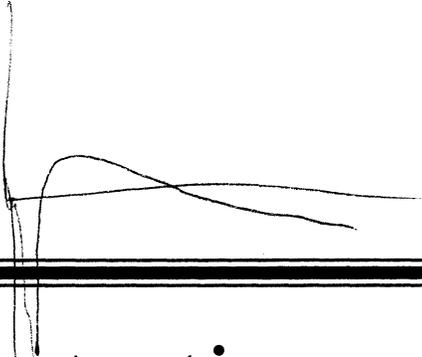


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Reconcentration of Radioactive Material Released to Sanitary Sewers in Accordance with 10 CFR Part 20

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**Prepared for
U.S. Nuclear Regulatory Commission**

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Abstract

The objectives of this study were to 1) assess whether radioactive materials that are released to sanitary sewer systems undergo significant reconcentration within WWTPs and 2) determine the physical and/or chemical processes that may result in their reconcentration within the WWTPs. The results of this study will assist in developing strategies for assessing whether changes in the NRC sanitary sewer disposal regulations are needed.

This one-year study addressed these objectives by collecting information and data from the open literature, NRC reports, EPA surveys, and interviews with licensees and staff of the WWTPs that may be impacted by these discharges. The literature review encompassed wastewater treatment, important geochemical processes, and individual radionuclide behavior in WWTPs. Metal/radionuclide mass balance and removal efficiencies were calculated from data provided by licensees and the WWTPs at Oak Ridge, TN; Erwin, TN; and the WWTPs associated with the Northeast Ohio Regional Sewer District (NEORS). In addition, the current state-of-the-science in modeling metal/radionuclide behavior in WWTPs was reviewed.

A review of the literature clearly demonstrated that radioactive materials discharged to sanitary sewer systems can be reconcentrated in sludge produced as a result of wastewater treatment. Initial reconcentration occurs as a result of primary and/or secondary treatment where physical/chemical processes remove radioactive materials from sewage to the sludge phase. Secondary reconcentration, a purely physical phenomenon, occurs as a result of sludge handling techniques. The degree to which a

given radionuclide is reconcentrated during the initial phase depends on 1) the partitioning of the radionuclide between the suspended solids and the aqueous (dissolved) phase, 2) the concentration of suspended solids, 3) the suspended solids removal efficiency, 4) the degree to which the dissolved radionuclide is partitioned to solids during primary and secondary treatment, and 5) the wastewater treatment processes used.

Mass balance calculations for radionuclides based on licensee discharge data and WWTP sludge data were not shown to be reliable. Generally, the licensee release data underestimated the mass of radionuclide found in the sludge. It was uncommon to find any agreement between the licensee(s) discharge and sludge mass balance. These disparities between licensee discharge and sludge content are centered around the fact that the data used in this study were collected to address regulatory concerns not to perform mass balance calculations. There is very limited data currently available or collected during WWTP investigations that could be used to make generic quantitative calculations of the potential for radionuclide reconcentration.

Although the results of our limited modeling study indicate that empirical models hold some promise for successfully predicting metal/radionuclide behavior in WWTPs in some instances, their general applicability remains uncertain. With the data and models currently available, it is not possible to quantitatively determine the physical and chemical processes that cause reconcentration or to calculate, *a priori*, reconcentration factors for specific WWTP unit processes or WWTPs in general.

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Foreword

Following identification of several incidents whereby radioactive material in particulate form was found to have concentrated in sewage sludge, the NRC revised its regulations to only permit the release of soluble radioactive material to sanitary sewers. In consideration that many treatment processes may, in fact, cause soluble material to become insoluble, the NRC contracted with Pacific Northwest Laboratories (PNL) to evaluate the possible mechanisms for reconcentration of radioactive material into sewage sludge. This report presents the results of PNL's evaluation.

In addition to other available information, the NRC will evaluate the results from this report to determine whether additional rule changes are necessary regarding release of radioactive material to sewers. This report is not a substitute for NRC regulations. The approaches and/or methods described in this report are for information only. Publication of this report does not necessarily constitute NRC approval or agreement with the information contained herein.



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Abbreviations/Acronyms

AA	atomic absorption spectroscopy
ALI	annual limit of intake
BOD	biological oxygen demand
CBOD	carbonaceous biological oxygen demand
COD	chemical oxygen demand
CSO	combined sewer overflow
DAF	dissolved air flotation
DCr	dissolved chromium
DOC	dissolved organic carbon
DTPA	diethylenetriaminepentaacetate acid
EDTA	ethylenediaminetetraacetic acid
EPA	U.S. Environmental Protection Agency
ICP	inductively-coupled plasma
MCRT	mean cell residence time
MEI	maximally exposed individual
M _D	dissolved metals
MGD	million gallons per day
MSC	Manufacturing Sciences Corporation
M _T	total metals
NCRP	National Council on Radiation Protection and Measurements
NEORS	Northeast Ohio Regional Sewer District
NFS	Nuclear Fuel Services
NPDES	National Pollutant Discharge Elimination System

Abbreviations/Acronyms

NRC	U.S. Nuclear Regulatory Commission
NTA	nitritotriactic acid
ORAU	Oak Ridge Associated Universities
PCBs	polychlorinated biphenyls
PNL	Pacific Northwest Laboratories
RBC	rotating biological contactor
SOC	soluble organic compound
STP	sewage treatment plant
TCr	total chromium
TSS	total suspended solids
VDS	volatile dissolved solids
VSS	volatile suspended solids
WWTP	wastewater treatment plant

1 Introduction

1.1 Background

The objectives of wastewater treatment have been evolving since their inception in the late 1800's and early 1900's (Metcalf and Eddy, Inc. 1991). From early times to the 1970's, these objectives were concerned primarily with: 1) removal of solids, 2) treatment of biodegradable organic compounds, and 3) the elimination of pathogenic organisms. Since the 1970's, these same objectives have continued to be used (albeit at higher efficiencies). In addition, the treatment also began to incorporate actions for aesthetic and environmental concerns such as 1) removal of plant nutrients, 2) removal of toxic organic compounds, and 3) removal of toxic and heavy metals. Many of the recent changes in wastewater treatment are responses to the Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500; referred to as the Clean Water Act). As a result of this evolution of objectives, wastewater treatment operations and processes have become more efficient and new technologies have been incorporated. For example, in 1974, over 2,800 wastewater treatment plants (WWTPs) used only primary treatment. By 1988, this number had been significantly reduced, primarily as a result of WWTPs upgrading to higher levels of treatment (U.S. Environmental Protection Agency [EPA], as reported by Metcalf and Eddy, Inc. 1991). While the total number of WWTPs in the United States is expected to grow by about 10 percent over the next 20 years, the number of WWTPs that will be upgraded to higher levels of treatment (that is, secondary and advanced treatment) will be significantly greater.

Today, the primary objective of wastewater treatment is to reduce and/or remove wastewater contaminants through the use of an engineered facility, such as a WWTP, as a way to maintain the water quality of liquid effluent discharged to receiving streams. Many different types of treatment processes are implemented in a typical WWTP to provide three classes of wastewater treatment: primary, secondary, and advanced (tertiary). The end result is a reduced

and/or contaminant free liquid effluent that satisfies regulatory limits for discharge into a designated receiving stream. The major byproduct of wastewater treatment is the sludge generated and collected from the various treatment processes. As a result of wastewater treatment and its evolution, it is no surprise that many dissolved and dispersible metal contaminants are retained and concentrated in the sewage sludge. Similarly, it is not surprising that radionuclides can also be concentrated in the sludge. Reconcentration of radioactive material could conceivably occur during most stages of treatment.

U.S. Nuclear Regulatory Commission (NRC) regulations permit release of radioactive materials into sanitary sewer systems in accordance with 10 CFR 20. Since that time, there has been a number of documented cases where radioactive materials have been discharged to sanitary sewer systems in accordance with applicable regulations and were subsequently concentrated in sanitary sewage sludge to levels of potential concern (U.S. Environmental Protection Agency 1986; Kennedy et al. 1992). As a result of these occurrences and because these occurrences seemed to involve particulate material, revisions to NRC regulations were implemented in January 1994 to prohibit the release of radioactive non-biological particulate material. The release of soluble materials and readily dispersible biological materials are still allowed under these regulations. It is not known whether this change in 10 CFR 20 is sufficient to prevent other reconcentration occurrences of radioactive material in sewage sludge at levels which present undue risks to the public.

1.2 Study Objectives and Scope

The processes currently used in WWTPs are numerous, and include physical, biological, and chemical techniques. Overlaid on this complexity are the chemical differences in the interactions of radionuclides with other radionuclides, with dissolved materials in the wastewater, and with organic and

1 Introduction

inorganic solid materials that constitute sludge. Past studies and surveys have documented many characteristics of WWTPS, such as 1) the fate of priority pollutants (heavy metals, etc.), 2) influent loads, 3) disposal practices, 4) technologies in use, 5) effluent flow, 6) sludge content, and 7) engineering data. However, these studies/surveys were not designed to study radioactive material at WWTPs. As a result, very few studies/surveys have been reported that have investigated radionuclide or radioactive material content of WWTPs with respect to 1) influent and effluent concentrations, 2) influence of treatment processes, 3) chemical form, or 4) reconcentration in sewage sludge.

The objectives of this study conducted by the Pacific Northwest Laboratory (PNL) are to 1) assess whether radioactive materials that are released to sanitary sewage systems undergo significant reconcentration within the WWTPs and 2) determine which physical and/or chemical processes result in nuclide reconcentration within the WWTPs. This one-year study addressed these objectives by collecting information and data from the open literature, NRC reports, EPA surveys, and interviews with licensees and staff at WWTPs that may be impacted by these discharges. The results of this study may assist in developing strategies for assessing whether changes in the NRC sanitary sewer disposal regulations are needed.

The radionuclides originally intended for study were selected by NRC; these were ^{241}Am , ^{60}Co , ^{137}Cs , ^{131}I , ^{54}Mn , ^{90}Sr , ^{232}Th , ^{234}U , ^{235}U , and ^{238}U .

However, the lack of available data for some of the radionuclides led the study efforts to concentrate on ^{60}Co , ^{137}Cs , ^{234}U , ^{235}U , and ^{238}U , as well as the heavy metals Zn, Cr, and Ni. These heavy metals were studied because Zn and Cr are commonly measured metals at WWTPs and radioactive isotopes of Zn and Cr (^{65}Zn and ^{51}Cr) may be discharged to sanitary sewer systems; Ni was used as a possible surrogate for Co. Three WWTPs were selected by the NRC for study because of the likelihood of radioactive materials having been released to their sanitary sewer systems. These are the Oak Ridge and Erwin, TN, WWTPs and the Northeast Ohio Regional Sewer District's (NEORS) Southerly Plant. Quantitative geochemical mass balance and process analysis of WWTP unit operations and processes were attempted. However, aqueous and solids analyses of wastewater treatment processes are

often driven by regulatory or engineering needs rather than those associated with scientific investigations. Lack of appropriate data can make geochemical fate calculations difficult.

1.3 Report Organization

This report on the reconcentration of radioactive materials released to sanitary sewer systems contains the following:

- the results of a literature review encompassing wastewater treatment, important geochemical processes, and individual radionuclide behavior in WWTPs (Chapters 2, 3, and 4)
- metal/radionuclide mass balance and removal efficiencies calculated from data provided by licensees and the WWTPs at Oak Ridge, TN; Erwin, TN; and the WWTPs associated with the NEORS (Chapter 5)
- the current state-of-the-science in modeling metal/radionuclide behavior in WWTPs (Chapter 6)
- the conclusions drawn from this study (Chapter 7).

In addition, Appendix A provides a set of tables/diagrams, that serve as a simple calculational tool allowing rapid understanding and assessment of the relationship between the amount of various radionuclides released by a licensee into a sanitary sewer system and the magnitude of potential radiation doses that may be received by a member of the public. The models and scenarios provided in NUREG/CR-5814 (Kennedy et al. 1992), as well as simplified intermediate steps, are used as the basis for this calculational tool.

The literature review is incorporated in three chapters. Chapter 2 is given as a primer to wastewater treatment unit operations and various processes used in primary, secondary, and advanced treatment techniques. It is not an in-depth analysis of wastewater treatment. The main source of information for this chapter was Metcalf and Eddy, Inc. (1991). Chapter 3 describes geochemical processes that may govern the fate of inorganic contaminants (that is, radionuclides, heavy

metals, cations, and anions) in various wastewater treatment processes. Chapter 4 describes the chemical data relevant to wastewater treatment that is currently available for each radionuclide of interest. This chapter includes a compilation of documented studies of radionuclide concentration measurements on influent wastewater, effluent, and sludge.

The DIALOG[®] Information Retrieval Service (Dialog Information Services, Inc. 1994) was used to conduct the computer-assisted literature search. The DIALOG service at the Hanford Technical Library, Richland, Washington, is connected to over 160 databases containing over 10 million records. The first step in the search was to scan all 160 databases for entries matching the keywords of "sewage" and "radio-isotope? or radionuclide? or radioactive?" and "not irradiation." The final qualifier, "not irradiation," was used to exclude numerous articles that reported on the use of gamma irradiation to sterilize sewage sludge, which was not in the scope of this study. This initial scan identified 12 databases that contained >99 percent of all possible citations or records matching the qualifying sets. The 12 databases used for the literature searches conducted in November 1993 are described in Table 1.1.

From the 12 databases, 499 different titles were identified as being potentially applicable to this study. Upon review of the titles and abstracts of these articles, more than 250 articles were determined to be relevant to this study. These articles were obtained and reviewed. From these articles, approximately 60 additional references were cited that dealt primarily with specific WWTP reports and articles dealing with metal interactions with sewage sludge. These were also obtained and reviewed.

As a quality control check of the computer-assisted literature review process, we chose to evaluate whether relevant articles cited in an EPA report on radionuclides in sewage ("Radioactivity of Municipal Sludge," EPA 1986), appeared among the 499 titles identified by the DIALOG search. Ten of 19 relevant citations appearing in the EPA document (1986) also appeared in the DIALOG report. Of the nine articles that did not appear in the DIALOG report, five were narrowly released annual reports from WWTPs, two were personnel communications, one was a NRC Information Notice, and one was a NRC internal memorandum.

Chapter 5 discusses the detailed calculations of metal/radionuclide mass balance and removal efficiencies from data provided by licensees and the WWTPs at Oak Ridge, and Erwin, TN, and the WWTPs associated with the NEORS. The present study collected information from selected licensees discharging to sanitary sewer systems and WWTPs related to 1) the radionuclides and activities discharged, 2) the chemical form of discharged radionuclides, 3) the volume of the discharges, 4) radionuclide activity in processed sludge, and 5) sludge production values. The working hypotheses behind these investigations were twofold: 1) the most easily determined factor for metals removal is the removal efficiency of an entire plant (simply the difference between influent and effluent masses divided by the influent mass), and hence, potentially could be used as a metal reconcentration factor, and 2) for radionuclides, where often only licensee discharge and total activity in the sludge was known, mass balance calculations could yield an effective estimate of a reconcentration factor. The latter hypothesis was based on the belief that, ideally, the mass of radionuclide discharged by a licensee(s) should be greater than the mass of radionuclide determined in the sludge and be a function of the radionuclide's propensity to associate with the sludge; that is, a reconcentration factor.

The results of these investigations are presented and include 1) a description of the WWTPs, 2) descriptions of the metal/radionuclide data collected from licensees and WWTPs, 3) results of calculations of WWTP metal/radionuclide removal efficiencies and mass balances, and 4) conclusions concerning the usefulness of the data collected and calculations performed. All data presented in Chapter 5 were provided by either NRC or Agreement States licensees or the WWTPs: the radioactive materials release data were provided by licensees who are required to maintain records on sewer discharges as a result of regulatory considerations; the sludge data were provided by the WWTPs or licensees as a result of monitoring programs.

Chapter 6, entitled "Mechanisms and Modeling of the Reconcentration of Radionuclides in Sewage Sludge," was originally designed to evaluate the data collected in Chapter 5 with respect to 1) the processes in which reconcentration of radionuclides occurred, 2) the chemical/physical forms of each radionuclide and how these forms affect reconcentration, 3) a mechanistic-based reconcentration pathway for the radionuclides

1 Introduction

Table 1.1 Databases used in computer-assisted literature search

Database	Description	Years Scanned
BIOSIS PREVIEW	Several biological listings including Biological Abstracts and Bioresearch Index	1969 to Dec. 1993
CA Search	Chemical Abstracts	1967 to Nov. 1993
Ei Compendex Plus	The Engineering Index	1970 to Dec. 1993
Energy Science & Technology	DOE database on energy and related topics	1973 to Nov. 1993
ENVIROLINE	Interdisciplinary information on environmental research and technology	1970 to Oct. 1993
INSPEC	Database for physics, electronics, and computing	1969 to Nov. 1993
NTIS	Government sponsored research, development, and engineering	1964 to Nov. 1993
Pascal	Multidiscipline international index of science and technology	1973 to Nov. 1993
Pollution Abstracts	Pollution, its sources, and its control	1970 to Nov. 1993
SciSearch	Multidiscipline index of science and technology	1974 to Nov. 1993
Toxline	Toxicology	1965 to Oct. 1993
Water Resources Abstract	Water resource topics	1969 to Nov. 1993

(or surrogate compounds), and 4) calculation of a theoretical reconcentration factor. As will be seen in Chapter 5, the available data on radionuclide concentrations were so limited as to preclude the evaluations mentioned above. However, during the literature search a number of models designed to evaluate trace metal behavior in particular WWTP processes, or WWTPs as a whole, were identified. To evaluate the effectiveness of these models on a full scale WWTP, metal data collected by the NEORS at the Easterly

Plant was used for model testing. In addition, a detailed description of models potentially applicable for predicting the behavior of metals/radionuclides in WWTPs is presented. A limited discussion of the mechanistic details of these models and the ramifications of this information with regards to the intended goal of predicting radionuclide behavior in WWTPs and its general applicability to WWTPs is also given.

2 Wastewater Treatment Processes Primer

2.1 Introduction

Effective management of wastewaters generated by municipalities and communities is important for protecting the environment in a manner commensurate with public health, economic, social, and political concerns (Metcalf and Eddy, Inc. 1991). Wastewater is a combination of liquid and solids, including sewage, paper products, infiltrated groundwater, and, in some cases, storm water that is collected in sewer piping systems. In the past, the sewer systems were designed to discharge directly to a surface water body, such as a river or ocean (that is, a receiving stream), without any treatment. However, wastewater characteristics (such as oxygen demand and suspended solids) and specific contaminants (such as disease-causing microorganisms and heavy metals) were found to adversely impact the water quality of the receiving streams. Therefore, wastewater treatment was implemented to reduce the adverse impacts of discharged wastewater on the receiving stream water quality. Consolidated in a WWTP, wastewater treatment is accomplished using a combination of numerous treatment processes and is directed toward the reduction and/or removal of constituents that contribute to oxygen demand, solids, and contaminants.

Many different types of processes are implemented within a plant to provide as many as three levels of treatment: primary, secondary, and tertiary. The objective of combining these three levels is to achieve a reduced or contaminant-free liquid effluent that satisfies the regulatory limits for discharge into a designated receiving stream. The treatment schemes are designed individually for each plant and are based on site-specific considerations, such as age of the plant, population served, type of waste received, geographic location, and water quality of the receiving stream. Figure 2.1 illustrates a general process flow diagram of a municipal WWTP. The prevalence of the common processes used in WWTPs in the United States is indicated in Table 2.1. The data for frequency of use of various WWTP processes were derived from the 1988 National Sewage Sludge

Survey (U.S. Environmental Protection Agency 1988) that examined 462 publicly owned WWTPs. The data obtained in the survey have been extrapolated to provide a representative estimate for all of the municipal WWTPs existing in the United States in 1988.

The major byproduct of wastewater treatment is the sludge generated and collected from the various treatment processes. Thus, a treatment plant contains facilities designed to process and handle sludge for ultimate disposal. Sludge handling and disposal are primary concerns for wastewater management and account for approximately 65 percent of the cost associated with operating a typical municipal WWTP.

This chapter presents an overview of the physical, biological, and chemical processes involved in wastewater and sludge treatment and is meant to be used as a primer. Therefore, the objectives and applications of the most commonly used processes utilized in the three levels of treatment (primary, secondary, and tertiary), are discussed as separate entities. Each treatment includes summary tables and simplified illustrations to give a more complete overview. Furthermore, the objectives and applications of the processes used for sludge handling and disposal are presented with a summary table, simplified illustrations, and process frequency of use. Throughout this primer, references are made to Chapter 3 (Biological, Chemical, and Physical Processes Affecting the Speciation of Radionuclides During Wastewater Processing) to indicate where additional information can be found pertaining to the effect of the wastewater treatment processes on radionuclides reconcentration.

2.2 Primary Treatment

In the early 1900s, wastewater treatment was initiated to remove floating and settleable solids from the influent wastewater using physical treatment processes. This first level of treatment, today referred to as "primary treatment," is accomplished in two steps: 1) preliminary treatment, and 2) primary settling.

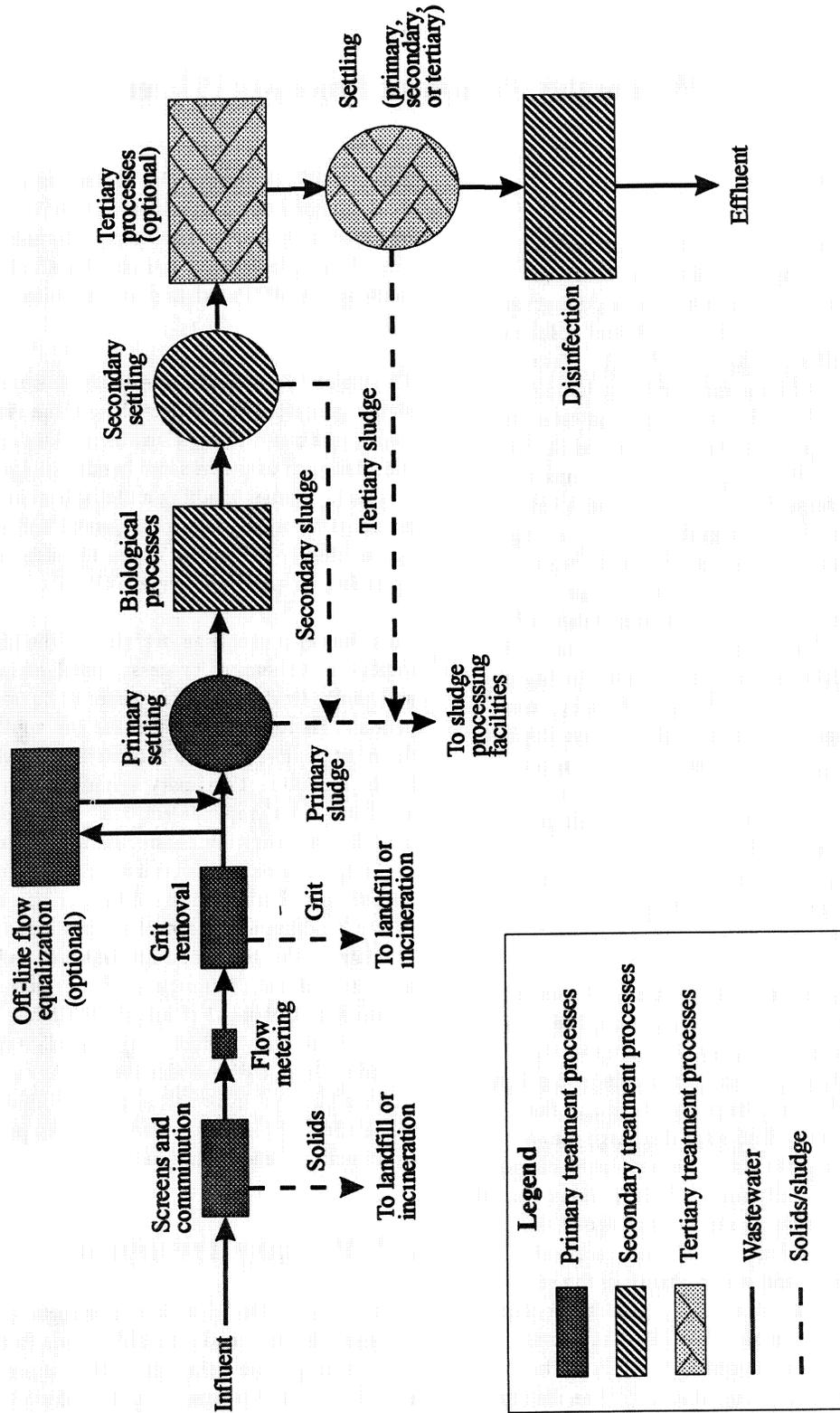


Figure 2.1 General process flow diagram of a wastewater treatment plant

Table 2.1 Treatment processes frequency of use by municipal wastewater treatment plants with at least secondary treatment

Treatment level	Process	Estimated percentage of wastewater treatment plants utilizing treatment processes ^(a)
Primary	Bar racks, screen, and grit removal	63.2
	Primary settling	30.2
Secondary	Biologically activated sludge	55.7
	Biological denitrification	3.5
	Biological nitrification	12.3
	Aerated lagoons	17.6
	Rotating biological contactor	4.0
	Trickling filter	11.1
	Chemical addition for precipitation and flocculation	13.1
	Disinfection	67.1
	Secondary settling	59.8
Tertiary	Multimedia filtration	13.7
	Other processes	22.3

(a) From EPA (1988).

Wastewater typically contains a wide variety of solid matter, including large solids of either biological or anthropogenic origin and grit (inorganic particles that can be easily removed by sedimentation). Different methods of removal are required for the types of solids involved. Preliminary treatment operations include screening, comminution, grit removal, flow measurement, and flow equalization. The latter two operations are conducted to facilitate the operation of the entire WWTP. Following preliminary treatment, the influent wastewater is discharged to primary settling tanks, where a majority of primarily organic solids and floating material is removed from the bulk wastewater. Primary treatment processes, their functions, and the equipment and chemicals used are summarized in Table 2.2. Figure 2.2 shows a schematic of the primary treatment phase of a typical municipal WWTP.

Before the passage of the Federal Water Pollution Control Act Amendment in 1972, primary treatment was the only level of treatment conducted in the majority of municipal WWTPs in the United States. Since 1972, many of the existing plants have been retrofitted with secondary and, in some cases, tertiary treatment facilities to maintain the water quality of

receiving streams in accordance with the Amendment. The results of a 1988 survey on the levels of treatment used at 15,708 WWTPs indicated that only 11 percent of these plants provided primary treatment alone (U.S. Environmental Protection Agency 1988). The importance of primary treatment in the reconcentration of metals and radionuclides varies greatly with the propensity of these constituents to associate with or precipitate as easily removable solids (Lester 1987a) (Section 3.5.1).

Removal efficiencies of various primary treatments generally range between 33 to 56 percent (Lester 1987a). Generally, removal efficiencies of metals are not related to influent concentration and they follow a general trend that is consistent with the reported propensity of the metals to sorb [adsorb, absorb, precipitate, coprecipitate (Sections 3.31 and 3.3.3)] to mineral and organic surfaces: Pb > Hg >> Cu > Zn >> Cr > Cd > Ni (Davis and Jacknow 1975; Lester et al. 1979; Stoveland et al. 1979). Primary treatments generally remove only trace amounts of anions and therefore would not be likely pathways in reconcentrating such radionuclides as ¹³¹I (I⁻ or IO₄⁻) and ^{99m}Tc (TcO₄⁻)—the two radionuclides that emit over 90 percent of the gamma radiation in

2 Wastewater

Table 2.2 Primary treatment process

Process	Function	Equipment and chemicals
Screening	Remove coarse to medium solids from the waste stream	Bar racks, screens
Comminution	Break up coarse solids into smaller ones without removing them from the waste stream	Vertical drum and cone comminutors
Flow measurement	Monitor the flow rate of the wastewater stream	Open channel: flumes, weirs Closed conduit: rotameters, pitot tubes, turbines
Grit removal	Remove grit, sand, or gravel from the waste stream	Grit chambers: horizontal flow, aerated, vortex type
Flow equalization	Maintain constant waste stream flow rate	Equalization basin
Primary settling	Removal of easily settleable solids and floating material	Rectangular settling tanks, clarifiers, flocculation chambers; alum, lime, and iron salts settling aids

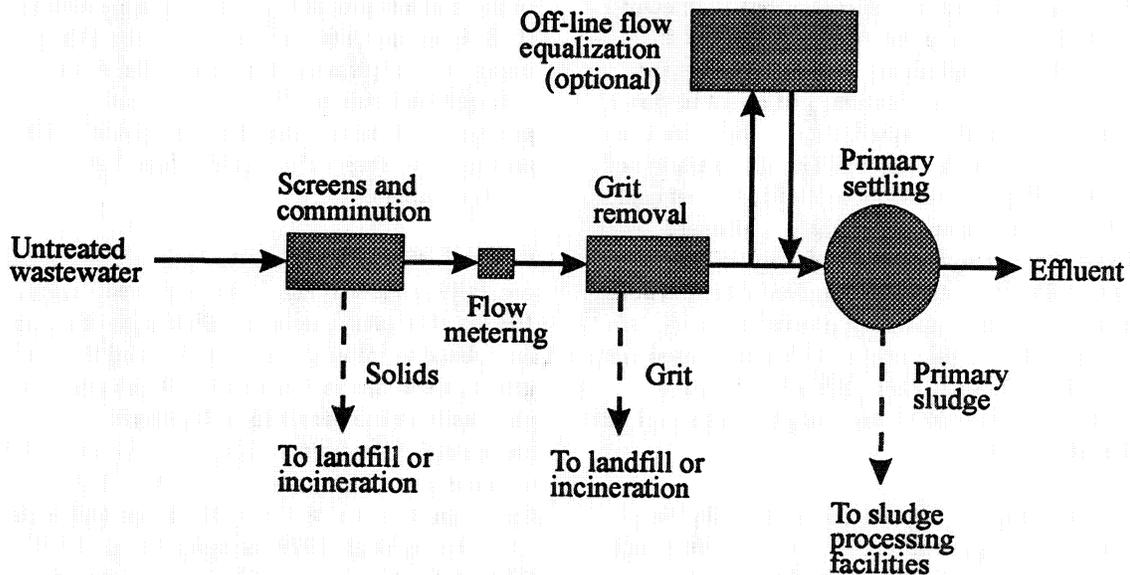


Figure 2.2 Primary treatment phase of a typical wastewater treatment plant

many domestic wastewater treatment facilities (Sections 4.5 and 4.8) (Moss 1973; Sodd et al. 1975; Testoni et al. 1988).

2.2.1 Preliminary Treatment Processes

Preliminary treatment operations are located at the beginning (headworks) of the plant to remove coarse solids and grit from the influent wastewater. Removal of these problematic solids at the plant headworks prevents adverse impacts on subsequent equipment (such as pumps) and processes used in the plant. Flow measurement and equalization are also conducted at the plant headworks for monitoring and downstream process optimization purposes.

2.2.1.1 Screening

Screening is the first physical operation applied to the influent untreated wastewater. The objective of

screening is to remove coarse floating and suspended solids from the bulk wastewater. As the wastewater enters the treatment plant, it is passed through bar racks or screens, where the solids are collected and removed.

Bar racks (Figure 2.3) contain a row of parallel bars spaced 15 mm or greater apart. The rack is partially submerged in the wastewater conduit and collects debris as the wastewater flows through the bar spacings. The bar racks are cleaned by hand or with mechanical devices. The material collected on the bar racks (coarse screenings) includes, for example, rocks, branches, pieces of lumber, leaves, paper, tree roots, plastics, and rags. Coarse screenings generally have a dry solids content of 15 to 25 percent, a density range of 640 to 960 kg m⁻³, and a volatile solids content (solids which combust at 600°C) of 80 to 90 percent or more (Metcalf and Eddy, Inc. 1991).

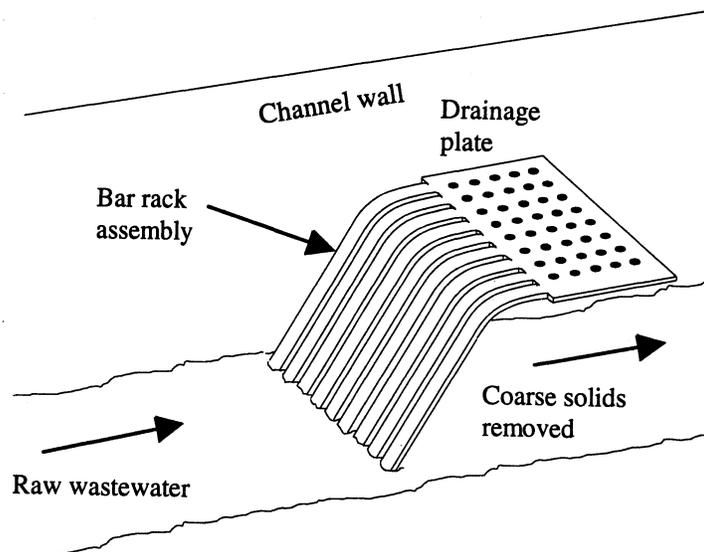


Figure 2.3 Wastewater screening process using a bar rack assembly

2 Wastewater

Screens are typically used in place of bar racks at small-scale treatment plants, where smaller solids are removed from the incoming wastewater, or at plants where headloss through the screens does not pose a problem. The screening material is usually made of stainless steel or nonferrous wire mesh. Static (fixed) or rotary drum are the types of configurations used. Typical screen openings range from 0.2 to 6 mm. Both types of screens are cleaned with mechanical devices. Depending on the size of the screen opening, an influent suspended solids removal of 10 to 15 percent can be achieved. The collected solids (fine screenings) have volatile solids contents ranging from 65 to 95 percent and contain grease and scum materials.

There are many handling and disposal options for both coarse and fine screening materials. Some of these options are 1) dumping in landfills, 2) burial on the treatment plant site (for small plants only), 3) incineration (for large plants only), 4) disposal with municipal solids wastes, or 5) onsite grinding and returning the resulting grounds to the wastewater.

2.2.1.2 Comminution

Comminution is occasionally used in place of bar racks and screens to handle the coarse solids in the influent wastewater. Comminutors are mechanical cutting devices that cut up (comminute) coarse solids. The resulting smaller-sized solids eliminate the need for removing, handling, and disposing the coarse solids that would be collected using bar racks and screens. However, comminuted solids often present downstream problems. Rags are especially problematic because they have a tendency to recombine into ropelike strands that can clog pump impellers, sludge pipelines, and heat exchangers and to accumulate on air diffusers. Comminutors are often used in plants serving small communities.

2.2.1.3 Grit Removal

Downstream from the flow-measurement facility, the influent wastewater enters a grit chamber, where the grit is either allowed to or forced to settle. Grit chambers are used to 1) protect mechanical moving equipment from abrasion and abnormal wear, 2) reduce the formation of heavy deposits in pipelines, and 3) reduce the frequency of digester cleaning caused by excessive accumulations of grit. Grit chambers are

typically placed between the bar racks, screens, or comminutors and the primary settling tanks (see Figure 2.2). Both grit removal and bar screening are frequently used as preliminary treatment processes (63.2 percent of the time) in municipal WWTPs with at least secondary treatment (see Table 2.1).

The specific gravity of grit solids is generally higher than the specific gravity of the organic solids in wastewater. Therefore, grit chambers are designed to effectively separate (by sedimentation) the inorganic/inert solids from organic solids and bulk wastewater. The separation of the organic solids occurs downstream in the primary settling tanks. The specific gravity of the grit material ranges between 1.3 g/cm³ (when substantial organic matter is agglomerated to inert solids) and 2.7 g/cm³ (for inert solids only). The size distribution of collected grit varies, depending on the geographic location of the plant, collection system characteristics, and grit-removal efficiencies. A 100-mesh (0.15-mm) screen will retain most grit particles (Metcalf and Eddy, Inc. 1991).

Grit chambers are designed to remove grit particles with a specific gravity of 2.65 g/cm³ at a wastewater temperature of 15.5°C. The three types of grit chambers are: horizontal flow (rectangular or square configuration), aerated, and vortex type. Horizontal-flow chambers are settling basins designed to allow the grit to undergo gravity settling. The accumulated grit is removed mechanically (by such devices as skimmers or scoop buckets) from the chamber bottom. Aerated grit chambers are rectangular-shaped settling basins with a sloping bottom, where the settled grit is collected and removed with grab buckets. Air diffusers are positioned along the chamber bottom, where air is bubbled into the wastewater causing a helical flow pattern that promotes settling of the dense grit material. Vortex-type chambers use a vortex-flow pattern to promote grit settling to achieve effective separation from the bulk wastewater and organic solids. A vortex-type chamber consists of a funnel-shaped tank with a rotating turbine that creates a downward-spiralling flow path for the dense grit material. The grit accumulated at the chamber bottom is removed by a grit pump. The collected grit solids are disposed in a landfill or, in some cases (in large treatment plants), incinerated. Some states require material collected from grit and screenings to be lime stabilized before disposal in a landfill. The grit chamber wastewater effluent is discharged to the

equalization basin or basins without the problem of abrasive effects of grit causing damage to pumps and other vital equipment.

2.2.1.4 Flow Equalization

Flow rates of incoming waste streams can vary widely according to the time of day, amount of rainfall, and other factors. To make the flow more constant, equalization basins are used. If flow equalization is necessary, the grit chamber effluent is diverted to a large open basin, where the influent flow rate can vary but the effluent flow rate remains relatively constant. Because the basin area is so large, the cost of removing naturally settling solids is quite high. Therefore, constant mixing in the equalization basin is necessary to prevent sedimentation.

2.2.2 Primary Settling

The wastewater from the grit chamber or equalization basin is discharged to the primary settling tanks, where settleable solids (primarily organic) and floating material are removed from the bulk wastewater. The settling tanks are typically rectangular or circular (called clarifiers) and are equipped with mechanical cleaning equipment to remove settled solids and floating material, such as oil and grease. An efficiently designed settling tank can remove from 50 to 70 percent of the influent suspended solids and from 25 to 40 percent of the biological oxygen demand [(BOD); the oxygen demand required to biologically degrade carbonaceous organic matter in the influent wastewater over a five-day period]. The general concept of quiescent settling, using a rectangular primary settling tank, is illustrated in Figure 2.4. Figure 2.5 illustrates the general operation of a primary clarifier. The sedimentation/flocculation process is described in detail in Section 3.2.1. The solids collected in the primary settling tanks are discharged to the sludge-handling and sludge-disposal operations of the treatment plant.

Flocculation and chemical additives are used to improve the performance of primary settling tanks. Flocculation is a physical process whereby suspended solids in the wastewater are slowly mixed to promote aggregation of fine solids that are more easily settled. Flocculation can occur upstream from the primary settling tanks in a separate flocculation chamber or in

the pipeline connecting the grit chamber or equalization basin(s) and primary settling tank(s). Primary clarifiers can be equipped with a flocculating chamber that promotes a mixing zone for solids aggregation. Chemical additives (precipitants) can enhance primary settling by forming a gelatinous floc in the wastewater that easily settles and entraps fine solids that are otherwise not easily removed in the settling tank. Specific chemical additives include alum, polymers, ferric chloride, ferric sulfate, ferrous sulfate, and lime.

Section 3.2.1.2 provides additional information about the mechanisms by which these chemical additives achieve sedimentation/flocculation. The effect of chemical additives on radionuclide reconcentration will vary with the radionuclide and the chemical additive (Section 3.5.3). Those additives that behave as flocculents, such as polymers, would tend to reconcentrate those radionuclides like ^{232}Th and ^{241}Am that sorb strongly to solid organic or inorganic surfaces. Conversely, they would have relatively less effect on those radionuclides, such as ^{131}I (as iodide) and $^{99\text{m}}\text{Tc}$ (as pertechnetate), that sorb relatively weaker to surfaces.

2.3 Secondary Treatment

Today, secondary treatment is a minimum standard for municipal wastewater treatment facilities using chemical and/or biological processes to remove constituents that are not effectively removed during primary treatment. The primary constituents targeted for removal by secondary treatment are natural and unnatural organic compounds, phosphorus, and nitrogen.

Biological processes use microorganisms to consume organic components and other nutrients, such as nitrogen and phosphorus, converting them to microbial biomass, carbon dioxide, water, and ammonia. Chemical processes facilitate the removal of certain species by 1) precipitating or vaporizing the unwanted constituents out of the wastewater or 2) flocculating suspended solids that may contain the unwanted constituent. Chemical additives are also used to disinfect the wastewater stream. One of the inherent disadvantages associated with most chemical wastewater treatment processes, as compared with the physical treatment operations, is that they use additives. In most cases,

2 Wastewater

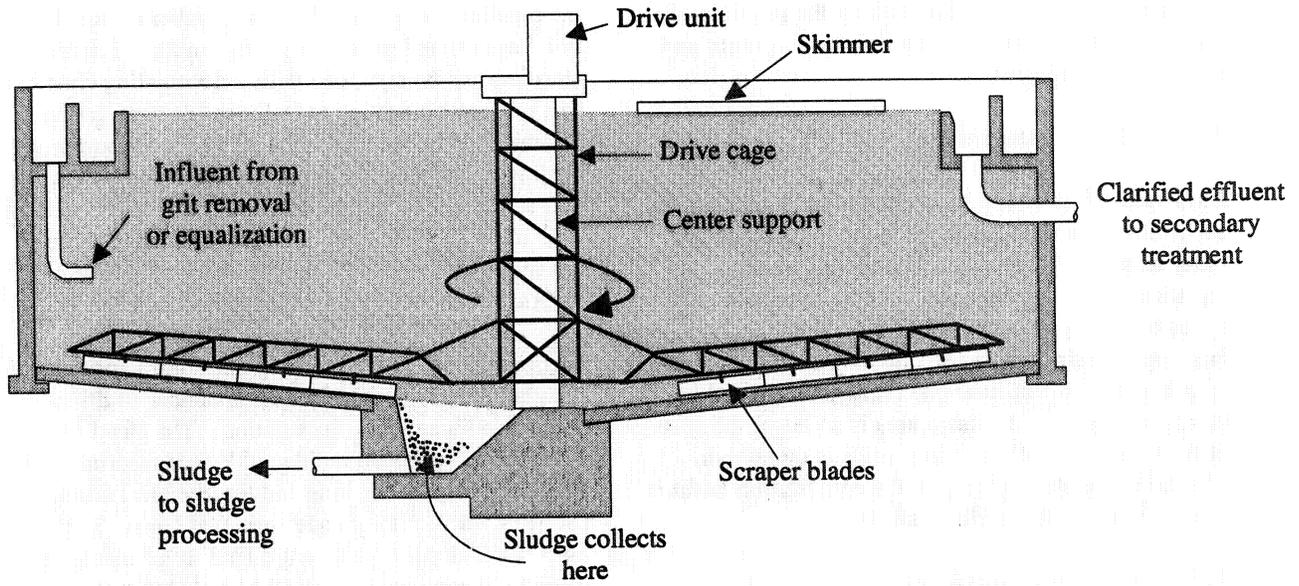


Figure 2.4 Primary sludge settling basin

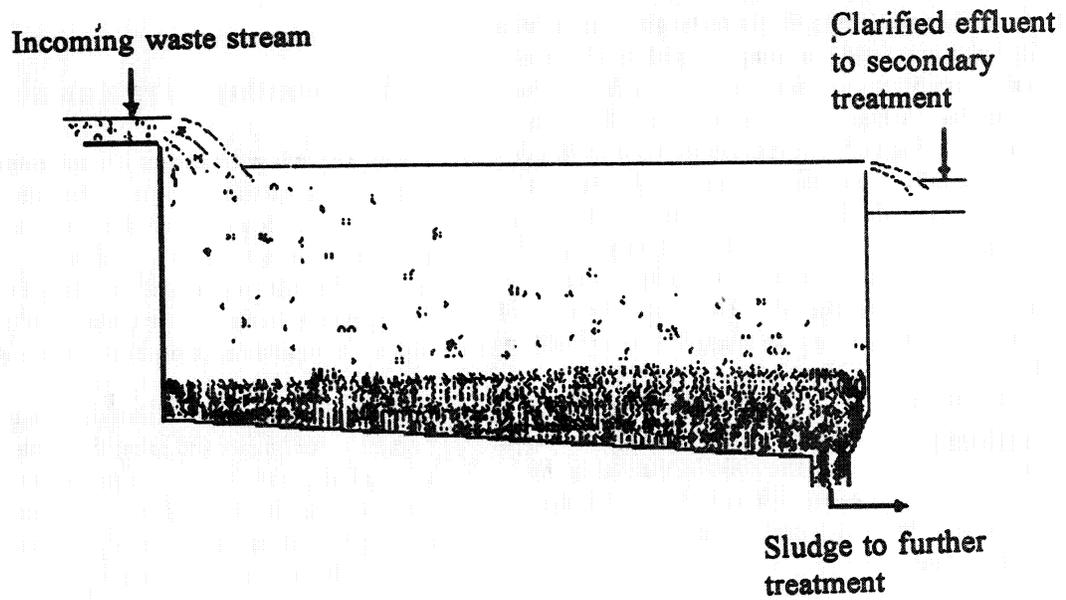


Figure 2.5 Primary clarifier

the wastewater experience a net increase in mass. For example, where chemicals are added to enhance the removal efficiency of sedimentation (that is not enhanced by chemical additives), the total dissolved solids concentration of the wastewater is always increased.

The secondary treatment phase of a WWTP is designed to meet the unique requirements of the area it serves; consequently, each plant is different. The age of the plant, the number of people it supports, the type of wastes it receives, and its geographic location influence the design of the plant. Figure 2.6 presents a generalized schematic of a secondary treatment configuration. Tables 2.3 and 2.4 summarize the biological and chemical processes currently used in secondary treatment.

Metal removal during secondary treatment has been extensively studied (Section 3.5.2) (reviewed by Lester 1987b). Secondary treatments typically have a greater removal efficiency, ranging from 24 to 86 percent, than primary treatments. Fe(III), Cu, Cr, and Zn generally have higher removal efficiencies as a result of secondary treatment than Ni, Mn, Ca, and Mg (Neufeld and Hermann 1975; Forster 1976). In general, a current relationship does not exist between metal concentration entering the secondary treatment and metal removal (Lester 1987b). Secondary treatment is likely to induce radionuclide reconcentration, especially for ^{241}Am (Section 4.2), ^{131}I (Section 4.5), and ^{232}Th (Section 4.9).

2.3.1 Biological Processes

The primary objectives of the biological treatment processes are to 1) reduce the concentrations of dissolved and solid organic materials, 2) reduce the concentration of inorganic solids, and 3) stabilize the organic waste (remove offensive odors and eliminate disease-causing organisms) (Grady and Lim 1980). Additional objectives may include reducing the concentration of nutrients, specifically nitrogen and phosphorus, or reducing the concentration of contaminant organic and inorganic compounds. In the case of the latter, pretreatment may be required because industrial wastes may be toxic to the microorganisms.

Removing constituents that contribute to BOD, flocculation of suspended colloidal solids, and stabilization of organic matter is accomplished biologically, using a variety of microorganisms, principally aerobic or anaerobic bacteria. These microorganisms are used to convert the colloidal and dissolved organic matter into various gases and biomass. The gases are then captured and, if necessary, destroyed, and the biomass is removed by gravity settling.

A wide variety of microorganisms are used in wastewater treatment, including bacteria, fungi, algae, protozoa, and rotifers. The type, as well as the species, of microorganisms used varies with the objective of the treatment process. Aerobic treatment environments generally contain a highly diverse group

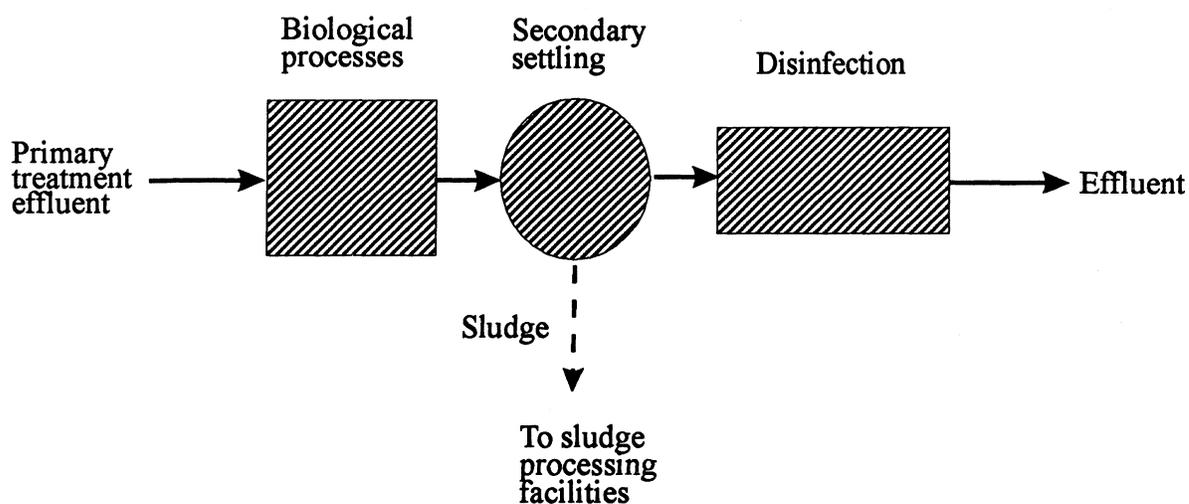


Figure 2.6 Secondary treatment phase of a typical wastewater treatment plant

Table 2.3 Secondary treatment biological processes

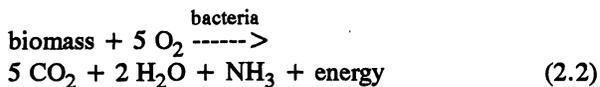
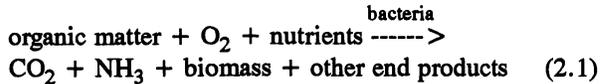
Process	Function	Chemicals and equipment
Aerobic suspended growth	Carbonaceous BOD ^(a) removal (nitrification)	Biologically activated-sludge processes, deep tank, aerated lagoons
Aerobic attached growth	Carbonaceous BOD removal (nitrification)	Trickling filters, roughing filters, packed bed reactors
Combined aerobic suspended and attached growth	Carbonaceous BOD removal (nitrification)	Biologically activated-biofilter processes, trickling filter solids-contact processes
Anaerobic suspended growth	Carbonaceous BOD removal and stabilization	Anaerobic digestion, contact processes
Anaerobic attached growth	Carbonaceous BOD removal and stabilization	Anaerobic filter processes, expanded beds
Anoxic suspended growth	Denitrification	Suspended growth nitrification
Anoxic attached growth	Denitrification	Fixed-film denitrification

(a) BOD = biological oxygen demand

Table 2.4 Secondary treatment chemical processes

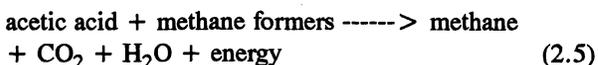
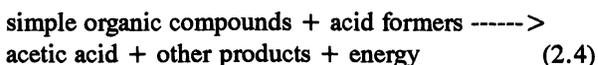
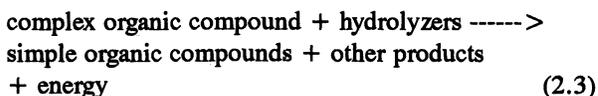
Process	Function	Chemicals and equipment
Chemical precipitation	Removal of settleable and colloidal solids by the addition of a precipitation agent	Commonly used precipitating agents are alum, ferric chloride, ferric sulfate, ferrous sulfate, and lime
Adsorption	Removal of organics not removed by conventional chemical and biological methods; most often used as a polishing agent before release from point source	Commonly used adsorption agent is activated carbon
Disinfection	Selective destruction of disease-causing organisms	Commonly used disinfecting agents are chlorine (most common), chlorine dioxide, bromine chloride, ozone, and ultraviolet radiation
Dechlorination	Removal of total combined chlorine residual that exists after chlorination	Commonly used dechlorinating agents are sulfur dioxide, activated carbon, sodium sulfite, and sodium metabisulfite
Odor control	Removal or decreased amount of odor-causing components	Commonly used agents are chlorine, hydrogen peroxide, and ozone

of organisms (primarily bacteria) that break down organic compounds in the presence of oxygen, forming carbon dioxide, ammonia, biomass, and other end products (Equation 2.1). The bacteria process these materials into basic components such as carbon dioxide, water, and ammonia during cellular respiration (Equation 2.2).



Although the endogenous respiration reaction results in relatively simple end products and energy, stable organic end products (that is, biomass) are also formed.

Anaerobic treatment environments also contain diverse groups of organisms. Anaerobic destruction of organics is generally a more complex process, requiring at least two separate types of microorganisms to break down wastes. The first group of organisms, hydrolyzers, breaks down the complex organics into simpler forms, such as amino acids and monosaccharide (Equation 2.3). Acid formers then break these products down further into simple organic acids, such as acetic acid (Equation 2.4). The last group of organisms, methane formers, takes these acids and further breaks them down to methane gas and carbon dioxide (Equation 2.5).



2.3.1.1 Aerobic Suspended Growth

Aerobic suspended growth processes use aerobic organisms suspended in wastewater. Typical processes used to accomplish aerobic suspended growth are biologically activated sludge, aerated lagoons, and sequencing batch reactors. Of these, the biologically activated-sludge process is clearly the most used process at municipal WWTPs (Table 2.1). Aerobic digestion is sometimes considered a secondary treatment step, but for the purposes of this report, this process is addressed in detail under Sludge Handling and Disposal in Section 2.5.

Biologically activated-sludge processes involve the introduction of wastewater into a reactor, where an aerobic bacterial culture is maintained in suspension. The aerobic environment in the reactor is achieved by using diffused or mechanical aeration, which also serves to keep the waste and aerobic organisms well-mixed (Figure 2.7). The concentration of microorganisms in the reactor depends on the desired treatment efficiency and the growth kinetics of the microbial population. The residence time of the wastewater varies greatly from days to weeks, depending on a number of factors, including the objective of the process, the stage of growth of the microbial population, the temperature, and the influent chemical composition. The mixture of new and old microbes (mixed liquor) is then passed into a settling tank, where the cells are separated from the treated wastewater. A portion of the settled biomass is recycled to maintain the desired concentration of organisms in the reactor, and a portion is removed for disposal (Figure 2.7). The degree of treatment achieved by biologically activated sludge is presented Table 2.5.

Aerated lagoons are similar to conventional biologically activated-sludge processes, except that an earthen basin is used as the reactor and the oxygen is supplied by surface or diffused aerators. In an aerobic lagoon, all the solids are maintained in suspension. The large surface area associated with aerated lagoons can cause more significant temperature effects than are normally encountered in the conventional biologically activated-sludge process.

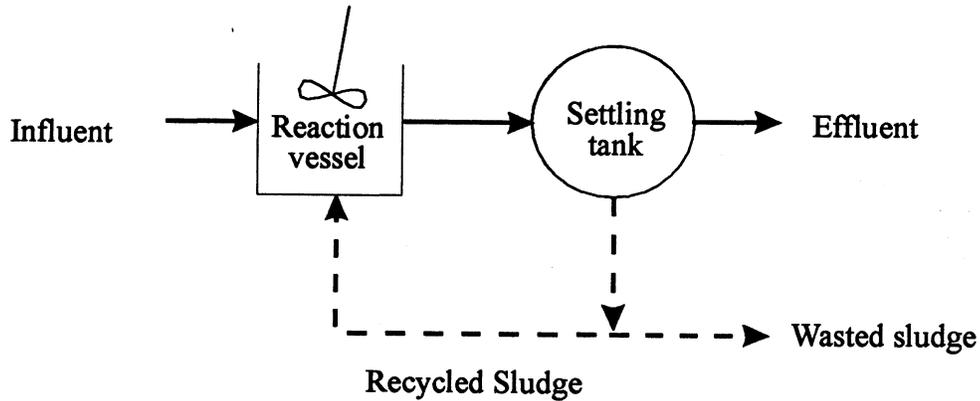


Figure 2.7 Biologically activated-sludge process

Table 2.5 Degree of treatment achieved by process used in primary and secondary treatment (adapted from Qasim 1985)

Process	% Constituent removal efficiency				
	BOD ^(a)	SS ^(a)	P ^(a)	Org-N ^(a)	NH ₃ -N ^(a)
Bar racks	nil	nil	nil	nil	nil
Grit chambers	0 to 5	0 to 10	nil	nil	nil
Primary sedimentation	30 to 40	50 to 65	10 to 20	10 to 20	0
Biologically activated sludge (conventional)	80 to 95	80 to 90	10 to 25	15 to 50	8 to 15
Trickling filters	65 to 80	60 to 85	8 to 12	15 to 50	8 to 15
Rotating biological contactors	80 to 85	80 to 85	10 to 25	15 to 50	8 to 15
Chlorination	nil	nil	nil	nil	nil

(a) BOD = biological oxygen demand; SS = suspended solids; P = total phosphorus; Org-N = organic nitrogen; NH₃-N = ammonia nitrogen.

Sequencing batch reactors are open vessels that cycle through a series of treatment steps (Figure 2.8). The individual operations involved are identical to those in conventional biologically activated-sludge systems (that is, aeration and sedimentation/clarification are carried out in both systems). However, in conventional plants, the operations are carried out simultaneously in separate tanks, whereas in sequencing batch reactors, the operations are carried out sequentially in the same tank, as follows. A reactor containing biologically activated sludge is filled with wastewater. The reactor is aerated to mix the wastewater with the biologically activated sludge and to provide the necessary oxygen for aerobic growth.

The mixture is then allowed to settle and clarify. The treated water is withdrawn off the top, and a portion of the biologically activated sludge is taken off the bottom. The remainder of the biologically activated sludge is left in the reactor for the next batch of wastewater.

2.3.1.2 Aerobic Attached Growth

Aerobic attached-growth biological treatment processes are usually used to remove organic matter from wastewater and to achieve nitrification. The attached-growth processes include trickling filter, roughing filter, rotating biological contactor, and fixed-film

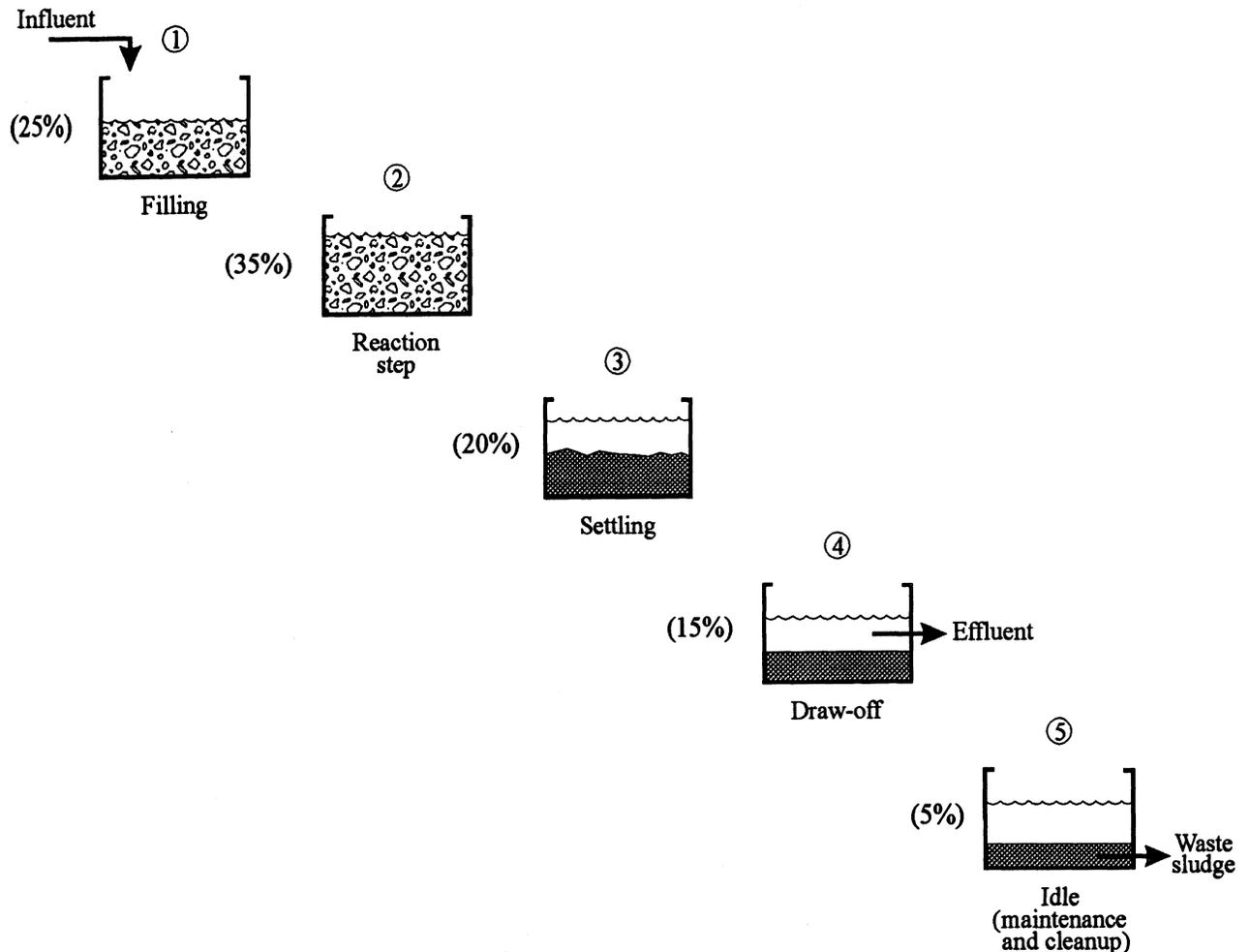


Figure 2.8 Sequencing batch reactor process (cycle time, percent)

nitrification reactor. The trickling-filter process is used most commonly (Table 2.1).

A trickling filter (Figure 2.9) consists of a bed of highly permeable medium that is coated with microorganisms. The wastewater is usually sprayed on top of the medium and then permitted to slowly trickle through to the bottom, where it is removed. The filter medium is usually rocks (2 to 10 cm in diameter) or plastic packing material. Trickling filters that use rocks are usually limited to approximately 2.5 m in height, whereas plastic packing filters can be as high as 12 m. A drain is located below the filters

to carry away treated wastewater and any biomass that has become detached from the medium. The drain system is important both as a collection unit and as a porous structure through which air can be introduced to the lower strata of the filters. The collected liquid is passed to a settling tank where the solids are separated from the treated wastewater.

The organic material present in the wastewater is degraded by a population of microorganisms attached to the filter medium. Organic material from the liquid is adsorbed onto the biological film or slime layer.

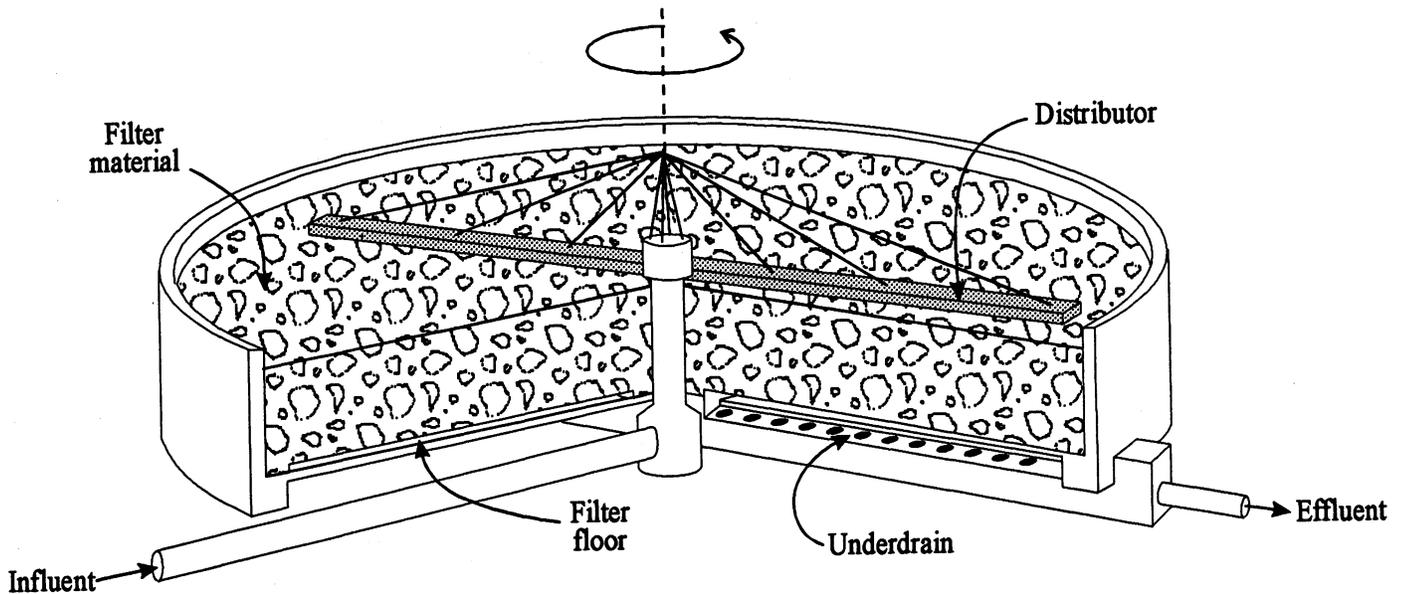


Figure 2.9 Trickling filter for treatment of wastewater

In the outer portions of the biological slime layer (0.1 to 0.2 mm), the organic material is degraded by aerobic microorganisms. As the microorganisms grow, the thickness of the slime layer increases and the available oxygen is consumed before it penetrates the full depth of the slime layer. Thus, an anaerobic environment is established near the surface of the filter medium. As the slime layer increases in thickness, the adsorbed organic matter is metabolized before it can reach the microorganisms near the filter medium face. As a result of having no oxygen or external source for carbon, the microorganisms near the medium face enter into an endogenous phase of growth and lose their ability to cling to the medium surface. The liquid then washes the slime off the medium, and a new slime layer starts to grow. This phenomenon of losing the slime layer is called sloughing and is primarily a function of the amount of organic material and the flow rate of the waste added to the filter. The sloughed organic solids are discharged with the treated wastewater effluent to the secondary settling tanks for removal.

Rotating biological contactors (Figure 2.10) consist of closely spaced circular disks of polystyrene or polyvinyl chloride. The disks are submerged in and rotated through the wastewater. The microorganisms

grow on the disks, receiving nutrients from the wastewater and oxygen from the air. Sloughing occurs when the buildup of microorganisms is sufficient to be unable to withstand the shearing force of the rotation of the disk in and out of the water. While rotating biological contactors are not commonly employed (Table 2.1), they are generally quite reliable because of the large amount of biological mass present.

Like other attached-growth processes, the packed-bed reactor (Figure 2.11) is used for nitrification and removal of BOD. Typically, a packed-bed reactor consists of a container that is packed with a medium to which the microorganisms can become attached. Wastewater is introduced from the bottom of the container through an appropriate drain system. Air or pure oxygen must also be fed in with the wastewater.

2.3.1.3 Anaerobic Suspended Growth

Within the last 15 years, a number of different anaerobic processes have been developed to 1) reduce the volume of sludge, 2) reduce the concentration of organic compounds that are difficult to degrade, and 3) stabilize organic materials. In the anaerobic digestion process, many different microorganisms break down organic materials and sludge into a variety

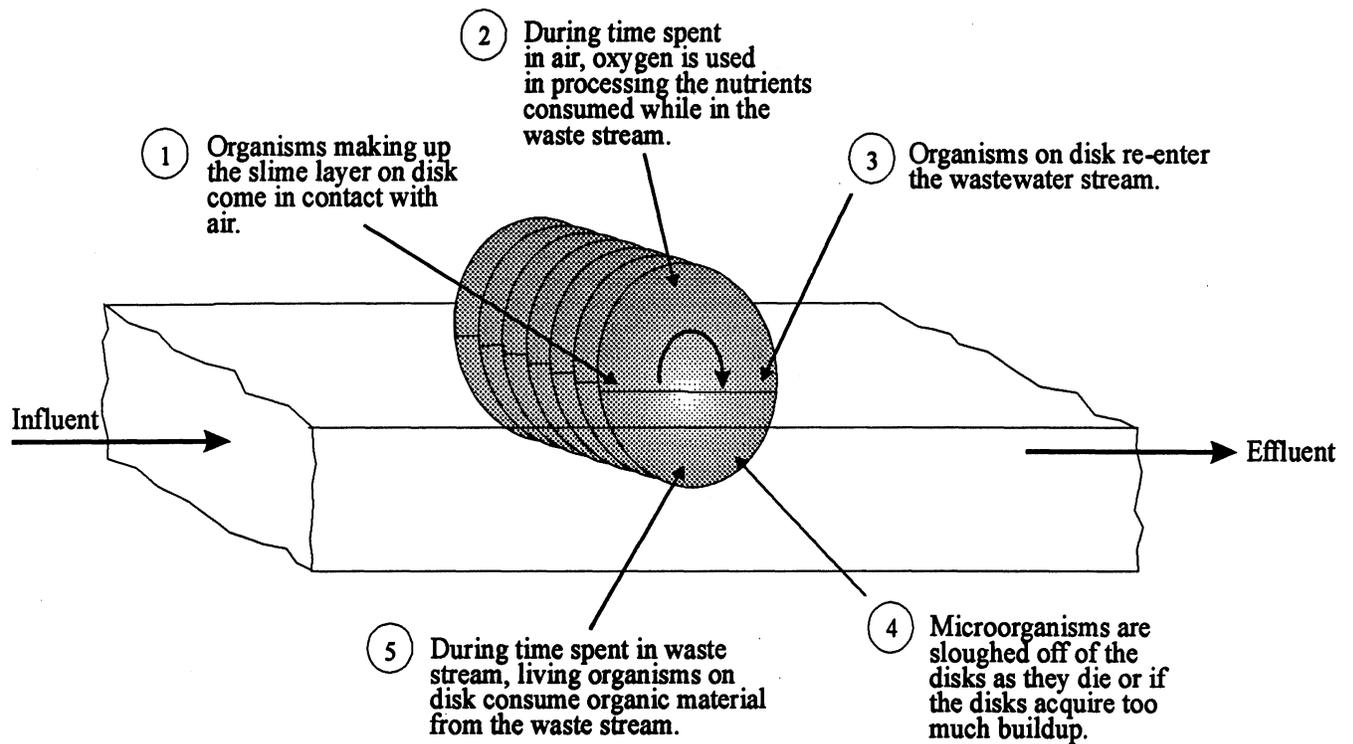


Figure 2.10 Rotating biological contactor for aerobic attached-growth biological treatment of wastewater

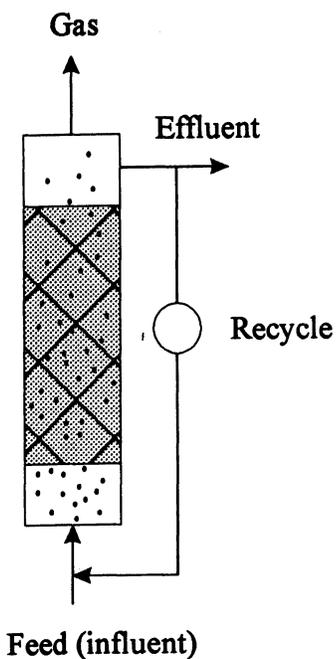


Figure 2.11 Packed-bed reactor for nitrification and removal of BOD from wastewater

of end products, including methane and carbon dioxide (Equations 2.3, 2.4, and 2.5). The anaerobic sludge-blanket process is the most commonly used anaerobic suspended-growth process. Other anaerobic digestion waste processes are described in Section 2.5.

The upflow anaerobic sludge-blanket process involves pumping wastewater up through a reactor, where it comes in contact with floating biological granules (Figure 2.12). During the respiration of these biological granules, gases are formed that buoy the particles until they bounce against the degassing baffles, releasing the gases and allowing the particle to drop back into the blanket portion of the mixture. Effluent is drawn off the top of the reactor and sent to a sedimentation tank. A portion of the settled sludge is returned to the blanket. Typical wastewater velocity through this process is 0.5 to 1.0 m h^{-1} .

Anaerobic conditions significantly affect the chemical reactivity of oxidation-reduction (redox) sensitive

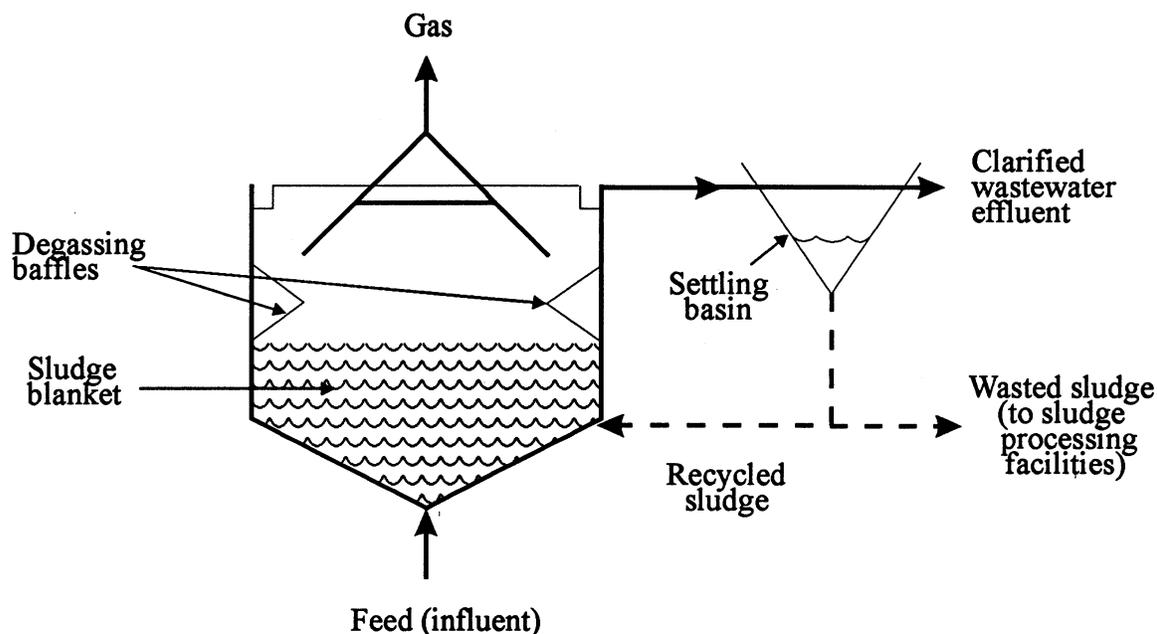


Figure 2.12 Upflow anaerobic sludge blanket with settler for anaerobic suspended-growth treatment of wastewater

elements. As discussed in more detail in Section 3.3.2, redox-sensitive elements include C, N, O, S, Mn, Fe, Co, I, Tc, and U. Changes induced by converting a wastewater stream from an aerobic to an anaerobic system may indirectly affect radionuclide reconcentration. For instance, such a change would be likely to significantly increase the solubility of Mn- and Fe-containing precipitates or coprecipitates while decreasing the solubility of S containing precipitates or coprecipitates. Changing the redox status of the wastewater stream will also have some direct effects on radionuclide reconcentration. Under more reduced (anaerobic) conditions, U(VI) as UO_2^{2+} , converts to U(IV), a radionuclide that forms much less soluble complexes and sorbs much more strongly to surfaces. Hence, U (as is the case with Tc and, to a lesser extent, I) is more likely to reconcentrate under anaerobic conditions than aerobic conditions. Redox chemistry is discussed in detail in Section 3.3.2 and the effect of redox conditions on redox-sensitive radionuclides is discussed separately in Chapter 4.0: Co in Section 4.3.1, I in Section 4.5.1, Mn in Section 4.6.1, Tc in Section 4.8.1, and U in Section 4.10.1.

2.3.1.4 Anaerobic Attached Growth

Anaerobic attached-growth processes include anaerobic filters and expanded-bed processes. Anaerobic filters are generally used for low-strength wastes and consist of an upflow reactor similar to a packed-bed reactor. Expanded-bed processes involve pumping the wastewater through a bed of filter medium (sand, coal, or expanded aggregate) that has anaerobic microorganisms attached. Much of the effluent is recycled to maintain the flow rate necessary to keep the bed in an expanded state.

2.3.2 Chemical Processes

Chemical processes are used to 1) precipitate unwanted constituents in the wastewater, 2) flocculate suspended organic or inorganic solids, and 3) disinfect wastewater. These processes are always used in conjunction with physical or biological processes to meet treatment objectives. About 13 percent of the wastewater treatment plants surveyed, used chemical additives (Table 2.1) (U.S. Environmental Protection Agency 1988). The mechanism by which these additives achieve their objective and impact on contaminant

Table 2.6 Summary of important chemical reactions that cause phosphate coprecipitation when limestone, alum, or iron(III) is added to sewage waste

Reaction	Precipitates
Limestone - CaMg(CO₃)₂	
1. $5 \text{Ca}^{+2} + 3 (\text{PO}_4)^{-3} + \text{OH}^- \rightarrow \text{Ca}_5(\text{PO}_4)_3(\text{OH})$	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$
2. $\text{Mg}^{+2} + 2 \text{OH}^- \rightarrow \text{Mg}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$
3. $\text{Ca}^{+2} + (\text{CO}_3)^{-2} \rightarrow \text{CaCO}_3$	CaCO_3
Alum - Al₂(SO₄)₃•18 H₂O or Al₂(SO₄)₃•14 H₂O	
4. $\text{Al}^{+3} + (\text{PO}_4)^{-3} \rightarrow \text{AlPO}_4$	AlPO_4
5. $\text{Al}^{+3} + 3 \text{OH}^- \rightarrow \text{Al}(\text{OH})_3$	$\text{Al}(\text{OH})_3$
Iron(III) - FeCl₃ or Fe₂(SO₄)₃	
6. $\text{Fe}^{+3} + (\text{PO}_4)^{-3} \rightarrow \text{FePO}_4$	FePO_4
7. $\text{Fe}^{+3} + 3 \text{OH}^- \rightarrow \text{Fe}(\text{OH})_3$	$\text{Fe}(\text{OH})_3$

reconcentration is further discussed in Sections 3.2.1 and 3.5.3.

2.3.2.1 Precipitation

The primary objective of chemical precipitation techniques used in secondary treatment is the removal of inorganic phosphate (Equations 4 and 6 in Table 2.6). This removal is accomplished by adding chemicals that will precipitate phosphate, typically as the pyrophosphate anion. The most common chemicals used today are alum [Al₂(SO₄)₃•18H₂O and Al₂(SO₄)₃•14H₂O], ferric chloride (FeCl₃), ferric sulfate [Fe₂(SO₄)₃ and Fe₂(SO₄)₃•3H₂O], ferrous sulfate (FeSO₄•7H₂O), lime [Ca(OH)₂], and limestone [CaMg(CO₃)₂] (Table 2.6). The decision to use one precipitating compound over another is usually driven not only by its performance but also by its availability and cost.

Iron(III) salts and alum can be added at a variety of different points in the treatment process, but adding them after the secondary treatment usually results in greater phosphate removal. The reason for this is that the secondary treatment usually transforms the polyphosphates and organic phosphates to orthophosphates, a form more easily removed from solution via precipitation. Iron(III) salts and alum react with soluble orthophosphate to produce a precipitate of low

solubility. Organic phosphates and polyphosphates are removed by more complex reactions and by adsorption onto floc particles. The amount of alum and iron(III) chloride added to a wastewater stream is primarily dictated by the amount of phosphates and the likely chemical form of the phosphates. These trivalent metals are generally applied in a molar ratio in the range of 1 to 3 metal ions to 1 phosphate ion. The typical Al (from alum):P molar ratio required for a 75, 85, and 95 percent reduction in phosphate concentration in wastewater is 1.4:1, 1.7:1, and 2.3:1, respectively (U.S. Environmental Protection Agency 1987). Lime is commonly added in association with these metal salts to neutralize the acid conditions produced by the hydrolysis of the metal moiety. Theoretically, the minimum solubility of AlPO₄ occurs at pH 6.3 and that of FePO₄ at pH 5.3; however, practical applications yield good phosphate removal anywhere in the range of pH 5.5 to 7.0, which is compatible with most biological treatment processes.

Lime is not used by itself for phosphate removal because of 1) the substantial increase in the mass of sludge to be handled compared to metal salts and 2) the operation and maintenance problems associated with the handling, storing, and feeding of lime. Because lime reacts with the alkalinity of the wastewater (Equation 3 in Table 2.6), the quantity of lime required will, generally, be independent of the amount of

2 Wastewater

phosphate present and will depend primarily on the alkalinity of the wastewater. The quantity of lime required to precipitate wastewater phosphate is typically 1.4 to 1.5 times the total alkalinity, expressed as CaCO_3 . Coprecipitation solely with lime is usually not feasible because a high pH value is required to precipitate phosphate. When lime is added to raw wastewater or to secondary effluent, pH adjustment is usually required prior to subsequent treatment or disposal. The calcium and the hydroxide of the lime react with any orthophosphate present to form an insoluble hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH}$] (Equation 1 in Table 2.6). A typical dosage for lime treatment is in the range of 75 to 250 mg L^{-1} as $\text{Ca}(\text{OH})_2$ when the pH of the effluent is between 8.5 and 9.5. Ferrous sulfate and lime are sometimes added together for the removal of phosphates. The ferrous sulfate is converted to ferrous bicarbonate that, in turn, reacts with dissolved oxygen and lime to form ferrous hydroxide. The ferrous hydroxide is next oxidized by O_2 to ferric hydroxide, the desired form of the iron. Ferric sulfate may take the place of ferrous sulfate, and its use often eliminates the need for lime and dissolved oxygen.

The addition of these chemicals also will affect the concentration of nontargeted dissolved species, such as radionuclides and heavy metals, through the formation of mixed oxide and phosphate coprecipitation that provides surfaces for sorption. For instance, the addition of iron(III) chloride to a wastewater stream may form not only the low-solubility precipitate of FePO_4 (Equation 6 in Table 2.6), but it may also form $\text{Fe}(\text{OH})_3$ (Equation 7 in Table 2.6). This solid may act as a sorbent for metals, if the pH of the system is sufficiently high ($\text{pH} > 6.0$) to give a negative charge on the particle surface. Therefore, radionuclide metals, such as Co, Cs, Mn, and especially Am, Th, and U, may be reconcentrated by the addition of Al- and Fe(III)-salts in high pH systems. Conversely, the radionuclides, I and Tc, are more likely to be reconcentrated via sorption by those chemical additives in low pH systems ($\text{pH} < 5$). This pH dependency for concentration is described in more detail in Sections 3.3.1 and 3.3.2.

2.3.2.2 Flocculation

Chemical additives are also used to facilitate the sedimentation of suspended solids through flocculation. The process by which this is accomplished via

chemical additives is discussed in more detail in Section 3.2.1. Because flocculation and precipitation can occur concurrently, it is impossible to differentiate between the two processes. Similar chemicals used to precipitate phosphates are also used to flocculate phosphate from the wastewater stream. For every mole of alum added to the wastewater stream, two moles of aluminum hydroxide are produced (Equation 5 in Table 2.6). The sparingly soluble aluminum hydroxide is a gelatinous floc that settles slowly through the wastewater, sweeping out suspended material and producing other changes. For every mole of iron(III) added to the wastewater stream, one mole of iron hydroxide is produced (Equation 7 in Table 2.6). The iron hydroxide also forms a gelatinous floc that removes dissolved and particulate phosphates from the solution. Alum and iron(III) additions are likely to induce radionuclide reconcentration via coprecipitation (Section 3.3.1).

Polymers are long-chained organic molecules containing ionizable subunits and may act as flocculants by lowering the surface charge of the wastewater particles, thereby reducing particle-particle repulsive forces that keep the particles in suspension. Because wastewater particles are normally charged negatively, cationic polyelectrolytes are used for this purpose. Polymers may also induce flocculation of suspended solids by bridging. In this case, polymers that are anionic and nonionic become attached at a number of adsorption sites to the surface of the particles found in the settled effluent. A bridge is formed when two or more particles become adsorbed along the length of the polymer. Bridged particles become intertwined with other bridged particles during the flocculation process. The size of the resulting three-dimensional particles grows until they can be removed easily by sedimentation. Finally, polymers may also induce flocculation by a combination of these two phenomena, referred to as the flocculation-bridging phenomenon. These polymers are typically extremely high-molecular-weight molecules that flocculate suspended solids by bridging and lowering the surface charge.

2.3.2.3 Adsorption

Adsorption is the process describing the partitioning of dissolved inorganic or organic constituents at the solid-liquid interface (Sections 2.4.5.1 and 3.3.3). Adsorption is not a common wastewater treatment process, with <5 percent occurrence (U.S. Environmental

Protection Agency 1988). In the past, the adsorption process has not been used extensively in wastewater treatment, but demands for a higher quality treated wastewater effluent have led to an intensive re-examination and use of the process of adsorption onto activated carbon. Many adsorbents are available, but activated carbon is by far the most commonly used compound (in both granular and powdered forms). Activated-carbon treatment of wastewater is usually thought of as a polishing process for water that has already received normal biological treatment. The activated carbon, in this case, is used to remove a portion of the remaining dissolved organic matter and, therefore, is likely to promote the re-concentration of those radionuclides that form strong complexes with dissolved organic matter, such as Am, Th, and U. Depending on the means of bringing the carbon in contact with the water, the particulate matter that is present may also be removed. Activated carbon can be regenerated and the waste removed by combustion. Gas-phase adsorption of the volatile odorous compounds and trace organic pollutants that may be emitted from various wastewater operations are also usually recovered via adsorption to activated-carbon products.

2.3.2.4 Disinfection

Disinfection is the selective destruction of disease-causing organisms, primarily bacteria, viruses, and amoebic cysts. Disinfection can be accomplished by chemical, physical, mechanical, and radiation sources. Chemical agents used for disinfection include chlorine and its compounds, bromine, iodine, ozone, phenol and phenolic compounds, alcohols, heavy metals and related compounds, dyes, soaps and

synthetic detergents, quaternary ammonium compounds, hydrogen peroxide and various alkalis, and acids. Physical agents used include heat and sunlight. Mechanical disinfection agents include screens, filters, and sedimentation tanks.

Chlorine is the most popular disinfectant being used today. The most common chlorine compounds used in wastewater treatment plants are chlorine gas (Cl_2), calcium hypochlorite [$\text{Ca}(\text{OCl})_2$], sodium hypochlorite (NaOCl), and chlorine dioxide (ClO_2). Calcium and sodium hypochlorite are most often used in very small treatment plants, where simplicity and safety are far more important than cost. Because chlorine dioxide does not react with ammonia, it is also used in a number of treatment facilities.

Many organic compounds in wastewater may react with the chlorine to form toxic refractory compounds that are resistant to physical or biological degradation. To minimize these adverse effects, dechlorination of wastewater is usually necessary. Dechlorination through the addition of sulfur dioxide gas is a very reliable process. In practice, 1.0 mg L^{-1} of sulfur dioxide will be required for the dechlorination of 1.0 mg L^{-1} of chlorine residue (expressed as Cl_2). Because the reactions of sulfur dioxide with chlorine and chloramine are nearly instantaneous, contact time is not usually a factor and contact chambers are not used; however, rapid mixing at the point of application is required. Chlorination is usually performed in a baffled contact chamber (Figure 2.13). Dechlorination usually follows chlorination and is performed in the same type of reactor. If the two additional areas are far enough apart, the steps can be performed in a single reactor.

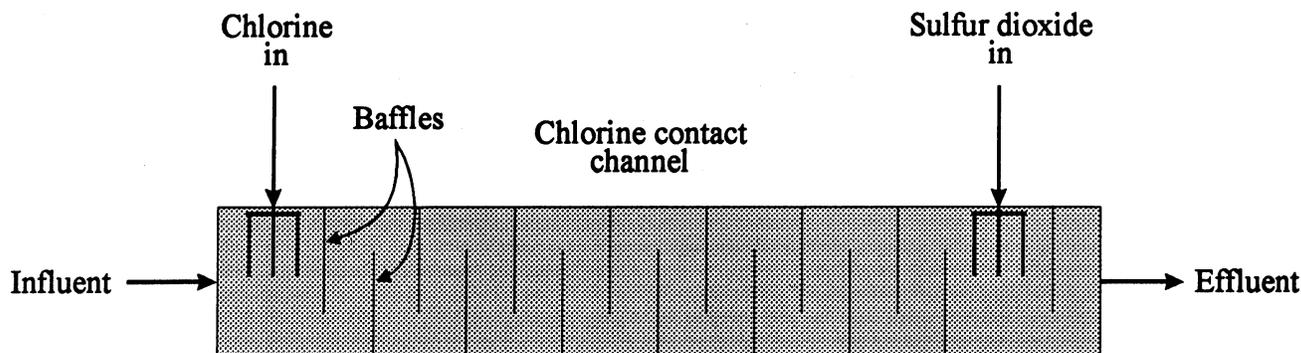


Figure 2.13 Chlorination/dechlorination contact chamber for disinfection of wastewater

2.4 Tertiary Treatment

The effluent from secondary treatment often contains suspended and dissolved substances that can adversely impact the water quality of receiving streams. These environmentally threatening constituents may include organic matter, suspended solids, nutrients (such as nitrogen and phosphorus) and specific toxic compounds (such as volatile organic compounds and heavy metals). To comply with the increasingly stringent permit requirements, additional treatment (that is, tertiary treatment) is often implemented downstream from conventional secondary treatment processes (Figure 2.1). The type of tertiary processes used depends on the target constituent(s) to be removed and the water quality of the receiving stream. Table 2.7 summarizes the various treatment processes used in tertiary treatment. Many of the tertiary treatment processes discussed are used in primary and secondary treatment. However, they can also be considered tertiary processes when they are implemented downstream from the secondary treatment phase of the plant.

The extent to which radionuclide reconcentration is likely to occur during tertiary treatment will clearly depend on the specific treatment processes involved. Because tertiary treatments are designed to remove targeted constituents and the targeted constituents to date have never been radionuclides, the ability of these processes to reconcentrate radionuclides will depend on how similar the chemistry of the radionuclide is to that of the targeted constituent. For instance, if the treatment process is the addition of sodium bisulfite to remove Cr(VI) [via reductive precipitation of Cr(III); Section 3.5.3; Patterson (1985) and Cushnie (1985)], it is very likely that dissolved Tc and U will also be removed from solution and reconcentrated in the sludge. However, this treatment process would have little effect on redox insensitive radionuclides, such as Cs and Sr.

2.4.1 Filtration

Filtration processes are used to remove residual inorganic and organic solids and dissolved species from secondary treatment effluents. However, in some cases, primary treatment effluent is filtered. Specific filtration processes, which are often referred to as effluent-polishing techniques, include granular med-

ium filters, microscreening, ultrafiltration, and reverse osmosis. The type of filtration and how it is implemented depend on the target solid or dissolved species to be removed. Each of the four specific filtration processes are further discussed in the following subsections.

2.4.1.1 Granular Medium Filtration

Removal of suspended biological floc (that is, small, nonsettleable organic solids) from the effluent of secondary settling basins and clarifiers is typically achieved using granular medium filters. This physical separation process is also implemented to remove residual suspended precipitates generated by chemical precipitation treatment for the removal of phosphorus. In addition to serving as a polishing (that is, particle removal) step for secondary biological treatment and chemical precipitation, granular medium filters can function as a pretreatment step for the removal of suspended solids before discharging secondary treatment effluent to activated-carbon contactors (Section 2.4.5.1).

Many types of granular medium filters are used in wastewater treatment and are classified according to their mode of operation, filter-bed characteristics, direction of flow, and cleaning process. The two phases of the filtration operation are filtration and regeneration/cleaning (referred to as backwashing).

The mode of operation depends on how these two phases are conducted. Semicontinuous filters conduct the filtration and cleaning phases in sequence, while continuous filters conduct the filtration and cleaning phases simultaneously. The filter-bed characteristics include the type of medium used, stratification (that is, layering of granules in the bed) of the medium, and depth. The type of backwashing technique determines if the filter medium is stratified.

The type of filter bed can be designated mono-medium, dual-medium, and multi-medium, depending on the number of media contained in the filter bed. Medium characteristics important to the filter design include grain size, grain-size distribution, grain shape, density, composition, and surface charge. These characteristics affect the particle-removal efficiency.

Table 2.7 Tertiary treatment processes

Process	Type	Function	Equipment and Chemicals
Filtration	Physical	Suspended solids and dissolved inorganic substances removal	Granular medium filters, microstrainers, ultrafiltration, reverse osmosis; alum and polymer filter aids
Biological nitrification	Biological	Ammonia oxidation	Combined- and separate-stage suspended-growth and attached-growth processes
Biological nitrification and denitrification	Biological	Nitrogen removal	Four-Stage Bardenpho process, oxidation ditch
Separate-stage biological denitrification	Biological	Nitrate removal	Suspended-growth processes
Mainstream phosphorous removal	Biological	Biological phosphorus removal	A/O process
Sidestream phosphorous removal	Biological	Biological phosphorus removal	PhoStrip process
Biological nitrification - denitrification and phosphorus removal	Biological	Combined nitrogen and phosphorus removal	A ² /O, five-stage Bardenpho, University of Cape Town, Virginia Initiative Plant processes
Air stripping	Physical	Nitrogen and volatile organic compounds removal	Packed towers, diffused aeration
Breakpoint chlorination	Chemical	Nitrogen removal	Chlorine contact chamber
Ion exchange	Chemical	Nitrogen and dissolved inorganic solids removal	Ion exchange columns
Chemical precipitation	Chemical	Phosphorus and dissolved inorganic substances removal	Metal salts, lime
Electrodialysis	Chemical	Dissolved inorganic substances removal	Stacked membrane systems
Carbon adsorption	Chemical	Toxic compounds and refractory organics removal	Fixed-bed contactors
Chemical oxidation	Chemical	Toxic compounds and refractory organics removal	Contact chambers

Mono-medium filters typically use sand or anthracite (a type of coal) (Figure 2.14a). Shallow-bed mono-medium filters (stratified) have a bed depth of 0.40 m or less. Conventional mono-medium filters (stratified) are designed with a typical bed depth range of 0.60 to 0.90 m. Both of these mono-medium filters are operated in the semicontinuous mode. Deep-bed mono-medium filters (unstratified) are operated in the

continuous mode and have a typical bed depth of 1.80 m.

Dual-medium filters (stratified) typically consist of 1) anthracite and sand, 2) activated carbon and sand, 3) resin beads and sand, or 4) resin beads and anthracite (Figure 2.14b). Typical bed depth is 0.90 m, and this type of filter can be operated in either the

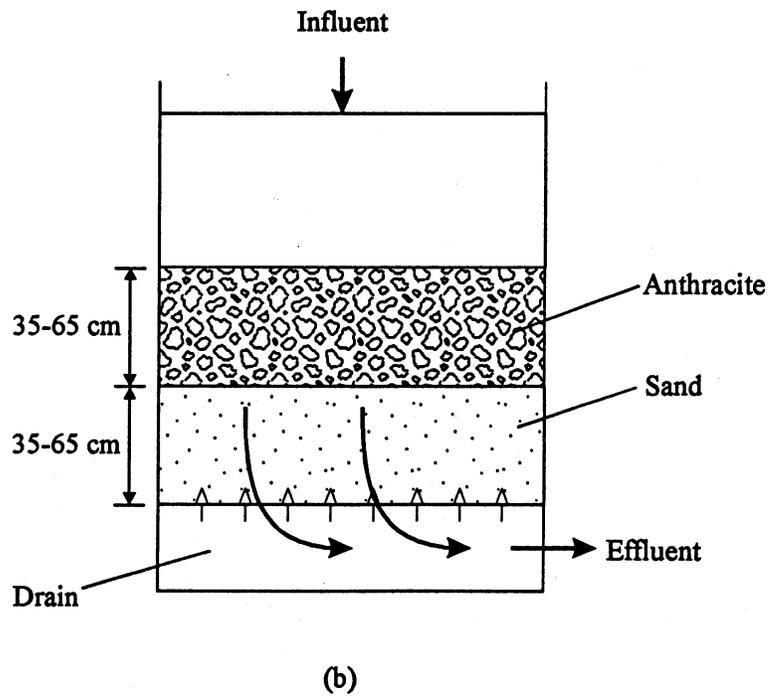
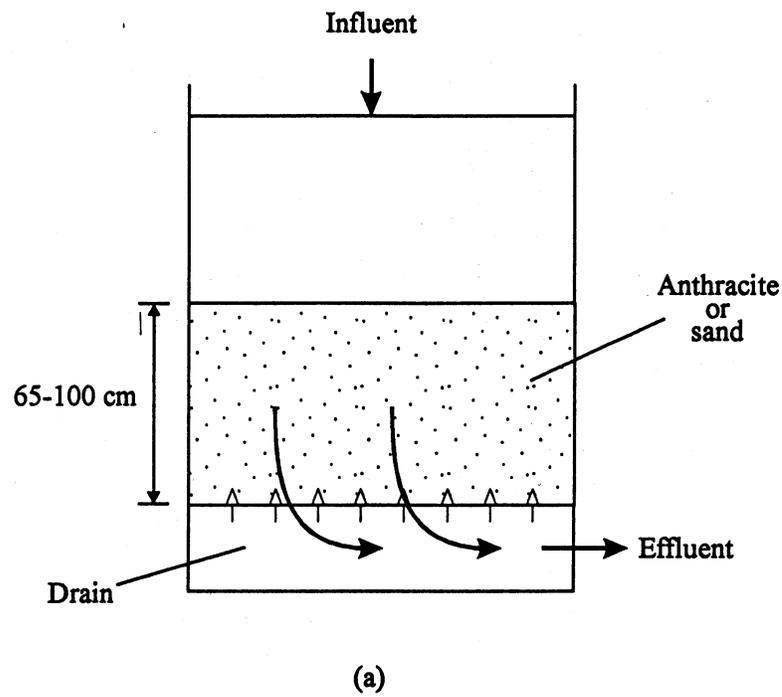


Figure 2.14 Granular medium filters for tertiary treatment of wastewater. (a) mono-medium downflow; (b) dual-medium downflow

semicontinuous or continuous modes. A schematic of a conventional dual-medium, downflow, granular medium filter is shown in Figure 2.14b.

Multi-medium filters typically consist of 1) anthracite, sand, and garnet or ilmenite (FeTiO_3); 2) activated carbon, anthracite, and sand; 3) weighted, spherical resin beads (charged and uncharged), anthracite, and sand; or 4) activated carbon, sand, and garnet or ilmenite. A typical multi-medium semicontinuous filter has a bed depth of 0.90 m.

Filter backwashing systems are used to regenerate and clean the filter medium(s). The backwash step is achieved by reversing the flow through the filter bed until the filter medium is fluidized (expanded). After the bed is fluidized, the material accumulated in the filter bed is washed away. The washwater is collected and returned either to the primary settling facilities or to the biological treatment processes. Surface water wash agitation or an auxiliary air scour are often included in the backwashing system to enhance the cleaning process.

Organic polymers and alum are chemical additives commonly used to enhance granular medium filter performance for settled secondary effluent filtration. These chemical filter aids are added to the settled secondary effluent prior to the filtering process to promote fine-particle aggregation, insoluble precipitate formation, and dissolved constituent sorption. The end result is an increase in particle size that is more easily entrapped and accumulated in the granular medium filter downstream (Section 3.2.1 and 3.5.3).

2.4.1.2 Microscreening

Microscreening is a filtration technique used to remove a portion of residual suspended solids from secondary settling tank effluents and stabilization pond effluents (Figure 2.15). The filter is composed of a screening material (stainless steel or polyester screen cloths) with openings ranging from 15 to 60 μm . The screen is fixed to the periphery of a rotary drum, which is partially submerged in the wastewater (approximately 75 percent of the drum diameter). The wastewater enters one end of the drum, which is rotating at a very slow speed (no more than

4 revolutions/min), and flows outward through the filter. The solids collected on the filter are backwashed into a collection trough using high-pressure jets. The collection trough is located at the highest point of the drum above the wastewater surface. This technique typically achieves 55 percent suspended solids removal.

2.4.1.3 Ultrafiltration

Ultrafiltration is a pressure-driven filtration process used to remove colloidal particulates (typically 0.001 to 1 μm) and large molecules (> 5000 molecular weight) from liquid streams. Typical operating pressures range from 70 to 690 kN/m^2 (American Water Works Association 1990). This physical separation process has been investigated in various tertiary treatment applications, specifically for the removal of dissolved inorganic substances. Although ultrafiltration has proved to be technically feasible, cost and operational requirements have limited its municipal wastewater treatment applications. However, given the success of ultrafiltration for effective separation of colloids and macromolecules, this process is a potential treatment option for future tertiary treatment applications.

Full-scale ultrafiltration systems are operated in the continuous mode. The filter is typically made of a polymeric membrane material, such as cellulose acetate, constructed in a spiral wound or hollow-fiber configuration. The membrane material is designed with a uniform pore size, ranging from 0.003 to 1 μm in diameter. The influent stream comes into contact with the membrane surface using an applied pressure-driving force. Colloids and macromolecules with effective sizes in excess of the membrane pore size are held back, while the remainder of the influent passes through the membrane pores (that is, the filtrate). Ideally, the target species to be removed are concentrated in the fraction held back, thus achieving the desired separation. The type of species and their respective concentrations will determine how the held back waste stream is handled and disposed. Recent studies indicate that ultrafiltration is a suitable pretreatment step for reverse osmosis and also could be used for the removal of phosphates (Water Pollution Control Federation 1983).

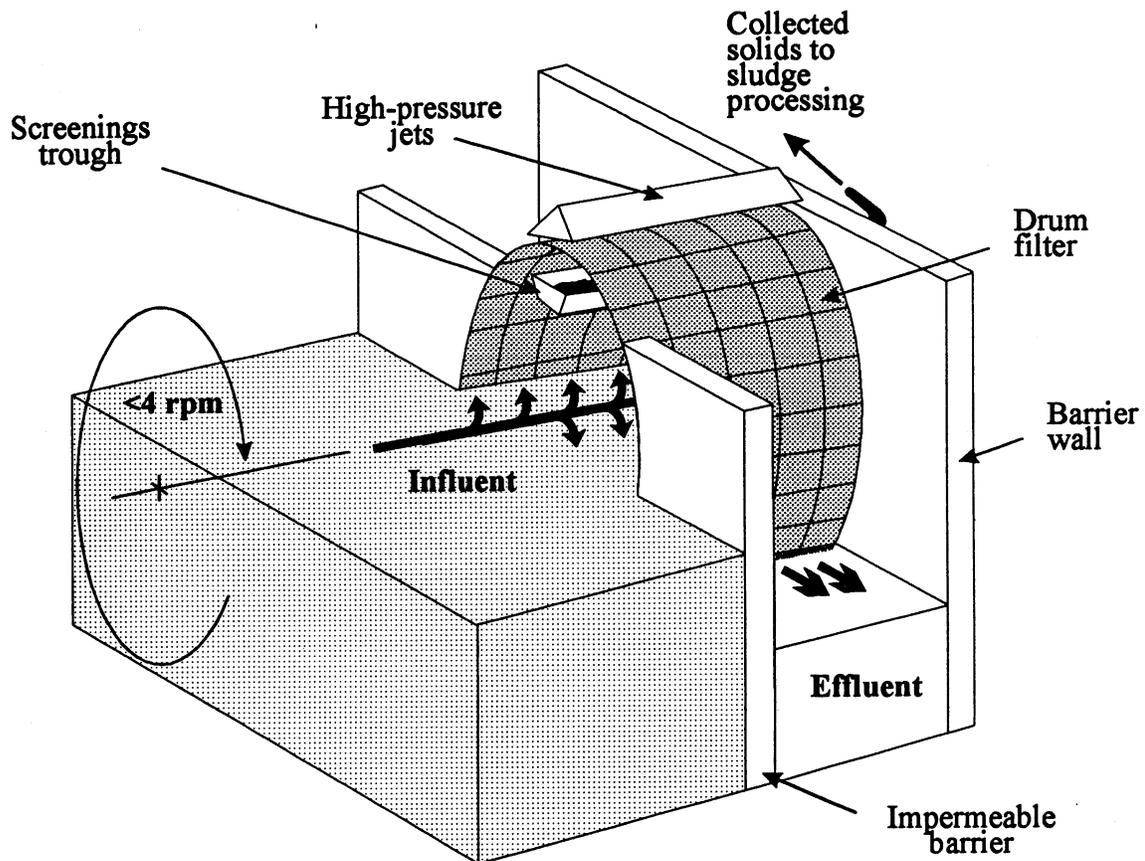


Figure 2.15 Microscreen filtration technique for clarification of effluents of secondary treatment processes

2.4.1.4 Reverse Osmosis

Similar to ultrafiltration, reverse osmosis is a pressure-driven filtration process that uses a semi-permeable membrane filter typically made of cellulose acetate or nylon. However, reverse osmosis is used to separate dissolved salts from water, requires much higher operating pressures than ultrafiltration (1380 to 10,340 kN/m^2), and results in a higher operating cost (American Water Works Association 1990). The separation is achieved by filtering the influent through the semipermeable membrane at a pressure greater than the osmotic pressure caused by the salts present in the influent. The salts are held back and concentrated, thus achieving the desired separation. Handling and disposal of the held back waste stream depend on the type and concentration of salts present.

Reverse osmosis has been used as a tertiary treatment process for the removal of phosphorus. Removal efficiencies of 90 to 100 percent for phosphorus entering the treatment plant have been reported (Metcalf and Eddy, Inc. 1991). However, reverse osmosis is not frequently used because of its high operating cost. Also, prefilters (such as granular medium and ultrafiltration) are required to remove particulate matter that can easily clog the reverse osmosis membrane. Despite its limitations, reverse osmosis is a treatment option for future tertiary treatment applications.

2.4.2 Biological Nutrient Control Processes

The primary nutrients of concern in treated wastewater are nitrogen and phosphorus. Discharged wastewater

containing these nutrients can accelerate eutrophication (the depletion of dissolved oxygen from natural waters) of lakes and reservoirs and the growth of algae and rooted aquatic plants in shallow streams. Stimulated algae and aquatic plant growth can adversely impact the beneficial uses of the receiving waters, especially when these waters are used for fish propagation, recreation, and water supplies. Significant concentrations of nitrogen can deplete the dissolved oxygen of receiving waters, exhibit toxicity toward aquatic life, affect chlorine disinfecting efficiency (which poses a public health hazard), and degrade the suitability of wastewater for reuse. Thus, control of nitrogen and phosphorus in primary and secondary treatment effluents is becoming increasingly important for water quality management and is a primary objective of tertiary treatment.

Biological, chemical, and physical processes are used to control wastewater nitrogen and phosphorus concentrations before discharge to the receiving water. The following discussion will focus on the biological nitrogen- and phosphorus-removal techniques.

2.4.2.1 Biological Nitrogen Removal

Nitrogen in municipal wastewater can exist in many forms (Figure 2.16). As the wastewater is treated, nitrogen undergoes several transformations that affect its final form in the discharged wastewater. Biological treatment processes are designed to achieve specific nitrogen transformations, resulting in a final nitrogen form that will not pose adverse impacts on the receiving stream or can be easily removed from the

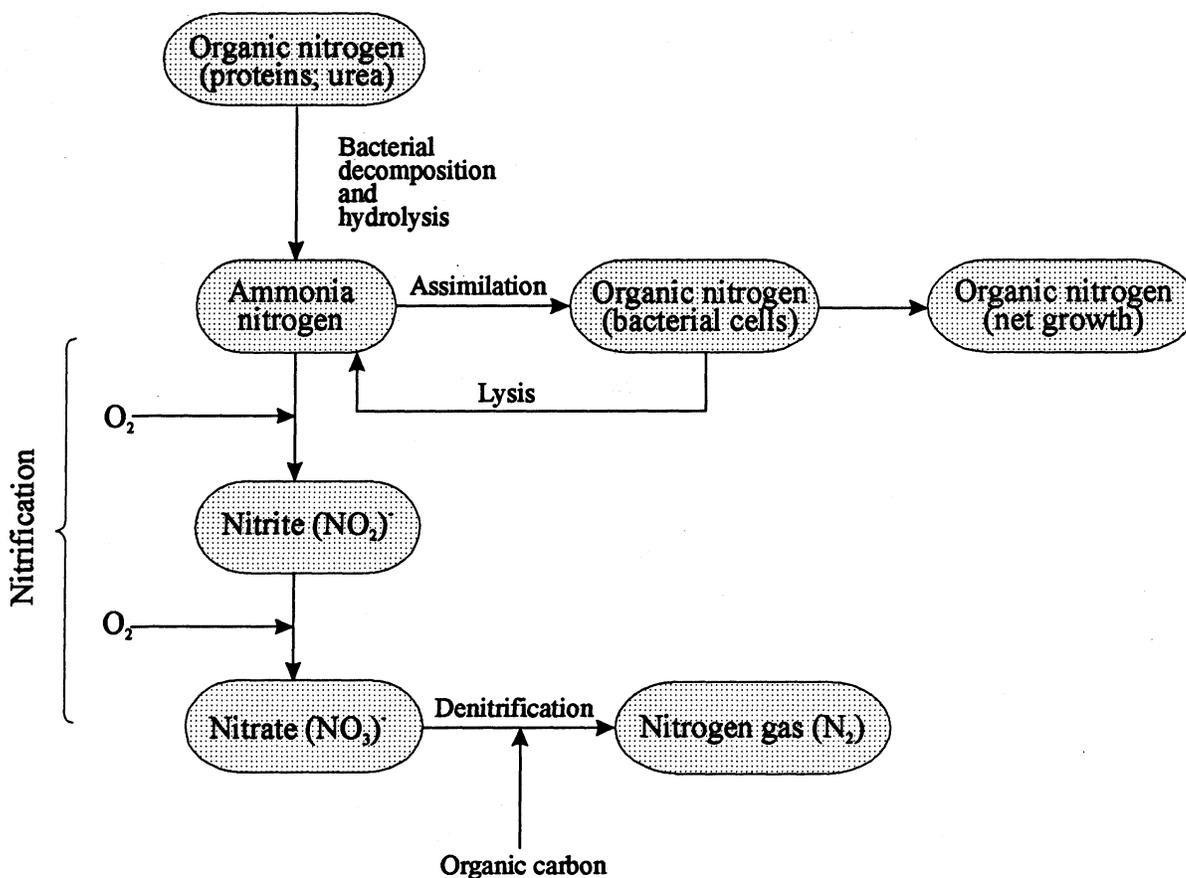


Figure 2.16 Nitrogen transformations occurring in biological treatment of wastewater

wastewater prior to discharge. The two principal mechanisms for removal of nitrogen are assimilation and nitrification/denitrification.

Assimilation of ammonia nitrogen by microbes occurs in both suspended-growth and attached-growth biological process used in secondary treatment for the removal of carbonaceous BOD (Section 2.3.1) because nitrogen is a microbial nutrient. The assimilated nitrogen is incorporated into the cell mass, which is eventually collected as sludge. The fraction of influent nitrogen not removed by assimilation is removed using nitrification followed by denitrification. Nitrification converts ammonia nitrogen to nitrate; denitrification converts the nitrate to nitrogen gas for removal. Nitrification, separate-stage denitrification, and nitrification/denitrification are discussed in the following paragraphs.

The objective of biological nitrification is to convert ammonia nitrogen, which can exert both an oxygen demand and ammonia toxicity on the receiving stream, to nitrate. Nitrification is a two-step aerobic process that uses two bacteria genera, *Nitrosomonas* and *Nitrobacter*. In the first step, *Nitrosomonas* converts ammonium (NH_4^+) to nitrite (NO_2^-). In the second step, *Nitrobacter* converts nitrite to nitrate (NO_3^-). This conversion process effectively reduces the concentration of ammonia nitrogen in the wastewater and, in some cases, will satisfy the receiving water requirements for nitrogen oxygen demand and ammonia toxicity. Nitrification typically removes 5 to 20 percent of the total nitrogen entering the nitrification process reactor (U.S. Environmental Protection Agency 1979). Carbon oxidation is the removal of carbonaceous BOD using secondary biological treatment (Section 2.3.1).

Nitrification processes are classified as single or separate stage. Single-stage nitrification uses a single process facility to conduct both nitrification and carbon oxidation. Any of the suspended-growth aerobic biological processes discussed in Section 2.3.1.1 (Figure 2.17a) apply in nitrification and carbon oxidation. The biomass generated (such as from cell growth) from the carbon oxidation and nitrification processes are settled and collected in the secondary settling tank.

Nitrification conducted in a separate reactor downstream from the biological carbon oxidation reactor is referred to as separate-stage nitrification (Figure 2.17b). Greater process flexibility, reliability, and optimization are the major advantages for using separate-stage versus single-stage processes. Both suspended-growth and attached-growth aerobic processes can be used to achieve separate-stage nitrification. Separate-stage suspended-growth nitrification processes are designed in a similar manner to the biologically activated-sludge process (Section 2.3.1.1). Trickling filters and rotating biological contactors are two attached-growth aerobic processes typically used for separate-stage suspended-growth nitrification. Removal of the biomass produced in the nitrification process requires a subsequent settling facility, designated as the nitrification clarifier.

The objective of separate-stage denitrification is the removal of nitrate generated from an upstream nitrification process (Figure 2.18a). Denitrification is the biological conversion of nitrate to nitrogen gas under anoxic (without oxygen) conditions (Figure 2.16). The nitrite is then further reduced by the bacteria to the following gaseous products for removal: nitric oxide, nitrous oxide, and nitrogen gas. Denitrification requires carbon (organic matter) in the wastewater to provide an energy source for the nitrogen-reducing bacteria. Because denitrification is conducted in a separate reactor, an external carbon source (typically methanol) is required. Both suspended-growth and attached-growth processes are used.

Suspended-growth, separate-stage denitrification systems are designed similarly to the biologically activated-sludge process (Section 2.3.1.1). The nitrogen gas released during denitrification becomes attached to the organic solids and adversely impacts their ability to settle in the downstream denitrification clarifier. Therefore, a final aeration basin or aeration channel between the denitrification zone and the clarifier is used to strip the nitrogen gas bubbles from the solids. In the early 1970s, separate-stage denitrification was the generally accepted method for biological denitrification. However, the associated space requirements, external carbon source requirement, and cost for additional denitrification basins and clarifiers, compared to combined nitrification/denitrification systems, are some major disadvantages of the separate-stage denitrification process.

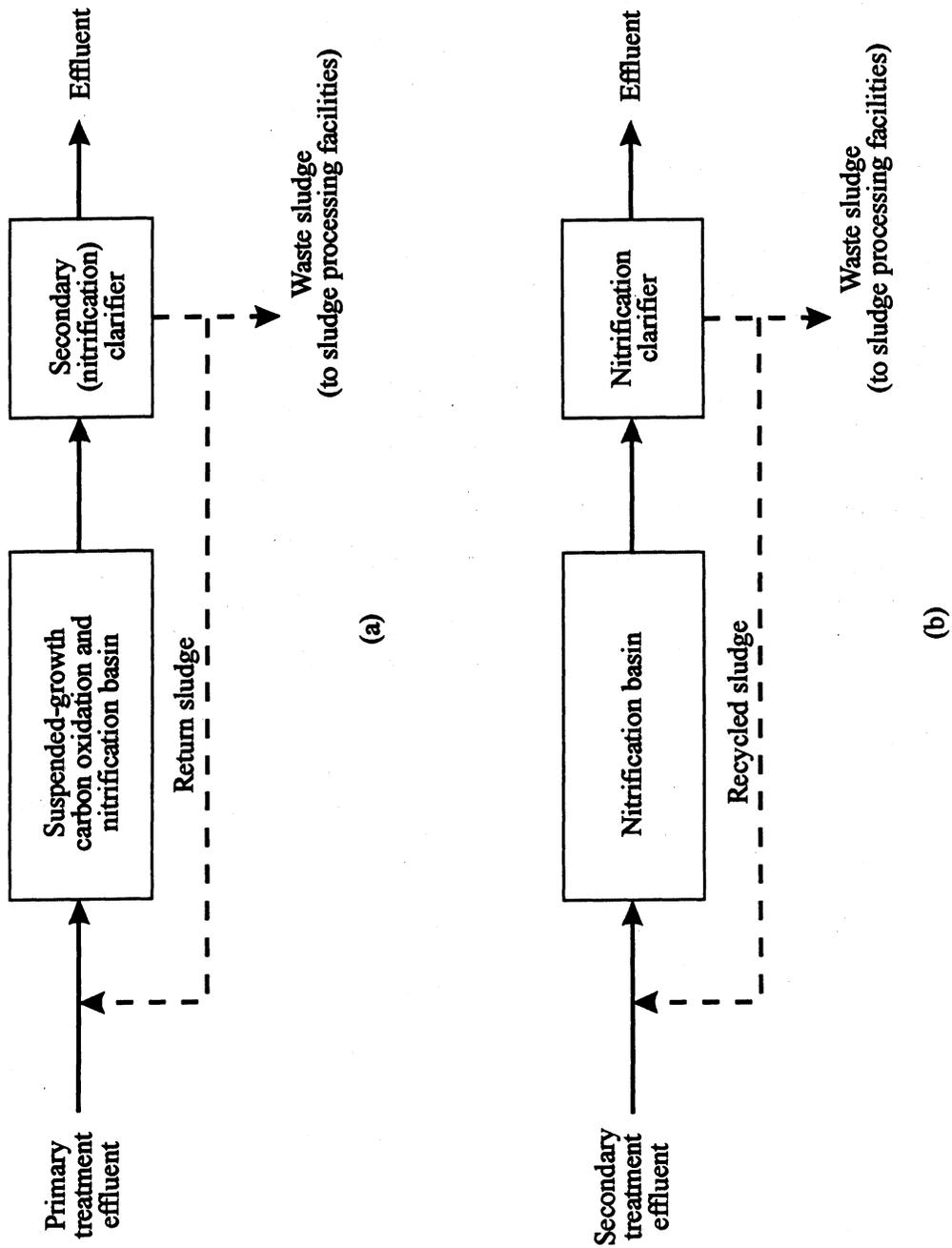


Figure 2.17. Suspended-growth nitrification processes. (a) single-stage nitrification; (b) separate-stage nitrification

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Biological nitrification/denitrification is a two-step nitrogen removal process conducted in the same process reactor. Nitrification, the first step, is followed by denitrification, the second step. In combined nitrification/denitrification process reactors, single-sludge systems, naturally occurring organic matter, and biomass from endogenous decay are the primary sources of carbon for the denitrification step.

Biological nitrification/denitrification is a good nitrogen removal method for the following reasons: 1) high potential removal efficiency (70 to 95 percent), 2) good process stability and reliability, 3) easy process control, 4) small land area requirements, and 5) moderate cost (Metcalf and Eddy, Inc. 1991).

Combined nitrification/denitrification systems are designed to achieve carbon oxidation, nitrification, and denitrification. They use suspended-growth biological processes to achieve both carbon oxidation and nitrification in an aerobic zone (see discussion of combined carbon oxidation and nitrification in Section 2.4.2.1) and denitrification in an anoxic zone. The four-stage proprietary Bardenpho process and the oxidation ditch are common single-sludge systems (Figure 2.18b). Specific advantages for using a combined system include 1) reduction in the volume of air needed to achieve nitrification and BOD removal, 2) supplemental sources of carbon (such as methanol) for denitrification are not required, and 3) intermediate clarifiers and recycled sludge facilities required for staged nitrification/denitrification systems are not necessary (Metcalf and Eddy, Inc. 1991).

The Bardenpho process (Figure 2.18b) is a four-stage system containing two anoxic and two aerobic zones. Raw wastewater or primary effluent initially enters the first anoxic denitrification basin, where the carbon present in the wastewater provides the energy source for denitrification of recycled mixed liquor from the downstream carbon oxidation and nitrification aeration basin. The ammonia nitrogen present in wastewater passes unchanged through the first anoxic denitrification zone to the first aeration basin, where it is nitrified. Additional denitrification of the nitrified mixed liquor from the first aeration basin is achieved in the second anoxic zone. A final aerobic zone is used to strip the gaseous nitrogen generated from the denitrification process. The effluent from the second aerobic zone is clarified in the secondary settling tanks.

The oxidation ditch (Figure 2.18c) consists of an oval-shaped channel that houses a mechanical aeration device (such as a paddle wheel). The aerator is positioned to create one aerobic zone (downstream from the aerator) and one anoxic zone (upstream from the aerator). The wastewater enters the ditch at the upstream limit of the anoxic zone, where the carbon present in the wastewater is used for denitrification. Carbon oxidation and nitrification occur in the aerobic zone. Gaseous nitrogen, generated in the anoxic zone, is air stripped from the wastewater by the aerator.

The effluent from the ditch is removed at the end of the aerobic zone and transferred to a settling facility for clarification.

2.4.2.2 Biological Phosphorus Removal

Microorganisms use phosphorus in wastewater, which primarily exists as orthophosphate (PO_4^{3-}), polyphosphate (P_2O_7), and organically bound phosphorus, during cell synthesis and energy transport. The resulting biomass production (that is, cell growth and multiplication) is separated from the wastewater stream by settling, which effectively reduces the influent wastewater phosphorus concentration. Thus, biological treatment is an efficient and effective means of removing phosphorus from the bulk wastewater to prevent eutrophication and stimulated aquatic plant growth in the receiving stream. However, conventional secondary biological treatment only removes 10 to 30 percent of the influent wastewater phosphorus concentration (Metcalf and Eddy, Inc. 1991). Thus, additional (tertiary) biological treatment is often required to reduce the treated wastewater effluent phosphorus concentrations to levels required for the receiving stream's water quality.

The uptake of phosphorus by microorganisms (*Acinetobacter* is the primary phosphorus-removal organism) can be increased above normal levels if the microorganisms are exposed to anaerobic conditions, followed by aerobic conditions. Therefore, biological phosphorus-removal reactors are designed with alternating anaerobic and aerobic zones. The resulting sludge, containing excess phosphorus, is collected in a downstream settling facility where it is wasted (that is, discharged to sludge-processing facilities) or sent to a separated anaerobic reactor. In this separate anaerobic reactor, phosphorus is released from the microorganisms and subsequently removed from the

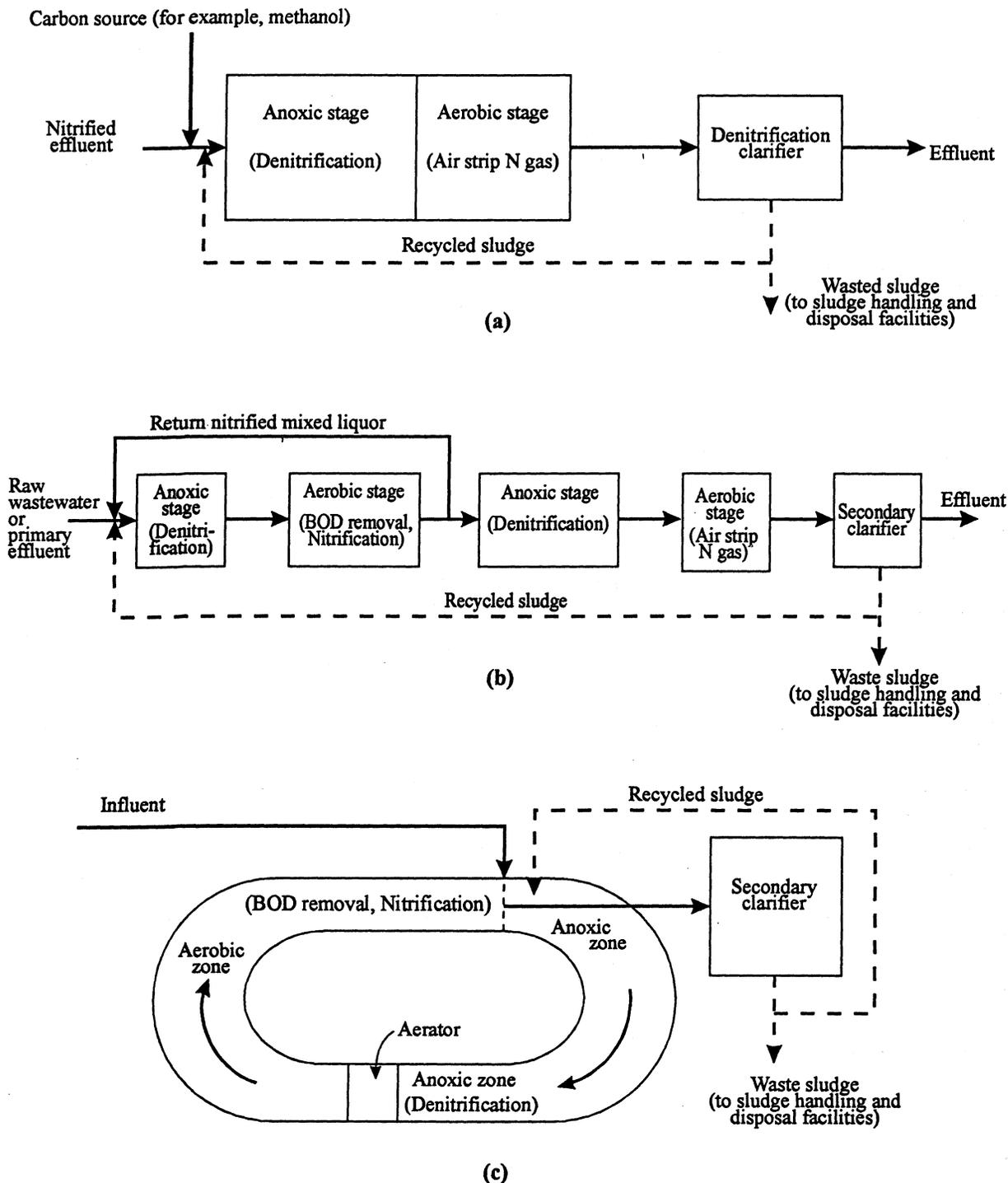


Figure 2.18 Denitrification and nitrification/denitrification processes. (a) suspended-growth separate-stage denitrification; (b) four-stage Bardenpho process; (c) combined carbon oxidation and nitrification/denitrification using the oxidation ditch

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reactor supernatant by chemical precipitation. Biological-phosphorus removal is accomplished in the main secondary biological treatment process (designated mainstream) or in a separated (sidestream) process reactor.

2.4.3 Chemical and Physical Nutrient Control Processes

Both chemical and physical treatment processes are used to remove nitrogen from wastewater. Specific processes include air stripping, breakpoint chlorination, and ion exchange. These nitrogen removal processes, however, are rarely used in tertiary treatment facilities because of cost, inconsistent performance, and operating and maintenance problems.

Removal of phosphorus from wastewater can be accomplished chemically by using chemical precipitation (Section 2.3.2.1). Prior to the development of biological phosphorus-removal processes, chemical precipitation was the standard technique used and is still often used in primary, secondary, and tertiary treatment.

2.4.3.1 Air Stripping

The objective of air stripping is the removal of gaseous ammonia nitrogen from wastewater. The ammonia nitrogen is converted from a liquid to a gaseous phase (referred to as volatilization) by adjusting the pH from 10.5 to 11.5 (usually by adding lime). The wastewater is then contacted with ambient air, using an aeration device, to expedite the transfer of the ammonia gas from the liquid to the gas phase (referred to as air stripping). Packed towers, diffused aeration (that is, bringing air bubbles in contact with the wastewater), and spray nozzles are common air-stripping operations. Air stripping can be controlled for selected ammonia removals, may be able to meet total nitrogen standards, and is not sensitive to toxic substances. This process is most applicable if required seasonally in combination with a lime addition system for phosphorus removal. However, this process is temperature sensitive, is limited to special cases where high pH is required, and is susceptible to fogging and icing in cold weather. Further, ammonia reaction with sulfur dioxide may cause air pollution problems.

Air stripping also has tertiary treatment applications for the removal of volatile organic compounds (such as trichloroethylene) from wastewater. Because they are volatile, these compounds are easily transferred from the liquid to the gas phase, which makes air stripping a feasible removal technology. Diffused aeration is a common air-stripping method for the removal of volatile organic compounds. Among the radionuclides, the concentration of I may be reduced by air stripping. Iodine, particularly when complexed to organic matter, such as ICH_3 , may volatilize at atmospheric pressures (Section 4.5.1).

2.4.3.2 Breakpoint Chlorination

The chemical oxidation of ammonia in wastewater to nitrogen gas and other stable compounds can be achieved using breakpoint chlorination. With proper control, all the ammonia nitrogen in the wastewater can be oxidized. However, the process is sensitive to pH and has a high operating cost because of chemical requirements. Also, high chlorine residuals, which are toxic to aquatic life, are produced. Breakpoint chlorination can also promote trihalomethane formation, which impacts the water quality of the receiving stream. Breakpoint chlorination can be accomplished in the disinfection facility of the WWTP.

2.4.3.3 Ion Exchange

Ion exchange is a chemical process used to remove ammonium (NH_4^+) from wastewater. The wastewater is contacted with an insoluble exchange material, such as resins, that contains cation exchange sites (that is, the exchange material contains chemical functionalities that are negatively charged, electrostatically attached, and bind with cationic species in the solution). Zeolite (such as clinoptilolite) is an effective natural exchange resin that exhibits an exchange selectivity for ammonium (Metcalf and Eddy, Inc. 1991). When wastewater is passed through a column containing zeolite resin, cations attached to the zeolite exchange sites are preferentially displaced by ammonium in the wastewater. When the ion exchange column is exhausted (that is, all of the sites contain ammonium ions), the column is taken off-line and regenerated with lime [$\text{Ca}(\text{OH})_2$]. During regeneration, Ca^{2+} displaces the NH_4^+ accumulated on the zeolite exchange material. The displaced ammonium ion is converted to NH_3 , and this concentrated solution is typically sent to an air-stripping facility to remove the ammonia prior to

discharge. Pretreatment by filtration is usually required to remove suspended solids from the wastewater and to prevent plugging the ion exchange column. Ion exchange is an advantageous nitrogen-removal process because it can be used where climatic conditions prohibit biological nitrification and where stringent effluent standards are required. Also, ion exchange produces a relatively low total dissolved solids effluent, a reclaimable product (aqueous ammonia), and may be able to meet total nitrogen effluent standards. On the other hand, disadvantages associated with ion exchange include resin binding caused by organic matter in the wastewater from biological treatment, pretreatment with filtration to prevent plugging the column with suspended solids, high concentrations of other cations that reduce the ammonia-removal capacity, high capital and operating costs, regeneration products that must be disposed of, and the need for a highly skilled operator (Metcalf and Eddy, Inc. 1991).

2.4.3.4 Chemical Precipitation

Chemical precipitation is a phosphorus-removal technique used in primary, secondary, and tertiary treatment. The location of chemical addition in the treatment plant determines the designated treatment level. The process descriptions, chemical additives, and applications for secondary treatment are discussed in Section 2.3.2. Chemical precipitation used in primary treatment is discussed in Section 2.3.2.1. Chemical precipitation is considered a tertiary treatment process when the location of the chemical addition occurs after the secondary settling facility. This consideration is typically the case when a separate clarifier downstream from the secondary clarifier is used to remove the phosphate precipitates. Chemical addition takes place between the secondary and tertiary clarifier. Tertiary chemical precipitation achieves the lowest phosphorus concentration in the effluent. However, chemical requirements are expensive, and handling and disposal of the chemical sludge are required.

In addition to phosphorus, chemical precipitation also has potential applications for the removal of dissolved inorganic substances (Metcalf and Eddy, Inc. 1991). During phosphorus removal, various inorganic ions (such as heavy metals) can also be removed. This coincidental removal of inorganic ions can have adverse impacts on other treatment processes in the

plant. For example, when chemical precipitation is used in primary settling clarifiers, the heavy metals concentrated in the sludge prohibit the option of anaerobic digestion as a sludge-stabilization process because of the toxicity exhibited by the heavy metals in the primary sludge. Despite its limitations, chemical precipitation is a treatment option for the removal of soluble inorganic substances in many tertiary treatment applications.

2.4.4 Removal of Toxic Compounds and Refractory Organics

The adverse impacts on water quality of the receiving streams caused by the discharge of wastewater containing toxic and refractory organic compounds (resistant to microbial degradation) have necessitated the implementation of treatment methods designed to remove these environmentally threatening compounds from wastewater using, in many cases, tertiary treatment facilities. Specific classifications of these priority pollutants include refractory organic compounds, heavy metals, ammonia, halogenated aliphatic and aromatic compounds, and hydrogenated hydrocarbons. Specific treatment processes for removal of these pollutants from wastewater include 1) chemical precipitation, sedimentation, and filtration for removal of heavy metals and polychlorinated biphenyls (PCBs); 2) conventional biological treatment, PCBs, and selected hydrogenated hydrocarbons; 3) air stripping for removal of ammonia and volatile organic compounds; 4) activated carbon adsorption for removal of natural and synthetic organic compounds and heavy metals; and 5) chemical oxidation for removal of ammonia and refractory and toxic halogenated aliphatic and aromatic compounds. The first three treatment processes listed were discussed in the previous section, and the remaining two treatment processes are discussed below.

2.4.4.1 Carbon Adsorption

Carbon adsorption is a chemical and physical process used primarily to remove dissolved-refractory organic compounds and dissolved organic matter. Those radionuclides associated with the dissolved organic matter may reconcentrate as a result of being processed through a carbon adsorption unit. Removal is achieved by bringing the solution in contact with a solid medium, whereby the soluble species adhere to the

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solid medium. The most common medium used in wastewater treatment is granular or powdered activated carbon. Carbon adsorption is used as a secondary treatment polishing step for removing residual dissolved organic matter from biologically treated and clarified wastewater. If removal of additional dissolved species (such as refractory organics, nitrogen, sulfides, and heavy metals) from secondary treated wastewater is required, carbon adsorption is implemented as a tertiary treatment process.

Granular activated-carbon adsorption systems (such as contactors) typically consist of two or three down-flow, fixed-bed (that is, the carbon remains fixed and the wastewater flows through) columns, operated in parallel or series. Upflow, expanded-bed columns, operated in series, are also used. Flow through the columns is achieved by gravity or applied pressure. Fixed-bed systems require backwashing (that is, flushing the columns in the direction opposite of normal operational mode) to remove accumulated particulate matter. When the adsorptive capacity of a fixed-bed column is depleted, the column is taken off-line and sent to an offsite regeneration facility. Regeneration is typically accomplished using a thermal process (such as a furnace), whereby thermal oxidation of the entrapped organic matter removes it from the surface of the carbon. In expanded-bed systems, the wastewater flows upward through a descending bed of fixed carbon. When the adsorptive capacity of the lower portion of the carbon bed is depleted, it is removed and replaced with an equal amount of fresh activated carbon at the top of the bed. The expanded-bed contactor cannot be backwashed, so low concentrations of particulate matter in the influent are required to prevent plugging. For both fixed-bed and expanded-bed systems, pretreatment with granular medium filters to remove particulate matter is required to prevent plugging the carbon contactor columns.

2.4.4.2 Chemical Oxidation

The objectives of chemical oxidation as a tertiary treatment process are the removal of ammonia, the reduction of residual organics, and the reduction of bacterial and viral species prior to discharging the wastewater to a receiving water. Breakpoint chlorination, previously discussed in Section 2.4.3.2, is a

chemical oxidation process used for ammonia removal. Chlorine dioxide and ozone have been investigated as alternatives to chlorine to prevent the formation of trihalomethanes when chlorine is added to wastewater. The selection of chemical oxidant and specific process configuration depends on the target species for removal. Typical chemical dosages (kilogram oxidant/kilogram destroyed organic) for the oxidation of organics in secondary treatment effluent are 2.0 for chlorine and 6.0 for ozone (Metcalf and Eddy, Inc. 1991).

2.5 Sludge Handling and Disposal

Sludge is defined as the byproduct of wastewater treatment and consists of both liquid and solid components. The treatment processes used are dependent on many factors, including the sludge source and characteristics, what the final disposal method will be, geographic location, and cost limits. Table 2.8 contains some typical sources and characteristics of municipal sludge.

In a WWTP, sludge is derived from primary and secondary sedimentation tanks and other solids collection areas. The sludge is then subjected to a series of treatment steps that may include pretreatment, thickening, stabilization, conditioning, disinfection, dewatering, drying, composting, thermal reduction, and final disposal. Conditioning, disinfection, drying, and thermal reduction are optional steps that are not included in all sludge treatment plants. Table 2.9 contains a list of the processes with the function, equipment, and chemicals used in each step. Figure 2.19 contains a generalized schematic of sludge processing. All of the water removed from the sludge during these steps (especially the thickening and dewatering steps) is normally returned to the plant's primary treatment influent.

Significant amounts of reconcentration of radionuclides may occur during the handling of sludge after it has gone through a treatment process. The concentration occurs not by increasing the radionuclide concentration, but by decreasing the concentration of other constituents. For instance, the ^{241}Am activity on a per weight basis increased nearly three-fold after the sludge of a New York State waste treatment plant underwent dewatering (New York State Department of Health 1986). Further reconcentration occurred upon

Table 2.8 Typical sludges (Eckenfelder and Santhanam 1981)

Sludge Source	Concentration (% solids)	Characteristics
Primary sedimentation tanks	4 to 8	Bad odor; gray-brown; does not drain well on drying beds but can be dewatered mechanically
Anaerobic primary digestion tanks	6 to 10	Dewaters well on drying beds; black; musty; produces gas
Filter humus	3 to 4	Fluffy; brown
Waste biologically activated sludge	0.5 to 1.5	Yellow-brown; fluffy; difficult to dewater; very active biologically
Aerobic digestion tanks	1 to 3	Yellow-brown; sometimes difficult to dewater; biologically active
Waste alum (chemical precipitation)	0.5 to 1.5	Gray-yellow; odorless; very difficult to dewater

Table 2.9 Handling and disposal processes for sludge

Process	Function	Chemicals and Equipment
Preliminary operations	Size reduction, grit removal, blending, and storage	Sludge grinding, blending, storage, and degritting
Thickening	Volume reduction	Gravity thickening, rotary drum, flotation, centrifugation, gravity belt thickening
Stabilization	Stabilization	Lime, heat, anaerobic digestion, aerobic digestion, composting
Conditioning (optional)	Conditioning	Filter aids, chemical conditioning, heat treatment
Disinfection (optional)	Disinfection	Pasteurization, long-term storage
Dewatering	Volume reduction	Vacuum filter, pressure filter, horizontal belt filter, centrifuge, drying bed, lagoon
Drying (optional)	Weight and volume reduction	Flash drying, spray drying, rotary drying
Thermal reduction (optional)	Volume reduction and stabilization	Incineration, wet air oxidation, pyrolysis, and starved-air combustion
Ultimate disposal	Removal from plant to final location of solids	Landfill, land application, lagoon, reuse

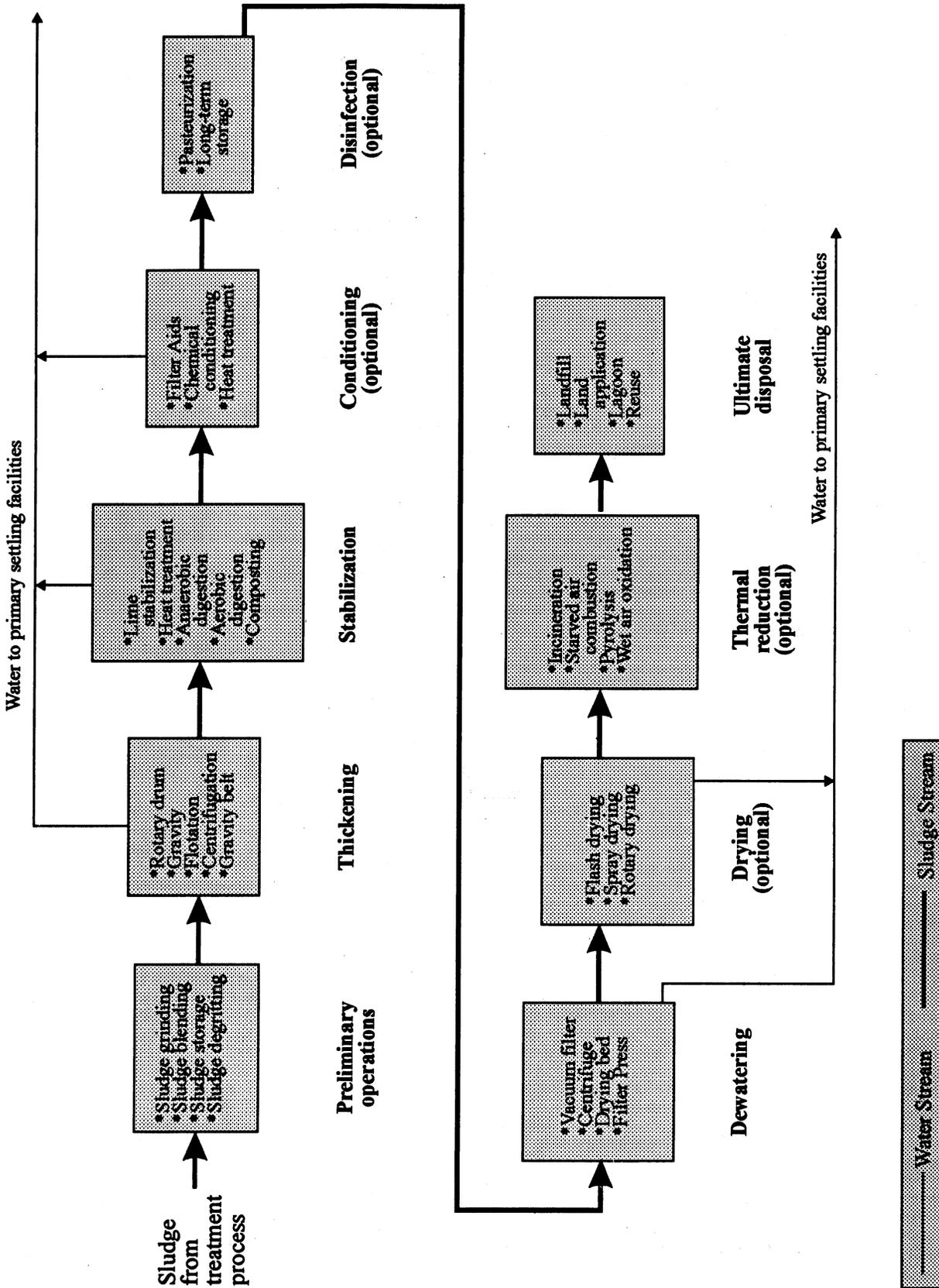


Figure 2.19 Processes of sludge handling and disposal

ashing the sludge whereby the ^{241}Am activity on a per weight basis increased an order of magnitude.

2.5.1 Preliminary Operations

Preliminary processes are used to homogenize the incoming sludges. Thicker sludges are mixed with the more diluted sludges, and those sludges that are primarily chemical are sometimes mixed with those that are biological. Waste volumes are equalized by sludge storage, allowing a homogenous constant flow into the sludge-treatment processes. Most of these equalization processes are similar to those used in primary pretreatment (Section 2.2.1.4). Preliminary treatment includes blending, grinding, grit removal, and storage of sludges.

2.5.2 Thickening

The purpose of thickening is to remove excess water, thereby decreasing the volume of sludge to be processed. Thickening processes include gravity thickening, flotation thickening, centrifugal thickening, gravity belt thickening, and rotary drum thickening. These processes are described in following subsections.

2.5.2.1 Gravity Thickening

Gravity thickening is essentially the same process as sedimentation (Figure 2.4), with settled, thickened sludge withdrawn from the bottom of the tank and clarified water decanted from the top. Thickening tanks normally have a steeper floor slope to minimize retention time and to increase the depth of the sludge over the withdrawal pipe. Thickeners also have vertical pickets that help in the release of water and gases from the sludge (Eckenfelder and Santhanam 1981). Gravity thickening is estimated to be used in 17.9 percent of municipal WWTPs (Table 2.10).

2.5.2.2 Flotation Thickening

Flotation thickening is used primarily to treat activated sludge or trickling filter sludge wastes. Flotation thickening is more cost effective for the biological sludges because of their inherent tendency to form aggregates that float. The most common method, dissolved air flotation, functions by introducing dissolved air into a pressurized tank containing

the sludge. The tank is then depressurized, allowing the dissolved air to form very small bubbles to which organic solids will attach. The bubbles will rise to the top, thereby lifting the attached solids to the top where they are removed by skimmers. Flotation thickening is estimated to be used in 6.1 percent of municipal wastewater treatment plants (Table 2.10).

2.5.2.3 Centrifugal Thickening

Centrifugal thickening uses centrifugal force to accelerate the natural sedimentation rate of the waste. The most common types used are perforated basket centrifuges, solid-bowl conveyor centrifuges, and disk nozzle centrifuges. Basket and solid-bowl conveyor centrifuges have the advantage of being able to process large particles, which the disk nozzle centrifuges cannot handle. Centrifuges have the advantage (or disadvantage in some cases) of producing a high solids content sludge. Follow-on treatment steps must be capable of handling the very thick sludge. In the centrifuge equipment shown in Figure 2.20, the solids collect against the walls into a thick cake. The water can be decanted off easily at the end of the cycle.

2.5.2.4 Gravity Belt Thickening

Gravity belt thickening is a process where the sludge travels on a moving belt that passes through a series of rollers and plow blades. The rollers press the water through the belt, and the plow blades form ridges and valleys in the sludge, allowing the water to drain more easily.

2.5.2.5 Rotary Drum Thickening

In rotary drum thickening, the sludge stream travels slowly through the center of a rotating drum. Water drains through the porous drum walls into a receiving tank located below the drum and the concentrated sludge exits at the end of the drum.

2.5.3 Stabilization

Thickened sludges are discharged to sludge-stabilization facilities. The purpose of stabilization is to reduce pathogens in the sludge, eliminate offensive odors, and reduce or eliminate the potential for putrefaction (that is, the decomposition of organic matter). This result is accomplished by biological

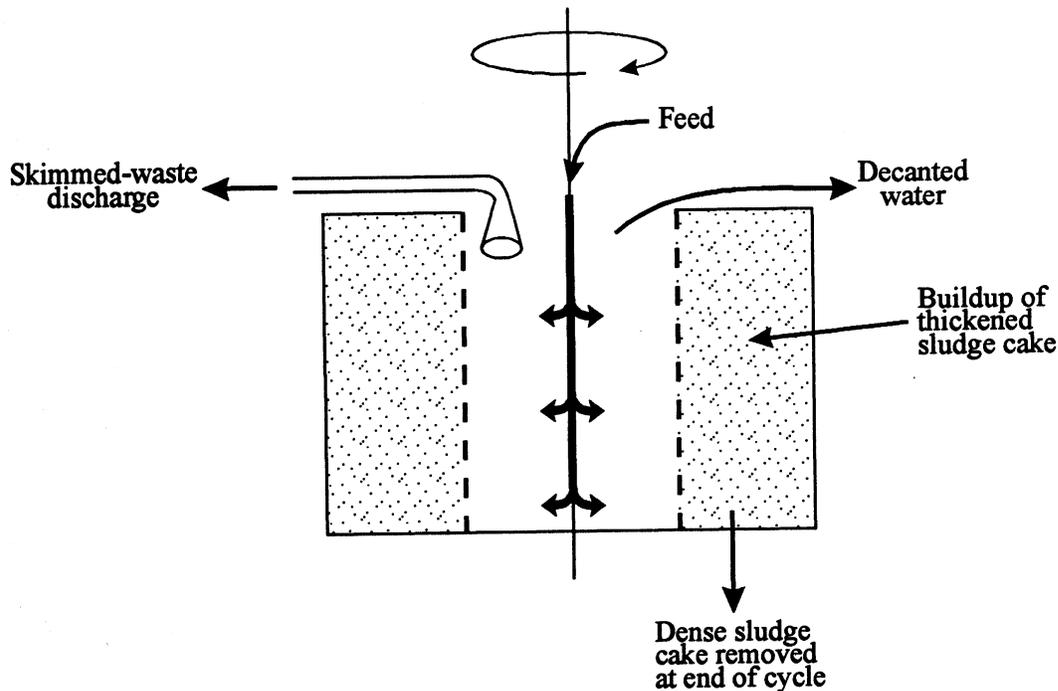


Figure 2.20 Centrifugal thickener for sludge processing

reduction, chemical oxidation, chemically altering the microorganisms' environment, or heat. Stabilization processes used include lime stabilization, heat, anaerobic sludge digestion, aerobic sludge digestion, and composting.

2.5.3.1 Lime Stabilization

Lime stabilization of sludge is achieved by adding enough lime to bring the solution pH up to 12 or more. The extreme basic environment inhibits growth of or destroys pathogenic microorganisms. This method has the disadvantage of increasing the volume of the sludge to be disposed of and is not effective against many organisms. Lime stabilization is estimated to be used in 4.8 percent of municipal WWTPs (Table 2.10).

2.5.3.2 Heat Stabilization

By heating the sludge (up to 260°C) at elevated pressures (up to 2760 kN/m²) several beneficial changes can occur such as reduction in volume and

disinfection. Heat stabilization is estimated to be used in only 0.7 percent of municipal WWTPs (Table 2.10).

2.5.3.3 Anaerobic Digestion

Anaerobic digestion is one of the oldest and most commonly processes for stabilizing sludge. Although anaerobic digestion can be used to treat sludges from many sources in the WWTP, it is most suitable for primary sludges, which typically contain large amounts of nonmicrobial organic matter and high-strength wastewaters. Anaerobic digestion reduces the organic matter to methane and carbon dioxide with minimal production of biomass (Section 3.1). Digestion rates can be increased by mixing and heating the sludge, requiring 15 days or less to treat the sludge, as opposed to standard digestors that can take 30 to 60 days. Anaerobic digestors can be designed to operate in either batch or continuous modes, mixed or unmixed, and are normally covered to reduce odor emissions and to recover methane (Metcalf and Eddy, Inc. 1991). Figure 2.21 shows a completely mixed, heated digester. Sludge heating is normally performed

Table 2.10 Frequency of handling and disposal processes for sludge used by municipal wastewater treatment plants with at least secondary treatment

Treatment	Process	Estimated percentage of wastewater treatment plants utilizing treatment processes ^(a)
Thickening	Gravity thickening	17.9
	Flotation thickening	6.1
	Centrifugal thickening	(b)
	Gravity belt thickening	(b)
	Rotary drum thickening	(b)
Stabilization	Lime stabilization	4.8
	Heat stabilization	0.7
	Anaerobic digestion	24.5
	Aerobic digestion	44.5
	Composting	1.0
Conditioning	Heat	(b)
	Filter aids	(b)
	Chemical conditioners	17.7
Disinfection		(b)
Dewatering	Sand drying beds	38.1
	Vacuum filtration	3.6
	Centrifuges	2.4
	Filter presses	7.5
Drying		(b)
Thermal reduction	Incineration	16.1

(a) From U.S. Environmental Protection Agency (1988)

(b) Not included in survey

in a heat exchanger outside of the digester because of the buildup of solids on the stationary heat sources.

The primary advantages of anaerobic digesters are 1) a minimal amount of biomass is produced during organic degradation, 2) the ability of the anaerobic microorganisms to survive in nutrient-deficient environments that aerobic organisms cannot live in, 3) the ability of the anaerobic microorganisms to disinfect the sludge, and 4) the methane produced can be recovered for fuel use. The primary disadvantage of anaerobic digestion is the necessity of monitoring the processes to ensure that the balance between the different types of microorganisms is maintained. Other disadvantages are that the process is slow, the sludge usually must be thickened before being sent to the digester, and the reactor effluent normally

contains high concentrations of soluble organic matter that must be treated prior to discharge (Grady and Lim 1980). Anaerobic digestion is estimated to be used in 24.5 percent of municipal WWTPs (Table 2.10).

2.5.3.4 Aerobic Digestion

The primary objective of aerobic digesters is to remove insoluble organic matter. Aerobic digesters may be used to treat primary sludge and secondary chemical process sludge but are most suitable for secondary sludges generated by biological processes. The predominant products of aerobic digestion are carbon dioxide, water, and ammonia (Section 2.3.1). Two process variations include conventional and pure oxygen digestion. In conventional aerobic digestion,

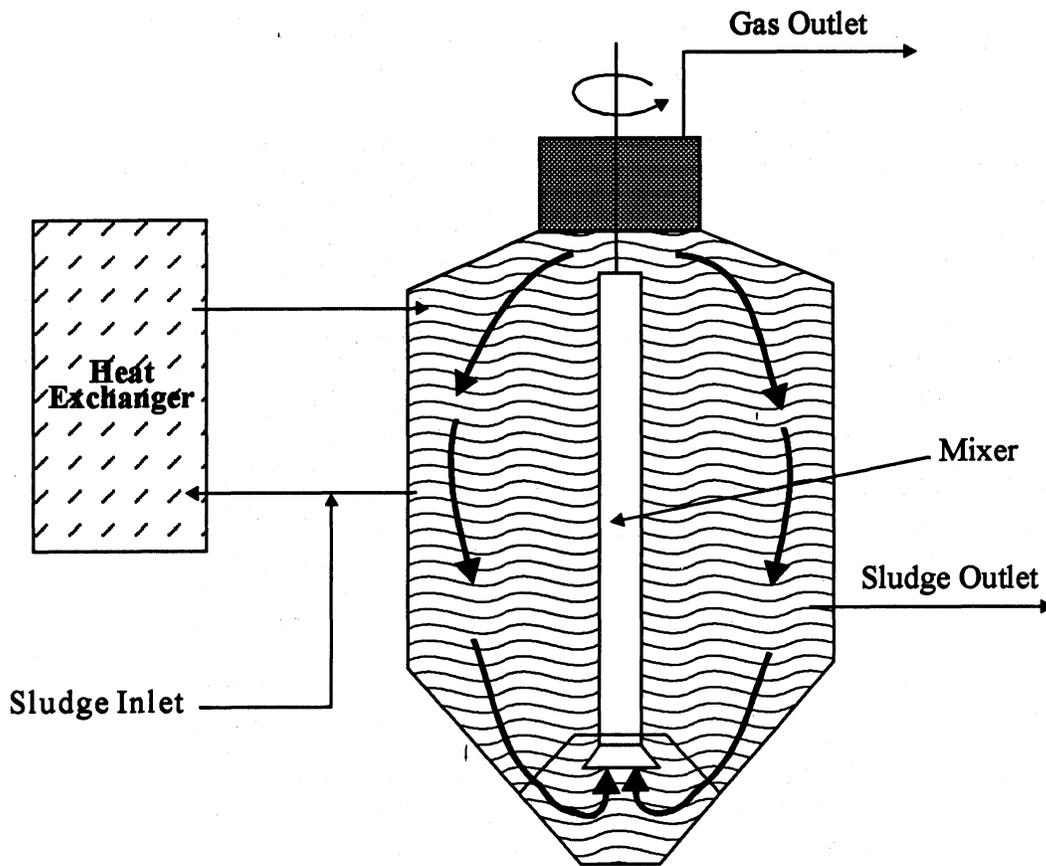


Figure 2.21 Heated, anaerobic digester for sludge processing

the sludge is aerated for an extended period of time in an open, unheated tank, using conventional air diffusers or surface aeration equipment. This process can occur in both continuous and batch modes. Pure oxygen digestion is similar, except oxygen is used instead of air and the tank is usually covered to recover unused oxygen for recycling. Thermophilic aerobic digestion is also similar, except thermophilic bacteria are used at a higher temperature to shorten the retention time of the sludge to 3 to 4 days.

The advantages of this type of digester are 1) supernatant of aerobic digesters normally contains little soluble biodegradable organic matter, 2) aerobic digesters can process low sludge concentrations (decreasing the need for thickeners), 3) aerobic digesters can achieve organic solids reductions similar to anaerobic digestion (that is, 45 to 50 percent) for

secondary sludges, 4) aerobic digestion is a better process, if the end use of the sludge will be fertilizer, and 5) aerobic digesters experience fewer operational difficulties. Some disadvantages of aerobic digesters are that they 1) provide no energy recovery in the form of methane, 2) oxygen must be added, 3) more residual sludge is formed, and 4) the efficiency is highly dependent on temperature (Grady and Lim 1980). Aerobic digestion is estimated to be used in 44.5 percent of municipal WWTPs (Table 2.10).

2.5.3.5 Composting

Composting is similar to a digestion process, in that the organics in the waste are degraded by micro-organism activity. Composting can be achieved in either aerobic or anaerobic environments, although municipal composting is usually done aerobically.

Composting generally requires several months to stabilize the sludge (Metcalf and Eddy, Inc. 1991). Composting is estimated to be used in 1.0 percent of municipal WWTPs (Table 2.10).

2.5.4 Conditioning

Stabilized sludges are sometimes discharged to conditioning facilities. The purpose of conditioning is to increase the efficiency of the sludge-dewatering process that follows. The ability of sludges to retain water is dependent on many factors, including solids concentration, particle-size distribution, pH, alkalinity, ionic constituents, and surface charge. The surface charge exhibited by particles (usually negative) interferes with flocculation because electrostatic repulsion inhibits particle aggregation. Most conditioners function by reducing the surface charge of the particles, allowing van der Waals' attractive forces to overcome the electrostatic repulsion. Conditioning can be achieved by adding heat, filter aids, or chemical conditioners (Eckenfelder and Santhanam 1981).

2.5.4.1 Heat

Heating sludges under pressure breaks down the structure of water-particle conglomerates. Typical conditions used are 149 to 199°C, pressures of 1000 to 1400 kN/m², and residence times of 30 to 45 minutes. Heat treatment has the added advantage of also disinfecting the sludge (Eckenfelder and Santhanam 1981).

2.5.4.2 Filter Aids

Filter aids improve cake production and filter efficiency when processing compressible sludges that might plug or slime the filters. Such filter aids include fly ash, diatomaceous earth, and many other relatively inert compounds. They function primarily by sorbing the water away from the sludge and by partially solubilizing metal constituents. The primary advantages of filter aids are their low costs and uncomplicated processes (Eckenfelder and Santhanam 1981). They have the disadvantages of increasing the volume of the sludge to be processed and decreasing the incineration fuel content of the sludge.

2.5.4.3 Chemical Conditioners

Chemical conditioners function by neutralizing the surface charge on sludge particles, binding dispersed particles into aggregates, and affecting sludge characteristics, such as pH, dissolved oxygen concentration, carbonate concentrations, and redox potentials. Chemical conditioners are divided into organic (polymers) and inorganic conditioners. Inorganic conditioners include ferric and ferrous salts, aluminum salts, and lime (Section 2.3.2.1). Typically, organic conditioners are long chains, are water soluble, have high molecular weights, and have numerous active functional groups. Organic conditioners are further divided by their functional group ionization into anionic, cationic, nonionic, and ampholytic (both positive and negative functional groups). Anionic conditioners (negatively charged) include polyacrylic acid, hydrolyzed polyacrylamide, and polystyrene sulfonate. The most common cationic conditioner is polydiallyl-dimethyl ammonium. Nonionic conditioners are used primarily as a structural binding site for sludge particles and include polyethylene polymers and polyacrylamide. Ampholytic polymers are predominantly protein-like synthetic organics (Eckenfelder and Santhanam 1981). Polymers are added in an estimated 17.7 percent of municipal WWTPs (Table 2.10).

2.5.5 Disinfection

Disinfecting sludge enhances the possibility that it may be used in land applications or reused in some other manner. Disinfection can be achieved through pasteurization, heat treatment, chemical modification, chlorination, irradiation, and long-term storage in lagoons. Pasteurization is used widely in Europe, while the United States primarily uses long-term storage in lagoons.

Lagoon storage involves leaving sludge in earthen basins for two or more months, depending primarily on temperature. Microorganisms can remove much of the pathogenic constituents in a process similar to digestion. Monitoring of lagoons is required to limit percolation and possible contamination.

2.5.6 Dewatering

Sludge that has been stabilized and possibly conditioned or disinfected is discharged to dewatering facilities. Dewatering of sludge is performed for one or more of the following reasons: sludge disposal is often based on weight or volume of the sludge, landfills require a dewatered sludge to reduce leachate production, dewatered sludge is easier to handle, and dewatering increases the efficiency of any incineration and composting processes that may follow. Dewatering is accomplished using drying beds and lagoons, vacuum filters, centrifuges, and filter presses.

2.5.6.1 Drying Beds

Drying beds are the most common type of dewatering processes used. Dewatering is accomplished by allowing the water in the sludge to drain and/or evaporate over time. Several different types of beds are used, varying primarily in the construction material. The most common beds used are conventional drying beds, vacuum-assisted drying beds, and lagoons.

Drying beds can be made of various materials, including sand, pavement, and artificial media. Sand drying is generally done only in smaller communities because of the amount of land needed for the drying beds and the cost of replacing the sand. Sand beds accounted for 38.1 percent of all municipal WWTPs (Table 2.10). Paved drying beds must be especially designed to allow for drainage at the bottom. They are easier to clean out and do not need a replacement material. Figures 2.22a and b display typical paved drying beds. Artificial media, such as stainless steel wedge wire or high-density polyurethane formed into panels, are becoming more popular because of the increased rate of drying that can be achieved with these materials. These materials allow excess water to drain easily out the bottom and are easy to maintain.

Vacuum-assisted drying beds are similar to conventional drying beds, except that a vacuum is applied to the bed to increase the rate of water removal.

Lagoons can be used in lieu of drying beds when the sludge has been previously digested. However, lagoons are not suitable for untreated sludges, limed

sludges, or watery sludges because of the possible formation of noxious odors.

2.5.6.2 Vacuum Filtration

Vacuum filtration involves applying a vacuum across a filter medium placed in the sludge. A cake of solids will build up on the filter, and the liquid will pass through the filter. The cake is then removed and disposed. Chemical conditioning almost always precedes vacuum filtration of sludge. Vacuum filtration is estimated to be used in 3.6 percent of municipal WWTPs (Table 2.10).

2.5.6.3 Centrifuges

Centrifuge devices are used occasionally (2.4 percent) in municipal WWTPs for dewatering. The equipment used is identical to that described in Section 2.5.2.3.

2.5.6.4 Filter Presses

Two main types of filter presses are used today: the belt filter press and the plate filter press. The belt filter presses are similar to the gravity belt thickeners discussed in Section 2.5.2.4. Plate filter presses are similar to belt filter presses, except that the sludge is passed between a series of plates under pressure (690 to 1550 kN/m²). Water is pressed through filters surrounding the plates, flows through holes in the plates, and is removed. Filter presses are estimated to be used in 7.5 percent of municipal WWTPs (Table 2.10).

2.5.7 Drying

Dewatered sludges are sometimes discharged to drying facilities. Drying is required if the sludge is to be incinerated or recycled into fertilizers. Drying is accomplished by applying heat to the sludge to vaporize the water to less than ten percent of the total sludge weight. Several methods are in use, including flash dryers, spray dryers, and rotary dryers. Removing water from sludge before incineration increases the efficiency of the incinerator. Drying is required before sludge is processed into fertilizer to slow or stop biological activity and reduce sludge volume.

Flash dryers are the most common type of dryer used today. In flash drying, the sludge is mixed vigorously

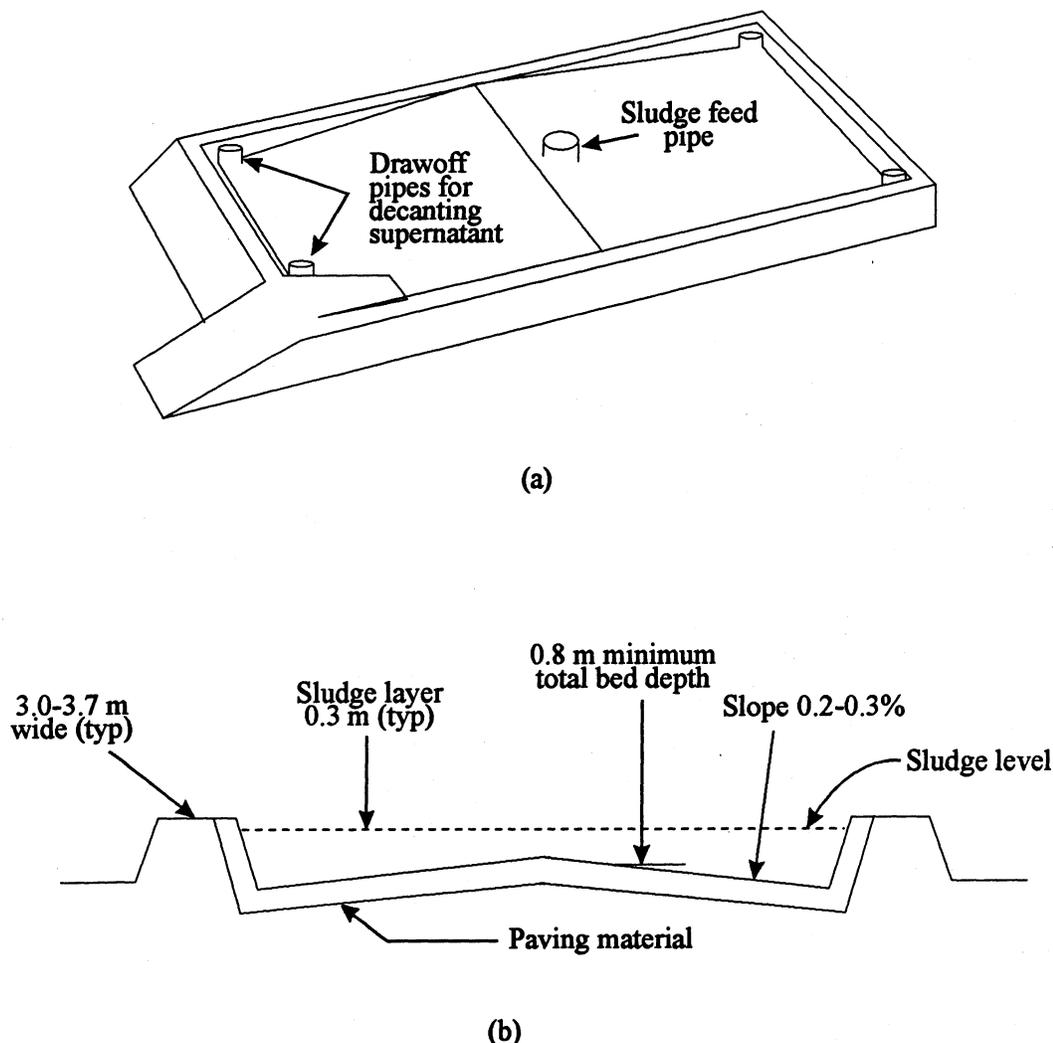


Figure 2.22 Decanting type paved drying bed for sludge processing. (a) isometric view; (b) side view

while being subjected to a flow of hot gases that pull out the moisture. Spray dryers, another type of dryer, use centrifugal forces to atomize the sludge into very small particles that are sprayed into a drying chamber. Rotary dryers, yet another type of dryer, are similar to the rotary drum thickener described in Section 2.5.2.5. In rotary drying, the drum is heated or hot gases are passed through the sludge as it rotates and mixes in the drums.

2.5.8 Thermal Reduction

The primary purpose of thermal reduction is to reduce the volume of sludge prior to disposal. Thermal reduction of sludge wastes can be accomplished by

several means, including incineration, wet air oxidation, pyrolysis, and starved air combustion. Incineration and wet air oxidation of organics primarily yield carbon dioxide, water, and ash. Wet air oxidation is estimated to be used in two percent of municipal WWTPs (Table 2.10). Starved air combustion and pyrolysis processes yield products that have a limited energy content that can be extracted beneficially at a later time. Incineration is the simple burning of the organic material in an environment containing surplus oxygen. Pyrolysis involves breaking down the organic in an oxygen-free environment at high temperatures. Starved air combustion is the burning of organics in an environment that contains a controlled amount of oxygen. Wet combustion is the

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burning of liquids at high temperatures and pressures (Metcalf and Eddy, Inc. 1991).

2.5.9 Ultimate Disposal

Dewatered sludges that also may have been processed in drying and/or thermal reduction facilities are ready for disposal. The ultimate fate of the treated sludges generated during wastewater treatment is dependent on many factors, including the availability and type of land, the characteristics of the treated sludge, and the relative costs to the community (such as sludge transportation and land costs). The most common methods of disposal are land application, land-filling, and lagooning.

Land application involves spreading sludge on or just below the soil surface. This application can be used on agricultural lands, where the nutrient value of the treated sludge can be used or on marginal lands (that is, formerly strip-mined land) that would otherwise be unusable for human needs. Land application is a permanent treatment method in which natural microorganisms are used to adapt the waste into usable soil.

Agricultural land, forested land, disturbed land, and dedicated land-disposal site application are the most common end uses of sludges in the United States.

Sludges that were not stabilized or contain components that would make the sludge unusable in land applications (such as pathogens) must be land-filled. As a result of the increasing regulatory awareness in the United States, this method of disposal is declining in popularity.

The disposal of treated sludge into lagoons is generally only relevant to smaller communities, where land is relatively inexpensive, and in areas that have low annual rainfall. The large surface area of these lagoons facilitates evaporation of water, and the layers of thickened sludge compress the solids over time. One major advantage of this type of disposal is that many of the treatment steps can be eliminated (especially dewatering, drying, disinfection, and thermal reduction). The major disadvantage of this type of storage is the odor generated, which cannot be reduced by any type of covering.

3 Biological, Chemical, and Physical Processes Affecting the Speciation of Radionuclides During Wastewater Processing

3.1 Introduction

On average, approximately one percent of the total flow entering a wastewater treatment facility is ultimately produced as sludge, and because 50 to 90 percent of the metals contained in the raw sewage are removed during treatment, a considerable amount of metals is reconcentrated during the wastewater treatment process (Lester et al. 1983). The extent to which this reconcentration takes place is greatly affected by the chemical form (species) of the metal. Sposito (1989) calculated that a typical soil solution will easily contain 100 to 200 different soluble species and 50 to 100 surface-associated or precipitated species. Although it has never been calculated, it would be reasonable to assume that sewage wastewater would have at least this many species. Surfaces or precipitated metal species would be more easily removed from the wastewater stream than other species and, therefore, more prone to reconcentration than those that have a propensity to exist as dissolved species. Consequently, an understanding of the processes affecting chemical speciation is necessary to predict how and under what conditions radionuclides may become reconcentrated during wastewater treatment.

Sewage wastewater is a mixture of water, dissolved substances, gases, and solids. Table 3.1 provides the typical composition of untreated domestic wastewater. Depending on the concentrations of these constituents, wastewater is classified as low, medium, or high. Both the constituents and the concentrations of the constituents vary with the hour of the day, the day of the week, the month of the year, and other local conditions. As evidenced by Table 3.1, there is a considerable amount of solid material in sewage wastewater. These solids are usually the easiest fraction of the unwanted constituents to remove from the wastewater stream and are characterized by a set of operationally defined analytical methods used throughout the wastewater treatment industry (Figure 3.1). In the medium-strength wastewater described in Figure 3.1, approximately half of the

Table 3.1 Typical composition of untreated domestic wastewater with low, medium, and high constituent concentrations^(a)

Constituent	Concentration (mg L ⁻¹)		
	Low	Medium	High
Total solids ^(b)	350	720	1200
Total dissolved ^(c)	250	500	850
Fixed ^(d)	145	300	525
Volatile ^(d)	105	200	325
Suspended solids ^(c)	100	220	350
Fixed ^(d)	20	55	75
Volatile ^(d)	80	165	275
Biological oxygen demand	110	220	400
Total organic carbon	80	160	290
Nitrogen	20	40	85
Organics	8	15	35
Free ammonia	12	25	50
Nitrites	0	0	0
Nitrates	0	0	0
Phosphorous	4	8	15
Organic	1	3	5
Inorganic	3	5	10
Chlorides	30	50	100
Sulfates	20	30	50
Alkalinity (as CaCO ₃)	50	100	200
Grease	50	100	200
Total microbial count	10 ⁶	10 ⁷	10 ⁷

(a) After Metcalf and Eddy, Inc. (1991).

(b) Total solids is all the matter that remains as residue after evaporation at 105°C.

(c) Total dissolved and suspended solids is the filtrate and retentate of wastewater passed through a glass-fiber filter (nominal pore size of about 1-2 μm), respectively.

(d) The volatile solids are the fraction that can be volatilized at 500°C. The fixed solids are that fraction not volatilized at 550°C. In general terms, the fixed is generally thought of as the inorganic fraction and the volatile as the organic fraction.

solids are organics and half are inorganics. The organic fraction is composed of between 40 and 60 percent protein, 25 and 50 percent carbohydrates, and 10 percent fats and oils. This composition is appreciably different from that of naturally occurring

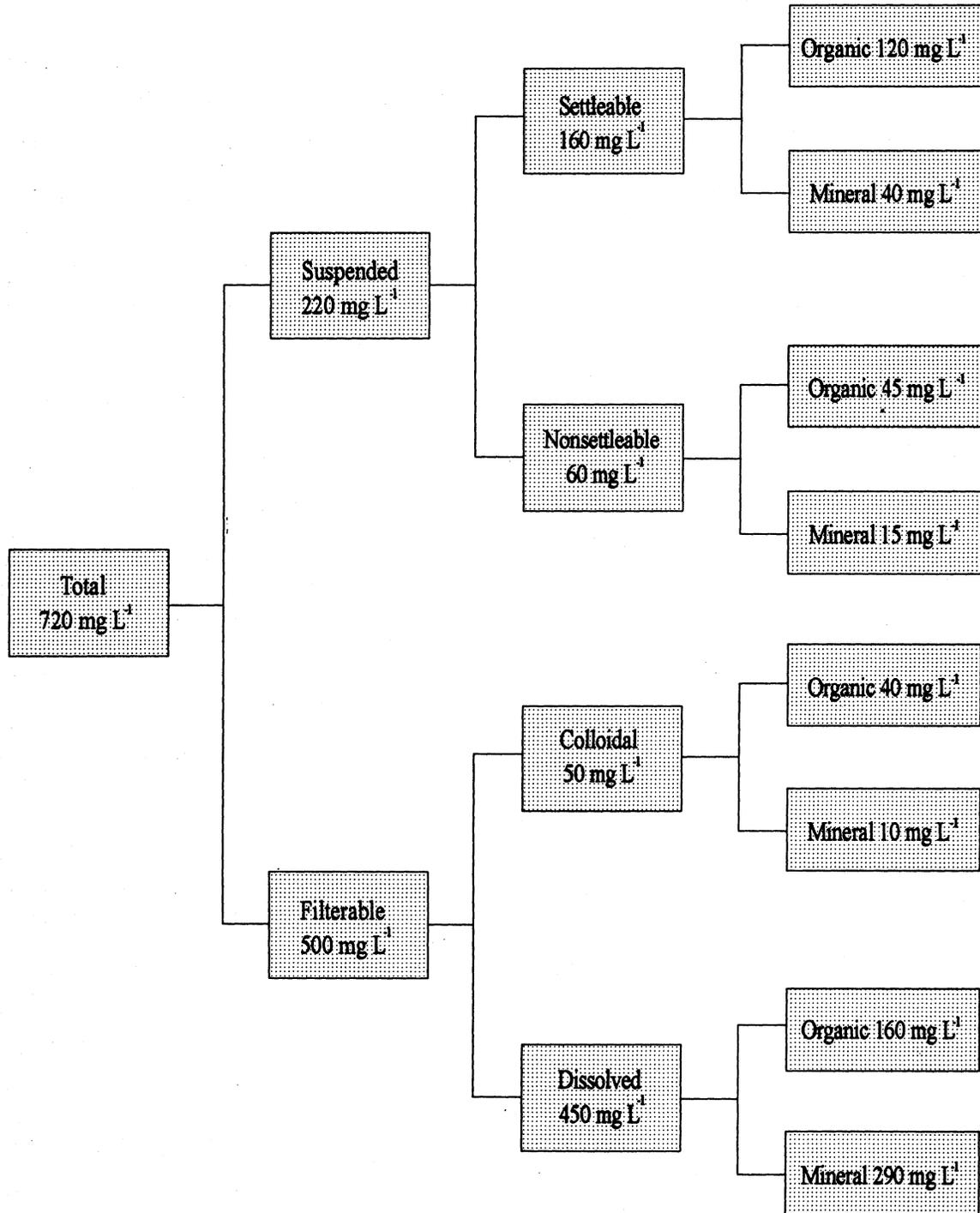


Figure 3.1 Classification and concentrations of solids found in medium-strength wastewater (Metcalf and Eddy, Inc. 1991)

organic matter, which contains less than three percent of proteins, fats, and oils. This difference is primarily the result of the much higher concentration of microorganisms (approximately 30 percent on a weight-to-weight basis) existing in the sewage wastewater as compared to natural surface waters (approximately five percent). The inorganic solids in the wastewater influent come from landscape runoff and are primarily made up of silt (2 to 50 μm) and especially clay ($<2 \mu\text{m}$) particles. Therefore, their mineralogical composition will depend on that of the regional soils. The organic and inorganic solids in the wastewater stream are usually quite small; approximately 30 percent of the solids described in Figure 3.1 can pass through a 0.45- μm -pore-sized filter, of which 30 percent will not settle under quiescent conditions after a 60-min period (that is, considered as being the nonsettleable fraction). At present, an operational definition of 0.45- μm -pore-sized filtration is currently being used as one of several available methods for solubility determination for filtration of suspended solids (NRC 1994).

Radionuclides have several important characteristics that relate to reconcentration during wastewater treatment. First, the rate that these materials emit radiation cannot be modified by any physical, chemical, or biological process. The process of reconcentration results from the physical transfer of radionuclides as chemical elements from the suspended solids or dissolved form to a settled solid form. During this transition, their nature of radioactivity remains unchanged except for radioactive decay that occurs during this process. Second, radionuclides react chemically like their stable counterparts. For example, if a process removes the stable form of cobalt, it will generally also remove the radioactive form of cobalt. This property is important because relevant information regarding the possible behavior of a radionuclide can be inferred from its stable counterpart (or chemical analogs). Third, the concentrations of radioactive material present in wastewater systems are exceedingly low. In many cases, radionuclides can only be measured because of their radioactive emissions and the analytical techniques available that have extremely low radiation detection limits. The detection limits for their nonradioactive counterparts is often several orders of magnitude higher. The low concentration of radionuclides, particularly in the presence of a high

concentration of the stable counterpart, may significantly affect the radionuclide speciation and, therefore, its propensity to reconcentrate during wastewater treatment.

The three main factors affecting the reconcentration of radionuclides during wastewater treatment will be discussed in this chapter: physical, chemical, and biological factors. Particular attention will be directed at indicating 1) how the different factors result in reconcentration, and 2) where in the wastewater treatment process these factors come into play. The final section describes the removal efficiency of some of the wastewater treatment processes.

3.2 Physical Factors

The two principal physical factors affecting the reconcentration of radionuclides in wastewater treatment facilities are sedimentation/flocculation and temperature. Sedimentation and flocculation are the fundamental sludge collection processes used during primary (Section 2.2), secondary (Section 2.3), and tertiary (Section 2.4) treatment. If radioactive materials are present in the form of discrete particles, it is possible that if they combine with other suspended solids they can be removed from the wastewater stream. The flocculation/sedimentation process may also remove the radionuclides that are sorbed to particles from the wastewater stream.

Temperature has an effect on a number of properties that, in turn, affect radionuclide biogeochemistry. Temperature has a profound effect on 1) the water viscosity, which in turn influences flocculation/sedimentation and particle surface charge; 2) the solubility of gases, which in turn affects the oxidation-reduction (redox) status of the system, amount of alkalinity or dissolved solids (that is, CO_3^{2-} and HCO_3^-), the oxidation state of some constituents, including radionuclides, and the propensity of some radionuclides to sorb to solid surfaces; and 3) the rate of biological (that is, microbial) growth that, in turn, affects the ability of secondary treatment processes to remove radionuclides from the wastewater stream. Finally, temperature has a direct affect on chemical-reaction kinetics, complexation, and solubility.

3.2.1 Sedimentation/Flocculation

Sedimentation is the process by which particles are separated from water by gravitational forces. Flocculation is the aggregation of discrete particles. Together, these processes are the most widely used of the wastewater treatment (Table 2.1). A settling/clarifying unit process follows almost every aerobic (Sections 2.3.1.1 and 2.3.1.2), anaerobic (Sections 2.3.1.3 and 2.3.1.4), and chemical addition (Sections 2.3.2, 2.4.3, and 2.4.5) process (Figures 2.1 and 2.6). On the basis of the concentration and the tendency of particles to interact, four types of sedimentation can occur: discrete particle, flocculent, hindered, and compression. During the sedimentation of suspensions with a high-particulate load, it is common to have all four types of settling occurring at the same time. The settling phenomenon that occurs when a concentrated suspension, initially of uniform concentration throughout, is placed in a graduated cylinder is schematically presented in Figure 3.2.

The settling of discrete, nonflocculating particles can be analyzed by means of the classic laws of sedimentation described by Stokes (van Olphen 1977; Hillel 1980). Stokes' law yields the terminal particle velocity, μ_t , by equating the gravitational force of the particle with the frictional resistance, or drag. The frictional resistance force, F_r , is defined as

$$F_r = 6\mu\eta ru \quad (3.1)$$

where η is the viscosity of the fluid and r and u are the radius and velocity of the particle. Initially, as the particle begins its fall, its velocity increases. Eventually, a point is reached at which the increasing resistance force equals the constant downward force of gravity. The particle then continues to fall without acceleration at a constant velocity, known as the "terminal velocity."

The downward force from gravity, F_g , is

$$F_g = \frac{4}{3} \pi r^3 (\rho_s - \rho_f) g \quad (3.2)$$

where $4/3(\pi r^3)$ is the volume of the spherical particle, ρ_s is the particle density, ρ_f is the fluid density, and g

is gravitational acceleration. By setting the two forces equal, we have Stokes' law

$$\mu_t = \frac{2r^2 g}{9\eta} (\rho_s - \rho_f) = \frac{d^2 g}{18\eta} (\rho_s - \rho_f) \quad (3.3)$$

where d is the diameter of the particle. In the design of sedimentation basins, the usual procedure is to select a particle with a terminal velocity μ_t and to design the basin so that all particles that have a terminal velocity equal to or greater than μ_t will be removed. In the instance where the wastewater is considered to contain a high load of contamination, studies may be conducted to determine the particle-size distribution containing the greatest amount of contamination. With this knowledge, the facility designers can then apply Equation 3.3 to determine the depth of the sedimentation basins (U.S. Environmental Protection Agency 1979; Lester 1987a). Four unrealistic assumptions that must be made when using Equations 3.1, 3.2, and 3.3 for wastewater treatment purposes are 1) the particles do not aggregate during settling, 2) the particles are spherical, 3) the particles have the same density, and 4) the water is motionless.

Particles in dilute suspension may not act as discrete particles but may flocculate during sedimentation. As flocculation occurs, the mass of the particle increases and it settles faster. This type of settling is referred to as flocculent settling (Figure 3.2). The extent to which flocculation occurs is dependent on the surface charge of the particles and the opportunity for contact, which in turn varies with the stream flow rate, the depth of the settling basin, the concentration of particles, particle surface charge, and the range of particle sizes (Hillel 1980; Metcalf and Eddy, Inc. 1991). The effects of these variables on flocculation cannot be predicted from mechanistic models, thus empirical models are sometimes used for these determinations. But more often, simple batch-type experiments simulating the conditions of the settling basin are conducted (U.S. Environmental Protection Agency 1979; Hillel 1980).

In systems that contain high concentrations of suspended solids, such as in the clarifying tanks that follow biological or chemical addition treatment processes, both hindered settling and compression settling usually occur in addition to discrete and flocculent settling (Figure 3.2). Because of the high

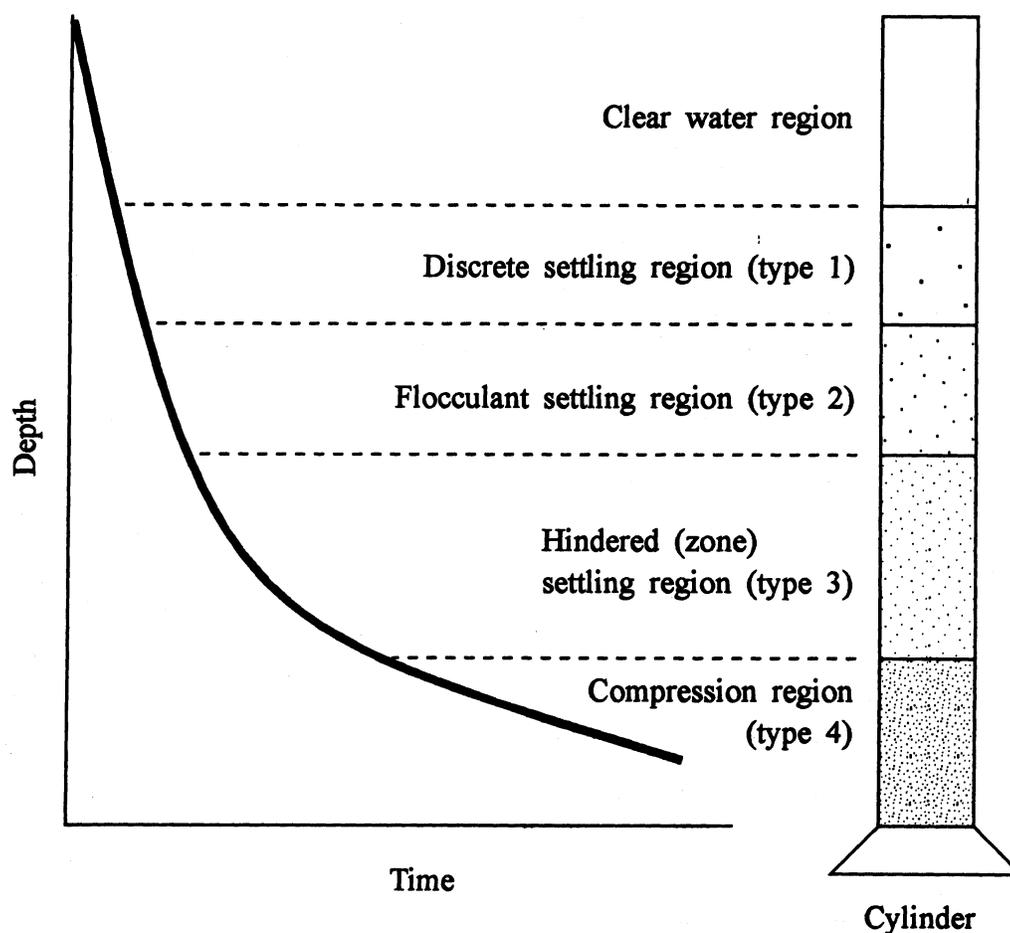


Figure 3.2 Schematic of settling regions for suspended solids

concentration of particles, the contacting particles tend to settle as a blanket, maintaining the same relative position with respect to each other. This phenomenon is known as "hindered settling." As the particles in this region settle, a relatively clear layer of water is produced above the particles in the settling region. The scattered, relatively light particles remaining in this region usually settle as discrete or flocculent particles. In most cases, an identifiable interface develops between the more or less clear upper region and the hindered settling region shown in Figure 3.2. The rate of settling in the hindered settling region is a function of the concentration of solids and the solids density and surface charge.

As settling continues, a compressed layer of particles begins to form on the bottom of the cylinder. The particles in this region apparently form a structure with close physical contact between the particles. As the compression layer forms, regions containing successively lower concentrations of solids than those in the compression region extend upward in the settling basin. Thus, in actuality, the hindered settling region contains a gradation in particle concentration, from the highest concentration at the bottom of the region to the lowest concentration at the top of the region. The forces of physical interaction between the particles that are especially strong in the compression settling region lessen progressively with height (Dick and Ewing

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1967). These forces exist only to a limited extent in the hindered settling region.

3.2.1.1 Surface Charge

To bring about particle flocculation (or aggregation), steps must be taken to reduce particle charge or to overcome the effect of this charge. Surface charge develops in two ways: isomorphic substitution and ionization of functional groups. These two processes give rise to the permanent and variable charge of the solids in the wastewater stream, respectively. Permanent charge is limited to inorganic particles. Variable charge is found on both inorganic (such as Fe and Al oxides) and organic matter (humic materials). Although inorganic and organic solid materials typically contribute equal amounts to the total solids mass (Figure 3.1), organic matter contributes by far the greater fraction of the total surface charge in the system. Organic matter may have 10 to 100 times more charge per gram than inorganic solids (Stumm and Morgan 1981). This factor not only has important ramifications regarding particle sedimentation/flocculation, but it also greatly affects the reconcentration of contaminants that are electrostatically attracted to these charged surfaces. This latter point is discussed in more detail in Section 3.3.3.

Isomorphic substitution is the substitution of one ion for another of similar size within the crystal lattice of a mineral. If a cation of lower valence substitutes for one of higher valence, such as Mg^{2+} for Al^{3+} or Al^{3+} for Si^{4+} , the negative charge of O^{2-} and OH^- ions of the mineral structure is left unbalanced, yielding a net negative charge on the mineral surface. The charge formed through isomorphic substitution is essentially independent of the particle's environment. Isomorphic substitution is the principal source of charge on most clay minerals in soils. Often, these clay minerals make up a large fraction of the inorganic particles in the wastewater influent as a result of runoff from the landscape. Permanent positively charged particles are rare in nature.

The charge of variable-charged surfaces is influenced by the chemical composition of the aqueous phase. Many surfaces contain ionizable functional groups: hydroxyl (OH), carboxyl (COOH), phosphate (H_3PO_4), and amino (NH_2). The charge of these surfaces is dependent on the degree of ionization (proton transfer) and, consequently, on the pH of the

medium. For example, the surface charge of proteins or microorganisms is acquired through the ionization of carboxyl and amino groups (Figure 3.3). At low pH, both of these groups are protonated, resulting in a positively charged surface/molecule. As the pH of the system increases, the carboxyl groups start to deprotonate to produce a negatively charged functional group COO^- . This process causes the surface/molecule to become less positively charged. As the pH increases slightly, the concentrations of COO^- and $COOH$ become equal; this is referred to as the pK_a of the carboxyl group. Further increases in the pH result in the surface/molecule acquiring a net charge of zero. This level is the pH_I , or the isoelectric point, of the surface/molecule. The pH levels above the pH_I impose a net negative charge on the surface/molecule, whereas pH levels below the pH_I impose a net positive charge on the surface/molecule. The surface/molecule becomes more negatively charged when the pH is increased above the pK_a of the amino group, the point where the concentration of NH_3^+ and NH_2^0 groups are equal.

The zero-point-of-charge (analogous to the isoelectric point) of some variable-charge materials found in wastewater treatment facilities is presented in Table 3.2. Because wastewater treatment facilities maintain a pH between seven and eight, gibbsite particles and α - NH_3 functional groups on organic matter would generally be expected to be positively charged, goethite particles to have little to no charge, and hematite, silica, feldspar, kaolinite, and α -COOH functional groups on organic matter to have negative charges. The presence of positively and negatively charged surfaces in the same system result in the

Table 3.2 Zero-point-of-charge (pH_{zpc})^(a)

Material	pH_{zpc}
Gibbsite ($\alpha - Al_2O_3$)	9.1
Hemitite (Fe_3O_4)	6.5
Goethite ($\alpha - FeOOH$)	7.8
Silica (SiO_2)	2.0
Feldspar	2.4
Kaolinite	4.6
$\alpha - COOH$	1.7 to 2.6 ^(b)
$\alpha - NH_3$	9.0 to 10.4

(a) After Stumm and Morgan (1981) and Lehninger (1979).

(b) These values represent the range of pK_a values for amino acids.

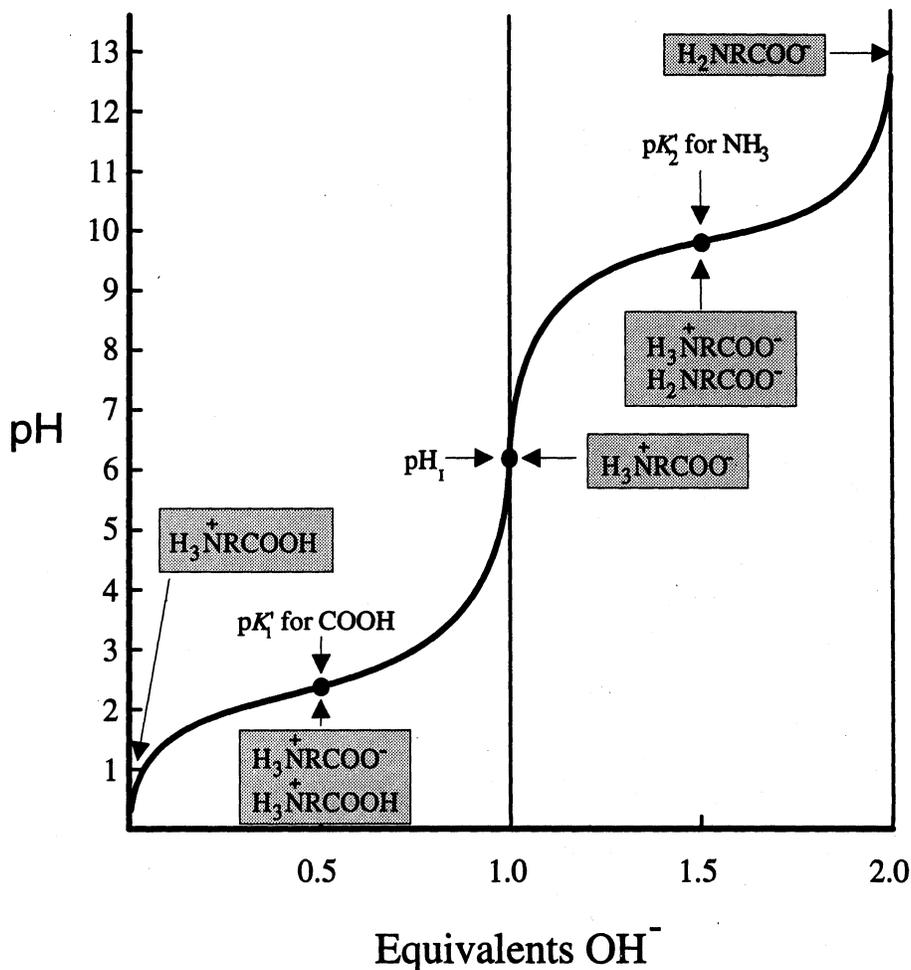


Figure 3.3 Generalized titration curve of an organic compound containing a carboxyl and amino functional group. The predominant ionic species at each cardinal point in the titration is given. R represents an organic moiety

sorption of cations and anions and increased flocculation as a result of electrostatic bonding. The first point suggests that both cationic and anionic radionuclides can be reconcentrated by the organic and (to a lesser extent) inorganic fraction via electrostatic attraction to wastewater solids. This point is discussed further in Section 3.3.3.

Inorganic clays tend to form a single sigmoidal titration curve because they generally have only one functional group affecting the variable charge of their surfaces. This information is indirectly depicted in

Figure 3.4, where surface charge of various particles that can be found in wastewater are plotted as a function of aqueous pH. Note that at lower pH levels, the particles tend to have a net positive charge, whereas at higher pH levels, the particles tend to have a net negative charge. The pH where the charge is zero corresponds to the zero-point-of-charge tabulated in Table 3.2 (gibbsite and goethite are included in Figure 3.4 and Table 3.2). Also shown in Figure 3.4 is the effect of pH on electrophoretic mobility. Electrophoretic mobility is a measure of the velocity of a particle when it is placed in an electrolyte solution

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containing a voltage field. Depending on its surface charge, the particle will be attracted to the anode or cathode; the velocity that it moves toward one of these electrodes is proportional to its surface charge. At pH 7 or higher, most wastewater treatment particles will have a net negative charge, except for perhaps gibbsite (Line F in Figure 3.4). The net charge of particles from the effluent of a wastewater treatment facility is negative (Line G in Figure 3.4).

When a colloid or particle surface has a charge, ions of opposite charge, called "counter ions," are attracted to it. The counter ions may either attach directly to the colloid surface to form a fixed layer of ions, called the Stern layer, or they may be distributed more or less diffusely in the liquid (Figure 3.5). The fixed layer of counter ions is held on the colloid surface through electrostatic and van der Waals' forces strongly enough to overcome thermal agitation. The counter ions in the diffuse layer are more thermally agitated than those in the Stern layer. As shown in Figure 3.5, the potential (Ψ) drops in the Stern layer and drops again in the diffuse layer until it approaches zero in the bulk solution. The bulk solution is that part of the aqueous phase whose chemistry is not affected by the presence of the charged particle. It has a potential equal to zero. These two layers contain an excess of counter ions and a deficit of ions of the same sign as the surface. The Stern model is one of several models that have been proposed to describe the spatial distribution of charges at the surface. Some reviews of surface charge models have been made by Adamson (1976), van Olphen (1977), and Sposito (1984).

3.2.1.2 Chemistry of Flocculating Agent

To bring about particle aggregation, steps must be taken to reduce particle charge or to overcome the effect of this charge. The effect of the charge can be overcome by 1) the addition of potential-determining ions (such as H^+ or OH^- ions) that will react with the colloid surface to lessen the surface charge, 2) the addition of indifferent electrolytes (electrolytes that do not sorb to the surface) that reduces the thickness of the diffuse double layer, 3) the addition of polyelectrolytes (long-chained organic polymers containing ionizable subunits) to bring about the removal of particles by neutralizing the surface charge and bridging, and 4) the addition of chemicals that form hydrolyzed metal ions. Chemical additions to the

wastewater stream can be made during primary treatment (Section 2.2), but are more frequently made during secondary (Section 2.3) and tertiary (Section 2.4) treatment.

Potential-determining ions include any ions that chemically bond to the colloid surfaces, thereby altering their charge. Clearly, the most common ions used to lessen surface charge are H^+ ions from strong acids and OH^- ions from strong bases, as illustrated in Figure 3.3. By adding these ions to a system, repulsive forces between particles are reduced, thereby promoting aggregation. Phosphates also have the capability to behave as potential-determining ions, but it would be counterproductive to add them to wastewater treatment systems for the purpose of flocculating particles from the wastewater stream.

When two particles approach each other in dilute colloid suspensions as a result of their Brownian motion, their counter-ion atmospheres begin to interfere with each other. The balance of attractive and repulsive forces determine whether these random collisions will result in aggregation. Attractive forces, V_A , between particles are primarily those attributed to van der Waals' force. The van der Waals' force is analogous to the gravitational force between two masses and is the sum of the intermolecular attractive forces

$$V_A = -Ar/12d \quad (3.4)$$

where A is Hamaker's constant, r is the particle radius, and d is the interparticle distance. Hamaker's constant is a function of the composition of the solid and the composition of the solution phase. It typically has a value between 2×10^{-20} to 5×10^{-20} J for minerals in water (van Olphen 1977).

Repulsive forces arise from the interaction of double-layer-repulsive forces. Based on the Stern model (Figure 3.5), the distribution of charge in the diffuse layer is governed by the equation

$$X_x = X_s \exp(-Kx) \quad (3.5)$$

where X_x is the surface charge at distance x from the Stern boundary (the Stern layer/diffuse-double-layer interface), X_s is the surface charge at the Stern boundary, and K is the Debye-Huckel parameter. The

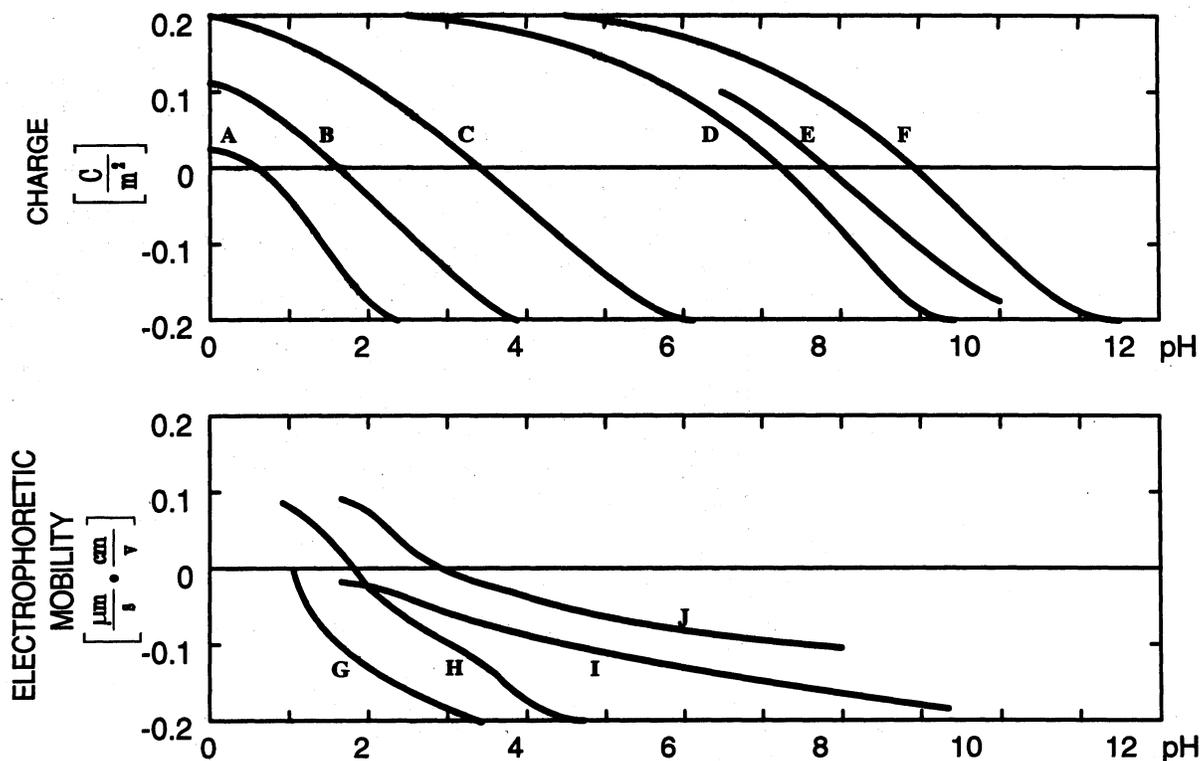


Figure 3.4 Charge and electrophoretic mobility of various colloidal materials found in wastewater as a function of suspension pH (adapted from Stumm and Morgan 1981)(A = silica, B = montmorillonite, C = MnO_2 , D = goethite, E = calcite, F = gibbsite, G = effluent from a waste water treatment facility, H = oil, I = the bacteria *Aerobacter aerogens*, J = algae).

Debye-Huckel parameter is defined (with some simplifying assumptions) by the equation:

$$K = 2 \times 10^9 (\sum c_i z_i^2)^{0.5} \quad (3.6)$$

where c_i is the activity of constituent i and z_i is the valence of constituent i . The value $1/K$ is equal to the double-layer thickness. Equation 3.6 indicates that, as the concentration or the valence of ions in solution is increased, the double layer progressively collapses; the valence of the ions in solution has a greater impact on the double-layer thickness than does the ion concentration. Hence, the choice of trivalent metals, Al^{3+} and Fe^{3+} , as flocculents. As an illustration of the salt-concentration effect, the value of $1/K$ for a

clay particle in water is approximately 1000 nm, whereas the value of $1/K$ for a particle in a 0.01-M salt solution of $CaCl_2$ is approximately 1 nm. Thus, the concentration of indifferent salts in solution has a rather dramatic effect on surface charge.

The repulsive forces (V_R) of identical particles in a dilute concentration of indifferent ions can be described by the equation

$$V_R = 32\pi\epsilon(kT/ze)^2\delta^2\exp(-Kd) \quad (3.7)$$

where ϵ is the dielectric constant (proportional to the ability of a phase to conduct current), k is the Boltzmann constant, e is the electron charge, d is the

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interparticle distance, T is temperature, z is valence, and δ is

$$\delta = \tanh(zeX_g/4kT). \quad (3.8)$$

The saline aspects of Equation 3.7 are that particle repulsive forces are directly proportional to the particles' radius and double-layer thickness ($1/K$), and inversely proportional to the particles' interparticle distance, the solution ionic strength ($0.5[\sum c_i z_i^2]^{0.5}$), and the indifferent counter-ion valence.

The effect of ion concentration, c_i , on the attractive force (Equation 3.4), repulsive force (Equation 3.7), and total force ($V_T = V_R + V_A$) is shown in Figure 3.6. The attractive forces do not change as a function of ion activity; however, the repulsive and total forces do change. When the total force is in the repulsive force zone (that is, above the horizontal line in each figure), little aggregation is expected. Aggregation is expected when the total force of the two particles is in the attractive force region of the diagrams (that is, the region below the horizontal lines). As the ion activity increases, the total force is decreasingly repulsive. Near the surface, the repulsive and total forces increase sharply as a result of forces other than those described by the Stern model. These other forces include steric hinderance (physical obstruction by extruding points on the less-than-perfectly-smooth particle surfaces), hydrologic hinderance (adsorbed water molecules inhibit particles from making contact), and the Born effect (a specific type of steric hindrance).

The effects of pH, or more specifically the effect of the potential-determining H^+ and OH^- ions, on V_R , V_A , and V_T are shown in Figure 3.7. As the pH gets well above or below the zero point of charge, dispersion of particles is expected because the repulsive and, therefore, total forces between particles increase. At or near the zero point of charge, flocculation is expected to occur. The attractive force of particles is not influenced by potential-determining ions.

By setting V_T to zero and making a few assumptions (van Olphen 1977), it is possible to calculate the critical flocculation concentration, the minimum electrolyte concentration for a counter ion of a given valence to induce flocculation. According to this calculation, referred to as the "Schultz-Hardy rule," an increase in the valence of the electrolyte by one

unit (such as use Mg^{2+} instead of Na^+ as an electrolyte) makes it possible to flocculate particles with a electrolyte solution 10^6 times less concentrated. In practice, a 10^2 -times decrease in electrolyte concentration has been observed to induce flocculation.

Polyelectrolytes may be divided into two categories: natural and synthetic. Important natural polyelectrolytes include polymers of biological origin and those derived from starch products, cellulose derivatives, and alginates. Synthetic polyelectrolytes consist of simple monomers that are polymerized into high-molecular-weight substances. Depending on whether their charge when placed in water is negative, positive, or neutral, these polyelectrolytes are classified as anionic, cationic, and nonionic, respectively.

The action of polyelectrolytes may be divided into three general categories. In the first category, polyelectrolytes promote aggregation by lowering the charge of the wastewater particles. Because wastewater particles normally are negatively charged, cationic polyelectrolytes are used for this purpose. The second category of polyelectrolytes promotes flocculation by forming interparticle bridges; anionic and nonionic polyelectrolytes attach to a number of surface-adsorption sites on more than one particle (Figure 3.8). A bridge is formed when two or more particles become adsorbed along the length of a single polymer. Bridged particles become intertwined with other bridged particles during the aggregation process. The size of the resulting three-dimensional particles grows until they can be removed easily by sedimentation. The third category of polyelectrolytes achieves flocculation by an aggregation-bridging phenomenon, which results from using cationic polyelectrolytes of extremely high molecular weight. Besides lowering the charge, these polyelectrolytes also form particle bridges.

In contrast with the aggregation brought about by the addition of chemicals acting as electrolytes and polymers, aggregation brought about by the addition of a hydrolyzable metal, such as Al^{3+} or Fe^{3+} , is a more complicated process. In the past, it was believed that free Al^{3+} and Fe^{3+} were responsible for the effects observed during particle aggregation by collapsing the double layer, as described in Equations 3.5 and 3.6. However, it is now known that hydrolysis products of these trivalent metals are more important in the flocculation process (Stumm and Morgan 1962; Stumm

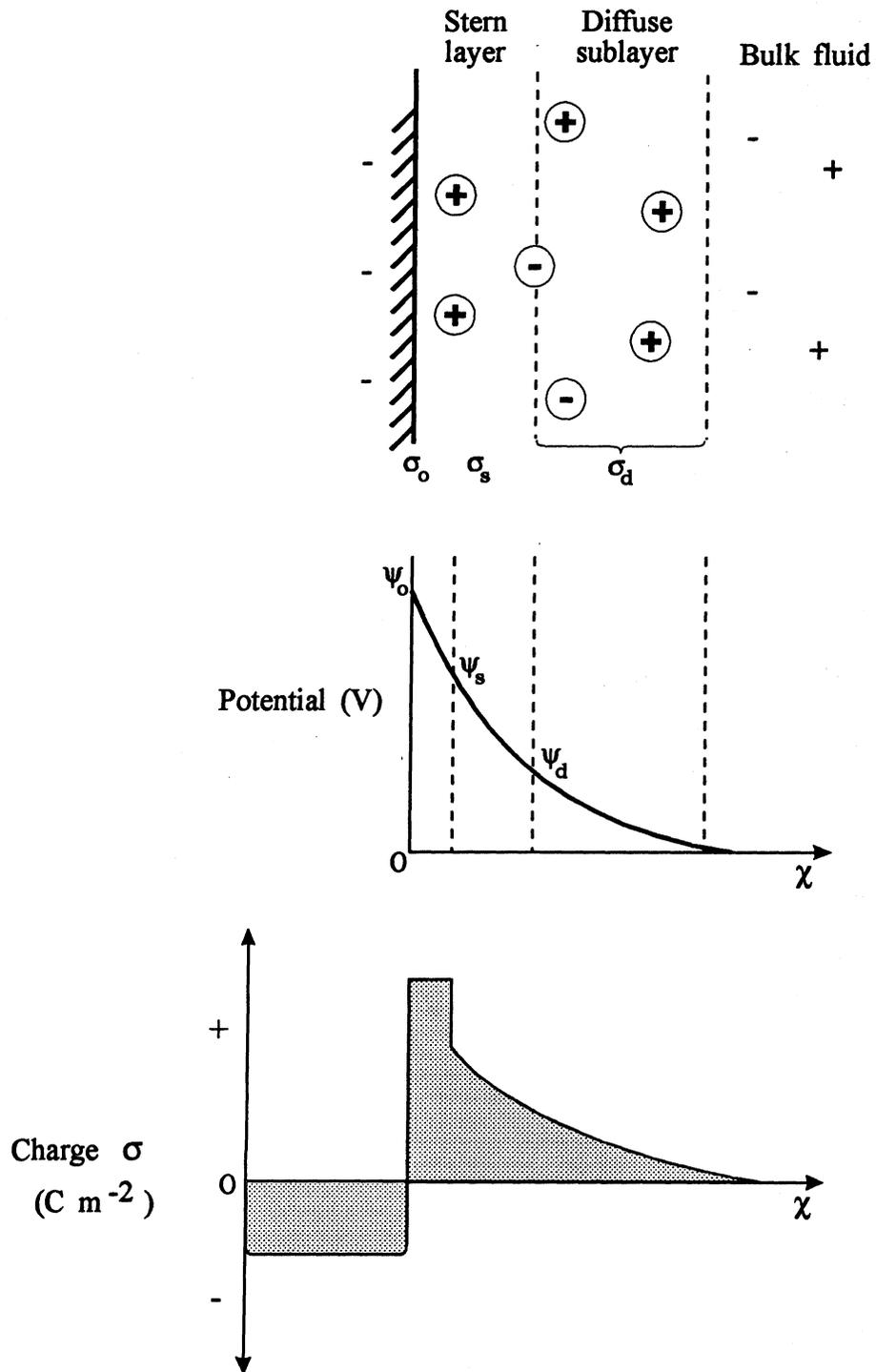


Figure 3.5 Distribution of charge and potential at a solid-solution interface as described by the Stern model of the electric-double layer

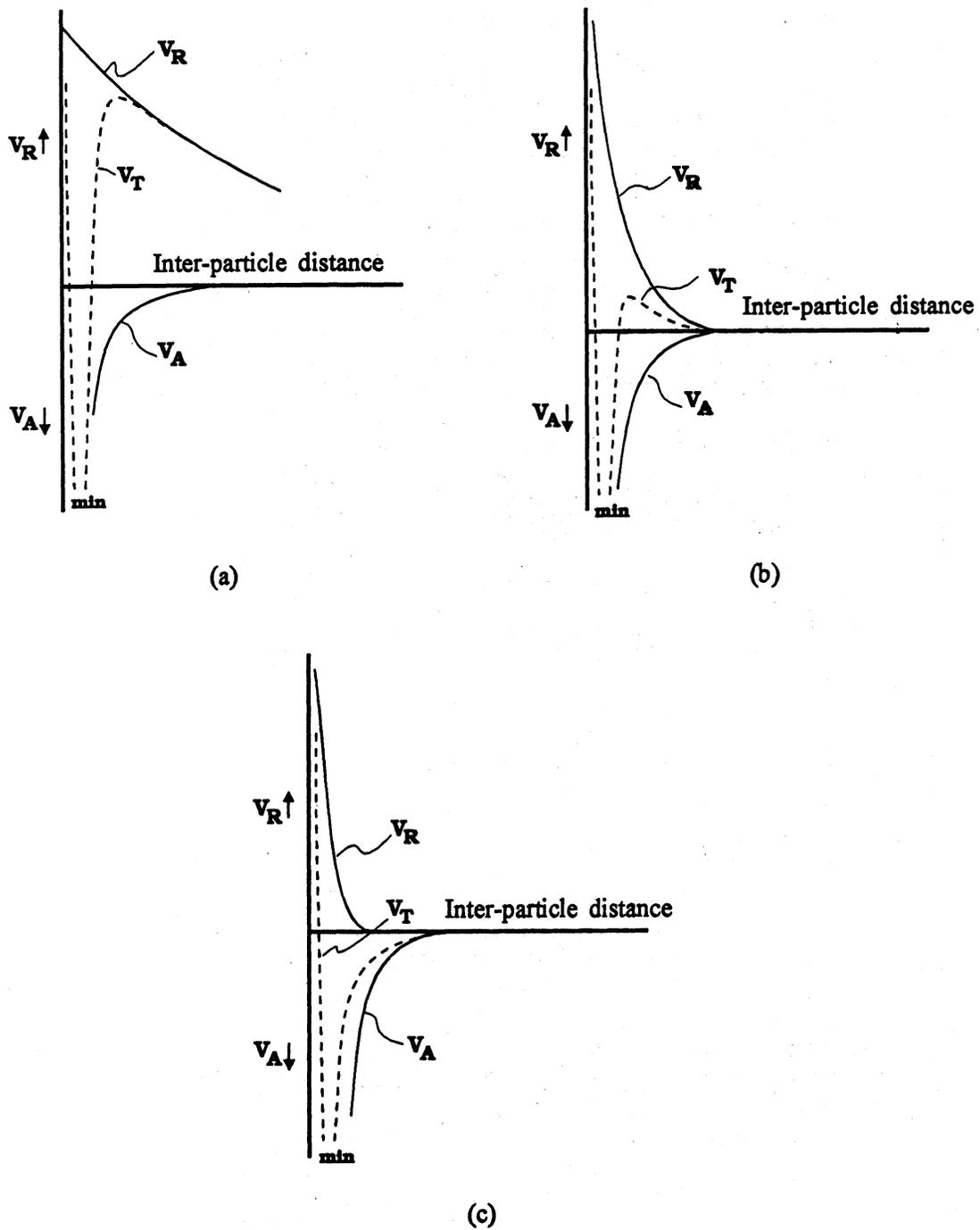


Figure 3.6 Total (V_T), repulsive (V_R), and attractive (V_A) forces as a function of particle separation distance. (a) low electrolyte concentration, (b) intermediate electrolyte concentration, (c) high electrolyte concentration (adapted from van Olphen 1979).

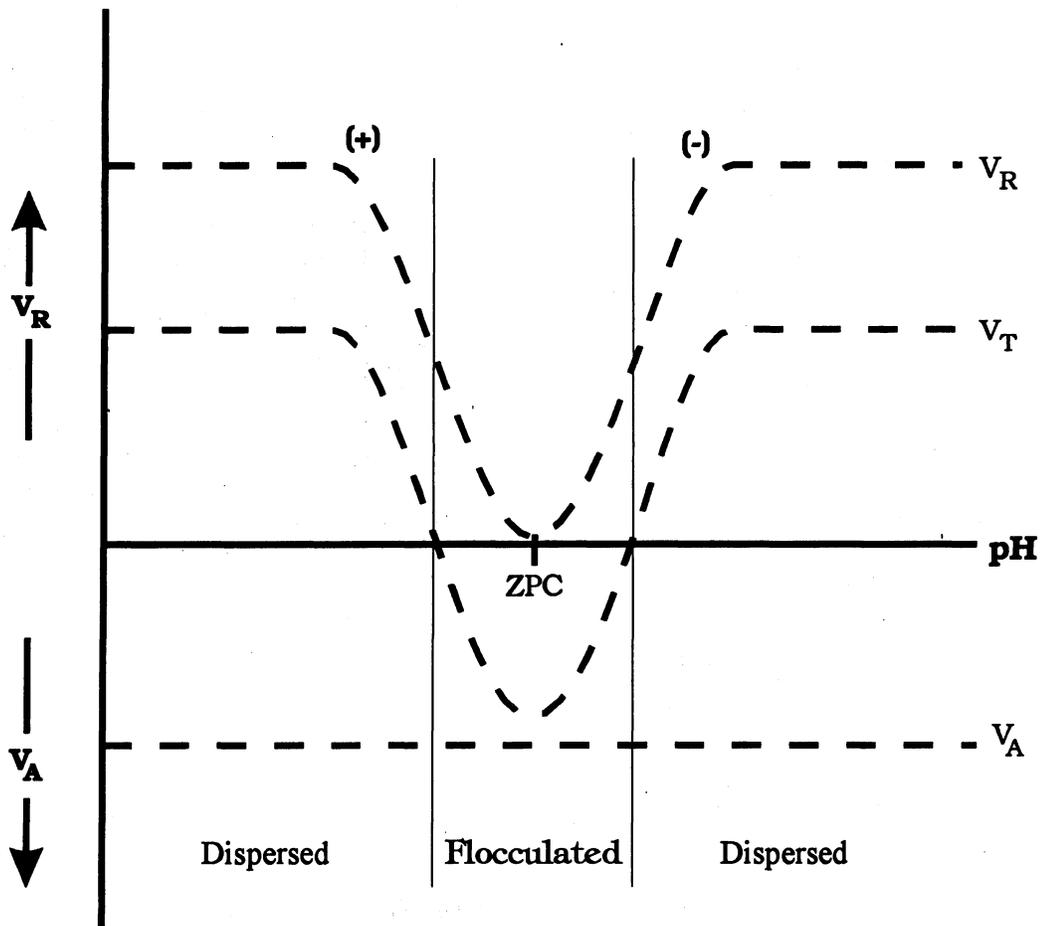


Figure 3.7 Generalized diagram of the repulsive (V_R), total (V_T), and attractive (V_A) forces of particles with variable-charged surfaces as a function of solution pH

3 Biological, Chemical, and Physical Processes

and O'Melia 1968) (Figure 3.9). Aluminum and iron hydrolysis forms monomeric molecules (one metal ion per molecule; such as FeOH^{2+} , AlOH^{2+} , $\text{Al}(\text{OH})_2^+$) and complex polymeric (more than one metal ion per molecule; such as $(\text{Al}_8\text{OH}_{20})^{+4}$ and $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}]^{7+}$) molecules. Stumm and Morgan (1981) proposed that the active polymeric molecules in these systems were composed of six $([\text{Al}_6(\text{OH})_{15}]^{3+})$ or eight $([\text{Al}_8(\text{OH})_{20}]^{4+})$ Al atoms. More recently, Bertsch (1989) proposed that the most common species of polymeric Al species were made up of 13 Al atoms $([\text{Al}_{13}\text{O}_4(\text{OH})_{24}]^{7+})$. Another complicating factor is that effectiveness of Al and Fe as flocculents will vary with time because the hydrolysis reactions to form these polymeric species follow a step-wise process (that is, more polymeric species are likely to exist in an aged solution than in a freshly prepared solution). Consequently, an alum slurry that has been prepared and stored will flocculate suspended solids differently than a freshly prepared solution. Aluminum and iron hydrolysis chemistry is complicated, and a full description of the chemistry has not been attempted here.

What is important, however, is the realization that one or more of the hydrolysis products may be responsible for the observed action of adding Al^{3+} or Fe^{3+} to aqueous systems. Review articles by Stumm and Morgan (1962), Stumm and O'Melia (1968), and Bertsch (1989) are recommended for a more detailed discussion of trivalent metal hydrolyses and its use as a flocculating agent.

3.2.2 Temperature

Temperature affects almost every biological and geochemical process in wastewater treatment: rate of chemical reactions, solubility of mineral phases, solubility of gases, growth of microorganisms, rate of aerobic digestion, rate of anaerobic digestion, molecular O_2 diffusion, aqueous-phase viscosity, and flocculation/dispersion. Because of its far-reaching effects on the biology and chemistry of these systems, it is very likely that temperature indirectly affects the reconcentration of radionuclides during secondary treatment. However, little to no attempt is usually made to control the temperature of most unit operations because they are open to the air (except anaerobic and a few types of aerobic digestion units). The purpose of this section is to discuss the effect of

temperature on some biological and geochemical processes.

Temperature has an important effect on the survival and growth of bacteria: the faster bacteria grow, the faster the removal of wastewater constituents. In general, optimal growth occurs within a fairly narrow range of temperatures, though the bacteria may be able to survive within much broader limits (Stanier et al. 1986). Temperatures below the optimum typically have a more significant effect on growth rate than temperatures above the optimum. Growth rates have been observed to double with approximately every 10°C increase in temperature until the optimum temperature is reached (Metcalf and Eddy, Inc. 1991). According to the temperature range in which they function best, bacteria may be classified as psychrophilic (optimum range of 12 to 18°C), mesophilic (optimum range of 25 to 40°C), and thermophilic (optimum range of 55 to 65°C). The species that compose the population of microorganisms often change within a given facility in response to changes in chemistry and temperature of the facility (Higgins and Burns 1975; Stanier et al. 1986). When temperatures are lower than usual, biological treatment of wastewater is slower than usual; consequently, wastewater requires a greater residence time for contaminant removal. The importance of bacteria in wastewater treatment is discussed in more detail in Section 3.4.

The concentration of gases in solution is also strongly influenced by temperature and has a profound effect on dissolved oxygen, methane, and carbon dioxide content and the oxidation state of wastewater constituents via oxidation-reduction chemistry. Controlling the concentration of gases during digestion is critical and is, in part, accomplished by controlling temperature. The oxidation state of wastewater constituents has a significant effect on the reconcentration of radionuclides. For instance, a poorly oxygenated (reduced) system would be much more likely to reconcentrate uranium (U) than a well-oxygenated system. The effects of oxidation-reduction reactions on the geochemistry of wastewater are discussed further in Section 3.3.2.

Gases, in particular oxygen, may also affect the types of microbes in the system (Sections 2.3 and 3.4). The equilibrium, or saturation concentration, of gases dissolved in a liquid is a function of the type of gas and the partial pressure of the gas adjacent to the liquid.

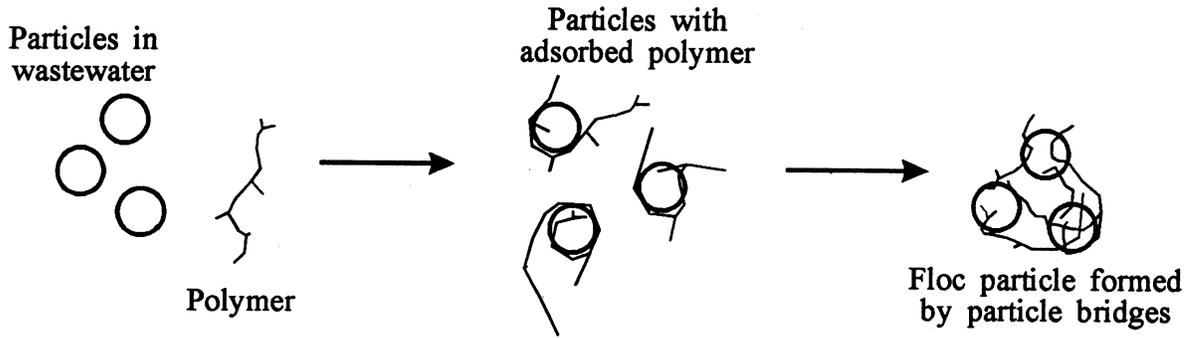


Figure 3.8 Interparticle bridging with polyelectrolytes

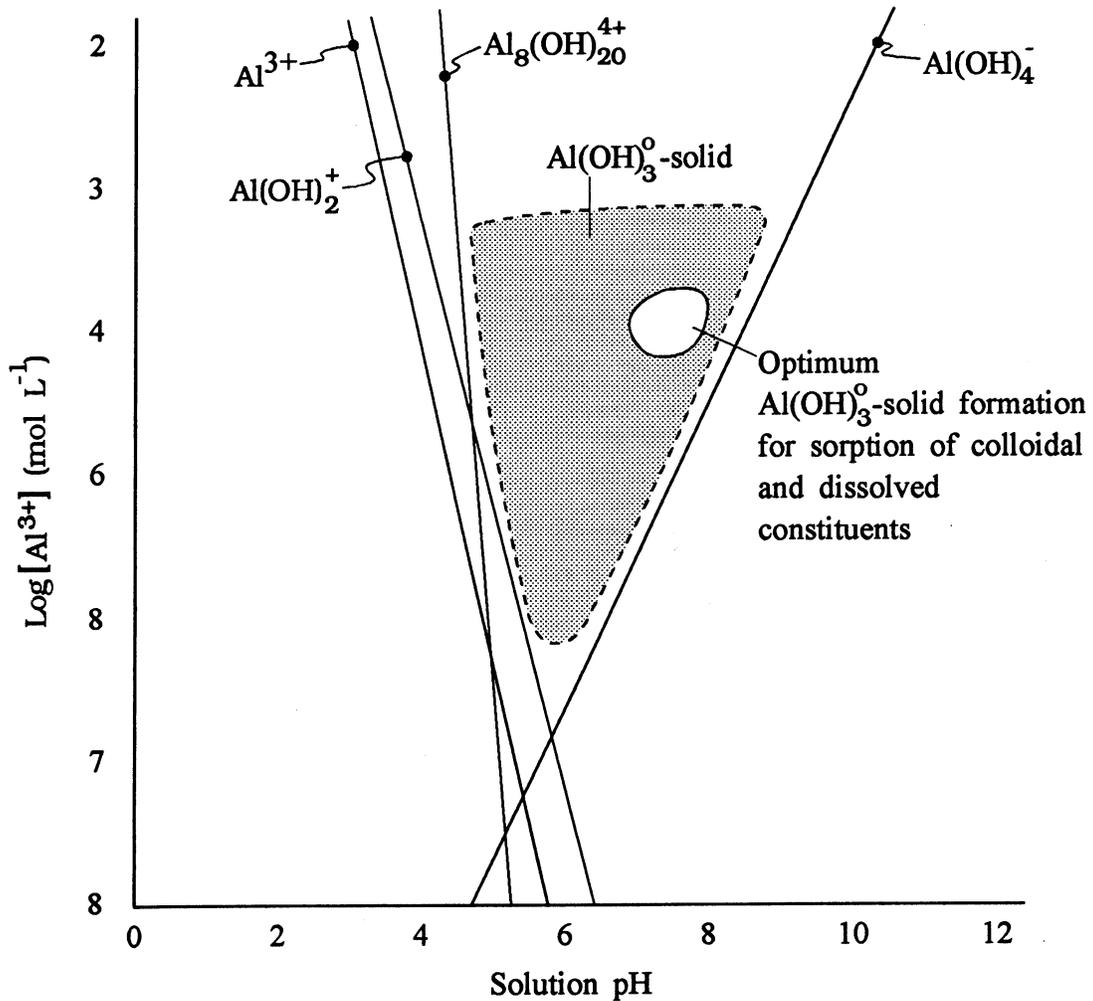


Figure 3.9 Aluminum speciation and optimal aluminum concentrations for removal of colloidal and dissolved constituents via sorption to aluminum hydroxide solids

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The relationship between the partial pressure of gas in the atmosphere, P_g , and the equilibrium mole fraction of dissolved gas in the liquid, χ_g , is given by Henry's law

$$P_g = H\chi_g \quad (3.9)$$

where H is Henry's law constant. Henry's law constant is a function of the type, temperature, and constituents of the liquid. For example, Henry's law constant for oxygen increases from 4.01×10^{-4} to 5.88×10^{-4} atm (mol fraction)⁻¹ as the temperature increases from 20 to 50°C. Temperature also alters chemical equilibrium and reaction kinetics. The basic relationship for the influence of temperature on chemical equilibrium is described by the van't Hoff equation

$$d(\ln K)/dT = \Delta H^\circ/RT^2 \quad (3.10)$$

where K is an equilibrium constant (discussed in Section 3.3.), T is temperature in degrees Kelvin, H° is enthalpy, and R is the gas constant. In 1889, Arrhenius proposed the equation

$$d(\ln k)/dT = E_a/RT^2 \quad (3.11)$$

to describe the influence of absolute temperature, T, on the second-order rate constant, k. E_a is the activation energy (approximately the energy required for a reaction to occur) and R is the gas constant. The central concept of the Arrhenius equation is that reactant molecules must attain an activated state before they can react to form products. His results were derived from analysis of a reversible equilibrium



and drew on the van't Hoff equation (Equation 3.10). In this handling of reaction kinetics, temperature is expected to increase the number of successful collisions and to decrease the activation energy; hence, such processes as radionuclide adsorption to solid phases will generally be increased as temperature increases. The effect of temperature on aquatic chemistry is discussed thoroughly in Alberty (1987).

3.3 Chemical Factors

Sewage wastewater is a mixture of water, dissolved substances, gases, and solids. As described in Section 3.1, the proportion of each of these fractions varies greatly as a function of facilities, seasons, time of day, and weather. Recently, wastewater treatment facilities have been required by law to analyze for the total concentration of a number of contaminants.

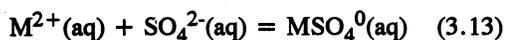
While total concentrations of these constituents indicate the extent of contamination, they give little insight into the forms in which the metals are present in the waste, their potential for reconcentration during the treatment process, or their mobility and bioavailability on dispersal in the environment. Contaminants can occur in sewage sludge as soluble-free, inorganic-soluble-complexed, organic-soluble, complexed, adsorbed, precipitated, coprecipitated, or solid structural species (Lake 1987). The geochemical processes that contribute to the formation of these species/solids and their potential effect on reconcentration of radionuclides are discussed in this section.

3.3.1 Complexation and Precipitation

A complex is said to be formed whenever a molecular unit, such as an ion, acts as a central group to attract and form a close association with other atoms or molecules. The aqueous species $\text{Th}(\text{OH})_4^0$, $\text{UO}_2(\text{OH})^+$, and HCO_3^- are complexes, with Th^{4+} , U^{6+} , and CO_3^{2-} , respectively, acting as the central group. The associated ions, OH^- or H^+ , in these complexes are termed "ligands." If two or more functional groups of a single ligand are coordinated to a metal cation in a complex, the complex is termed a "chelate." The complex formed between Al^{3+} and citric acid $[\text{Al}(\text{COO})_2\text{COH}(\text{CH}_2\text{COOH})]^+$, in which two COO^- groups and one COH group are coordinated to Al^{3+} , is an example of a chelate. If the central group and ligands in a complex are in direct contact, the complex is called "inner-sphere." If one or more water molecules is interposed between the central group and a ligand, the complex is called "outer-sphere." If the ligands in a complex are water molecules (as, for example, in $\text{Ca}(\text{H}_2\text{O})_6^{2+}$), the unit

is called a "solvation complex" or, more frequently, a "free species." Inner-sphere complexes usually are much more stable than outer-sphere complexes (because the latter cannot easily involve ionic or covalent bonding between the groups).

Most of the complexes likely to form in wastewater are metal-ligand as compared to metal-chelate complexes. Metal-ligand complexes may be either inner-sphere or outer-sphere. As an example, consider the formation of a neutral sulfate complex with a bivalent metal cation (M^{2+}) as the central group



where the metal M can be Co, Sr, Ca, Mn, or Cu. The conditional equilibrium constant, c_K , corresponding to Equation 3.8 is

$$c_K = \frac{[MSO_4^0(aq)]}{[M^{2+}(aq)][SO_4^{2-}(aq)]} \quad (3.14)$$

where [] represents the concentration of the species. The conditional equilibrium constant can describe the distribution of a given constituent among its possible chemical forms if complex formation and dissociation reactions are at equilibrium. The conditional stability constant is affected by a number of factors, including the ionic strength of the aqueous phase and the presence of competing reactions, such as hydrolysis or complexation with competing reactants.

Complexing anions present in substantial amounts in wastewater treatment systems are HCO_3^-/CO_3^{2-} , Cl^- , SO_4^{2-} , PO_4^{3-} , and organic materials. Their relative propensity to form complexes with many metals are: $CO_3^{2-} > SO_4^{2-} > PO_4^{3-} > Cl^-$ (Stumm and Morgan 1981). Uranium, as the UO_2^{2+} species, forms extremely strong complexes with CO_3^{2-} and SO_4^{2-} ions (Rai et al. 1990). The presence of these anions, even at trace levels, has dramatic effects on the chemical behavior of U (Kim 1986). A large number of dissolved, small-chain organic materials are present in wastewater and their complexation properties with metals/radionuclides are not well understood. Because of the omnipresence of organic materials in wastewater treatment facilities and their tendency to form strong complexes, complexation of many radioactive metals by organic materials is likely an

important chemical reaction (Kim 1986). The chelate anion, ethylenediaminetetraacetic acid (EDTA) (introduced into sewage systems from industrial sources), forms strong complexes with many cations, much stronger than carbonate and organic materials (Kim 1986). The role of organic materials in the chemical speciation of wastewater is discussed further in Section 3.3.3.

The precipitation reaction of dissolved species is a special case of the complexation reaction (Equations 3.14 and 3.15) in which the complex formed by two or more aqueous species is a solid. As an example, consider the formation of a sulfide precipitate with a bivalent metal cation as the central group



where M can be a radionuclide metal. The solubility product constant, K_{sp} , corresponding to Equation 3.15 is

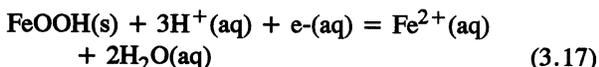
$$K_{sp} = \frac{[MS(s)][H^+]}{[M^{2+}(aq)][HS^-(aq)]^2} \quad (3.16)$$

It must be emphasized that species in the denominator of Equation 3.16 are the activities of the free species, not the total concentration. Hence, complexation, as illustrated in Equation 3.13, has a direct impact on the propensity of a given species to precipitate. Precipitation of radionuclides is not likely to be a dominant reaction in untreated wastewater streams because the radionuclide activities, even in the absence of complexation, are not likely to be high enough to cause the quotient of Equation 3.16 to exceed the K_{sp} . Precipitation is more likely to occur if the radionuclide has a stable counterpart in the wastewater that exists at an activity that would cause the K_{sp} to be exceeded. Under such conditions, the radioactive isotope will precipitate with, and in direct proportion (on a mass basis) to, the stable isotope because the two are chemically identical. However, it is very likely that coprecipitation of radionuclides in wastewater could occur. Coprecipitation is the simultaneous precipitation of a chemical element with other elements (Sposito 1984). The three broad types of coprecipitation are inclusion, surface precipitation, and solid solution formation. Inclusion is the occasional substitution of a foreign ion for the matrix ion in the solid. Surface precipitation is the formation of a three dimen-

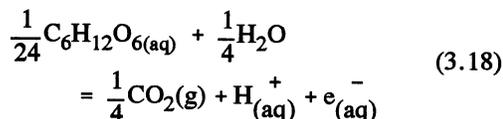
sional solid phase at the surface of an existing solid. Solid solution formation is the formation of a solid phase containing more than one central atom where substitution for one atom/molecule is generally greater than that which occurs via inclusion. For example, the addition of alum or Fe(III) salts may result in the coprecipitation of divalent radionuclides.

3.3.2 Redox Chemistry

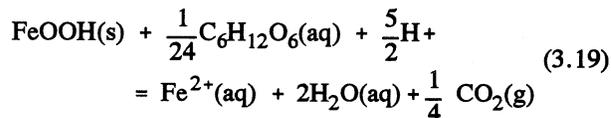
An oxidation-reduction (redox) reaction involves the complete transfer of electrons from one species to another. The chemical species that loses electrons in this charge-transfer process is called oxidation, where the one receiving electrons is called reduction. For example, in the reaction involving Fe species



the solid phase, goethite, is the oxidized species, and $\text{Fe}^{2+}(\text{aq})$ is the reduced species. Equation 3.17 is a reduction half-reaction, in which an electron in aqueous solution, denoted $\text{e}^-(\text{aq})$, serves as one of the reactants. This species, like the proton in aqueous solution, is understood in a formal sense to participate in charge-transfer processes. The overall redox reaction in a system must always be the combination of two half-reactions, an oxidation- and reduction-half reaction, such that species $\text{e}^-(\text{aq})$ does not exist explicitly. For example, in wastewater treatment systems, Equation 3.17 could be combined (or coupled) with the half reaction involving the oxidation of a organic materials (typified by glucose oxidation to CO_2):



Combining Equations 3.17 and 3.18 results in the cancellation of the aqueous electron and represents the reduction of Fe^{3+} via the oxidation of the organic materials in the wastewater treatment system:



The electron is a very useful conceptual device for describing the redox status of aqueous systems, just as the aqueous proton is useful for describing the acid-base status of soils. Similar to pH, the propensity of a system to be oxidized can be expressed by the negative common logarithm of the free-electron activity

$$\text{pE} = -\log(\text{e}^-) \quad (3.20)$$

The range of pE in wastewater treatment systems may vary between approximately 7.0 to 1.7 in aerobic treatment systems. If an anaerobic digestion process is included in the treatment, the pE may be as low as -3.0. The most important chemical elements affected by redox reactions in wastewater treatment facilities are C, N, O, S, Mn, and Fe. In radioactively contaminated systems, this list would grow to include Co, I, Ir, Np, Pu, Tc, and U. If the wastewater treatment process is behaving in effect like a closed system (such as flooded sludge under stagnant ponding) and abundant sources of carbon and energy are available to support microbial-mediated catalysis, a well-defined sequence of reduction of inorganic elements appears. This sequence is presented in Table 3.3 by representative reduction half-reactions. Also presented in Table 3.3 is the range of pE values over which the

Table 3.3 Sequence of principal electron acceptors in neutral aquatic systems

Reduction half-reactors	Range of initial pE
$1/2 \text{O}_2 + 2\text{e}^- + 2\text{H}^+ = \text{H}_2\text{O}$	5.0 to 11.0
$\text{NO}_3^- + 2\text{e}^- + 2\text{H}^+ = \text{NO}_2^- + \text{H}_2\text{O}$	3.4 to 8.5
$\text{MnO}_2 + 2\text{e}^- + 4\text{H}^+ = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	3.4 to 6.8
$\text{FeOOH} + \text{e}^- + 3\text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{O}$	1.7 to 5.0
$\text{SO}_4^{2-} + 6\text{e}^- + 9\text{H}^+ = \text{HS}^- + 4\text{H}_2\text{O}$	0 to -2.5
$\text{H}^+ + \text{e}^- = 1/2 \text{H}_2$	-2.5 to -3.7
$(\text{CH}_2\text{O})_n = n/2 \text{CO}_2 + n/2 \text{CH}_4$	-2.5 to -3.7

After Sposito (1989) and Bohn et al. (1979)

reductions are initiated in neutral pH aquatic systems. In each case, it may be imagined that reduction half-reaction is coupled with the oxidation of organic materials, as in Equation 3.19.

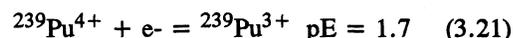
As the pE of the system drops below +11.0, enough electrons become available to reduce $O_2(g)$ to $H_2O(aq)$ (Table 3.3). Below pE 5, O_2 is not stable in neutral systems; above pE 5, O_2 is consumed in the respiration processes of aerobic microorganisms. As the pE decreases below 8.0, electrons become available to reduce NO_3^- . This reduction is catalyzed by nitrate respiration (that is, NO_3^- serving as a biochemical electron acceptor like O_2) involving bacteria that ultimately excrete NO_2^- , N_2 , N_2O , or NH_4^+ . Denitrification is the special case of nitrate respiration, in which $N_2(g)$ and other nitrogenous gases are produced (Section 2.3).

As the system pE value drops into the range of 7.0 to 5.0, electrons become plentiful enough to support the reduction of Fe and Mn in solid phases. Iron reduction does not occur until O_2 and NO_3^- are depleted, but Mn reduction can be initiated in the presence of NO_3^- . In the case of Mn and Fe, decreasing pE results in solid-phase dissolution because the stable forms of Mn(IV) and Fe(III) are solid species. Besides the increase in Mn and Fe solubility expected from this effect of lowered pE, a marked increase in the aqueous-phase concentrations of metals like Cu, Zn, or Cd, and of ligands like $H_2PO_4^-$ or $HMoO_4^-$, accompanying Mn and Fe reduction is usually observed. The principal cause of this secondary phenomenon is the desorption of metals and ligands that occurs when the adsorbents (such as Fe and Mn oxides) to which metals are bound become unstable and dissolve. Typically, the metals released in this fashion, including Mn and Fe, are soon reabsorbed by solids that are stable at low pE (such as clay minerals or organic matter) and become exchangeable surface species. These surface changes have an obvious influence on the availability of the chemical elements involved, particularly phosphorus. If a radionuclide were involved in this dissolution/exchange set of reactions, the latter radionuclide species is expected to be less strongly associated with the solid phase.

As pE becomes negative, the reduction of S(VI) can take place. If radioactive metals, such as Co are present in the aqueous phase at high enough concen-

trations, they can react with bisulfide (HS^-) to form metal sulfides that are quite insoluble. Thus, anoxic wastewater conditions can diminish significantly the solubility of radioactive metals, thereby reconcentrating them in a solid phase.

Redox chemistry also has a direct effect on radionuclide chemistry in wastewater treatment facilities. The oxidation state and, therefore, the potential of reconcentration of Co, I, Ir, Np, Pu, Tc, and U are affected. For example, the reduction of Pu



makes ^{239}Pu appreciably less reactive in complexation (that is, $^{239}\text{Pu}^{3+}$ stability constants are much less than those of $^{239}\text{Pu}^{4+}$) and sorption/partitioning reactions (Kim 1986). The reduction of U(VI) as the UO_2^{2+} ion to U(IV) has the opposite effect [that is, U(IV) forms stronger complexes and sorbs more strongly to surfaces than U(VI)]. Therefore, changes in redox may increase or decrease the tendency for reconcentration of radionuclides in wastewater treatment, depending on the aqueous-phase chemical composition and the radionuclide in question. However, if the redox status becomes low enough to induce sulfide formation, generally reconcentration of radionuclides can be expected.

The pE at the bottom of settling tanks, the bottom of aerobic-attached-growth unit operators (Section 2.3.1.2), and thorough anaerobic digestors (Section 2.3.1.3 and 2.3.1.4) are lower than the rest of the wastewater stream (Metcalf and Eddy, Inc. 1991). In the case of the first two unit operators, sulfide generation may occasionally occur (Metcalf and Eddy, Inc. 1991); therefore, these aerobic-like processes may have a low enough pE status to cause the reduction of several radionuclides. Another treatment process that has a direct effect on the redox status of the wastewater treatment stream is the disinfection process using strong oxidizers (Sections 2.3.2.4 and 2.5.5). Many redox-sensitive constituents may oxidize during this step because very strong oxidizing agents (chloride gas, ozone, sodium or calcium hypochlorite) are used.

3.3.3 Aqueous Phase/Solid Phase Sorption

When a wastewater constituent of interest is identified as existing in the filterable fraction of a sample, it is

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not known if that constituent was adsorbed onto the surface of a solid, absorbed into the structure of a solid, precipitated as a three-dimensional molecular structure on the surface of the solid, or partitioned into an organic structure. Such detailed information is often very difficult to obtain. A generic term, devoid of mechanism used to describe the partitioning of aqueous-phase constituents to a solid phase, is sorption. This term, frequently quantified by the distribution coefficient, K_d , is defined as

$$K_d = \frac{q_i}{C_i} \quad (3.22)$$

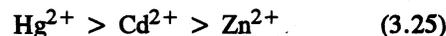
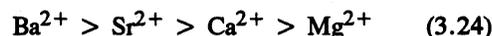
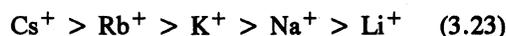
where q_i is the amount of constituent sorbed to the surface and C_i is the concentration of constituent i in the equilibrium aqueous phase that is in contact with the solid phase (Sposito 1984).

Adsorption, as discussed in this text, is the net accumulation of matter at the interface between a solid phase and an aqueous-solution phase.

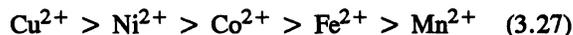
Adsorption differs from precipitation because it does not include the development of a three-dimensional molecular structure. The matter that accumulates in two-dimensional molecular arrangements at the interface is the adsorbate. The solid surface on which it accumulates is the adsorbent. Adsorption on clay particle surfaces can take place via three mechanisms: 1) The inner-sphere complex that resides in the Stern layer (Figure 3.5), 2) The outer-sphere surface complex that has a solvation shell (at least one water molecule between it and the surface), and 3) If a solvated ion does not form a complex with a charged surface functional group but instead neutralizes surface charge only in a delocalized sense, it is said to be adsorbed in the diffuse-ion swarm (Figure 3.5). The diffuse-ion swarm and the outer-sphere surface complex mechanisms of adsorption involve, almost exclusively, electrostatic bonding; whereas inner-sphere complex mechanisms are likely to involve ionic, as well as covalent, bonding.

As a rule of thumb, the relative affinity of a wastewater adsorbent for a free-metal cation will increase with the tendency of a cation to form inner-sphere surface complexes. The higher the valence or the ionic potential (the ratio of the valence to the ionic radius) of a cation, the greater the tendency the cation has of forming an inner-sphere complex (Sposito

1989). Based on these considerations and laboratory observations, the relative-adsorption affinity of metals has been described as follows (Sposito 1989):



With respect to transition metal cations, however, ionic potential is not adequate as a single predictor of adsorption affinity because electron configuration plays a very important role in the complexes of these cations. Their relative affinities tend to follow the Irving-Williams order:



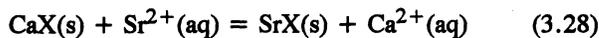
The molecular basis for this ordering is discussed in Huheey (1983).

The effect of pH on metal cation adsorption is principally the result of changes in the variable-charge component of the surface charge and hydrolysis of metal cations. As discussed in Section 3.2.2, most of the suspended materials in wastewater treatment facilities have variable-charged surfaces. As the pH increases, the surface charge decreases toward negative values (Figure 3.4), and the electrostatic attraction of a wastewater adsorbent for a metal cation is enhanced. The presence of complex-forming ligands in the wastewater solution greatly complicates the prediction of the relative adsorption affinity of a metal cation. For example, radioactive $^{60}Co^{2+}$ usually adsorbs very strongly to inorganic surfaces, but if EDTA is present to form nonadsorbing-soluble complexes with the $^{60}Co^{2+}$, its electrostatic attraction to a clay surface will be diminished appreciably (Means et al. 1978). Decreases in Am, Pu, and U sorption have also been observed when these radionuclides form complexes with naturally occurring humic substances (Means et al. 1978; Kim 1986).

The mechanisms by which nonpolymeric anions adsorb are surface complexation and diffuse-ion swarm association. Outer-sphere surface complexation of anions involves coordination with a protonated hydroxyl or amino group or to a surface metal cation

(such as water-bridging mechanisms). Inner-sphere surface complexation of anions, such as borate, phosphate, and carboxylate, involves coordination with created or native Lewis acid sites. Almost always, the mechanism of this coordination is hydroxyl-ligand exchange (Sposito 1984). In general, ligand exchange is favored by $\text{pH} < \text{zero point of charge}$ (Table 3.2 and Figure 3.3). The anions Cl^- and NO_3^- , and to a lesser extent HS^- , SO_4^{2-} , and HCO_3^- , are considered to adsorb mainly as diffuse-ion and outer-sphere-complex species.

In its most general meaning, an ion-exchange reaction involves the replacement of one ionic species in or on a solid phase by another ionic species taken from an aqueous solution in contact with the solid. In the cation-exchange reaction



Sr^{2+} replaces Ca^{2+} from an exchange site, X. The equilibrium constant, K_{ex} , for this exchange reaction is defined by

$$K_{\text{ex}} = \frac{[\text{SrX(s)}][\text{Ca}^{2+}(\text{aq})]}{[\text{CaX(s)}][\text{Sr}^{2+}(\text{aq})]} \quad (3.29)$$

Numerous ion-exchange models are described by Sposito (1984) and Stumm and Morgan (1981).

Relevant to radionuclide chemistry in wastewater treatment facilities is a phenomenon referred to as "isomorphic exchange" (Friedlander et al. 1966). This may best be described through an example. Strontium can exist naturally as the nonradioactive isotope, ^{88}Sr , in many carbonate systems at a concentration of approximately 10^{-6} M. If the ^{88}Sr is in equilibrium with a solid-exchange phase and a very large dose of the anthropogenic ^{90}Sr (such as 1000 pCi L^{-1}) is introduced into the system, it is likely the resulting K_{ex} for the ^{90}Sr would be appreciably less than if no other Sr isotopes were in the system. The reason for this is the solid-exchange phase cannot distinguish between the two isotopes. Although the radioactivity of the ^{90}Sr is quite high, its mass addition to the system is minimal (approximately 10^{-12} M in this example). Hence, addition of ^{90}Sr to the system has essentially no effect on the already existing mass-based equilibrium described by K_{ex} .

The solids in a typical wastewater treatment facility are composed primarily of organic materials. Organic materials make up approximately 75 percent of the suspended solids and 40 percent of the filterable solids in a typical wastewater stream (Figure 3.1). Of the organic fraction, approximately 40 to 60 percent are proteins, 25 to 50 percent are carbohydrates, and 10 percent are fats and oils (Hernandez et al. 1988; Garcia et al. 1989; Metcalf and Eddy, Inc. 1991). Urea is also present in large concentrations but decomposes very rapidly, so it is seldom found in wastewater other than raw sewage. Proteins contain primarily amino (NH_3^+), sulfhydryl (SH^-), and carboxyl (COO^-) functional groups; carbohydrates contain primarily carboxyl and alcohol groups; fats and oils contain primarily quinone carbonyl ($\text{C} = \text{O}$), ketonic carbonyl, carboxyl, and alcohol functional groups.

Each of these functional groups has a unique pK_a value and imposes a variable charge to these substances (Figure 3.3). Because most of the functional group acidity of these substances dissociates between pH 5 and 7 (Hernandez et al. 1988), these organic molecules are expected to bear a net negative charge in wastewater treatment facilities where the pH is often maintained between 7 and 9. Even in the acidic pH range, these organic materials likely have a net negative charge. However, variable-charge materials with a net-negative charge may still possess positively charged functional groups, although usually not many. Basic amino acids like arginine, that contain two protonatable NH_2 groups, are good examples of an organic material that may possess some positively charged functional groups when the entire molecule has a net negative charge. Even without the development of net-positive charge, protonated functional groups like COOH and NH_3^+ can form hydrogen bonds with functional groups containing electronegative atoms, such as O, N, and F. As an example, the carbonyl groups in the phenylcarbamate pesticides can form a hydrogen bond with NH in humic substances.

Much of the molecular framework of organic matter found in wastewater is not electrically charged. This nonionic structure can nevertheless react strongly with the uncharged part of another organic compound through van der Waals' interactions (Stevenson 1982). This provides a mechanism by which weakly charged metal/organic complexes that are not electrostatically

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attracted to solid surfaces can partition to solid phases and eventually be flocculated from suspension. The van der Waals' interaction between just two molecules is very weak, but when many molecules in a polymeric structure like sludge interact simultaneously, the van der Waals' component is additive and strong. The van der Waals' interaction between nonionic compounds, or nonionic portions of compounds, and organic matter is often stronger than the interactions between these compounds and water. Water molecules in the vicinity of large nonpolar molecules are not attracted and so cannot orient their very polar OH bonds in ways that are compatible with the normal structure of liquid water. The resultant disorder of this situation produces a low water solubility of the nonpolar molecule and a propensity for it to react with organic matter through van der Waals' interactions. This phenomenon is referred to as "hydrophobic attraction" and is frequently described by the distribution coefficient defined in Equation 3.22.

3.4 Biological Factors

Biological treatment of wastewater takes place during secondary treatment (Section 2.3). It is the principal process used to remove unwanted dissolved and colloidal materials from the wastewater stream (Lester 1987b) and, therefore, a likely process where radionuclide reconcentration may occur. Material removal during biological treatment has been extensively studied, although the overwhelming majority of results presented are for biologically activated-sludge facilities (Lester 1987b). Several mechanisms are possible for the removal of materials in this process, including 1) physical trapping of materials associated with particulates in the sludge-floc matrix, 2) sorption of soluble materials to bacterial extracellular polymers, and 3) accumulation of soluble materials by the microbial cell (Brown and Lester 1979). It is difficult to distinguish between precipitated metals that have settled independently but are removed with the sludge, and precipitated metals that have interacted with the floc matrix and become physically entrapped and settled with the floc. Because of the difficulty in differentiating between these three mechanisms, researchers usually calculate a distribution coefficient value (Equation 3.22) of the entire sludge material (Rudd et al. 1983; Lester 1987b).

Evidence for the direct involvement of extracellular polymers in metal adsorption comes from several sources. Freidman and Dugan (1968) compared the uptake of metal ions by two strains of *Z. ramigera*: a strain that produced extensive amounts of polymers and a strain that produced no extracellular polymers. They found the strain that did not produce any extracellular polymers accumulated only half as much metal as the strain that produced extracellular polymers. They suggested that extracellular polymers may be responsible for half the metal uptake and that total metal uptake is determined by the combined influence of the cell and its extracellular matrix.

Brown and Lester (1982) attempted to quantify the contribution of metal uptake by extracellular polymers to the total percentage uptake by biologically activated sludge. This quantification was investigated by using a relatively nondisruptive method to extract the polymer from the biomass, followed by assessing the uptake of Cd and Ni by intact biomass, biomass stripped of its polymer, and isolated polymer. At added metal concentrations of 0.1 and 1 mg L⁻¹, extraction of the polymer from the biomass reduced the uptake of Cd by approximately 85 to 95 percent for Cd and 28 to 30 percent for Ni. The uptake of the metals by the extracted polymer did not completely account for these differences, but generally about twice as much Cd as Ni was complexed with the polymer.

The accumulation of metals by the cells of living organisms is a well-documented phenomenon (Lester 1987b). An organism may accumulate metals to varying degrees, depending on the bacterial strain and the metal. Metals may be either actively taken up (assimilated) by the organism or passively adsorbed to the cell wall. Copper and Ni tend to be actively taken up, whereas Mn, Co, Cd, and Th tend to be more passively adsorbed onto the cell surface (Lawson et al. 1984a).

In experiments to determine the relative contribution of adsorption and precipitation to metal removal in laboratory experiments, eight metals, including trivalent and hexavalent Cr, were added at two concentrations to identical samples of biologically activated-sludge suspensions and filtrates of biologically activated sludge (Sterritt and Lester 1981). The samples were filtered (refiltered in the case of the biologically activated-sludge filtrate samples), and the

metals in the filtrates were determined. A severe limitation of this study is that metals were introduced into the suspensions in the dissolved free form (M^{m+}), instead of as a complex. The net effect is that metal removal by biologically activated sludge is likely to be greater in the experiment than in an actual treatment facility. Cadmium, Cr(VI), Mn, and Ni were almost completely soluble in the sludge filtrate, and removal was, therefore, almost entirely caused by sorption to the biological solids because no precipitates (filterable metal in the spiked activated sludge filtrates) were detected. Cobalt was predominantly nonfilterable (soluble), and because its removal from suspension appeared not to be concentration-dependent, the formation of insoluble salts may have been limited by the concentration of species able to coprecipitate. The removal of Pb was almost entirely due to precipitation (large amounts of metals were removed by filtering the spiked sludge filtrates). Removal of Cr(III) by precipitation exhibited a concentration dependence that contrasted with the behavior of Pb. The relative contribution of adsorption and precipitation to Cu removal appeared to be dependent on concentration. At the lower concentration of Cu added (2×10^{-5} M), 50 percent of the total removal was the result of precipitation; whereas of the total removal at the added concentration of 2×10^{-4} M, 92 percent was the result of precipitation. It appears that precipitation is important in the removal of some metals, notably Pb, Cu, and Cr(III).

3.5 Removal Efficiency of Various Wastewater Treatment Processes

One measure of the ability of a given process to remove materials from wastewater is called the removal efficiency, R , defined as

$$R = \frac{C_i - C_e}{C_i} \times 100 \quad (3.30)$$

where C_i and C_e are the concentrations of the influent and effluent constituents. No shortage of this type of data exists (Lester 1987a, 1987b; Metcalf and Eddy, Inc. 1991; Krishnan et al. 1992). Unfortunately, such data rarely provide any insight into the mechanisms

responsible for the observed change in constituent concentration. Furthermore, usually no attempt is made in these studies to separate the solids from the entrained liquids; therefore, it is not possible to determine if the constituent of interest is truly partitioned to the solid phase. As presented previously, several mechanisms for the removal of unwanted constituents are possible in any given wastewater treatment process. For instance, the addition of alum may remove the unwanted constituent via precipitation or flocculation. The following paragraphs discuss the reported efficiencies of three kinds of wastewater treatment processes. Additionally, whenever possible, efforts are made to provide some insight as to the possible mechanism underlying the removal of the targeted constituent and the ramification of these mechanisms on radionuclide reconcentration. Most of the literature referenced is on the subject of heavy metal removal; therefore, most of the examples provided will deal with heavy metals.

3.5.1 Primary Treatment

The removal of contaminant metals during primary sedimentation is important for two reasons: 1) it reduces the metal loading on the biological stage of treatment, thus reducing the possibility of impairment of the efficiency of treatment as a result of metal toxicity (Barth et al. 1965); and 2) it contributes to the overall removal efficiency for the treatment facility, thus reducing contamination of surface waters into which final effluents are discharged. Metal removal during primary sedimentation is a physical process dependent on the settlement of precipitated metal or metals associated with particulate matter (Section 3.2). Minimal removal of dissolved metals occurs during this process and the proportion of dissolved metal to total metal in the effluent increases as a result (Oliver and Cosgrove 1974).

A great deal of variability in the efficiency of metal removal by primary sedimentation would be expected because the factors that affect suspended-colloid sedimentation, as well as those affecting contaminant speciation, vary widely between treatment facilities (Lester 1987a). Lester tabulated the removal efficiencies of seven wastewater treatment facilities, and an abridged version of his tabulation is presented in Table 3.4. The results of Lester's study indicated that removal efficiencies of metals were not related to

influent concentrations and that they followed a general trend consistent with the reported propensity of these metals to sorb to mineral and organic surfaces: $Pb > Hg \gg Cu > Zn \gg Cr > Cd > Ni$. Nickel consistently had the lowest removal efficiencies in the seven studies reported by Lester (1987a), as well as in several other studies (Davis and Jacknow 1975; Lester et al. 1979; Stoveland et al. 1979). Nickel removal was <2 percent during a six-month study at a full-scale treatment plant in the United Kingdom (Davis and Jacknow 1975).

Table 3.4 Metal concentrations in raw sewage and their removal during primary sedimentation^(a)

Metal	Number of Observations	Influent Concentration Range ($\mu g L^{-1}$)	Average Removal (%) (\pm Std. Err.)
Cadmium	6	5 to 85	37 \pm 15
Chromium	6	90 to 786	38 \pm 10
Copper	7	120 to 560	45 \pm 17
Mercury	2	1 to 7	56 \pm 2
Nickel	5	80 to 1,126	33 \pm 15
Lead	7	51 to 630	58 \pm 15
Zinc	6	600 to 2,400	44 \pm 17

(a) After Lester (1987a)

Removal data, based on total concentrations of contaminant metals, do not provide an indication of removal mechanisms involved. Contaminant removal in primary sedimentation depends on the presence of the metal in a settleable or potentially settleable form. Contaminants that are removed may exist in insoluble forms or forms that have the capacity for binding to settleable solids. Lester (1987a) reported the ratio of soluble to insoluble species increases as a result of primary sedimentation. Thus, the speciation of contaminants in the influent sewage will influence their removals. For instance, Bailey et al. (1970) showed that Cr(III) was largely removed in sedimentation, leaving the hexavalent species in solution.

Kempton et al. (1987a) partitioned the metal concentrations in raw sewage into two groups: metals associated with volatile suspended solids (mostly organic solids) and nonvolatile suspended solids

(inorganic solids). They concluded that two main groups of contaminants could be discerned. Silver, Co, and Mo were strongly associated with the volatile suspended solids. The second group of metals, consisting of Cu, Mn, Pb, and Zn, was primarily associated with the nonvolatile suspended solids fraction. The authors did not attempt to explain why Cu and Pb existed primarily in the nonvolatile instead of the volatile fraction, since both metals typically form extremely strong organic complexes (Schnitzer and Kahn 1972; Stevenson 1982; Sposito 1989).

3.5.2 Secondary Treatment

Secondary treatment primarily involves the use of biological processes to remove constituents that are not effectively removed during primary treatment (Section 2.3). Metal removal during biological treatment has been extensively studied (reviewed by Lester 1987b). However, most studies have dealt exclusively with biologically activated-sludge facilities because this is the most common process in use (Table 2.1). As described in Section 2.3, biological treatment can be divided into two parts: a biological reactor and a phase separator (settling). In the reactor, large populations of microorganisms grown under aerobic conditions oxidize the dissolved or suspended organic compounds present in wastewater and convert them into CO_2 , water, and cellular material. The bacteria and other microorganisms form aggregates. The suspension then passes into a settling tank. Any substance that is sorbed by the bacterial flocculent is removed from the wastewater stream. A combination of flocculation and settling is, therefore, the mechanism by which material removal is achieved during this process. Any factor affecting the flocculation or settling properties of a suspension will also affect its capacity to remove materials.

As was observed for primary sedimentation, removal efficiencies of metals by biologically activated-sludge facilities vary a great deal (Table 3.5). The wide range of removal efficiencies observed for any one metal demonstrates the variability of conditions prevailing in biologically activated-sludge facilities. Iron, Cu, Cr, and Zn had the highest removal-efficiency values (Table 3.5) while Ni, Mn, Ca, and Mg had the lowest removal-efficiency values. These generalized metal-removal efficiencies are consistent with the findings of Neufeld and Hermann (1975) and

Table 3.5 Metal-removal efficiencies during activated sludge treatment^(a)

Element	Number of Observations	Range	Average
		Activated Sludge Effluent ($\mu\text{g L}^{-1}$)	Removal (%)
Aluminum	2	250 to 1,750	72 \pm 29
Cadmium	19	0.3 to 120	49 \pm 22
Chromium	20	10 to 47,000	58 \pm 23
Cobalt	2	17 to 79	2 \pm 1
Copper	25	10 to 54,500	62 \pm 23
Iron	3	457 to 2,950	86 \pm 13
Lead	19	4 to 25,500	60 \pm 25
Nickel	21	71 to 25,300	24 \pm 18
Zinc	21	180 to 20,000	55 \pm 23

(a) After Lester (1987b). Includes data from laboratory simulations, pilot plant studies, and full-scale facility studies.

Forster (1976). The data presented in Table 3.5 do not suggest that a trend exists between metal loading and metal removal; however, Brown et al. (1973) reported that such a relationship existed for Cr, Cu, Pb, Zn, and Cd in a study of six treatment plants.

Oliver and Cosgrove (1974) reported that much of the Pb and Fe introduced as soluble species was converted into an insoluble form upon reaction with municipal sewage; these metals were very efficiently removed. The same authors observed that the ratio of dissolved to total metal concentration increased as metals passed through the treatment process.

In the case of Cr, the oxidation state or valence has been found to affect removal efficiency (Sections 3.3.2 and 3.5.3). Although Cr normally enters the treatment plant in the hexavalent form (Moore et al. 1961), it has been demonstrated that during secondary treatment it may be reduced to the trivalent form (Brown et al. 1973). As mentioned in Section 3.3.2, reducing environments can exist toward the bottom of aerobic digesters. Removal efficiency for Cr(III) in biologically activated-sludge treatments has been reported to be 70 to 90 percent, while Cr(VI) removal efficiency was approximately 20 percent (Lester 1987b).

Extracellular polymers may exist in the form of loose slime, which causes an increase in the viscosity of the medium, or capsules, that adhere to the cell wall. Dudman and Wilkinson (1965) have proposed that the more soluble extracellular polymers become detached from cells and remain in colloidal suspension. One strain of *K. aerogens* produced an extracellular polymer of the capsular type and another strain produced a slime extracellular polymer; both had exactly the same composition and immunological specificity. From the standpoint of treatment removal efficiency, the capsule polymers are more desirable because they can be more easily settled than the slime polymers that remain in the dissolved and colloidal phases of the effluent.

Conditional stability constants from metal complexes of extracellular polymers and sludge floc extracted from biologically activated sludge have been reviewed by Lester (1987b). The constants determined for the extracellular polymers were similar to those determined for the entire sludge floc, suggesting the polymer may have conferred considerable complexation ability on the biomass. The affinity of the polymers and sludge floc for metals was $\text{Cu} > \text{Co} > \text{Cd} > \text{Ni}$.

3.5.3 Chemical Additives

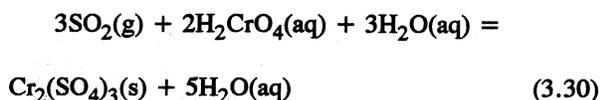
The addition of chemicals to the wastewater stream can occur during primary, secondary, or tertiary treatment. During primary treatment, the chemicals added to the wastewater stream are flocculents, such as polyelectrolytes, lime, alum, and ferrous salts (Section 2.2). During secondary treatment, the chemicals added include flocculents, compounds to promote phosphate precipitation (such as alum, lime, and sodium sulfide), and disinfectants (such as chlorine gas and calcium hypochlorite) (Section 2.3.2). During tertiary treatment, the chemicals added include those used during secondary treatment and compounds to remove a specific constituent (Sections 2.4.3 and 2.4.5). Because the addition of flocculents and precipitators has the expressed objective of removing solid associated- or dissolved-unwanted constituents from the wastewater stream, such addition is also likely to result in the removal and, therefore, reconcentration of most radionuclides.

The EPA conducted a comprehensive study using 21 well-characterized wastewater samples to evaluate the

3 Biological, Chemical, and Physical Processes.

metal-removal efficiencies of lime, sodium sulfide, and several sulfide sources for reducing Cr(VI) (Krishnan et al. 1992). Addition of lime to the wastewater stream was effective in removing As, Cd, Cr(III), Cu, Fe, Mn, Ni, Pb, and Zn from solution (Table 3.6). Sulfide precipitation was effective for Cd, Co, Cu, Fe, Hg, Mn, Ni, and Zn (Table 3.7). It is likely that many of the radionuclide metals would also be removed from solution/suspension following lime or sulfide treatment. If lime were added to a wastewater stream containing U^{4+} and Th^{4+} , it is likely these radionuclides would precipitate/coprecipitate from solution as sparingly soluble hydroxide solids (Kim 1986). Similarly, the addition of sulfide salts would likely cause the precipitation/coprecipitation of Th, Am, Co, Sr, Mn, and U from the wastewater dissolved phase.

Four sulfide compounds (sulfur dioxide [SO_2], sodium bisulfite [$Na_2S_2O_4$], sodium metabisulfite [$Na_2S_2O_5$], and ferrous sulfate [$FeSO_4 \cdot 7H_2O$]) were also evaluated for their ability to remove Cr(VI) by reducing it to the more insoluble form, Cr(III). The reduction of Cr(VI) through the introduction of SO_2 can be described as follows:



The reduction reaction proceeds rapidly at a wastewater pH between two and three. Atmospheric oxygen consumes a major portion of the reducing agent; therefore, excess chemical reductant is required. After reduction, the Cr(III) is removed from the wastewater by precipitating it from solution by adding lime to increase the pH to above 8.0 (Krishnan et al. 1992). Of the four sulfide compounds evaluated for Cr(VI) removal, sodium bisulfite was the only one that did not perform adequately (Table 3.8). Radionuclides reportedly found in wastewater treatment facilities and known to become less soluble after reduction include Tc and U (Kim 1986; Wolfrum and Bunzl 1986). These two constituents would likely be reconcentrated if they were exposed to a sulfide-reduction tertiary treatment.

Table 3.6 Metal-removal efficiency by hydroxide precipitation^(a)

Metal	Inlet Concentration (mg L ⁻¹)	Residual Concentration (mg L ⁻¹)
Arsenic	0.2 to 0.5	0.03
Cadmium	3.10	0.21
Chromium, trivalent	1300	0.06
Copper	204 to 385	0.2 to 2.3
Iron	10	0.1
Lead	0.5 to 25	0.03 to 0.1
Manganese	21	1.1
Nickel	5	0.15
Zinc	16.1	0.02 to 0.23

(a) After Patterson (1985).

Table 3.7 Metal-removal efficiency by sulfide precipitation^(a)

Metal	Influent Concentration (mg L ⁻¹)	Residual Concentration (mg L ⁻¹)
Cadmium	440 to 1000	0.008
Copper	50 to 115	0.5
Mercury	6.0	0.05
Nickel	6.5	2.1
Zinc	3.2	0.09

(a) After Patterson (1985).

Table 3.8 Effect of sulfide additions on chromium(VI) concentrations in wastewater^(a)

Reducing Agent	Chromium(VI) Concentration (mg L ⁻¹)	
	Influent	Effluent
Sulfur dioxide	1,300	ND ^(b)
Sodium bisulfite	140	0.7 to 1.0
Sodium metabisulfite	70	0.5
Ferrous sulfate	1,300	0.01

(a) After Patterson (1985) and Cushnie (1985).

(b) ND = Not detectable.

4 Chemistry of Important Radionuclides During Wastewater Treatment

4.1 Introduction

The reconcentration and chemistry of ^{241}Am , ^{60}Co , ^{137}Cs , ^{131}I , ^{54}Mn , ^{90}Sr , $^{99\text{m}}\text{Tc}$, ^{232}Th , and ^{238}U during wastewater treatment are examined in this section. These radionuclides vary widely in their decay rates, sources, and chemical behaviors (Table 4.1). Thorium-232 and ^{238}U are of natural origin and their occurrence in sewage sludge are largely dependent on the regional mineralogy. These radionuclides may also become concentrated in sewage sludge where ore extraction or other types of processing occurs and Th or U waste enters the sewage system. The other radionuclides are primarily man-made and their occurrence in sludge will be dependent almost entirely on the amount discharged into the sewage system by licensees.

The discharge of radionuclides into municipal sewer systems has been regulated by the NRC in accordance with 10 CFR 20 and, in some instances, by state agencies in accordance with state regulations. These regulations were developed because of concerns about potential harmful concentrations of radioactive materials in WWTPs and in the effluents leaving the plants. A licensee is allowed to discharge licensed radioactive material to the sanitary sewer if the material is readily soluble (or is a readily dispersible biological material) in water and the quantity of radioactive material that the licensee releases in one month divided by the average monthly volume of wastewater released into the sewer by the licensee does not exceed the activity concentrations given in Table 3 of Appendix B of 10 CFR 20 (U.S. Nuclear Regulatory Commission 1991). These limiting concentrations are presented in Table 4.1 for radionuclides of interest in this study. (See the notation for Table 3 in Appendix B of 10 CFR 20 for a description of the method used by NRC to calculate these values.) In addition to these limitations, 10 CFR 20 also restricted the total annual activity of all radionuclides discharged to 185 GBq per year tritium, 37 GBq per year for ^{14}C , and 37 GBq total for all other radionuclides combined. Thus, a licensee who handles tritium, ^{14}C , as well as other radionuclides is

limited to a combined release not to exceed 259 GBq per year. Finally, these regulations provide an exclusion for excreta from individuals undergoing medical diagnosis or therapy with radioactive materials.

The sewage-release limit for a radionuclide is in part controlled by the half life ($t_{1/2}$) of the radionuclide: an inverse relationship exists between a radionuclide's half life and its sewage-release limit (Table 4.1). Technetium-99m has a rather large sewage release limit in part because of its short half-life of only 6 hours. Consequently, radiological decay likely plays a much greater role than any biological or chemical wastewater treatment process in $^{99\text{m}}\text{Tc}$ reconcentration. Conversely, ^{241}Am and ^{238}U have long half-lives and, therefore, physical and chemical processes likely play a more important role than radiological decay in their reconcentration.

Table 4.1 Half-life, natural abundance, common sources, and release limit into sanitary sewage systems of selected radionuclides

Radio-nuclide	$t_{1/2}$ (y) ^(a)	Natural Abundance (%) ^(a)	Sewage Release Limit (mBq/L) ^(b)	Common Sources (b, c, d)
^{241}Am	432	0	0.007	Smoke Detectors, W
^{60}Co	5.3	0	1.1	P, R
^{137}Cs	30	0	0.37	P, R, W
^{131}I	0.022	0	0.37	M, P
^{54}Mn	0.767	0	11.1	W, M
^{90}Sr	29	0	0.19	P, R, W
$^{99\text{m}}\text{Tc}$	0.0010	0	370	W, M
^{232}Th	1.39E10	100	0.01	N
^{238}U	4.51E9	99.27	0.11	N

(a) Friedlander et al. (1966).

(b) NRC (1991).

(c) Mattigod and Page (1983).

(d) P = Power Plants; R = Fuel Processing;

W = Weapons Testing; M = Medical; N = Natural.

The objective of this section is three-fold: 1) tabulate reported radionuclide concentrations in wastewater streams and removal efficiency values; 2) provide a description of the important biological, chemical, and physical processes likely to control the reconcentration of these radionuclides in wastewater treatment streams; and 3) identify the likely wastewater treatment processes where the radionuclides are likely to be reconcentrated. Each radionuclide is discussed in a separate subsection that contains a comprehensive table of reported radionuclide concentrations in wastewater streams and removal efficiency values.

4.2 Americium

Americium does not occur naturally in the environment (Table 4.1). However, because radioactive fallout contains ^{241}Pu (a parent to ^{241}Am), ^{241}Am distribution is worldwide (Perkins and Thomas 1980). Americium is produced as two long-lived isotopes: ^{241}Am (with a half-life of 432 years) and ^{243}Am (with a half-life of 7370 years); the former being more common in the geosphere. It can exist in four oxidation states, Am(III), Am(IV), Am(V), and Am(VI). The Am(III) oxidation state is the most stable under oxidizing atmospheric conditions. The higher oxidation states are strong oxidizing agents and, therefore, are prone to converting to Am(III) in most systems including wastewater treatment systems where a substantial amount of organic matter (an oxidizable material) exists (Coleman 1963).

4.2.1 Behavior in Wastewater Treatment Plants

Americium-241 has been detected in the sewage sludge of a number of WWTPs (Table 4.2). The sources of the Am found in two New York State WWTPs were companies producing foils for smoke detectors (New York State Department of Health 1986). In the Tonawanda, NY case, ^{241}Am was found in about 10,000 tons of ash that had been disposed of in a landfill. In April and May, 1984, the ash contained between 6.7 ± 1.5 Bq/g and 28 ± 7.0 Bq/g of ^{241}Am (Table 4.2). The activity decreased continually until 1986, when the last measurement was made. At this time, the activity was 0.4 ± 0.07 Bq/g ash. The decline in ^{241}Am activity was attributed to the foil manufacturer moving

his business to Mexico in May, 1983, thereby removing the contaminant source (Rimawi 1984a). These ^{241}Am data provide some insight regarding the propensities of the different wastewater treatment processes to concentrate ^{241}Am . The sequence of the wastewater treatment processes at the Tonawanda Sewage Treatment Plant are as follows: primary settling, conventional biologically activated sludge, settling tank, Zimbrow (heat treatment of sludge for stabilization and conditioning), and incineration. The data from 1984 indicates the average activity of the sludge at the end of the treatment process (0.1 Bq/g) was somewhat lower than the sludge recovered from the bottom of the settling tank (0.2 Bq/g). This suggests the solids removed downstream of the settling tank contained lower activities of ^{241}Am per gram of solid (that is, the settling tank reconcentrated ^{241}Am more effectively than the following processes). The biologically activated sludge (Section 2.3.1) had a greater activity (0.4 Bq/g) than the final sludge or the settling-tank sludge. Apparently, the biologically activated-sludge process and the settling tank are effective at removing ^{241}Am from the wastewater stream. The Zimbrow process had little significant affect on ^{241}Am activity in the sludge. Clearly, the greatest increase in ^{241}Am activity was measured after sludge incineration when ^{241}Am activity increased by over an order of magnitude (Table 4.2).

Because of the ^{241}Am contamination at the Tonawanda Site, the New York Department of Health also collected sludge samples at the Grand Island Wastewater Treatment Facility, which received effluent from another manufacturer that produced foils for smoke detectors. This manufacturing facility discharged about 0.9 GBq/y of ^{241}Am into the sewage system. The Grand Island Facility uses tertiary treatment prior to discharging effluent. Sludge is digested and pressed to increase the solids content to about 20 percent, and subsequently buried in a landfill. The average ^{241}Am activity in the dry sludge was 3.1 Bq/g dry weight when first measured in 1984. Upon the request of the New York Department of Labor, the manufacturer reduced the ^{241}Am activity in its discharges by filtering the waste prior to release from the waste-holding tanks. As can be seen in Table 4.2, the ^{241}Am activity in the waste generated from the Grand Island Facility gradually decreased during the following two years. This provides an example of the importance of removing particulate

Table 4.2 Americium-241 occurrence in wastewater treatment plants

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ²⁴¹ Am Activity	Effluent ²⁴¹ Am Activity	Stabilized Sludge ²⁴¹ Am Activity	RF	Reference	Comments
Chicago Metropolitan Sanitary District, Stickney, IL	Irnhoff process; Air dried and aged in large open-air piles; sludge dried as free fertilizer called "Nu Earth"	Summer 1974; Spring 1975	NR	NM	NM	0.074-0.16 Bq/kg ash 0.056-0.12 g d wt ^a	NR	Alberts and Walgren 1977; Alberts et al. 1974	²⁴¹ Am detection was below background levels Material in sludge appears to be in form not readily available for removal and is unlikely to remobilize a. Dry weight
Webster Wastewater Treatment Plant, Webster, TX	Dried processed sludge	3/22-31/83 8/17/83 9/29/83 1/14/86	NR	NM	NM	LLD (259)-740 Bq/kg ^a	NR	Texas DOH 1986	a. Types of sludge monitored include dried process, surface, process, sludge bin, from floor of drier bldg, on drier belt
Webster Wastewater Treatment Plant, Webster, TX	Dried processed sludge	5/5/87 10/18/88 1/4/89 3/21/89 6/21/89 1/10/90 4/25/90 7/24/90 10/31/90	From Licensee TX-B	<0.9 Bq/L <1.8 Bq/L <2.8 Bq/L NR <0.8 Bq/L LLD LLD LLD LLD	<0.5 Bq/L <0.2 Bq/L <0.3 Bq/L <0.4 Bq/L LLD LLD LLD LLD	<555 Bq/kg d wt ^a <100 Bq/kg d wt <74 Bq/kg d wt 629 Bq/kg d wt <122 Bq/kg d wt LLD LLD LLD LLD	NR	Texas DOH Environmental Monitoring Report for 1987; 1988 & 1989; and 1990	Receives input from Licensee TX-B which previously manufactured sealed sources a. Dry weight
Sims Bayou Sewage Treatment Facility, Houston, TX	Conventional bio. act. sludge, flash dried	5/5/87 1/4/89 6/22/89 1/11/90 4/27/90 7/25/90 11/2/90	Radioactive waste processors; medical center	<0.6 Bq/L <3.7E-03 Bq/L <4.1 Bq/L LLD LLD LLD LLD	<0.4 Bq/L <0.5 Bq/L <2.7 Bq/L LLD LLD LLD LLD	<22 Bq/kg d wt ^a <518 Bq/kg d wt <137 Bi/kg d wt LLD LLD LLD LLD	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	Receives input for Licensee TX-A - several processors of loose radioactive waste, and from Houston Medical Center a. Dry weight
Houston, TX	NR	7/5/88 4/24/90	From Licensee TX-A	NM	NM	74 Bq/kg d wt ^a LLD	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	Licensee TX-A in south-central Houston - is a processor of loose radioactive waste a. Dry weight

4 Radionuclide Geochemistry

Table 4.2 (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent 241 Am Activity	Effluent 241 Am Activity	Stabilized Sludge 241 Am Activity	RF	Reference	Comments
Webster, TX	NR	4/1/87 7/6/88 4/25/90	From Licensee TX-B	NM	NM	<4.1 Bq/L <1.7 Bq/L 15 Bq/kg	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	Licensee TX-B in south Houston - which previously manufactured sealed sources
Houston, TX	Septic tank	5/5/87 10/18/88 11/1/90	From Licensee TX-D	NM	NM	<14 Bq/L <10 Bq/L LLD	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	Licensee TX-D in south-eastern Houston - is a processor of loose radioactive waste and manufacturer of radioimmunoassay kits
Tonawanda Sewage Treatment Plant, Tonawanda, NY	Bio. act. sludge; Zimbrow Process	5/84-6/84 6/84-12/84 1/85-1/86	Smoke detector foils	< Detection limit	NM	167-444 Bq/kg 67-185 Bq/kg ^a 33-444 Bq/kg	NR	NY State DOH 1986	a. Excludes one sample of 100 pCi/g taken 8/7/84
Tonawanda Sewage Treatment Plant, Tonawanda, NY	Incineration; ash to landfill	4/84-5/84 5/84-12/84 1/85-1/86	Smoke detector foils	< Detection limit	NM	6.7-28 kBq/kg ash 0.2-0.8 kBq/kg ash 81-851 Bq/kg ash ^a	NR	NY State DOH 1986	a. Excludes 2 samples of 63 pCi/g and 80 pCi/g taken 2/7/85 and 12/16/85
Grand Island Sewage Treatment Plant, Grand Island, NY	Unpressed, pressed, and digester sludges; tertiary treatment	8/84-12/84 1/85-6/85 7/85-11/85 1/86	Smoke detector foils	NM	NM	2.1-4.4 kBq/kg 1.2-2.0 kBq/kg 0.6-1.6 kBq/kg 0.2 kBq/kg	NR	NY State DOH 1986	

NM = Not measured

NR = Not reported

RF = Reconciliation factor

LLD = Lower limit of detection

< = The quantity listed is the smallest amount that could be measured at the 95% confidence level, that is, lower limit of detection (LLD)

forms of radionuclides from waste prior to releasing it to a sewage system.

4.2.2 Aqueous Speciation and Complexation

Like other trivalent cations, Am generally forms very strong complexes with oxygen-containing ligands, such as OH^- , CO_3^{2-} , and organic acids (Allard et al. 1984; Kim 1986). Under the conditions commonly present in wastewater streams (Table 3.1), Am is more likely to form organic matter complexes than to undergo hydrolysis or form carbonate complexes (Bertha and Choppin 1978; Yamamoto and Sakanoue 1982; Choppin and Allard 1985; Kim 1986). The affinity of Am to complex/partition to organic materials is discussed in more detail in Section 4.2.3. In wastewater treatment processes where lime is added as a dispersant or precipitant (Sections 2.3.2 and 2.4.3), Am is likely to form hydroxycarbonate complexes (Lundqvist 1982; Kim 1986). Such complexes may have no charge [for example $\text{Am}(\text{OH})(\text{CO}_3)^0$] or a negative charge [such as $\text{Am}(\text{CO}_3)_2^-$, and $\text{Am}(\text{OH})_2(\text{CO}_3)_2^-$], resulting in these species being harder to remove from the wastewater stream via sorption to solid phases.

Americium complexation to F^- , NO_3^- , Cl^- , ClO_4^- , and phosphate ions is not likely to occur to a great extent because these anions typically exist at concentrations much lower than organic matter or carbonate (Table 3.1; Metcalf and Eddy, Inc. 1991).

Furthermore, these ligands also tend to form weaker complexes with Am than organic matter or carbonates. For univalent anions, complexing ability with Am follows the order $\text{F}^- > \text{NO}_3^- > \text{Cl}^- > \text{ClO}_4^-$; for bivalent anions, $\text{CO}_3^{2-} > \text{oxalate}^{2-} > \text{SO}_4^{2-}$. Phosphate forms a weaker complex than SO_4^{2-} and a stronger one than Cl^- (Keller 1971; Kim 1986). During chlorination, Cl^- and ClO_4^- concentrations may be sufficiently high to promote the formation of some Am/Cl and Am/ ClO_4 complexes. However, due to the very low complexation property of Cl^- and ClO_4^- , hydrolysis, carbonate complexation, or organic matter complexation reactions would likely dominate Am speciation at neutral or high pH systems (Kim et al. 1989).

4.2.3 Precipitation and Coprecipitation

Americium precipitation is not likely a dominant process in wastewater treatment facilities because the activity (chemical) of the free species of Am is not likely to exceed the K_{sp} of any solid-Am phase (Equation 3.16). Furthermore, the high concentration and high propensity of Am to complex with (or partition to) organic matter is likely to greatly reduce the already low activity of the free-Am species in solution (Table 4.2; Kim 1986; Keller 1971). Another factor that diminishes the likelihood of Am precipitation is that the pH of wastewater systems is generally seven or higher; based on thermodynamic calculations of an oxidized system, the solubility of oxides and hydrous oxide of Am is high at these pH levels (Ames and Rai 1978). This trend was also observed in an Am-contaminated soil system where the solubility-limited Am concentration was found to decrease approximately ten-fold with one unit increase in pH (Rai et al. 1981). The solubility of Am also decreases in oxidized systems (Kim 1986).

4.2.4 Sorption to Organic and Inorganic Solid Phases

The distribution coefficient (K_d ; Equation 3.22) of Am has been measured in simplified chemical systems (Allard et al. 1980; Rai et al. 1981; Ames and Rai 1978). Typically, these K_d values have been large, ranging from 100 to 44,000 mL/g. However, in complex chemical systems, such as wastewater treatment facilities in which hundreds of constituents exist, a number of conditions may affect the extent to which Am sorbs to inorganic surfaces. This compromises the value of most K_d measurements for use in wastewater systems. Reduced Am absorption to inorganic-solid phases has been reported 1) in the presence of dissolved organic matter (Bondietti 1982; Yamamoto and Sakanoue 1982; Kim et al. 1989), 2) in the presence of the organic chelating agent, EDTA (Section 3.3.1) (Kim 1986), 3) when a fraction of the Am existed in a colloidal form ($< 0.45 \mu\text{m}$) (Kim 1986), and in the presence of the competing trivalent Fe ion (Kim 1986).

The affinity of Am to complex/partition to organic matter was found to be dependent on the pH and ionic strength of the suspension (Kim et al. 1989). As pH increases and ionic strength decreases, more Am is partitioned to the organic material (Kim et al. 1989). This result is consistent with the theory of variable charge presented in Section 3.2.1.1. In solutions where the equivalent concentration ratio of humic acid to Am was larger than one, as is always the case in wastewater streams, a tridentate complexation (three-bonded chelation; Section 3.3.1) is formed (Kim 1986). Such a bond is extremely strong and because of the omnipresence of organic matter, Am organic matter species are likely to dominate Am speciation in the wastewater stream.

Organic materials can also indirectly influence Am speciation in wastewater streams by 1) sorbing to and changing the surface properties of inorganic mineral surfaces, and 2) directly competing for common sorption sites on mineral sorbents. These interactions can decrease or increase Am sorption depending on pH, sorbent surface charge, type and molecular size of the organic substance, stability constant of the metal with the organic substance, and a complex array of other factors. Because of the high affinity of many types of organic substances for FeOH and AlOH surface sites (Tipping 1981; Davis 1982), it is likely that mineral particles in wastewater streams are coated with organic matter. Such coatings alter the surface properties of mineral sorbents (Hunter and Liss 1979; Tipping and Cooke 1982) and the sorption reactions of metal contaminants. The sorption of humic substances by layer silicates has been shown to increase with decreasing pH in response to positive charge development on the mineral surface (Zachara et al. 1990). Allard et al. (1989) measured the adsorption of Am on alumina as a function of pH (4 to 10) at two different ionic strengths (0.10 and 0.01 M NaClO₄) and in the presence and absence of groundwater humic materials. They observed an enhanced removal of Am from solution when organic matter was included in the tertiary system at pH levels below seven. Furthermore, they concluded that the speciation of Am (in solution or in the solid phase) was likely to be entirely dominated by its association with organic matter in most systems containing even trace amounts of organic matter.

4.3 Cesium

Cesium (Cs) exists in the environment in the 1⁺ oxidation state. Stable Cs is ubiquitous in the environment with a crustal abundance of approximately 3.2 mg/kg; in soils, Cs concentrations range between 0.3 and 25 mg/kg (Lindsay 1979). Industrial uses for Cs include use as a catalyst for hydrogenation of certain organic compounds, photoelectric cells, and as oxygen scrubbers. A number of unstable isotopes of Cs exist, but in the context of the present topic only ¹³⁴Cs and ¹³⁷Cs are important; half-lives for these two isotopes are 2.05 years and 30.23 years, respectively. The production of these isotopes is through neutron activation and fission (United Nations Scientific Committee on the Effects of Atomic Radiation 1982). Medical use of ¹³⁷Cs in the United States is limited to sealed teletherapy sources (Ault 1989). Sources of ¹³⁴Cs and ¹³⁷Cs in WWTP sludge may be from research, decontamination, production of sealed sources, or as a result of soil particles contaminated with ¹³⁴Cs and ¹³⁷Cs entering the sewer systems. Furr et al. (1976) surveyed municipal sewage treatment plants throughout the United States and found that Cs concentrations in the sludge ranged from 0.45 to 1.6 mg/kg on a dry weight basis.

4.3.1 Behavior in Wastewater Treatment Plants

Cesium-134 and ¹³⁷Cs has been observed in sewage sludge throughout the United States, Canada, and Europe (Table 4.3). Unfortunately, mass balance and removal efficiency values can not be calculated because the influent and effluent ¹³⁴Cs and ¹³⁷Cs activities were either below detection limit or not determined. Crude ¹³⁷Cs removal efficiency calculations were conducted with the available data: Royerford removal efficiency was 97 percent; Blue Plains (Licensee A) removal efficiency was 33 percent, Blue Plains (Licensee B) removal efficiency was 25 percent; and Springfield removal efficiency was 0 percent. These values suggest that ¹³⁷Cs may be concentrated in the sludge produced by these WWTPs. Mass balance for the same WWTPs was within an order of magnitude {data from NRC safety inspection reports [Inspection No. 030-20934/85-04 (Royersford); 030-01786/86-01, 030-06922/86-01, 030-17872/86-01, 030-08478/86-01 (Blue Plains); 030-04632/86-01 (Springfield)]}.

Table 4.3 Cesium-134 and ¹³⁷Cs occurrence in wastewater treatment plants

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ¹³⁴ Cs and ¹³⁷ Cs Activity	Effluent ¹³⁴ Cs and ¹³⁷ Cs Activity	Stabilized Sludge ¹³⁴ Cs and ¹³⁷ Cs Activity	RF	Reference	Comments
Chicago Metropolitan Sanitary District, Stickney, IL	Imhoff process; Air dried and aged in large open-air piles; sludge dried as free fertilizer called "Nu Earth"	11/74	NR	1.2 mBq/L	1.0 mBq/L	52 Bq/kg ash ^a	18% ^c	Alberts et al. 1974	a. Measured in organic fertilizer b. Dry weight c. RF = [(influent-effluent)/influent] x 100 d. RF = (sludge/influent) x 100 e. RF = [sludge/influent (including storm runoff)] x 100
Hamilton Sewage Treatment Plant on Lake Ontario, Canada	Digester sludge (freeze dried for analysis)	NR	NR	NM	0.9 mBq/L	7.8 Bq/kg dry wt	NR	Durham and Joshi 1979	Most ¹³⁷ Cs radioactivity removed with sludge during sewage treatment Concentration of radionuclides in sludge are low enough to allow agricultural use
Dundas Sewage Treatment Plant on Lake Ontario, Canada	Digester sludge (freeze dried for analysis)	NR	NR	NM	ND	7.8 Bq/kg	NR	Durham and Joshi 1979	Most ¹³⁷ Cs radioactivity removed with sludge during sewage treatment Concentration of radionuclides in sludge are low enough to allow agricultural use
Webster Wastewater Treatment Plant, Webster, TX	Dried processed sludge	3/22-31/83 8/17/83 9/29/83 1/14/86	NR	NM	NM	LLD (0.04)- 3.0 kBq/kg ^a	NR	Texas DOH 1986	a. Types of sludge monitored include dried process, surface, process, sludge bin, from floor of drier bldg, on drier belt; measured ¹³⁷ Cs
Webster Wastewater Treatment Plant, Webster, TX	Dried processed sludge	5/5/87 10/18/88 1/4/89 3/21/89 6/21/89 1/10/90 4/25/90 7/24/90 10/31/90	From Licensee TX-B	<0.2 Bq/L <0.4 Bq/L <0.6 Bq/L NR <4.1 Bq/L LLD LLD LLD LLD	<0.06 Bq/L <0.04 Bq/L <0.04 Bq/L <0.1 Bq/L <0.6 Bq/L LLD LLD LLD LLD	44 Bq/kg d wt ^a 26 Bq/kg d wt 44 Bq/kg d wt <37 Bq/kg d wt <333 Bq/kg d wt LLD LLD LLD LLD	NR	Texas DOH Environmental Monitoring Report for 1987; 1988 & 1989; and 1990	Receives input from Licensee TX-B which previously manufactured sealed sources; measured ¹³⁷ Cs a. Dry weight

4 Radionuclide Geochemistry

Table 4.3 (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ¹³⁴ Cs and ¹³⁷ Cs Activity	Effluent ¹³⁴ Cs and ¹³⁷ Cs Activity	Stabilized Sludge ¹³⁴ Cs and ¹³⁷ Cs Activity	RF	Reference	Comments
Sims Bayou Sewage Treatment Facility, Houston, TX	Conventional bio. act. sludge, flash dried	5/5/87	Radioactive waste	<0.2 Bq/L	<1.4 Bq/L	<7.4 Bq/L	NR	Texas DOH Environmental	Receives input for Licensee TX-A - several processor of loose radioactive waste, and from Houston Medical Center; measured ¹³⁷ Cs
		1/4/89		<0.004 Bq/L	<0.07 Bq/L	<LLD			
		6/22/89	processors; medical center	<0.9 Bq/L	<0.6 Bq/L	<22 Bq/kg d wt ^a		Monitoring Reports for 1987; 1988 & 1989; and 1990	
		4/27/90		LLD	LLD	LLD			
		7/25/90		LLD	LLD	LLD			
11/2/90		LLD	LLD	LLD			a. Dry weight		
Houston, TX	NR	7/5/88 4/24/90	From Licensee TX-A	NM	NM	1.1 kBq/kg d wt ^a 1.4 kBq/kg d wt	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	Licensee TX-A in south-central Houston - is a processor of loose radioactive waste; measured ¹³⁷ Cs
Webster, TX	NR	4/1/87	From Licensee TX-B	NM	NM	0.1 Bq/L <0.3 Bq/L 255 Bq/kg	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	Licensee TX-B in south Houston - which previously manufactured sealed sources; measured ¹³⁷ Cs
		7/6/88							
		4/25/90							
Houston, TX	Septic tank	5/5/87	From Licensee TX-D	NM	NM	<2.8 Bq/L <0.6 Bq/L LLD - 1.4 Bq/L	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	Licensee TX-D in south-eastern Houston - is a processor of loose radioactive waste and manufacturer of radioimmunoassay kits; measured ¹³⁷ Cs
		10/18/88							
		11/1/90							
Royersford Waste Water Treatment Facility, PA	Primary and secondary treatment; anaerobic digestion; 2-stage biofiltration	10/85	Nuclear Laundry ^a	0.6 Bq/L ^b	0.02 Bq/L	141 Bq/L	NR	U.S. NRC Inspection Report No. 030-20934/85-04 1986a	a. Waste water from laundering of contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge; measured ¹³⁷ Cs
		10/85		107 Bq/L ^c	ND	10 Bq/L ^d	NR		b. From licensee's discharge tanks
		12/85		NM	4.8 Bq/L	555 Bq/L			c. From licensee's discharge tanks; measured ¹³⁴ Cs
		12/85		NM	ND	56 Bq/L ^d			d. Measured ¹³⁴ Cs

Table 4.3 (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ¹³⁴ Cs and ¹³⁷ Cs Activity	Effluent ¹³⁴ Cs and ¹³⁷ Cs Activity	Stabilized Sludge ¹³⁴ Cs and ¹³⁷ Cs Activity	RF	Reference	Comments
Blue Plains Water Treatment Plant, Blue Plains, PA	Modified bio. act. sludge process	2/86	Licensee A ^a - 0.06-0.09mBq/L ^b Medical research 1.5-1.9 Bq/L ^c	1.1 Bq/L	0.2 Bq/kg w wt ^d	NR	U.S. NRC Inspection Report No. 86-01 1986b	a. Liquid wastes discharged into underground discharge tanks, or directly into sewers; measured ¹³⁷ Cs b. Discharge concentration taken at manhole near facility c. From licensee's discharge tanks d. Wet weight	
Blue Plains Water Treatment Plant, Blue Plains, PA	Modified bio. act. sludge process	2/86	Licensee B ^a - 0.7-1.5 Bq/L ^b research & devel.; calib. 0.7-15 Bq/L ^c sources	1.1 Bq/L	0.2 Bq/kg w wt ^d	NR	U.S. NRC Inspection Report No. 070-00398/86-04 1986d	a. Liquid wastes discharged into underground discharge tanks, or directly into sewers; measured ¹³⁷ Cs b. Discharge concentration taken at manhole near facility c. From licensee's discharge tanks d. Wet weight	
Oak Ridge Water Treatment Plant, Oak Ridge, TN	Primary and secondary treatment; anaerobic digestion	12/86-5/88 6/88-6/89	Industrial; hospitals; nuclear weapons fallout	NM NM	444 Bq/kg d wt ^a 74 Bq/kg d wt	NR	Boston et al. 1990	Only maximum concentrations reported; study primarily looked at radionuclide movement in soils from sludge application; measured ¹³⁷ Cs a. Dry weight	
Oak Ridge Water Treatment Plant, Oak Ridge, TN	Primary and secondary treatment; anaerobic digestion	9/85 6/86	Industrial; hospitals; nuclear weapons fallout	6-2923 Bq/L ^a	19-200 Bq/L	7% ^b	Halsey 1986	a. Discharge from Company "Q"; measured ¹³⁷ Cs b. 0.024 Bq ¹³⁷ Cs in sludge/0.34 Bq released by Co. "Q"; with further manipulations results in 22.6 GBq/g dried sludge per μ Ci/mL in influent	

Table 4.3 (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ¹³⁴ Cs and ¹³⁷ Cs Activity	Effluent ¹³⁴ Cs and ¹³⁷ Cs Activity	Stabilized Sludge ¹³⁴ Cs and ¹³⁷ Cs Activity	RF	Reference	Comments
Oak Ridge Waste Water Treatment Plant, Oak Ridge, TN	Primary and secondary treatment; anaerobic digestion	1990	Industrial; hospitals; nuclear weapons fallout	NM	NM	0.3-11.5 Bq/kg w wt ^a	NR	City of Oak Ridge 1990 Land Application Report	a. Wet weight; measured ¹³⁷ Cs
Oak Ridge Waste Water Treatment Plant, Oak Ridge, TN	Primary and secondary treatment; anaerobic digestion	1991	Industrial; hospitals; nuclear weapons fallout	NM	NM	0.3-4.9 Bq/kg w wt ^a	NR	City of Oak Ridge 1991 Land Application Report	a. Wet weight; measured ¹³⁷ Cs
Oak Ridge Waste Water Treatment Plant, Oak Ridge, TN	Primary and secondary treatment; anaerobic digestion	1992	Industrial; hospitals; nuclear weapons fallout	NM	NM	0.2-1.1 Bq/kg w wt ^a	NR	City of Oak Ridge 1992 Land Application Report	a. Wet weight; measured ¹³⁷ Cs
Springfield Regional Waste Water Treatment Plant, Springfield, MA	Bio. act. sludge process	2/86	Nuclear laundry ^a	0.4 Bq/L ^b	0.6 Bq/L ^b	26 Bq/L	NR	U.S. NRC Inspection Report No. 030-04632/86-01 1986c	a. Waste water from laundering of contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge; measured ¹³⁷ Cs
		2/86		ND ^c	ND	7 Bq/L ^d	NR		b. Discharge concentration at company's fence line (via manhole) = 237 Bq/L; Filtered: Soluble = 152 Bq/L; Insoluble = 20 Bq/L
									c. Discharged concentration at company's fence line (via manhole) = 52 Bq/L; Filtered: Soluble = 44 Bq/L; Insoluble = ND
									d. Measured ¹³⁴ Cs

Table 4.3 (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ¹³⁴ Cs and ¹³⁷ Cs Activity	Effluent ¹³⁴ Cs and ¹³⁷ Cs Activity	Stabilized Sludge ¹³⁴ Cs and ¹³⁷ Cs Activity	RF	Reference	Comments
Kallby Waste Water Treatment Plant, Lund, Sweden	Primary and secondary treatment	10/85-12/85	Hospitals, NPP, nuclear weapons fallout	NM	1.2-5.4 MBq	1.8-3.1 MBq ^a	0.5 ^b	Erlandsson et al. 1989	a. Sludge data is decay corrected; measured ¹³⁷ Cs b. RF = sludge/(effluent + sludge) c. Measured ¹³⁴ Cs
Finland: 9 plants 1 plant 1 plant 1 plant 1 plant 3 plants 1 plant	-Simultaneous precip. -Oxidation ditch -Direct precip. -Chemical treatm. -Precipitation -Near NPP -Septic tank near NPP	9/85-8/87	Hospitals, NPP, nuclear weapons fallout ^a	NM	NM	240-810 Bq/kg d wt ^b 490-380 Bq/kg d wt 120-440 Bq/kg d wt 28-140 Bq/kg d wt NM 75-760 Bq/kg d wt 0-180 Bq/kg d wt NM	NR	Fuhakainen and Rahola 1989	a. Measured ¹³⁴ Cs b. Dry weight

ND = Not detected

NM = Not measured

NR = Not reported

RF = Reconciliation Factor

< = The quantity listed is the smallest amount that could be measured at the 95% confidence level, that is, lower limit of detection (LLD)

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The previously calculated Cs removal efficiencies vary widely and are determined from limited data. However, the lower efficiencies observed at Blue Plains and Springfield are comparable to those observed for ^{134}Cs in a tracer study performed at the Oak Ridge WWTP (Stetar et al. 1993). Prior to primary treatment, total and dissolved Cs concentrations were determined for the raw influent. Only about 6.6 percent of the total Cs was associated with the solids fraction. Cesium-134 removal efficiency for primary treatment (sedimentation only) was determined as about 3 percent (Stetar et al. 1993). Importantly, the raw sludge from primary treatment was about 3 percent solids and 80 percent of the Cs was associated with the solid phases. Within the same study, Stetar et al. (1993) observed that about 80 percent of the tracers ^{58}Co and ^{131}I present in the primary sludge were also associated with the solids fraction, even though the partitioning between the aqueous and solid phases of the raw influent for these latter two radionuclides was drastically different than Cs. This strongly suggests that only a fraction of ^{134}Cs associated with the influent solids will be removed, and that not all of that fraction is removable through sedimentation. During secondary treatment (activated sludge), approximately 9.4 percent of the remaining ^{134}Cs was removed. The overall efficiency for Cs removal was only about 12 percent and close to the percentage of Cs that was associated with the influent solids. These data suggest that little, if any, chemical reconcentration of Cs took place; most of the incorporation of Cs into the Oak Ridge WWTP sludge was accomplished by a physical means that captured solids. Aside from the preceding data, information detailing Cs behavior during wastewater treatment is not available because Cs is not routinely determined. Also, the behavior of Cs is not generally investigated as part of the normal suite of elements in WWTPs.

4.3.2 Aqueous Speciation and Complexation

The dominant aqueous species in influent systems is thought to be the free Cs^+ species. The Cs^+ ion forms only extremely weak aqueous complexes with SO_4^{2-} , Cl^- , and NO_3^- and therefore formation of inorganic complexes is not believed to a major influence on Cs speciation. Cesium is poorly complexed by organic substances, as shown by the

relative order of ion complexation to organic substances: $\text{Ce} > \text{Fe} > \text{Mn} > \text{Co} \geq \text{Ru} \geq \text{Sr} > \text{Cs} > \text{I}$ (Bovard et al. 1970). Further, complexation of Cs by chelates (such as EDTA) is believed to be poor due to generally low stability of Cs-chelates and the presence of other elements (such as Ca) at significantly higher concentrations than Cs. Therefore, aqueous speciation and complexation is not thought to greatly influence Cs behavior.

4.3.3 Precipitation and Coprecipitation

Neither precipitation or coprecipitation are expected to affect Cs incorporation into sewage sludge.

4.3.4 Sorption to Organic and Inorganic Solid Phases

Sorption of Cs to organic colloids should follow a relationship similar to that of dissolved organic humic materials (Section 4.4.3) and, hence, should not be an important sink for Cs. However, Larsen et al. (1992) discovered a ^{137}Cs hot particle in the primary sludge of the Oak Ridge WWTP that was characterized as a nonaggregated $\sim 50\text{-}\mu\text{m}$ diameter nonmetallic particle. They suggested the particle may be of organic origin. However, beyond this one discovery, association of Cs with particulate in WWTPs is unknown.

It has frequently been assumed that Cs would be associated with inorganic soil materials, such as clay minerals as a result of soils being washed into sewer systems. This theory is predicated on the knowledge that Cs exchange at the surface of clay minerals is characterized by high selectivity. Sorption of Rb, K, NH_4^+ , and Cs to clay minerals has been well-studied. The interlattice fixation of cations has long been recognized as the result of the ability of certain cations to dehydrate and, in this state, fit into the hexagonal holes (radius 1.40 Å) in the exterior oxygen plane of the tetrahedral layer (Bruggenwert and Kamphorst 1979). The energy gain associated with fixation, in the form of electrostatic attraction, must be balanced against the energy loss due to the dehydration process; this fact, in conjunction with cation radii, explains why cations with high energies of hydration like Ca, Mg, Na, and Li are not fixed and why Rb, K, NH_4^+ , and Cs with low energies of hydration are fixed. It has been suggested, however, that fixation of ^{137}Cs in soils, in carrier-free quantities, is an essentially

different process from those that predominate in the fixation of macro quantities of Cs, Rb, K, and NH_4^+ (Schultz et al. 1960). Regardless, exchange on the clay minerals is believed to be the greatest factor in determining the nature of Cs (that is, either dissolved or solid associated) in WWTPs. The extent to which exchange occurs would appear to be dependent on 1) the amount of clay or soil material that is present, 2) the quantity of macrocations that can effectively compete with Cs for exchange sites (K , NH_4^+), and 3) the size of the clay mineral materials.

The Cs removal efficiencies (three percent for primary treatment and nine percent for secondary treatment) reported by Stetar et al. (1993) and those calculated in Section 4.3.1 for the Blue Plains (25 and 33 percent) and Springfield (0 percent) WWTPs appear more reasonable than that calculated for the Royersford (97 percent) WWTP. This conclusion was reached because 1) complexation of Cs is believed to be negligible; 2) precipitation/coprecipitation will not control Cs aqueous concentrations; 3) even though no studies have been found detailing Cs sorption by extracellular polymers, it is believed to be of minimal importance; and 4) the quantity of clay minerals in raw sewage is not elevated, except during storm events, and, then, only in those systems where the sewage and storm systems are linked. Hence, it is believed that Cs will be poorly retained in sewage sludge.

4.4 Cobalt

Cobalt occurs naturally in the environment and its crustal abundance is about 25 mg/kg. Cobalt is an essential nutrient and has a number of industrial uses ranging from catalysts to use in alloys. In the uncomplexed form, only the cobaltous ion (Co II) is stable in aqueous environments, including wastewater treatment systems. However, the cobaltic ion (Co III) does form very stable complexes with certain organic ligands; cyanocobalamin, or vitamin B_{12} , is an example of a Co (III) complex found in soil, water, sewage sludge, manure, and dried estuarine mud (Trischan et al. 1981). Stable Co is ubiquitous in the environment, including wastewaters and the resulting sludges. Reported Co concentrations in sewage sludge from throughout the continental U.S. and Canada range from 3.4 to 80 mg/kg (Clark and Hill

1958; Fortescue et al. 1975; Carson and Cole 1981; Mumma et al. 1983). Few measurements of Co in wastewater (raw sewage) have been performed; however, 0.002 mg/kg was observed by Oliver and Cosgrove (1974) for a biological activated-sludge treatment plant. This is similar to Co levels observed in Adelaide, Australia and two Ukrainian cities (Matthews and Thomas 1975; Kostovetskii et al. 1975, as reported by Carson and Cole 1981).

Radioactive isotopes of cobalt (^{57}Co , ^{58}Co , ^{60}Co) result mainly from neutron activation. The cobalt isotopes have been used for both medical and industrial uses. For medical diagnostic uses, radiopharmaceuticals are made using ^{57}Co and ^{58}Co , namely ^{57}Co -bleomycin, ^{57}Co -vitamin B_{12} , and ^{58}Co -vitamin B_{12} (National Council on Radiation Protection and Measurements 1989); Teletherapy units using thousands of curies of ^{60}Co are used for external beam radiation therapy. The radioactive source unit used in radiation therapy units is made up of thousands of ^{60}Co pellets that have magnetic properties. A single pellet may contain up to 2.8 GBq of ^{60}Co activity (Mettler and Ricks 1990). In industry, ^{60}Co sources are used as radiography units for evaluating the integrity of metallic objects, such as pipe wells and airplane propellers (Mettler and Ricks 1990). Industrial radiography units are intensely radioactive sources (10-100 Ci) that are generally mobile so that they can be moved to the work site. The ^{60}Co sources are also used for sterilization of products, such as medical supplies, chemicals, or other objects. These stationary units may contain up to 185 PBq of ^{60}Co . Much smaller irradiation sources (<0.4 PBq)^(a) are also used in university research programs.

4.4.1 Behavior in Wastewater Treatment Plants

As evidenced from the data compiled in Table 4.4, ^{58}Co and ^{60}Co have been observed in sewage sludge throughout the United States, Canada, and Europe. However, influent and effluent ^{58}Co and ^{60}Co activities have been below detection limits (that is, not detected) in most of the cases listed in Table 4.4, making removal efficiency and mass balance calculations impossible. However, the tabulated data would

(a) PBq = 10^{15} Bq.

Table 4.4 Cobalt-57, ⁵⁸Co, and ⁶⁰Co occurrence in wastewater treatment plants

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ⁵⁷ Co, ⁵⁸ Co, and ⁶⁰ Co Activity	Affluent ⁵⁷ Co, ⁵⁸ Co, and ⁶⁰ Co Activity	Stabilized Sludge ⁵⁷ Co, ⁵⁸ Co, and ⁶⁰ Co Activity	RF	Reference	Comments
Oak Ridge Waste Water Treatment Plant, Oak Ridge, TN	Primary and secondary treatment; anaerobic digestion	12/86-5/88 6/88-6/89	Industrial; hospitals; nuclear weapons fallout ^a	NM NM	NM NM	740 Bq/kg d wt ^b 211 Bq/kg d wt ^b	NR	Boston et al. 1990	a. Only maximum ⁶⁰ Co concentrations reported; study primarily looked at radionuclide movement in soils from sludge application b. Dry weight
Oak Ridge Waste Water Treatment Plant, Oak Ridge, TN	Primary and secondary treatment; anaerobic digestion	1990	Industrial; hospitals; nuclear weapons fallout ^a	NM	NM	0.4-11 Bq/kg w wt ^b	NR	City of Oak Ridge 1990 Land Application Report	a. Measured ⁶⁰ Co b. Wet weight
Oak Ridge Waste Water Treatment Plant, Oak Ridge, TN	Primary and secondary treatment; anaerobic digestion	1991	Industrial; hospitals; nuclear weapons fallout ^a	NM	NM	0.4-3.7 Bq/kg w wt ^b	NR	City of Oak Ridge 1991 Land Application Report	a. Measured ⁶⁰ Co b. Wet weight
Oak Ridge Waste Water Treatment Plant, Oak Ridge, TN	Primary and secondary treatment; anaerobic digestion	1992	Industrial; hospitals; nuclear weapons fallout ^a	NM	NM	0.2-2.3 Bq/kg w wt ^b	NR	City of Oak Ridge 1992 Land Application Report	a. Measured ⁶⁰ Co b. Wet weight
Webster Waste Water Treatment Plant, Webster, TX	Dried processed sludge	9/29/83	NR	NM	NM	LLD (30)-37 Bq/kg ^a	NR	Texas DOH 1986	a. Types of sludge monitored include dried process, surface, process, sludge bin, from floor of drier bldg, on drier belt; measured ⁶⁰ Co
Webster Waste Water Treatment Plant, Webster, TX	Dried processed sludge	5/5/87	NR	<0.2 Bq/L	<0.04 Bq/L	<0.007 Bq/L	NR	Texas DOH Environmental Monitoring Report for 1987	Receives input from Licensee TX-B which previously manufactured sealed sources; measured ⁶⁰ Co

Table 4.4 (cont'd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ⁵⁷ Co, ⁵⁸ Co, and ⁶⁰ Co Activity	Effluent ⁵⁷ Co, ⁵⁸ Co, and ⁶⁰ Co Activity	Stabilized Sludge ⁵⁷ Co, ⁵⁸ Co, and ⁶⁰ Co Activity	RF	Reference	Comments
Sims Bayou Waste Water Treatment Facility, Houston, TX	Bio. act. sludge, flash dried	5/5/87	Radioactive waste	<0.4 Bq/L	<0.4 Bq/L	<22 Bq/kg d wt ^b	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	a. Receives input for Licensee TX-A which is a processor of loose radioactive waste; from another processor of loose radioactive waste and from Houston Medical Center; measured ⁶⁰ Co
		1/4/89		<0.004 Bq/L	<0.05 Bq/L	<48 Bq/kg d wt			
		6/22/89	processors; medical center ^a	<0.7 Bq/L	<0.6 Bq/L	<15 Bq/kg d wt			
		1/11/90		LLD	LLD	LLD			
		4/27/90		LLD	LLD	LLD			
		7/25/90		LLD	LLD	LLD			
		11/2/90		LLD	LLD				b. Dry weight
Houston, TX	NR	7/5/88	From Licensee TX-A	NM	NM	962 Bq/kg sewage	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	Licensee TX-A in south-central Houston - is a processor of loose radioactive waste; measured ⁶⁰ Co
		4/24/90		NM	NM	814 Bq/kg sewage			
Webster, TX	NR	5/5/87	From Licensee TX-D	NM	NM	<5.8 Bq/L	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	Licensee TX-D in south-eastern Houston - is a processor of loose radioactive waste and manufacturer of radioimmunoassay kits; measured ⁶⁰ Co
		10/10/88		NM	NM	<1.2 Bq/L			
		11/1/90		NM	NM	LLD			
Royersford Waste Water Treatment Facility, Royersford, PA	Primary and secondary treatment; anaerobic digestion; 2-stage biofiltration	10/85	Nuclear Laundry ^a	1.3 kBq/L ^b	2.6 Bq/L	518 Bq/L	NR	U.S. NRC Inspection Report No. 030-20934/85-04 1986a	a. Waste water from laundering of ⁶⁰ Co contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge; measured ⁶⁰ Co
		12/85		NM	0.5 Bq/L w wt ^c	2.2 kBq/L			b. From licensee's discharge tanks c. Wet weight
Blue Plains Waste Water Treatment Plant, Blue Plains, PA	Modified bio. act. sludge process	2/86	Licensee A ^a - Medical research	ND	ND	1.4 Bq/kg w wt ^{b,c}	NR	U.S. NRC Inspection Report No. 86-01 1986b	a. Liquid wastes discharged into underground discharge tanks, or directly into sewers; measured ⁶⁰ Co b. Discharge ⁶⁰ Co concentration taken at manhole near facility c. Wet weight

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Table 4.4 (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ⁵⁷ Co, ⁵⁸ Co, and ⁶⁰ Co Activity	Effluent ⁵⁷ Co, ⁵⁸ Co, and ⁶⁰ Co Activity	Stabilized Sludge ⁵⁷ Co, ⁵⁸ Co, and ⁶⁰ Co Activity	RF	Reference	Comments
Blue Plains Waste Water Treatment Plant, Blue Plains, PA	Modified bio. act. sludge process	2/86	Licensee B ^a - research & devel.; calib. sources	ND-33 Bq/L	ND	1.4 Bq/kg w wt ^c	NR	U.S. NRC Inspection Report No. 070-00398/86-04 1986d	a. Liquid wastes discharged into underground discharge tanks, or directly into sewers; measured ⁶⁰ Co b. Discharge ⁶⁰ Co concentration taken at manhole near facility c. Wet weight
Springfield Regional Waste Water Treatment Plant, Springfield, MA	Bio. act. sludge process	2/86	Nuclear laundry ^a	ND ^b (<851 Bq/L)	ND	122 Bq/kg	NR	U.S. NRC Inspection Report No. 030-04632/86-01 1986c	a. Waste water from laundering of contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge; measured ⁶⁰ Co b. Discharge ⁶⁰ Co concentration at company's fence line (via manhole) = 185 Bq/L; Filtered: Soluble = 89 Bq/L; Insoluble = 274 Bq/L
Borgeby Sewage Treatment Plant, Malmo Sweden	Primary and secondary treatment	3/81-5/81 8/81-9/81	Nuclear power plant	Entrance sludge ^a 183 Bq/kg	NM	Final Sludge ^b 91 Bq/kg	2.3 ^c	Erlandsson et al. 1983	a. Entrance sludge collected just after the first biological degrading step; measured ⁶⁰ Co b. Final sludge collected after the dehydrator c. RF = Entrance sludge conc./final sludge conc.
Royersford Waste Water Treatment Facility, Royersford, PA	Primary and secondary treatment; anaerobic digestion; 2-stage biofiltration	10/85 12/85	Nuclear Laundry ^a	59 Bq/L ^b NM	ND	20 Bq/L 56 Bq/L	NR	U.S. NRC Inspection Report No. 030-20934/85-04 1986a	a. Waste water from laundering of contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge; measured ⁵⁸ Co b. From licensee's discharge tanks

Table 4.4 (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ⁵⁷ Co, ⁵⁸ Co, and ⁶⁰ Co Activity	Affluent ⁵⁷ Co, ⁵⁸ Co, and ⁶⁰ Co Activity	Stabilized Sludge ⁵⁷ Co, ⁵⁸ Co, and ⁶⁰ Co Activity	RF	Reference	Comments
Springfield Water Treatment Plant, Springfield, MA	Bio act. sludge process	2/86	Nuclear laundry ^a	ND ^b	ND	41 Bq/L	NR	U.S. NRC Inspection Report No. 030-04632/86-01 1986c	a. Waste water from laundering of contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge; measured ⁵⁸ Co b. Discharge concentration at company's fence line (via manhole) = NR; Filtered: Soluble = 48 Bq/L; Insoluble = 41 Bq/L
Borgeby Sewage Treatment Plant, Malmö Sweden	Primary and secondary treatment	3/81-5/81	Nuclear power plant	Entrance sludge ^a <0.6-2.0 Bq/kg	NM	NM	NR	Erlandsson et al. 1983	a. Entrance sludge collected just after the first biological degrading step; measured ⁵⁸ Co a. Measured ⁵⁷ Co
Finland:		9/85-8/87	Hospitals, NPP, nuclear weapons fallout ^a	NM	NM	0-110 Bq/kg d wt ^b 0 Bq/kg d wt 0 Bq/kg d wt 0 Bq/kg d wt 0 Bq/kg d wt NM NM	NR	Puhakainen and Rahola 1989	b. Dry weight
Blue Plains Waste Water Treatment Plant, Blue Plains, PA	Modified activated sludge process	2/86	Licensee A - medical research ^a	Licensee A - 23 Bq/L	NM	NM	NR	U.S. NRC Inspection Report No. 86-01 1986b	a. Liquid wastes discharged into underground discharge tanks, or directly into sewers; measured ⁵⁷ Co

ND = Not detected
 NM = Not measured
 NR = Not reported
 RF = Reconcentration Factor
 < = The quantity listed is the smallest amount that could be measured at the 95% confidence level, that is, lower limit of detection (LLD)

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suggest that radioisotopes of Co are, or at least can be, concentrated in the sludge produced by WWTPs. Limited sewer system disposal data, coupled with limited effluent and sludge data from the Royersford, PA WWTP, allowed a crude calculation of ^{60}Co removal efficiency and mass balance. These calculations suggest a removal efficiency of approximately 88 percent and a mass balance that was within an order of magnitude [data from NRC safety inspection (Inspection No. 030-20934/85-04)]. McDuffie (1978) reported highly variable removal efficiencies for Co in two New York state WWTPs ranging from 0 to 85 percent, but the plant effluent Co levels were always $< 10\mu\text{g/L}$. If it is assumed that a particular set of reactions control the solubility of Co (or other metals) in a treatment facility, the Co effluent concentration will be similar [such as $< 10\mu\text{g/L}$ as reported by McDuffie (1978)], and the removal efficiency of a given plant may simply vary because of varying influent concentration. Removal efficiency is defined in Equation 3.30.

Probably the best data on the removal efficiency of radioactive Co in a WWTP were compiled by Stetar et al. (1993) at Oak Ridge, TN. These investigators spiked the influent sewage with ^{58}Co and followed the tracer through the plant. The overall removal efficiency for ^{58}Co was approximately 31 percent; removal efficiencies for the plant's primary and secondary treatment systems were 8.1 and 25 percent, respectively. Prior to primary treatment, approximately ten percent of the ^{58}Co was associated with the suspended solids, suggesting that removal of suspended solids by physical mechanisms (such as sedimentation) accounted for the primary treatment removal efficiency, not chemical mechanisms. During the secondary treatment, removal of 25 percent of the radiotracer may be attributed to either physical or chemical interactions. In addition, Stetar et al. (1993) observed that the ratio of dissolved Co (0.45 μm pore-size filtrate) to total Co increased, suggesting that little of the dissolved Co was removed to the sludge.

During primary treatment (sedimentation), metals are only removed from the WWTP influent stream if they are 1) present as particulate (inorganic or organic), 2) sorbed to suspended particles, and 3) if the particles are settleable (Oliver and Cosgrove 1974; Kempton et al. 1987a and b). Removal efficiencies for the truly soluble metal species (free metal or

complex) are < 1 percent during primary treatment (Oliver and Cosgrove 1974). The single most important factor that effects Co (and other metals) removal during primary treatment is the solids concentration. Cobalt removal efficiencies during a primary treatment study at a pilot plant at the Hogsmill Valley Water Pollution Control Works (Thames Water Authority, England) was found to increase from 15 to 34 percent as suspended solids increased from 405 to 888 mg/L, respectively. The results for Co were similar to that observed for nickel (Ni) and manganese (Mn) and agreed with the findings of Oliver and Cosgrove (1974) and Rossin et al. (1983). The low removal efficiency for ^{58}Co during primary treatment (8.1 percent) observed by Stetar et al. (1993) is probably the result of the low suspended solids concentration (100-150 mg/L). Prior to primary treatment, approximately ten percent of the ^{58}Co tracer was associated with the suspended solids; investigation of the primary sludge showed that approximately 80 percent of the ^{58}Co was associated with the solids (as determined by filtration using a 0.45 μm pore-size membrane filter).

During primary treatment, the dependence of Co removal on the suspended solids concentration should be seen simply as Co interaction with the solid phase, and, as the solid phase is increased, Co associated with the solid phase increases; that is, the ratio of solid to aqueous phase concentrations (K_d) is relatively constant. Hence, the removal of Co during primary treatment is essentially the result of sedimentation. Aside from the total solids concentration, the presence and quantity of selected solids subfractions in the raw sewage appear to be important. In studies by Kempton et al. (1987b), Co removal from the wastewater was significantly correlated to the volatile fraction of suspended solids. In addition, Co did not appear to be associated with particles $> 35\mu\text{m}$ in diameter.

During the biologically activated-sludge process (secondary treatment), metals are removed by 1) precipitation followed by independent settling or becoming enmeshed in the biological floc, 2) sorption of soluble metal to microbial cells, 3) soluble metal binding to microbial extra cellular polymers, and 4) volatilization to the atmosphere (Brown and Lester 1979). Lawson et al. (1984a and b) observed that dissolved Co removal was low and little affected by the activity of the biomass. Sludge floc or colloidal microbial extracellular polymers have only a low to

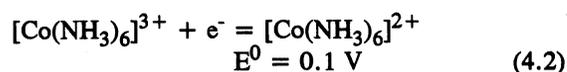
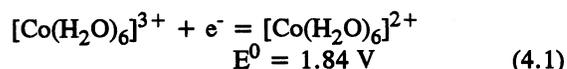
moderate affinity for Co at low concentrations (Kempton et al. 1983; Rudd et al. 1984; Stephenson and Lester 1987a and b). However, it has been suggested that Co can be complexed by soluble extracellular polymers (Brown and Lester 1982; Rudd et al. 1984). This interaction between Co and soluble polymers would keep the solubility of Co high and removal efficiency low. Kempton et al. (1983) observed extremely low Co removal efficiencies in biologically activated-sludge bench-scale studies (0-19 percent). They also observed Co effluent concentrations that were correlated to the waters chemical oxygen demand (COD) rather than effluent suspended solids; that is, Co was soluble and complexed with dissolved organic carbon (DOC) rather than associated with suspended particulate matter. While Co removal efficiencies were higher (< 41 percent) for biologically activated-sludge process pilot scale studies, the effluent Co was > 80 percent soluble (Stephenson and Lester 1987a and b). These results agree well with the studies of Stetar et al. (1993) performed in an operating WWTP. Stetar et al. (1993) observed Co removal efficiencies of approximately 25 percent in the biologically activated-sludge process.

Overall, Co removal efficiencies of 0 to 89 percent have been observed. However, the ratio of soluble to total Co tends to increase as influent moves through the primary and secondary treatment processes (Stetar et al. 1993; Stephenson and Lester 1987a and b). Previous studies with Co and other metals suggest this arises because the metals associated with particulate are removed throughout the process, but the soluble metal fraction is, or becomes, complexed by soluble organic ligands in the raw wastewater and the soluble materials present in the secondary treatment process (Nielsen et al. 1984; Rudd et al. 1984; Lawson et al. 1984; Brown and Lester 1982; Stoveland and Lester 1980; Bender et al. 1970). Complexation with soluble complexing agents will alter the potential for a given metal to interact with solids. Although the high variability in removal efficiencies observed for Co is probably the result of a number of factors including treatment processes used, age of the biologically activated sludge, and suspended solids concentration, the fluctuations in influent Co concentrations probably have the greatest effect. The presence of synthetic chelators (that is, NTA and EDTA), other process-produced soluble complexing agents, inorganic ligands, and pH have a substantial effect on Co

removal from wastewater as they dictate Co speciation and its solubility.

4.4.2 Aqueous Speciation and Complexation

In the uncomplexed form, only the cobaltous ion (Co II) is stable in aqueous environments, including wastewater treatment systems. However, the cobaltic ion (Co III) does form very stable complexes with certain ligands (Trischan et al. 1981).



As can be seen from Equations 4.1 and 4.2, complexation with organic ligands could conceivably make the Co(III) ion a viable oxidation state in the organic and NH_3 rich wastewater treatment environment. However, little is known about the oxidation state of Co in raw sewage or throughout WWTPs, but organic complexes of the Co(III) ion could be present. One such species that is known to be present is the cyanocobalamin, or vitamin B_{12} , which is found in soil, water, sewage sludge, manure, and dried estuarine mud (Trischan et al. 1981; Beck and Brink 1976). Inorganic ion pairs that could be of importance in WWTPs with regard to Co(II) are CoOH^+ , $\text{Co}(\text{OH})_2^0$, $\text{Co}(\text{OH})_3^-$, CoCl^+ , CoSO_4^0 , and CoCO_3^0 . All of these species could act to decrease the free divalent metal Co^{2+} species (Trischan et al. 1981; Morel 1983). Most inorganic species of Co(III) would probably not be stable in WWTPs.

Both NTA and EDTA form strong complexes with Co(II) and Co(III) ions; Co(II)NTA and Co(II)EDTA stability constants are, in general, between 0.2 to 3 log units lower than other divalent transition metals, such as Pb, Ni, Hg, and Cu. However, the log stability constant for Co(II)EDTA is approximately 16.2, whereas Co(III)EDTA is 36.0; as these stability constants suggest, the Co(III) complex is extremely strong (Trischan et al. 1981). The conversion of Co(II) to Co(III) in Equation 4.2, and other complexes such as Co(III)EDTA, may be accomplished easily in aerated systems (Trischan et al. 1981) or in the presence of an oxidant like MnO_2 (Crowther et al.

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1983; Murray and Dillard 1979). The stability of Co(III)EDTA [and presumably other Co(III) organic complexes] in environments where one would expect Co(II) is evidenced by the persistence of Co(III)EDTA in the soil and subsoil environment (Jardine et al. 1993). While NTA and EDTA are not commonly added to wastewater streams, they are often used in manufacturing processes discharging to WWTPs.

The majority of dissolved organic ligands in WWTPs are of a complex nature that is poorly defined in terms of the ligand structure, metal-ligand stability, and other chemical-physical parameters. However, the interaction of metals with dissolved organic fractions (such as fulvic acids) in the natural environment has been studied and could serve as an estimate of potential Co-DOC complexation in WWTPs. Conditional stability constants have been determined for a variety of dissolved humic and fulvic material (Stevenson and Fitch 1986). Cobalt and other metals tend to be complexed by the weakly acidic, phenolic, carboxyl, and enol groups of fulvic acid (Ephraim et al. 1989). Importantly, the stabilities of the complexes at pH 8 follow the approximate order of the Irving-Williams stability series (Equation 3.27) (Mantuora et al. 1978). With the level of DOC present in raw and treated sewage, complexation of metals and radionuclides with fulvic acid-type ligands could play an important role in maintaining their solubility in raw sewage and throughout the treatment process.

4.4.3 Precipitation and Coprecipitation

Cobalt precipitation is not likely to be a dominant process in wastewater treatment facilities because the activity of the free metal species (Co^{2+}) is not likely to exceed the K_{sp} of any solid Co phase (Equation 3.16). A previous study (Morel et al. 1975) using a chemical equilibrium model indicated that the two most likely Co solid phases, CoS and CoCO_3 , would be relatively soluble even when considering only inorganic speciation. In the presence of dissolved organic ligands, the Co solubility would be expected to increase further. The potential for Co to be coprecipitated with other solid phases (such as Fe oxide, CaCO_3 , and other carbonates) is feasible. However, little evidence is present in the literature that would lead to the conclusion that precipitation as

a pure or dilute mixed inorganic salt would control the aqueous Co concentration (Kempton et al. 1987a and b; 1983; Stephenson and Lester 1987a and b).

4.4.4 Sorption to Organic and Inorganic Solid Phases

Cobalt sorption phenomena during wastewater treatment may occur as a result of interactions between the dissolved Co and 1) inorganic particulate (Fe and Al oxide, carbonates), 2) particulate organic matter, and 3) biologically activated sludge. The magnitude of these interactions will vary, dependent on pH, aqueous speciation, ionic strength, ionic composition, and chemical additions. Although carbonate sorption of Co is thought to be important in soils and groundwater environments (Zachara et al. 1991), it is not believed to be an important mechanism in WWTPs because the pH generally observed in WWTPs is low with regard to Co sorption to carbonates.

Both FeCl_3 and alum [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] are used as coagulants and flocculents in wastewater treatment. On mixing with water and pH adjustment to near neutral conditions, both of these materials form oxide flocculent materials. Oxides and hydroxides of Al and Fe have long been recognized as important sorbents for a number of trace metal contaminants whose adsorption to and desorption from the surface of oxides influence sorbate behavior in the environment. Adsorption of trace metals, such as Co, to the oxide and hydroxide surface/water interface has been well characterized (Dzombak and Morel 1990; Girvin et al. 1993; Ainsworth et al. 1994). Cobalt adsorption to these oxides is cation-like (that is, sorption increases with increasing pH). The adsorption edge (fractional sorption as a function of pH) is very steep, typically going from 0 to 100 percent sorption over a pH range of about two units. Sorption of Co is minimally affected by changes in ionic strength. However, Co sorption to Fe and Al oxides, in the presence of a strong complexing anion, such as EDTA, reverses the Co sorption edge to where the CoEDTA behavior is more ligand-like; that is, sorption increases as pH decreases (Girvin et al. 1993). Additionally, the Co(II)/oxide interaction is thought to be an inner-sphere complex, but the CoEDTA/oxide interaction is characterized as an outer-sphere complex. The latter can be greatly affected by ionic strength changes. The presence of Co(III) as a complex can have significant

consequences on Co adsorption to oxides. In studies of Co(III)EDTA to Al_2O_3 surface, this species behavior was observed to be more ligand-like and sorption was reduced by about 70 percent compared to Co(II)EDTA (Girvin et al. 1993). It is assumed that other complexing ligands, including organic ligands associated with wastewater treatment, would affect Co(II) sorption in a similar manner as that observed with EDTA, or at the least, reduce the ability of Co to sorb to the surface. If chemical additions of Fe and Al flocculents are not added to the system, specific adsorption to oxides should not be a major source of Co(II) concentration in sludge.

Cobalt like Mn, is poorly sorbed to particulate humic materials. Schnitzer and Kerndorff (1980) investigated the sorption of a number of trace metals on particulate humic acids and found that sorption followed the order $Hg > Fe > Pb > Cu = Al > Ni > Cr = Zn = Cd = Co = Mn$ at pH 3.7. While the order shifted slightly with increasing pH, Co and Mn were always the least sorbed metals. Data using spectroscopic techniques have suggested the interaction between Mn and humic materials is an outer-sphere complex, the Mn retains its waters of hydration $[Mn(H_2O)_6^{2+}]$, and the complex is electrostatic in nature (Gamble et al. 1977; McBride 1978). This may explain the weak sorption of Mn and, by association Co, to humic materials. Because of the quantity of particulate organic material present in a WWTP's influent, however, even weak interactions between Co and particulate organic material will influence Co incorporation into sewage sludge. As was discussed previously, the single most important factor that affects the removal of Co (and other metals) during primary treatment is the solids concentration. Cobalt removal efficiencies during a primary treatment have been shown to be low, but directly related to the solids concentration.

The sorption of Co to the biologically activated sludge and settleable flocculants has been suggested to be minimal (Lawson et al. 1984a and b; Kempton et al. 1983; Rudd et al. 1984; Stephenson and Lester 1987a and b). Conditional stability constants determined for metal extracellular polymers from *K. aerogens* are similar for Co, Cd, and Ni. The complexation capacity is almost an order of magnitude below those of other metals (Rudd et al. 1984). In addition, specific uptake of Co to polymers extracted from

activated sludge were similar to that observed for extracellular polymers from *K. aerogens*. Further, Co uptake to the soluble fraction of extracellular polymers from *K. aerogens* was equal to, or greater than, the colloidal fraction. Stability constants developed for the extracellular polymers from *K. aerogens* (Rudd et al. 1984) are of the same order of magnitude as those for Co fulvic acid (Stevenson and Fitch 1986). This information would suggest that Co binding to the biomass of activated sludge would be low. This conclusion is in agreement with studies performed at pilot scale plants (Kempton et al. 1983; Stephenson and Lester 1987a and b).

Overall, little firm mechanistic data are found detailing Co behavior in WWTPs. From the information detailed in this brief review, however, it would seem that initial partitioning of Co between the influent solid and aqueous phases will forecast the removal of Co to sewage sludge. That is, Co incorporation into the sludge will greatly depend on the solids concentration and the subsequent removal efficiency of the solids. Little concentration of dissolved Co appears to occur because of Co complexation with the DOC. It is doubtful that inorganic precipitates will substantially affect the dissolved Co concentration, nor will sorption to the biologically activated sludge. Sorption to chemical additives, such as Al and Fe oxides at levels impacting Co solid-phase concentration, will depend on the magnitude of the additions, pH, and the aqueous Co complexes present. Unfortunately, no information is available that would suggest the impact of chemical additives on Co behavior.

4.5 Iodine

Of the 24 known isotopes of iodine, 18 have half-lives less than one day. Iodine-127 is the only stable isotope. Its average natural abundance is 5 mg/kg (Gu and Schultz 1991) and its concentration in uncontaminated surface waters is typically < 1 mg/L (Stumm and Morgan 1981). Only ^{129}I , with a half-life of 1.7×10^7 years is of long-term interest in high-level waste disposal. The fission product ^{131}I with a half-life of 8.07 days, and ^{125}I with a half-life of 60 days, are often short-term disposal hazards because of their poor retention by soils.

4.5.1 Behavior in Wastewater Treatment Plants

Because it is widely used in nuclear medicine for therapeutic purposes, Iodine-131 is frequently found in sewage sludge. Iodine exists predominantly in aqueous systems as an anion, forms weak complexes with inorganic constituents, can volatilize at atmospheric pressure, sorbs weakly to mineral surfaces, and sorbs somewhat more strongly to organic matter. Perhaps one of the most important properties of ^{131}I with regard to reconcentration during wastewater processing is its very short half-life, 8 days (Table 4.1). This greatly reduces the risk of a health threat as a result of reconcentration in sewage sludge. For example, assuming a 100 percent removal efficiency by the treatment plant, the amount of ^{131}I in the sludge after one month is only about ten percent of the amount that entered with the influent.

Moss (1973) conducted a 3-year study between 1969 and 1971 to obtain estimates of the magnitude of activity emitted from medical centers to the sewer system of Allegheny County, PA. Approximately 95 percent of the total activity (13 to 15 pCi/L) in the wastewater stream was either ^{131}I or $^{99\text{m}}\text{Tc}$, of which approximately 74 percent was ^{131}I . Hospital sewer lines contributed about 80 percent of all medical-isotope activity going into the local sewer system; the remainder was released into the local sewer lines from residential areas after the patients left the hospital. Moss (1973) calculated that approximately two percent of the radioactivity purchased by the county hospitals eventually reached the Ohio River through the public sewer system. This amounted to a total of 100 GBq in 1971, of which 70 GBq was ^{131}I . Moss did not report direct measurements of the activity in the influent, effluent, and sludge and made no attempt at determine the removal efficiency of ^{131}I by the sewage treatment facility.

In response to the report by Moss (1973), Sodd et al. (1975) conducted a similar type of survey of the radionuclides emitted to the Ohio River by the sewage system of Cincinnati, OH (Table 4.5). They measured, over a nine-day sampling period, the daily activity of a number of radionuclides in the sewage effluent and also the point where the sewage effluent enters the Ohio River. The isotopes ^{131}I and $^{99\text{m}}\text{Tc}$

accounted for approximately 90 percent of the activity measured in the effluent sewage; ^{131}I accounted for approximately 27 percent of the radiation. The ^{131}I activity did not change greatly on a time scale of days, ranging from 0.4 to 1.4 GBq/d. Only 0.01 Bq/L ^{131}I was measured in the Ohio River, a level that is 0.1 percent of the maximum permissible concentration in surface water (Sodd et al. 1975). According to the records obtained from the ten hospitals in the area, only 0.4 to 0.7 GBq/wk of ^{131}I was administered to patients prior and during the sampling period. However, approximately 3.4 GBq/wk of ^{131}I was measured in the sewage treatment plant effluent. No attempt was made to explain the apparent discrepancy of the quantity of ^{131}I reportedly administered by the hospitals and the amount found in the sewage. One possible source of the ^{131}I that was not accounted for in their report was release from nuclear power plants, numerous in this region of Ohio. Puhakainen and Rahola (1989) identified hospitals, nearby nuclear reactors, and fallout from the Chernobyl nuclear accident as sources for ^{131}I in the sewage sludge in several treatment plants in Finland.

Erlandsson and Mattsson (1978) collected information on the amounts of medically administered ^{131}I and measured the ^{131}I activities in the digested sewage sludge weekly for half a year in Malmo, Sweden (Table 4.5). The WWTP here generates $3.2 \times 10^6 \text{ m}^3$ of solid waste, and consists of a primary sedimentation pond, followed by biological secondary treatment and sludge digestion. The ^{131}I activity in the digested sludge (23 percent dry weight) due to medical use varied between 1.1 ± 0.4 and $4.4 \pm 0.7 \text{ Bq/kg}$. They also identified nuclear-weapons testing as another source of sewage sludge ^{131}I . An episodic high level of sludge ^{131}I activity of $15.5 \pm 0.4 \text{ Bq/kg}$ coincided with a test conducted by China on September 26, 1976. Air monitoring measurements confirmed the presence of ^{131}I in the air. The ratio of the amount of ^{131}I in the sewage sludge and the amount of ^{131}I reportedly administered by the hospital was $(2.6 \pm 0.6) \times 10^{-3}$. Assuming all the medically administered ^{131}I reached the wastewater treatment, the removal efficiency for ^{131}I was extremely low, 0.26 percent (on a dry weight basis this value only slightly increases to 1.1 percent). This low value may, in part, reflect errors associated with the assumptions underlying the calculation. Erlandsson et al. (1983) later determined that at the same treatment plant the reconcentration factor of the dehydrator (that is, the ^{131}I activity ratio

Table 4.5 Iodine-125 and ¹³¹I occurrence in wastewater treatment plants

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Stabilized Sludge ¹²⁵ I and ¹³¹ I			RF	Reference	Comments
				Influent ¹²⁵ I and ¹³¹ I Activity	Effluent ¹²⁵ I and ¹³¹ I Activity	Activity			
Sims Bayou Sewage Treatment Facility, Houston, TX	Bio. act. sludge, flash dried	88 d Spring to Summer 1975	NR	NM	163 mBq/d ^a	0.3-6.7 kBq/kg	1/3.3 ^b	Pritchard et al. 1981	a. Total discharge of ¹³¹ I from WWTP (sludge + effluent) b. RF = ¹³¹ I Dried Sludge/ ¹³¹ I Liq-Effluent
Sims Bayou Sewage Treatment Facility, Houston, TX	Dried and heat treated sludge	9/29/83	NR	NM		0.3-1.5 kBq/kg ^a	NR	Texas DOH 1986	a. Measured ¹³¹ I
Sims Bayou Sewage Treatment Facility, Houston, TX	Dried and heat treated sludge	5/5/87	Radioactive waste processors; medical center ^a	<3.7 Bq/L ^b	<2.6 Bq/L ^b	2.9 kBq/kg d wt ^{b,c}	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	a. Receives input for Licensee TX-A - several processors of loose radioactive waste, and from Houston Medical Center b. Measured ¹³¹ I
		5/5/87		<0.9 Bq/L ^d	<0.7 Bq/L ^d	<22.2 Bq/kg d wt ^{c,d}			
		1/11/90		LLD	LLD	LLD			
		4/27/90		LLD	LLD	2E-4 Bq/kg d wt ^{c,d}			
		7/25/90		LLD	LLD	3E-4 Bq/kg d wt ^{c,d}			
		11/2/90		LLD	LLD	LLD			
Webster Wastewater Treatment Plant, Webster, TX	Dried processed sludge	3/22-31/83 8/17/83 9/29/83 1/14/86	NR	NM		LLD (81)-237 Bq/kg ^a	NR	Texas DOH 1986	a. Types of ¹³¹ I sludge monitored include dried process, surface, process, sludge bin, from floor of drier bldg, on drier belt d. Measured ¹²⁵ I
Webster Wastewater Treatment Plant, Webster, TX	Dried processed sludge	5/5/87 10/18/88 1/4/89 3/21/89 6/21/89 1/10/90 4/25/90 7/24/90 10/31/90	From Licensee TX-B ^a	<0.5 Bq/L <0.8 Bq/L <1.6 Bq/L NM <2.5 Bq/L LLD LLD LLD LLD	<0.2 Bq/L <0.2 Bq/L <0.1 Bq/L <0.4 Bq/L <2.7 Bq/L LLD LLD LLD LLD	1.5 Bq/kg d wt ^b <41 Bq/kg d wt <33 Bq/kg d wt <59 Bq/kg d wt 144 Bq/kg d wt LLD LLD LLD LLD	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	a. Receives input from Licensee TX-B which previously manufactured sealed sources; measured ¹³¹ I b. Dry weight

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Table 4.5 (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ¹²⁵ I and ¹³¹ I Activity	Effluent ¹²⁵ I and ¹³¹ I Activity	Stabilized Sludge ¹²⁵ I and ¹³¹ I Activity	RF	Reference	Comments
Odessa, TX	Septic tank	4/1/87	From Licensee	NM	NM	<0.3 Bq/L	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	a. Licensee TX-E in Odessa - is a processor of loose radioactive waste; measured ¹³¹ I
		4/6/88	TX-E ^a			NR			
		4/6/89 3/20/90				<0.4 Bq/L LLD			
Odessa, TX	NR	4/1/87	From Licensee	NM	NM	1.2 Bq/L	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	a. Licensee TX-F in Odessa - is a manufacturer of sealed sources and a processor of loose radioactive waste; measured ¹³¹ I
		6/16/87	TX-F ^a			<0.8-2.1 Bq/L			
		3/30/88 4/6/89 3/20/90				<1.0-1.2 Bq/L <4.0-5.4 Bq/L LLD			
Between Midland and Odessa, TX	NR	4/1/87	From Licensee	NM	NM	1.7 Bq/L	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	a. Licensee TX-G in Odessa - is a processor of loose radioactive waste; measured ¹³¹ I
		4/6/88	TX-G ^a			<5.5 kBq/kg d w ^b			
Midland, TX	Septic tank	4/4/87	From Licensee	NM	NM	3.9 Bq/L	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	b. Dry weight a. Licensee TX-H in Odessa - is a processor of loose radioactive waste; measured ¹³¹ I
		10/28/87	TX-H ^a			8.6 Bq/L			
		1/11/89 4/6/89 3/19/90				4.7 kBq/kg d w ^b NR LLD			
Central Sewage Treatment Facility, Allegheny County, PA	NR	1969-1971	21 Nuclear Med. Depts. ^a	NM	0.4 Bq/L	NM	NR	Moss 1973	a. Estimated that 2 percent of total annual activity (all radionuclides) received by the 21 hospitals reaches the Ohio River via the sewer system. In 1971, 1.9 Ci of ¹³¹ I was received.
		8/6-14/73	Hospitals in Greater Cinn. area ^a	NM	NM	0.8-3.1 Bq/L	NR	Sodd et al. 1975	a. Sampling from outfall of settling basin; samples are cumulative samples taken twice a day; measured ¹³¹ I

Table 4.5 (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Stabilized Sludge			RF	Reference	Comments
				Influent ¹²⁵ I and ¹³¹ I Activity	Affluent ¹²⁵ I and ¹³¹ I Activity	Activity			
Blue Plains Waste Water Treatment Plant, Blue Plains, PA	Modified activated sludge process	2/86	Licensee A ^a - Medical Research	407 Bq/L ^b	NM	NM	NR	U.S. NRC Inspection Report No. 86-01 1986b	a. Liquid wastes discharged into underground discharge tanks, or directly into sewers
				NM	NM	ND-28 kBq/L ^c	NR	U.S. NRC Inspection Report No. 86-01 1986b	b. Discharge ¹³¹ I concentration taken at manhole near facility
Oak Ridge Waste Water Treatment Plant, Oak Ridge, TN	Primary and secondary treatment; anaerobic digestion	1990 1991	Industrial; hospitals; nuclear weapons fallout ^a	NM NM	NM NM	0.1-20 Bq/L w wt ^b 0.07-77 Bq/kg w wt	NR NR	City of Oak Ridge 1990 Land Application Report City of Oak Ridge 1991 Land Application Report	a. Measured ¹³¹ I b. Wet weight
Hamilton Sewage Treatment Plant on Lake Ontario, Canada	Digester sludge (freeze dried for analysis)	NR	NR ^a	NM	ND	1.7 Bq/kg d wt ^b	NR	Durham and Joshi 1979	a. Most radioactivity removed with sludge during sewage treatment; measured ¹³¹ I Concentration of radionuclides in sludge are low enough to allow agricultural use
									b. Dry weight

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Table 4.5 (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ¹²⁵ I and ¹³¹ I Activity	Effluent ¹²⁵ I and ¹³¹ I Activity	Stabilized Sludge ¹²⁵ I and ¹³¹ I Activity	RF	Reference	Comments
Dundas Sewage Treatment Plant on Lake Ontario, Canada	Digester sludge (freeze dried for analysis)	NR	NR ^a	NM	ND	6.8 Bq/kg d wt ^b	NR	Durham and Joshi 1979	a. Most radioactivity removed with sludge during sewage treatment; measured ¹³¹ I Concentration of radionuclides in sludge are low enough to allow agricultural use
Bologna Sewage System, Bologna, Italy	Primary decantation; active oxidation; active decantation; disinfection; sludge incineration	NR	2 Hospitals ^a	22 Bq/L (MAX) 0.3 Bq/L (AVG) 25 GBq/yr (TOTAL)	1.2 Bq/L (MAX) 0.02 Bq/L (AVG) 1.6 GBq/yr (TOTAL)	3330 MBq/yr (SLUDGE) 1665 MBq/yr (ASH)	93.5% ^b	Testoni et al. 1988	a. Measured ¹³¹ I b. [(Influent-Effluent)/Influent] x 100
Worcester Park Sewage Works, Kingston-upon-Thames, UK	Humus tanks; filter beds; digester; activated sludge plant	5/90-8/90	Hospital	NM	NM	*(See NRPB-M295 table below)	NR	McDonnell and Wilkins 1991	NRPB report on modeling doses to sewer workers associated with discharges from hospitals; measured ¹³¹ I
Sjölunda, Malmö Sweden	Partial biological cleaning; sedimentation; digester	7/76 11/76 10/76 ^a	Area hospitals and fallout ^a	3.2 GBq 1.7 GBq 8.3 GBq ^b	NM	6.4 MBq 5.4 MBq 14 MBq ^b	0.002 ^c 0.003 ^c 0.002 ^c	Erlandsson and Mattsson 1978	a. The mass ratio of input sewage/output sludge = 4.1E-4; measured ¹³¹ I b. Measured from runoff; done soon after 9/76 Chinese atmospheric testing c. RF = output sludge conc./reported medically administered conc.

Table 4.5 (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ¹²⁵ I and ¹³¹ I Activity	Effluent ¹²⁵ I and ¹³¹ I Activity	Stabilized Sludge ¹²⁵ I and ¹³¹ I Activity	RF	Reference	Comments
Borgeby Sewage Treatment Plant, Malmo Sweden	Primary and secondary treatment	3/81-5/81	Nuclear power plant ^a	Entrance sludge ^a NM	NM	Final Sludge ^c	1.7 ^d	Erlandsson et al. 1983	a. Measured ¹³¹ I
		8/81-9/81		183 Bq/kg	1750 Bq/kg	91 Bq/kg 1350 Bq/kg			b. Entrance sludge collected just after the first biological degrading step c. Final sludge collected after the dehydrator d. Entrance sludge conc./final sludge conc.
Kallby Waste Water Treatment Plant, Lund, Sweden	Primary and secondary treatment	7/85	Hospitals, NPP, nuclear weapon fallout ^a	NM	4.0 Bq/kg	265 Bq/kg ^b	c	Erlandsson et al. 1988	a. Study of uptake of radionuclides in tubificid worms; measured ¹³¹ I
		9/85		NM	NM	436 Bq/kg			b. Sludge values decay corrected for mean residence time of sludge is 14 d
		1/85		0.44 Bq/kg	87 Bq/kg	87 Bq/kg			c. Concentration data for turbidities
		1/86		1.54 Bq/kg	226 Bq/kg	226 Bq/kg			81 Bq/kg; 166 Bq/kg;
		8/86		NM	765 Bq/kg	765 Bq/kg			12 Bq/kg; 2 Bq/kg; 86 Bq/kg
Kallby Waste Water Treatment Plant, Lund, Sweden	Primary and secondary treatment	7/85-8/85	Hospitals, NPP, nuclear weapon fallout ^a	11-774 MBq (0.1-12 Bq/L)	NM	NM	0.08 ^c	Erlandsson et al. 1989	a. Measured ¹³¹ I
		7/85-12/85		53-1853 MBq	53-1853 MBq	2.6-256 MBq ^b			b. Sludge data is decay corrected
		10/85-12/85		159-4942 MBq	159-4942 MBq	27-256 MBq ^b	0.14 ^c		c. RF = sludge/ (effluent + sludge)

Table 4.5 (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ¹²⁵ I and ¹³¹ I Activity	Effluent ¹²⁵ I and ¹³¹ I Activity	Stabilized Sludge ¹²⁵ I and ¹³¹ I Activity	RF	Reference	Comments
Finland:									
9 plants	Simultaneous	9/85-8/87	Hospitals, NPP, nuclear weapon fallout ^a	NM	NM	21-7400 Bq/kg d wt ^b	NR	Puhakainen and Rahola 1989	a. Measured ¹³¹ I
1 plant	precip.					0 Bq/kg d wt			b. Dry weight
1 plant	Oxidation ditch					0-5 Bq/kg d wt			
1 plant	Direct precipitation					0 Bq/kg d wt			
1 plant	Chemical treatment					NM			
3 plants	Precipitation					0-7 Bq/kg d wt			
1 plant	Near Nucl. Plants					NM			
	Septic tank near NPP								
Pittsburg	NR	1971	NR	NR	0-1.5 Bq/L	NR	NR	Strong 1973 as cited in Prichard et al. 1981	Measured ¹³¹ I
Berkeley	NR	1973	0.3-9 Bq/L	0.1 Bq/L	NR	NR	NR		
Denver	NR	1973	NR	NR	NR	2.1 Bq/kg			
Baltimore	NR	1973	NR	NR	NR	2.0 Bq/kg			
Chicago	NR	1973	NR	NR	NR	1.7 Bq/kg			
Houston	NR	1973	NR	NR	NR	17 Bq/kg			
Boston	NR	1973	NR	NR	NR	ND			
Philadelphia	NR	1973	NR	NR	NR	ND			
New York	NR	1973	NR	NR	NR	5.3 Bq/kg			
Los Angeles	NR	1973	NR	NR	NR	25 Bq/kg			
San Francisco	NR	1973	NR	NR	NR	12 Bq/kg			
Cincinnati	NR	1973	NR	NR	0.2-3.1 Bq/L	NR			
Houston, TX	NR	10/18/88	From Licensee TX-A ^a	NM	NM	<10 Bq/L	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	a. Licensee TX-A in south-central Houston - is a processor of loose radioactive waste
		4/24/90				LLD ^b			b. Measured ¹²⁵ I

Table 4.5 (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ^{125}I and ^{131}I Activity	Effluent ^{125}I and ^{131}I Activity	Stabilized Sludge ^{125}I and ^{131}I Activity	RF	Reference	Comments
Houston, TX	Septic tank	1/88-1/89 11/1/90	From Licensee TX-D ^a	NM NM	NM NM	1.1 Bq/L ^b 6E-6 Bq/L ^b	NR	Texas DOH Environmental Monitoring Reports for 1987; 1988 & 1989; and 1990	a. Licensee TX-D in south-eastern Houston - is a processor of loose radioactive waste and manufacturer of radioimmunoassay kits b. Measured ^{125}I

ND = Not detected

NM = Not measured

NR = Not reported

RF = Reconciliation Factor

< = The quantity listed is the smallest amount that could be measured at the 95% confidence level, that is, lower limit of detection (LLD)

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of the sludge leaving the biological degrador divided by the activity of the final sludge collected after the dehydrator) was 1.7 (Table 4.5).

Prichard et al. (1981) reported that ^{131}I dominated the gamma spectra of dried sludge and effluent samples from a treatment plant serving the area containing the Texas Medical Center (Table 4.5). The conventional biologically activated-sludge facility in 1975 processed 190,000 m^3/d at an average residence time of 22 hours. The activity of ^{131}I varied considerably on a time scale of weeks. The ratio of ^{131}I activity between the dried sludge and the liquid effluent was 1:3.3. Twenty-three percent of the ^{131}I was in the dried sludge and 77 percent was in the effluent. Stated in yet another way, the removal efficiency of ^{131}I at this facility was 23 percent.

Puhakainen and Rahola (1989) conducted a survey of radionuclide activity in the air dried sludge produced by 19 wastewater treatment facilities in Finland (Table 4.5). The ^{131}I isotope accounted for most of the radioactivity in the sludge samples. They identified medical inputs as the dominant source of ^{131}I in the sludge. Other factors affecting the total activity of ^{131}I in sewage sludge included proximity to nuclear power plants, fallout, amount of rain, and amount of runoff. The method of wastewater treatment, (biological/ferric sulfate, ferric sulfate, or oxidation ditch) did not have a consistent affect on total activity or ^{131}I activity in the sludge. In spring when the snow melted and large quantities of run-off water flowed into the treatment plants, ^{131}I activity clearly increased (as did many other radionuclides), but decreased again by late spring and early summer. It was not possible to calculate a removal efficiency from the reported data.

Testoni et al. (1988) measured ^{131}I and $^{99\text{m}}\text{Tc}$ activity in the influent, effluent, sludge, and ashes from the WWTP in Bologna, Italy (Table 4.5). This facility processes 115,000 m^3/d by primary sedimentation, active oxidation, and chlorination. The process has a 12-hour residence time. The sludge is ashed and the effluent drains into the Adriatic Sea. A ratio of the known ^{131}I activities administered by the hospitals and the ^{131}I activity at the influent of the sewage facility was 0.3. A ratio of the weekly amount of ^{131}I in the effluent over that of the influent was 0.065. This suggests the treatment plant removed 93.5 percent of the ^{131}I in the influent. The percentage of moisture in

the sewage sludge was not reported and, therefore, the removal efficiency value cannot be normalized to a dry weight basis.

Erlandsson et al. (1989) measured the activity of a number of gamma emitting nuclides in the influent, effluent, and sludge of a treatment facility located in Lund, Sweden. The facility has mechanical and biological stages, as well as a chemical additive stage (the name was not included in the article). Sludge is produced at each stage. The sludge from the biological and chemical stages is recirculated to the inlet of the mechanical stage. The ratio of ^{131}I in the sludge to the total amount of ^{131}I entering the WWTP was 0.08 (an average of eight weekly ratios taken in the fall of 1985). A removal efficiency on a dry weight basis was 36 percent. The dry weight content of the sludge was 22 to 23 percent. The authors also passed an influent sample through an unspecified type of filter paper and determined that only 1.5 to 8.5 percent of the ^{131}I remained on the filter paper.

The literature review uncovered three removal efficiency values for ^{131}I : twenty-three percent for the sedimentation/biological (biologically activated sludge) process in Texas (Prichard et al. 1981), 93.5 percent for the sedimentation/active oxidation process in Bologna, Italy (Testoni et al. 1988), and eight percent for the sedimentation/biological/chemical precipitation process in Lund, Sweden (Erlandsson et al. 1989). Normalizing these values by sewage dry weight did not reduce the variability. By making certain assumptions, an additional removal efficiency of 0.26 percent was calculated for the sedimentation/biological/oxidation process in Malmo, Sweden (Erlandsson and Mattsson 1978). This value does not improve our understanding of how or to what extent ^{131}I is removed from the wastewater stream.

McDonnell and Wilkins (1991) measured the ^{131}I activity associated with the filtrate and suspended solids (retentate) from samples collected before and after a number of wastewater treatment processes of a sedimentation/biologically activated-sludge facility in Kingston-Upon-Thames, United Kingdom (Tables 4.5 and 4.6). The ^{131}I entered the treatment plant primarily in the filterable phase and remained in that phase through the primary settling process. Typically over 95 percent of the ^{131}I in the influent, grit, and primary setting samples were in the filterable fraction (Table 4.6). However, after the wastewater passed

Table 4.6 Iodine-131 activity associated with suspended solids and filtrate in the crude sewage, grit, primary sludge, settled sludge, activated sludge, and humus (after McDonnell and Wilkins 1991)

Sample Type	¹³¹ I Activity Concentration (Bq/kg wet sludge)													
	Collected 5/6/90				Collected 6/6/90				Collected 7/6/90				Collected 8/6/90	
	Total	Filtrate	Suspended Solids ^(a)	Total	Filtrate	Suspended Solids ^(a)	Total	Filtrate	Suspended Solids ^(a)	Total	Filtrate	Suspended Solids ^(a)	Total	Filtrate
Crude Sewage	5.0	4.3	0.7	232	231	0.93	160	156	5.0	37	36	1.30		
Grit ^(b)	NM ^(d)	NM	NM	NM	NM	NM	240	238	NM	NM	NM	NM		
Primary Sludge ^(b)	93	92.4	NM	323	323	NM	360	363	NM	370	366	NM		
Settled Sludge	5.5	5.3	0.25	178	177	0.65	206	204	2.7	60	58	1.35		
Bio. Act. Sludge	NM	NM	NM	NM	NM	NM	600	146	460	NM	NM	NM		
Humus	NM	NM	NM	NM	NM	NM	700	148	550	NM	NM	NM		

(a) Activity in suspended solids presented as Bq in filtered solids divided by weight of complete (liquid) sample in kg. Solids fraction is very much smaller than liquid and was not determined separately. Total activity concentration in sample is the sum of the activity concentration in liquid (filtrate) and the suspended solids.

(b) Primary sludges and grit were analyzed as collected without filtration. The activity concentration figures given in the filtrate column in fact refer to the total wet sample.

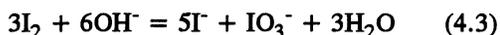
(c) Activity concentration expressed in Bq/kg in the wet sludge for this dried sample.

(d) NM = Not measured

through the biologically activated sludge process, only 24 percent of the ^{131}I in the wastewater stream was in the filterable fraction. The remainder existed as suspended solids. Thus, the biologically activated-sludge process converted the ^{131}I from a filterable species to an unfilterable (suspended solids) species.

4.5.2 Aqueous Speciation and Complexation

Although iodine is known to exist in the -1, 1, 3, 5, and 7 oxidation states, it usually occurs in the -1 (iodide, I^-) state in natural surface waters. Iodide is the most important species because its domain of predominance extends throughout the pH scale, completely covering a large part of the stability domain of water (Pourbaix 1966; Ticknor and Cho 1990). Oxidation of I^- to produce iodate, IO_3^- (the second most abundant form of iodine in aqueous systems), is easily accomplished in basic solution by the reaction:



(Cotton and Wilkinson 1972). Thus, the IO_3^- form of iodine is likely dominant in well-oxidized, high pH systems, as may exist in some wastewater treatment processes where lime is added. Iodide tends to form weak complexes with metal ions as a result of its large size (22-nm ionic radius). With a few exceptions, I^- forms weaker complexes than most anions, including other halides (Langmuir 1979). The IO_3^- species tends to form somewhat more stable complexes with metals than I^- (Ticknor and Cho 1990; Gu and Schulz 1991). The strongest iodine-bond formed is with organic matter where iodine may covalently bond to C (Walters and Winchester 1971). Iodine, especially when present as an organic-iodine molecule such as methyl iodide (CH_3I), can volatilize (more specifically, sublimate) at atmospheric pressure. The conditions under which iodine sublimates are not well understood and are poorly understood in complex systems, such as those existing in wastewater streams.

4.5.3 Precipitation and Coprecipitation

Precipitation and coprecipitation are not likely to be significant reaction paths of iodine in wastewater treatment systems. As stated in Section 4.5.1, iodine anions exist at very low concentrations and they tend

to form very soluble complexes with the common inorganic cations in wastewater streams. Some of the insoluble or sparingly soluble compounds include those formed with Ag, Ba, Hg, Pb, and Pd (Pourbaix 1966). In most wastewater streams, the concentration of these elements is very low. Therefore, these precipitates would not be expected to be present in most wastewater streams.

4.5.4 Sorption to Organic and Inorganic Solid Phases

Two types of reactions between anions and inorganic solids are recognized: specific adsorption and nonspecific adsorption (Section 3.3.3). Specific adsorption refers to incorporation of anions as a ligand in the coordination shell of an adsorbent, and nonspecific adsorption refers to adsorption of anions by simple coulombic (electrostatic) interactions with positive charges. Iodine anions are believed to sorb primarily through nonspecific, anion-exchange reactions on mineral surfaces (Gu and Schulz 1991) and through specific adsorption on organic matter (Walters and Winchester 1971). Nonspecific sorption may occur at the localized positive charges that occur 1) on Fe and Al oxide surfaces, 2) at the edges of aluminosilicate clay surfaces where the oxygen atoms are not fully coordinated by Al or Si atoms, and 3) on amine and amino groups of organic matter. These positive charges, which increase with decreasing pH (Section 3.2.1), attract anions electrostatically, and the anions are readily exchangeable with those in the aqueous phase (Gu and Schulz 1991). Several researchers have related charge characteristics with the mineralogical composition, organic matter content, and percentage of Fe and Al oxides of a system (Sakurai et al. 1989, 1990; Gu and Schulz 1991). They have pointed out the point-of-zero-charge reflects the overall mineral composition and the organic matter content of the systems (Section 3.3.1). In general, it seems clear the percentage of Fe and Al oxides tend to shift the point of zero charge towards higher pH values, while the presence of organic matter tends to shift the point-of-zero-charge towards lower pH values (Section 3.2.1 and Table 3.2). Therefore, the solids in wastewater treatment systems would probably have a low point of zero charge because of the abundance of organic matter in the system and the likelihood of organic coatings on many of the mineral surfaces, particularly the Al and Fe oxides (Tipping 1981; Tipping and

Cooke 1982). Because the pH of many wastewater systems is between seven and eight, most solid surfaces would be expected to have a net negative charge. Anions may still be electrostatically attracted to such surfaces, albeit to a limited extent, because positive charge sites usually exist, but less frequently than negative charge sites (Gu and Schulz 1991; Sposito 1984). The anion exchange capacity of a wide range of soils varied from 0.09 to 1.97 cmol/kg (Skjemstro and Koppi 1983). These values are appreciably less than the cation exchange capacities measured in the same soils: 2.41 to 8.11 cmol/kg.

The propensity of anions to sorb to mineral surfaces generally increases in the order: $I^- < NO_3^- < Cl^- < CH_3COO^- < SO_4^{2-} < PO_4^{3-}$ (Sposito 1984). Whitehead (1973) reported that sorption of I^- and IO_3^- by soil was associated with both soil organic matter and Fe and Al oxides, with the oxides being increasingly important under more acidic conditions. The maximum amounts sorbed by two surface soils at pH 6.6 to 6.8 were 25 and 6 mg/kg, respectively. At these pH levels, the amounts of I^- sorbed were found to be closely related to the contents of organic matter, but not to Fe or Al oxides or clay. At pH < 5, the removal of Fe and Al oxides resulted in a marked reduction in I^- sorption. Whitehead (1974) further observed that freshly precipitated ferric and Al oxides sorbed substantial amounts of iodide from solutions of pH < 5.5, but the amount decreased to zero as the pH approached seven. However, Muramatsu et al. (1990) reported that only ferric oxide sorbed substantial amounts of I^- and IO_3^- , while Al oxides sorbed very small amounts of I^- and IO_3^- . In calcareous soil systems, organic matter content was much more important than ferric and Al oxide concentrations in controlling I^- or IO_3^- removal from the aqueous phase (Whitehead 1978).

Ticknor and Cho (1990) studied the interaction of I^- and IO_3^- with a number of minerals (calcite, chlorite, goethite, gypsum, hematite, kaolinite, bentonite, muscovite, and quartz) at a pH range of 7.5 to 8.0. No I^- was removed from the aqueous phase by these minerals. Iodate, however, was removed from solution by all minerals except bentonite clay, calcite, gypsum, and muscovite. Chlorite and hematite showed the most sorption of IO_3^- under the widest range of experimental conditions. It was suggested that replacement of hydroxyl groups at exposed edge sites or H_2O ligands on hydrous oxide surfaces was

the mechanism accounting for high IO_3^- sorption on chlorite and hematite. Muramatsu et al. (1990) reported that neither I^- nor IO_3^- were sorbed by quartz sand. They also reported that IO_3^- was sorbed to a greater extent than I^- on organic matter and that sorption to organic matter was substantially higher than on clay minerals.

To extend these results conducted in soils to wastewater treatment systems, it would appear that 1) the addition of ferric salts and alum would remove dissolved I^- or IO_3^- only if the pH of the system was below neutrality, 2) organic matter is the solid phase most likely to remove iodine from the dissolved phase, 3) precipitation or coprecipitation is not a likely pathway of iodine in these systems, and 4) more iodine would be removed under oxidized conditions where IO_3^- is more abundant, than under reduced conditions where I^- is more abundant. Together these results suggest the process most likely to cause reconcentration of ^{131}I is the biological treatment of lime-amended wastewater streams.

4.6 Manganese

Manganese-55 is a naturally occurring element that may exist in a +2, +3, +4, and +7 oxidation states. Manganese(II) is the primary oxidation state in aqueous solutions. Very limited information is available on the precipitation/dissolution and adsorption/desorption mechanisms of Mn(II). The available data suggest that $MnCO_3$ may be the solubility-controlling solid under reducing conditions and high pH and high CO_2 levels. Manganese tends to form weak bonds with most ligands (Langmuir 1979). Manganese and organic matter complexes/solids may play an important role in Mn speciation because it forms somewhat stronger bonds with organic matter than with other ligands. Another factor is that organic matter exists in high concentrations in wastewater streams (Sections 4.6.1 and 4.6.3). Compared to other divalent metals, Mn partitions weakly to naturally occurring organic matter (Van Kijk 1971).

4.6.1 Behavior in Wastewater Treatment Plants

Manganese-54 is a gamma-emitting radionuclide with a half-life of 280 days that has been used in tracer

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studies in medical research. Relatively few cases of ^{54}Mn contamination have been found in sewage sludge (Table 4.7). The Royersford Wastewater Treatment Facility, Royersford, PA (U.S. Nuclear Regulatory Commission 1986a) and the Springfield Regional Wastewater Treatment Plant, Springfield, MA (U.S. Nuclear Regulatory Commission 1986b) receive sewage from two companies that launder radionuclide-contaminated clothing. The two companies are licensed to the same corporation. In addition to ^{54}Mn , these licensees also release several other radionuclides, the most abundant being ^{60}Co , ^{65}Zn , and ^{137}Cs .

The licensee disposing radioactive materials to the Royersford facility, pH adjusted the waste to between six and nine in a large holding tank prior to discharging the waste into the sewage system (U.S. Nuclear Regulatory Commission 1986a). How the pH was adjusted or whether the waste was filtered prior to discharge was not stated. However, it is company practice at the Massachusetts laundry operation to filter the waste before and after pH adjustment. The licensee discharges 60,000 L/d. In 1984, the average activity of the waste discharged to the sewage system was 2.1 mBq/L, and in 1986, the average activity was 0.9 mBq/L (U.S. Nuclear Regulatory Commission 1986a). The WWTP at Royersford consists of a primary settling tank, two secondary settling tanks, two aerobic biological digestors (where waste is heated and mixed to reduce organic contents of sludge), and two chlorinators.

Radioactivity at various stages during the treatment process was measured by holding a hand-held gamma radiometer one meter above the waste to provide the total radioactivity in units of microrems/h ($\mu\text{R}/\text{h}$) (U.S. Nuclear Regulatory Commission 1986a). The radioactivity in the influent (the effluent after the primary settling tanks), the primary biofilter, and the secondary biofilters was less than or equal to 20 $\mu\text{R}/\text{h}$, whereas the radioactivity in the secondary digester was approximately 1000 $\mu\text{R}/\text{h}$. The radioactivity levels in the primary digester were not measured. Essentially identical findings were obtained on two consecutive months. Unfortunately, these data do not permit differentiation between different gamma-emitting radionuclides, nor do they enable us to determine at which step this large reconcentration of radionuclides occurred. However, these data do indicate clearly that very low levels of

activity at the influent (below detection in the case of ^{54}Mn ; Table 4.7) can result in substantial reconcentration in the sludge and that settling, followed by biological treatment and digesting, is an efficient process for removing ^{54}Mn from this wastewater stream. As can be seen in Table 4.7, ^{54}Mn activity decreased from 0.08 mBq/L in the holding tanks of the licensee to below detection limit (numbers not reported) by the time the sewage reached the influent of the WWTP. Sludge ^{54}Mn activity was low, about 0.2 Bq/L.

The licensee disposing radionuclides to the Springfield Regional WWTP, as previously mentioned, filters their waste before and after pH adjustment (U.S. Nuclear Regulatory Commission 1986b). As was the case in Royersford, no detectable ^{54}Mn was measured in the influent or effluent of the treatment facility (Table 4.7). The sludge contained somewhat less ^{54}Mn activity than was detected in the Royersford sludge. Safety inspectors also collected some sewage within the licensee's fence line. They also measured soluble and insoluble levels (presumably determined by measuring the ^{54}Mn activity on a filter and in the corresponding filtrates of the sewage). About half of the ^{54}Mn existed in the insoluble fraction (Table 4.7). The presence of insoluble (particulate) ^{54}Mn in the sewage after the licensee had filtered the discharged solution may be attributed to 1) inspectors using a smaller pore-size filter than the licensee, or 2) soluble ^{54}Mn released from the holding tanks precipitated or became associated with filterable solids within the short time period of being introduced to the sewage system and reaching the sample site (this time period was not provided in U.S. Nuclear Regulatory Commission 1986b).

Erlandsson et al. (1983) determined the reconcentration factor of the dehydrator (that is, the ^{54}Mn activity ratio of the sludge leaving the biological degradation unit divided by the final sludge collected after the dehydrator unit) to be 1.4, approximately the same value as that calculated for ^{131}I (Reconcentration Factor = 1.7; Table 4.5).

4.6.2 Aqueous Speciation and Complexation

In terms of chemical speciation, radioactive ^{54}Mn behaves the same as stable ^{55}Mn . Therefore, ^{54}Mn

Table 4.7 Manganese-54 occurrence in wastewater treatment plants

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ^{54}Mn Activity	Effluent ^{54}Mn Activity	Stabilized Sludge ^{54}Mn Activity	RF	Reference	Comments
Springfield Regional Waste Water Treatment Plant, Springfield, MA	Bio. act. sludge process	2/86	Nuclear laundry ^a (<850 Bq/L)	ND	ND	7.4 Bq/L		U.S. NRC Inspection Report No. 030-04632/86-01 1986c	a. Waste water from laundering of contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge b. Discharge concentration at company's fence line (via manhole) = 34 Bq/L Filtered: Soluble = NM; Insoluble = 21 Bq/L
Royersford Water Treatment Facility, Royersford, PA	Primary and secondary treatment; anaerobic digestion; 2-stage biofiltration	10/85 12/85	Nuclear Laundry ^a	81 Bq/L ^b NM	ND ND	59 Bq/L 222 Bq/L	NR	U.S. NRC Inspection Report No. 030-20934/85-04 1986a	a. Waste water from laundering of contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge b. From licensee's discharge tanks
Borgeby Sewage Treatment Plant, Malmö, Sweden	Primary and secondary treatment	3/81-5/81 8/81-9/81	Nuclear power plant	Entrance sludge ^a 183 Bq/kg	NM 1750 Bq/kg	Final Sludge ^b 91 Bq/kg 1350 Bq/kg	1.4 ^c	Erlandsson et al. 1983	a. Entrance sludge collected just after the first biological degrading step b. Final sludge collected after the dehydrator
Finland: 1 plant	Septic tank near Nuclear Power Plant	9/85-8/87	NM	NM	NM	31 - 52 Bq/kg d wt ^a		Puhakainen and Rahola 1989	a. RF = Entrance sludge conc./final sludge conc.

NM = Not measured

NR = Not reported

RF = Reconciliation Factor

ND = Not detected

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equilibrium chemistry will be controlled largely by the concentration of ^{55}Mn that will always exist at much greater concentration than ^{54}Mn .

Compared to other divalent transition metals, Mn forms weak bonds with most ligands (Langmuir 1979). Stability constants at pH 7 of various ligand-Mn(II) complexes increase as follows: $\text{MnNO}_3^+ > \text{MnCl}_2^0 > \text{MnOH}^- > \text{MnHCO}_3^+ > \text{MnF}^+ > \text{MnCl}^+ > \text{MnSO}_4^0 > \text{MnHPO}_4^0$ (Langmuir 1979; Rai and Zachara 1984). Natural organic matter forms relatively stronger complexes with Mn than most inorganic ligands (Stumm and Morgan 1981). Because of the high concentration of organic matter in wastewater streams, it is likely that organic matter complexes dominate Mn(II) speciation in these systems.

Manganese is not readily removed from wastewater via primary treatment (Lester 1987a; Kempton et al. 1987a and b) or secondary (Lester 1987b; Stephenson and Lester 1987a and b). The poor removal efficiency of Mn by these treatment processes has been attributed to the formation of soluble organic complexes (Kempton et al. 1983; Lester 1987a and b). In a laboratory study in which Mn was added to filtered biologically activated-sludge liquor, the percentage of Mn removed by adding mixed liquor suspended solids (primarily biologically activated sludge) was ten percent (Kempton et al. 1983). The Mn in this laboratory study remained in a dissolved (< 15 nm) fraction as an organic complex. Similarly, Stephenson and Lester (1987b) observed that Mn (and Mo) remained in a soluble form whether biologically activated-sludge solids were or were not added to the studied system.

4.6.3 Precipitation and Coprecipitation

Lindsay (1979) has reviewed the thermodynamic data of Mn compounds and has calculated the relative stability of Mn compounds. His calculations show that Mn(IV) and Mn(III) compounds can occur under oxidizing conditions while Mn(II) compounds can occur under reducing conditions. Pyrolusite ($\beta\text{-MnO}_2$) is, thermodynamically, the most stable compound under oxidizing conditions. Because small quantities of foreign ions interfere with the formation of pyrolusite (McKenzie 1977), it is unlikely to form in wastewater streams. Manganese(III) and Mn(IV),

the second most stable species, are not likely to form MnOOH or Mn_2O_3 because carbonates, a common constituent of wastewater streams, greatly hamper the formation of these mineral phases. Manganese(III) and Mn(IV) may readily form nsutite, $\text{MnO}_{1.9}$, even in chemically complex systems (Zwicker et al. 1962). Nsutite is omnipresent in nature (Zwicker et al. 1962; Lindsay 1979; Stumm and Morgan 1981). Under reducing conditions (such as in anaerobic digestors or at the bottom of many bioreactors or settling basins) and in the presence of CO_2 , rhodochrosite (MnCO_3) may be expected to form. The most likely Mn solid to form in carbonate systems is MnCO_3 (Ponnampertuma et al. 1969; Schwab and Lindsay 1983). Based on Mn(II) levels in soils maintained at constant redox and CO_2 pressures, Schwab and Lindsay (1983) showed that Mn(II) levels at low redox potentials appear to be controlled by MnCO_3 and by Mn oxides at high redox potentials.

4.6.4 Sorption to Organic and Inorganic Solid Phases

Kempton et al. (1987a) reported that Mn removal, unlike Bi and Pb, from oxidized solutions appears to be controlled by adsorption on biologically activated sludge, and not precipitation. Manganese adsorption is complicated by redox reactions that affect aqueous species and transformations and formation of Mn compounds of different oxidation states. The available literature does not allow a clear definition of the most important adsorption process for Mn retention in wastewater systems (such as, specific adsorption, ion exchange or organic complexation). The presence of only trace amounts of organic matter in soils has been shown to greatly increase the amount of Mn adsorption (Hemstock and Low 1953). Clay minerals and iron oxides adsorb Mn less strongly than Co, Ni, Zn, and Cu (Takematsu 1979). Manganese is weakly, but specifically, adsorbed by iron oxide and more strongly by various Mn oxides (Takematsu 1979). In calcareous materials, chemical sorption to CaCO_3 surfaces may occur, possibly leading to the formation of MnCO_3 (McBride 1978). The oxidation of the Mn(II) ion at the surface of Mn oxides and incorporation into a new surface solid phase may also account for its removal from solution (McKenzie 1977). The adsorption of transition metals by Mn oxides may release Mn(II) from the solid (Murray 1975). This result is from an ion exchange of

adsorbed Mn by a more strongly binding metal or from structural replacement of Mn in the Mn oxide (Doner et al. 1982).

Manganese has been shown by nuclear magnetic resonance analyses to form outer-sphere bonds (Kempton et al. 1983; Deczky and Langford 1978). Such bonds are weak and, therefore, are less prone to affect speciation than inner-sphere bonds, such as those that exist between Cu(II) and organic matter (Deczky and Langford 1978). A combination of various researchers' stability sequences for metal-humic material complexes has been put together by Stumm and Morgan (1981): $\text{Hg(II)} > \text{Fe(III)} \geq \text{Pb(II)} \geq \text{Cu(II)} > \text{Cd(II)} \geq \text{Zn(II)} \geq \text{Ni(II)} > \text{Co(II)} \geq \text{Mn(II)} \geq \text{Ca(II)} \geq \text{Mg(II)}$. The placement of Mn towards the end of this series is indicative of the relative weakness of the Mn-organic matter complex. However, because Mn forms stronger complexes with organic matter than with most other ligands, and organic matter is abundant in wastewater streams, the partitioning of Mn to organic matter may play an important role in Mn chemistry in wastewater systems. Additionally, the higher pH of most wastewater streams will increase the variable charge of the organic matter, thereby increasing the likelihood of Mn partitioning to organic matter (Section 3.3.3). The association of Mn to large particulate organic matter may increase Mn removal, whereas the association of Mn to dissolved organic fragments may greatly reduce its removal from the wastewater stream.

4.7 Strontium

Strontium (Sr) exists in the environment in the Sr(II) oxidation state. While the crustal abundance of Sr is approximately 150 mg/kg, the total concentration range in soils is between 50 and 1000 mg/kg (Lindsay 1979). Strontium is usually present in the surface environment as a carbonate or a sulfate mineral, and can isomorphically substitute for Ca in carbonates and sulfates. The most important of the 12 nonstable isotopes of Sr are ^{85}Sr , ^{89}Sr , and ^{90}Sr . As a result of nuclear weapons testing, ^{90}Sr is distributed widely in the geosphere. The average activity in surface soils in the United States is approximately 3.7 GBq per square mile. The chemistry of Sr and Ca are closely related. As a Ca analog, Sr tends to accumulate in bone

(United Nations Scientific Committee on the Effects of Atomic Radiation 1982).

4.7.1 Behavior in Wastewater Treatment Plants

As evidenced from the data compiled in Table 4.8, ^{25}Sr , ^{89}Sr , and ^{90}Sr have been observed in sewage sludge in the United States and Sweden. A very crude estimate of the removal efficiency for ^{89}Sr and ^{90}Sr from the Royersford WWTP data is 87 to 96 percent [data from NRC safety inspection (Inspection No. 030-20934/85-04)]. In a survey of WWTP sludge from throughout the United States, the total Sr concentration ranged from 42 to 360 mg/kg on a dry weight basis (Furr et al. 1976). Because behavior of Sr has not generally been investigated as part of the normal suite of elements in WWTPs, no data were found detailing influent, effluent, and sludge Sr concentrations.

However, the tabulated data (Table 4.8) suggest that radioisotopes of Sr may be concentrated in the sludge produced by WWTP. Calcium, a chemical analog of Sr, is suggested to be present in a WWTPs' aqueous phase at levels 6 to 16 mg/L higher than local potable water (Metcalf and Eddie 1991). The total Ca concentrations in sewage sludge range from 0.77 to 11.64 percent on a dry weight basis; another Sr analog (Ba) was found at levels ranging from 268 to 1066 mg/kg (Furr et al. 1976).

4.7.2 Aqueous Speciation and Complexation

The dominant aqueous Sr species in influent systems over a broad pH range (two to nine) is the free divalent Sr^{2+} species. The solubility of Sr^{2+} is not greatly affected by the presence of most inorganic anions because Sr^{2+} forms only weak aqueous complexes with CO_3^{2-} , SO_4^{2-} , Cl^- , and NO_3^- . Since Sr and Ca form humic acid complexes of similar stability (Stevenson and Fitch 1986), Sr should not effectively compete with Ca for humic acid ligands because Ca will be present in concentrations of greater orders of magnitude. Therefore, natural organic ligand-Sr species are not thought to greatly affect the solubility of Sr.

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Table 4.8 Strontium-85, ⁸⁹Sr, and ⁹⁰Sr occurrence in wastewater treatment plants

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ⁸⁵ Sr, ⁸⁹ Sr, and ⁹⁰ Sr Activity			Effluent ⁸⁵ Sr, ⁸⁹ Sr, and ⁹⁰ Sr Activity			Stabilized Sludge ⁸⁵ Sr, ⁸⁹ Sr, and ⁹⁰ Sr Activity			Reference	Comments
				Activity	Activity	Activity	Activity	Activity	Activity	Activity	Activity	Activity		
Sjölunda, Malmo Sweden	Partial biological cleaning; sedimentation; digester	7/76	Medical diagnostic tests ^a	7.4 MBq/L from licensee	ND ^b	ND ^b	ND ^b	NR	Erlandsson and Mattsson 1978	a. Measured ⁸⁵ Sr	b. Problems in counting samples prevented accurate measurements			
		11/76												
		10/76 ^a												
Roversford Water Treatment Facility, Roversford, PA	Primary and secondary treatment; anaerobic digestion; 2-stage biofiltration	10/85	Nuclear Laundry ^a	16 Bq/L ^b	0.6 Bq/L	5.9 Bq/L	5.9 Bq/L	NR	U.S. NRC Inspection Report No. 030-20934/85-04 1986a	a. Waste water from laundering of contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge; measured ⁸⁹ Sr				
		12/85		NM	ND	NM								
Roversford Water Treatment Facility, Roversford, PA	Primary and secondary treatment; anaerobic digestion; 2-stage biofiltration	10/85	Nuclear Laundry ^a	22 Bq/L	2.7 Bq/L	12 Bq/L	12 Bq/L	NR	U.S. NRC Inspection Report No. 030-20934/85-04 1986a	a. Waste water from laundering of contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge; measured ⁹⁰ Sr	b. From licensee's discharge tanks			
		12/85		NM	2.8 Bq/L	23 Bq/L								
Blue Plains Waste Water Treatment Plant, Blue Plains, PA	Modified bio. act. sludge process	2/86	Licensee A ^a - medical research	0.04-0.1 Bq/L	NM	NM	NM	NR	U.S. NRC Inspection Report No. 86-01 1986b	a. Liquid wastes discharged into underground discharge tanks, or directly into sewers; measured ⁹⁰ Sr	b. From licensee's discharge tanks			
Springfield Regional Waste Water Treatment Plant, Springfield, MA	Bio. act. sludge process	2/86	Nuclear laundry ^a	NM ^b	NM	NM	NM	NR	U.S. NRC Inspection Report No. 030-04632/86-01 1986c	a. Waste water from laundering of contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge; measured ⁹⁰ Sr	b. Discharge concentration at company's fence line (via manhole) = 2.1 Bq/L			

ND = Not detected
 NM = Not measured
 NR = Not reported
 RF = Reconciliation Factor

4.7.3 Precipitation and Coprecipitation

Strontium aqueous concentrations during wastewater treatment would be expected to be controlled by inorganic solid phases. However, the aqueous Sr concentrations that may be maintained by SrSO_4 are significantly higher than what would be expected in a WWTP's influent and effluent. Therefore, Sr may coprecipitate with CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, or BaSO_4 (Ainsworth and Rai 1987, Felmy et al. 1993).

However, virtually no information is available on Sr behavior in a WWTP environment, and hence, the above precipitates are suggestions, based on how Sr behaves in other aqueous environments.

4.7.4 Sorption to Organic and Inorganic Solid Phases

For the same reasons as discussed for aqueous speciation, Sr sorption to organic and inorganic solids should have minimal impact on Sr behavior in WWTPs. In one of the few studies detailing sorption of Sr to microbial biomass and extracellular polymers, Sr was poorly partitioned to these phases.^(a) Sorption of Sr to particulate organic matter has not been widely investigated, but Sr partitioning to organic soils [as measured by K_d (L/kg)] has been reported to be 150, compared to 90 for Ca (Sheppard and Thibault 1990). In WWTPs that add alum or FeCl_3 , sorption of Sr to the resulting metal oxide should be minor considering that the surface complexation constants for Sr and Ca are very similar (Cowen et al. 1991).

4.8 Technetium

All isotopes of technetium (Tc) are radioactive. The primary Tc isotopes in sewage sludge are ^{99m}Tc , of medical origin, and to a much smaller extent, ^{99}Tc , a fission product from atmospheric fallout.

Technetium-99m accounts for over 80 percent of the gamma emitting radiation used by hospitals (Ault 1989). However ^{99m}Tc poses little risk as a reconcentrated radionuclide in sewage waste because it has an extremely short half-life: 6 hours (Table 4.1). For instance, after one day (four half-lives), ^{99m}Tc is reduced by 93.75 percent of its

original activity; after two days (eight half-lives), ^{99m}Tc is reduced by 99.6 percent of its original activity. Therefore, even if a treatment process had a 100 percent ^{99m}Tc -removal efficiency, after two days no more than 0.4 percent of the influent Tc would be present in the solids. Because ^{99m}Tc reconcentration in wastewater treatment is controlled more by its nuclear properties (that is, its short half-life) than by its chemistry, only a short description of its chemistry will be presented in this section.

4.8.1 Behavior in Wastewater Treatment Plants

Testoni et al. (1988) measured the ^{131}I (Section 4.5) and ^{99m}Tc activity in the influent, effluent, sludge, and ashes from the WWTP in Bologna, Italy (Table 4.9). This facility processes 115,000 m^3/d by primary sedimentation, active oxidation, and chlorination; the process has a 12-hour residence time. The sludge is ashed and the effluent drains into the Adriatic Sea. A preliminary tracer study was conducted during a period when no ^{99m}Tc was being introduced into the sewage system by patients of the two hospitals. They found the travel time of the spiked ^{99m}Tc was 3 hours and only 30 percent of the released ^{99m}Tc activity reached the WWTP. The WWTP removal efficiency was 99.8 percent. The percent moisture in the sewage sludge was not reported and, therefore, the removal efficiency value can not be normalized to a dry weight basis.

Sodd et al. (1975) reported a large day-to-day flux in ^{99m}Tc activity in the sewage influent: Monday through Friday the activity of the influent was 1.9 to 2.6 GBq/d, whereas during the weekend the activity dropped to an average of only 0.2 GBq/d. The authors attributed this large flux to the fact that two local hospitals did not administer ^{99m}Tc during the weekend.

Moss (1973) conducted a 3-year study between 1969 and 1971 to obtain estimates of the magnitude of activity emitted from medical centers to the sewer system of Allegheny County, Pennsylvania. Approximately 95 percent of the total activity (0.5 to 0.6 Bq/L) in the wastewater stream was either ^{131}I or ^{99m}Tc , of which approximately 26 percent was ^{99m}Tc . Hospital sewer lines contributed about 80 percent of all medical isotope activity going into the local sewer system, the remainder being released into the local

(a) H. Bolton, 1994, personal communication.

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Table 4.9 Technetium-99m occurrence in wastewater treatment plants

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ^{99m} Tc Activity	Effluent ^{99m} Tc Activity	Stabilized Sludge Activity	RF	Reference	Comments
Sims Bayou Sewage Treatment Facility, Houston, TX	Conventional bio. act. sludge, flash dried	88 d - Spring to Summer 1975	NR	NM	96-437 MBq/d ^a	NM	NR	Prichard et al. 1981	a. Total discharge from WWTP (sludge + effluent)
Bologna Sewage System, Bologna, Italy	Primary settling; active oxidation; active decantation; disinfection; sludge incineration	NR	2 Hospitals	93 Bq/L (MAX) 11 Bq/L (AVG) 1.0 TBq/y (TOTAL)	1.6 Bq/L (MAX) 0.02 Bq/L (AVG) 2.0 GBq/y (TOTAL)	1.7 Bq/L (SLUDGE) 7.6 GBq/y (ASH)	99.8%	Testoni et al. 1988 ^a	3-hr transit time between hospital and WWTP Only 30% of spiked ^{99m} Tc reached WWTP
Millcreek Treatment Plant, Cincinnati, OH	NR	8/6-14/73	Hospitals	NM	NM	0.3-5 Bq/L	NR	Sodd et al. 1975	a. (Influent-Effluent)/Influent x100 9-day (including weekend) sampling from outfall of settling basin; samples are cumulative samples taken twice a day. Large fluxuation in the day to day activity in influent; Monday through Friday had 1.9-2.6 GBq/d, Saturday and Sunday had 270 and 122 GBq/d, respectively; attributed activity flux to short half life and hospitals not administering ^{99m} Tc on weekends.

ND = Not detected
 NM = Not measured
 NR = Not reported
 RF = Reconciliation Factor

sewer lines from residential areas after the patients left the hospital. As reported in Section 4.5, Moss (1973) calculated that approximately two percent of the radioactivity purchased by the county hospitals eventually reached the Ohio River via the public sewer system. This total amounted to 100 GBq in 1971, of which 30 GBq was ^{99m}Tc . Moss (1973) did not report direct measurements of the activity in the influent, effluent, and sludge and made no attempt at determine the removal efficiency of ^{99m}Tc by the sewage treatment facility.

4.8.2 Aqueous Speciation and Complexation

The most common oxidation state of Tc in acid, neutral, or basic aqueous systems in equilibrium with the atmosphere is +7. The most common Tc(VII) free species is the pertechnetate ion, TcO_4^- (Coughtrey et al. 1983). This conclusion is also shown by the pE-pH diagrams of Tc (Hanke et al. 1986). Various Tc(V), Tc(IV), or Tc(III) species may be formed under reducing conditions (Pilkington 1990). However, the most stable of these reduced oxidation states is generally Tc(IV) (Bondietti and Francis 1979). The nature of the Tc(IV) species is uncertain: the most common suggestion is TcO_2 (Bondietti and Francis 1979). The reduced Tc species are rapidly oxidized to Tc(VII) by atmospheric oxygen (Coughtrey et al. 1983) and, therefore, Tc(VII) is the most likely form of Tc in air-exposed processes. Anaerobic digestion may cause Tc(VII) to temporarily reduce to Tc(IV).

The pertechnetate ion is highly soluble. For example, the solubility of sodium pertechnetate and potassium pertechnetate is 11 and 0.15 mol/L, respectively (Pilkington 1990). Pertechnetate also forms very soluble oxides (Baes and Mesmer 1976). In alkaline solutions and at low redox potential, the Tc(IV) species is more prevalent and its complexes are typically much less soluble, on the order of 10^{-7} to 10^{-8} mol/L over a range from pH 4 to 10 (Pilkington 1990). In the presence of air, Hanke et al. (1986) found the solubility of TcO_2 depended on the mass of TcO_2 and that it increased linearly with time. The solubility of Tc in contact with hydrated technetium dioxide was investigated by Pilkington (1990). He found that pH had little effect on the measured solubility of Tc over the pH range of 1 to 12.5. How-

ever, the presence of organic materials increased the measured solubility of Tc by a factor of 10, indicating that the complexation between the dissolved organic materials and the Tc occurred. Wildung et al. (1986) suggested that low molecular weight organic ligands may serve to increase the solubility of reduced forms of Tc, whereas complexation with the higher molecular weight organic ligands, particularly insoluble organic ligands, may lead to insolubilization. Schulte and Scoppa (1987) showed that Tc(IV) had a strong tendency to coordinate with ligands containing highly polar groups and positively charged ligands.

4.8.3 Precipitation and Coprecipitation

Precipitation and coprecipitation is not expected to be an important pathway for Tc(VII) reconcentration in wastewater processing. However, it is quite likely that Tc(IV) may precipitate as an oxide in reduced systems (Baes and Mesmer 1976). It is also quite possible that alum or Fe(III)-salt additions could induce the precipitation or coprecipitation (perhaps with phosphate) of Tc(IV).

4.8.4 Sorption to Organic and Inorganic Solid Phases

A number of studies have shown that retention of Tc by solid phases is related to the physicochemical properties of the solid phase (reviewed by Ames and Rai 1978; Gu and Shulz 1991). These studies indicate the extent to which Tc is sorbed to a solid phase is largely determined by the oxidation state of the system. Bowen (1966) reported that, in aerobic conditions, 90 percent of added Tc was readily extractable from soils. The Tc was assumed to remain in solution, either as the free ion or weakly adsorbed to soil ion-exchange sites. Less than ten percent of the added Tc was fixed by inorganic particles. Studies conducted in soils indicated that TcO_4^- sorbs most readily to Fe/Al oxides and organic matter (Gu and Schulz 1991). Similarly, Wildung et al. (1986) reported that 78 to 88 percent of the TcO_4^- added to soil could be extracted easily 30 days after application. In contrast, Cataldo et al. (1978) reported that under aerobic conditions sorption of Tc by soils could exceed 97 percent in two to five weeks.

In a study of 7 mineral soils and 27 organic⁴ soils, Sheppard et al. (1990) reported that in addition to the

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redox status, the organic matter content of soils play an important role in Tc sorption. Evidence of complexation between organic materials and Tc has also been presented by Toner et al. (1989). They indicated that such complexes can be readily synthesized by chemical reduction in the presence of organic matter.

Reduced Tc species as precipitates or organic matter-Tc complexes are not resolubilized by the chelating agent EDTA and diethylenetriaminepentaacetate acid (DTPA), which are known to form stable Tc complexes (Stalmans et al. 1986). This observation suggests that naturally occurring organic matter plays a significant role by forming relatively stable Tc complexes. The abundant organic matter in wastewater treatment streams is a likely complexing agent for reduced forms of Tc. Whether the organic matter-Tc(IV) complex can compete with Tc(IV) hydrolysis is not known.

4.9 Thorium

Six of the 13 isotopes of thorium (Th) are found in nature. Five of the six natural Th isotopes are unimportant (on a mass basis) members of the ^{238}U , ^{235}U , or ^{232}Th decay series. Thorium-232 is the most abundant isotope in nature (Table 4.1). Thorium-232 has a half-life of 1.39×10^{10} years, ranking it as a long-term health concern. Unlike the other radionuclides described so far in this section, ^{232}Th is an alpha emitting nuclide. Alpha radiation, unlike gamma or beta radiation, cannot even penetrate paper and, therefore, does not pose a serious health hazard through external exposure. Thorium-232 does however pose a serious health problem, if it enters the body.

The concentration of Th in sewage sludge will generally depend on the regional geologic Th levels. As a result of different Th levels in rocks and soils, regions containing granite, bauxite, bentonites, shales, and gneiss are expected to have higher levels of Th in their sewage sludge than those areas containing basalt, gabbros, sandstones, limestone, or marble (Ames and Rai 1978). Thorium measured in granite ranged from 10 to 20 mg/kg (Rogers 1964), granite/basalt intermediates ranged from 2 to 10 mg/kg (Heier and Carter 1964), and basalt and gabbros ranged from

0.5 to 2 mg/kg (Heier and Rogers 1963). Thorium may also concentrate in the clay-sized fraction of sediments via sorption (Adams et al. 1969). Up to 50 mg/kg Th in the Al hydroxide and weathering-resistant minerals in bauxite was reported by Adams and Richardson (1960).

Although other oxidation states of Th are known in the laboratory, only Th(IV) is found in nature. The combination of its high valence and small ionic size affords Th unique chemical properties, such as its exceptionally strong tendency to hydrolyse in aqueous systems, to form polynuclear species (Section 3.2.1.2), to form strong bonds with oxygen containing ligands (such as CO_3^{2-} , HCO_3^- , COOH organic groups, and OH^-), to sorb to solid surfaces, and to form several sparingly insoluble precipitates (Cotton and Wilkinson 1972). The oxide or hydroxide forms of Th are among the least soluble compounds in natural aquatic solution (Langmuir 1979). Consequently, Th(IV) is not likely to exist in aqueous systems as the free ionic species, Th^{4+} .

4.9.1 Behavior in Wastewater Treatment Plants

In a nationwide survey of 30 wastewater treatment facilities, Th concentrations in sewage sludge ranged from 1.9 to 29.5 mg/kg dry weight, with an average of 8.3 ± 6.3 mg/kg dry weight (Mumma et al. 1984). Thorium sludge concentrations were not correlated to the percent of wastewater from industrial sources that was processed by the treatment plants. No indication was made that Th-sludge levels were correlated to processes used by the wastewater treatment facilities. The greatest Th-sludge levels were from the Kuwahee plant in Knoxville, TN (15 percent industrial and 85 percent domestic waste volume using biologically activated sludge and ferric chloride treatment); the Fourth Creek plant in Knoxville, TN (11 percent industrial and 89 percent domestic waste volume using biologically activated sludge, ferric chloride, and lime treatment), and the Columbia Boulevard plant in Portland, OR (50 percent industrial and 50 percent domestic waste volume using biologically activated sludge and no chemical additive treatment). No information was presented to correlate regional mineralogy with Th-sludge levels (Mumma et al. 1984).

The Blue Plains WWTP in Washington, D.C., processes waste from a number of federal research facilities that use a broad spectrum of radionuclides (U.S. Nuclear Regulatory Commission 1986b) (Table 4.10). Some of the liquid waste from the licensees is released directly to the sanitary sewer system, whereas selected wastes are temporarily retained in holding tanks to permit decay of short-lived isotopes. One of the radionuclides investigated in this report was ^{228}Th . Thorium-228 has a half-life of 1.9 years, constitutes less than 0.01 percent of the total mass of Th under natural conditions, and is used in laboratory research. The licensee released a small amount of ^{228}Th , 1.2 GBq/y, directly into the sewer system (U.S. Nuclear Regulatory Commission 1986b). The influent, effluent, and sludge ^{228}Th levels at the Blue Plains WWTP were less than or equal to background levels.

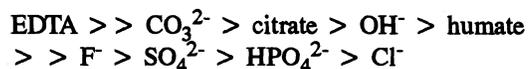
Thorium-228 activity was measured in the sewage sludge generated from two wastewater treatment facilities in Canada (Durham and Joshi 1979). The ^{228}Th activity at both facilities was quite low, about 9.3 Bq/kg, and the effluent of both plants was near or below background levels. It appears from the justification of this study that no *a priori* reason (a licensee or some natural point source) exists for investigating Th or, more specifically, ^{228}Th . In most environments, ^{232}Th is likely to be at least three orders of magnitude more abundant than ^{228}Th . The researchers had *a priori* reasons for investigating the activities of the latter radionuclides.

4.9.2 Aqueous Speciation and Complexation

The solution chemistry of Th is largely a study of its complexes. Thorium in solution is a small, highly charged ion that undergoes extensive chemical interaction with water and most anions. At pH values above three, Th undergoes hydrolysis in aqueous solutions (Ames and Rai 1978). The large effective charge of the Th ion can induce hydrolyses to the point that polynuclear and negatively charged complexes may form (Baes and Mesmer 1976; Allard et al. 1984). Present knowledge of the formation of polynuclear hydrolysed species is very poor because no unambiguous analytical technique to determine these species is known. Polynuclear species are believed to play an important role in Th aqueous

chemistry (Baes and Mesmer 1976). Our present inability to accurately account for their presence greatly compromises modelling efforts.

Like other ions with a +4 oxidation state, Th tends to form strong bonds with anionic ligands. The stability of Th complexes follows the order:



(Langmuir 1979; Kim 1986). EDTA is the strongest complexing agent; carbonate, humate, and citrate ions are appreciably weaker complexing agents. Thorium hydrolysis reactions out compete complexation reactions with humate, F^- , SO_4^{2-} , HPO_4^{2-} , and Cl^- . The stability constant for complexes formed between +4 actinides and F^- are high (Nash and Cleveland 1984; Felmy and Rai 1993). However, these complexes are not likely to play an important role in Th speciation because generally F^- concentrations in wastewater streams are insignificantly low. Sulfate complexation with Th would be expected to be even less important than F^- because of low sulfate concentration in these systems and the weaker strength of sulfate complexes with Th. The presence of carbonates may play a significant role in Th speciation. Carbonate complexation can compete with hydrolysis reactions, as evident from the previous complexation stability sequence. Carbonate complexes with Pu(IV) are so stable that in a carbonate-rich environment the complex undergoes neither disproportionation nor redox reactions, but remains stable (Kim et al. 1983).

Thorium will undergo hydrolysis or carbonate complexation before forming organic matter complexes (Nash and Choppin 1980; Ibarra et al. 1981; Kim 1986). However, it is important to remember that the Th-organic matter stability constant, although less than that for OH^- and carbonates, is extremely high in comparison with other metals.

4.9.3 Precipitation and Coprecipitation

The formation of Th oxide/hydroxide precipitates is prevalent in neutral solutions of low ionic strength (Baes and Mesmer 1976; Kim 1986). These precipitates are some of the least soluble ones in aqueous systems (Kim 1986). They can form in solution with pH levels as low as three (Ames and Rai 1978). In

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Table 4.10 Thorium-228 occurrence in wastewater treatment plants

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent ²²⁸ Th Activity	Effluent ²²⁸ Th Activity	Stabilized Sludge ²²⁸ Th Activity	RF	Reference	Comments
Hamilton Sewage Treatment Plant on Lake Ontario, Canada	Digester sludge (freeze dried for analysis)	NR	NR ^a	NM	ND	8.7 Bq/kg d wt ^b	NR	Durham and Joshi 1979	a. Most radioactivity removed with sludge during sewage treatment Concentration of radionuclides in sludge are low enough to allow agricultural use b. Dry weight
Dundas Sewage Treatment Plant on Lake Ontario, Canada	Digester sludge (freeze dried for analysis)	NR	NR ^a	NM	7.4E-4 Bq/L	11 Bq/kg d wt ^b	NR	Durham and Joshi 1979	a. Most radioactivity removed with sludge during sewage treatment Concentration of radionuclides in sludge are low enough to allow agricultural use b. Dry weight
Blue Plains Wastewater Treatment Plant, Washington, DC.	Modified bio. act. sludge; sludge composition	2/13/86	1.2 GBq/yr	ND	ND	ND	NR	U.S. NRC Inspect Report No. 86-01 1986b	

ND = Not detected
 NM = Not measured
 NR = Not reported
 RF = Reconciliation Factor

carbonate rich solution ($\text{pH} > 7$), Th tends to precipitate as hydroxycarbonate species, such as $\text{Th}(\text{OH})_2\text{CO}_3(\text{s})$ (Bernkopf and Kim 1984).

4.9.4 Sorption onto Inorganic and Organic Solid Phases

Thorium K_d (Equation 3.22) values have been determined on a wide range of inorganic solid phases (reviewed by Ames and Rai 1978). As stated in Section 3.3.3, these values do not differentiate between adsorption and precipitation mechanisms. This consideration is particularly important with regard to evaluating Th K_d values because of the propensity of Th to precipitate in solution. Thorium appears to sorb strongly to mineral surfaces with K_d values often over 1000 mL/g (Stumm and Morgan 1981). Particle size greatly affects Th sorption to inorganic solid surface: the smaller the particle size, the greater the K_d value. For example, K_d values for medium sand, very fine sand, and silt-clay sediments were 40 to 130, 310 to 410, and 2700 to 10,000 mL/g, respectively (Nishiwaki et al. 1972). As a function of pH, Rancorn (1973) measured the K_d values for two soils. For the soil consisting of quartz and clay with no calcite or organic matter, at pH 6, the K_d was 5×10^5 mL/g; at pH 4 the K_d was 1×10^3 mL/g; and at pH 2 the K_d was 5 mL/g. The mixed quartz/clay/calcite/organic matter soil could not be lowered in pH without removal of soil calcite, but at pH 8, the K_d was 10^6 mL/g and at pH 10, the K_d dropped to 100 mL/g. Dissolution of humic acids in the soil probably resulted in Th complexation and a decreased K_d with rising pH. Wastewater streams frequently obtained pH levels near ten after lime treatment (Metcalf and Eddy, Inc. 1991) that can result in the subsequent release of Th using this mechanism.

4.10 Uranium

Uranium can exist in the +3, +4, +5, and the +6 oxidation state; however, only the +4 and +6 oxidation states are typically observed in the environment. Naturally occurring U typically contains 99.283 percent ^{238}U , 0.711 percent ^{235}U , and 0.0054 percent ^{234}U by weight, the half-lives of these U isotopes are 4.51×10^9 years, 7.1×10^8 years,

and 2.47×10^5 years, respectively (Table 4.1).

Uranium is of great importance as a nuclear fuel and in the production of plutonium (^{239}Pu), as depleted U in inertial guidance devices, as shielding materials, and as military ordinance. Geologically, U occurs most often as U(IV) minerals, such as pitchblende, uraninite, carnotite, and autunite and as U(VI) uranophane; it is also found in phosphate rock, lignite, and monazite sands at levels that can be commercially recovered. In the presence of lignite and other sedimentary carbonaceous substances, U enrichment is believed to be the result of UO_2^{2+} transport, adsorption or complexation by humic materials, and reduction of dissolved U(VI) to U(IV), followed by the formation of uraninite. Understanding this process may help in understanding the incorporation of U into sewage sludge. Although a number of isotopes of U exist, the three isotopes noted previously, and perhaps ^{233}U ($t_{1/2} = 1.62 \times 10^5$ years), are of importance to this study. Uranium found in sewage sludge results from environmental sources and release by industrial sources.

4.10.1 Behavior in Wastewater Treatment Plants

As evidenced from the data compiled in Table 4.11, little information is known about U removal from WWTP influent as a result of sewage treatment processes. What data are available from Royersford, Springfield, and Oak Ridge WWTPs suggests no isotopic effect regarding U removal from influent sewage, as $^{233/234}\text{U}$, ^{235}U , and ^{238}U exhibit similar removal efficiencies: 94 to 96 percent. No data were found that detailed U partitioning between the solid-liquid phases of raw sewage, the primary treatment effluent, primary sludge, secondary treatment effluent, or digested sludge. In addition, major chemical considerations, such as oxidation state in the solid or liquid phases associated with the raw sewage, sludge or effluent, are not known.

4.10.2 Aqueous Speciation and Complexation

The aqueous U(VI) uranyl cation (UO_2^{2+}) is the most stable ion in oxidizing solutions; the U(III) species easily oxidizes to U(IV) under most environmental

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Table 4.11 Uranium-233/234, ²³⁵U, and ²³⁸U total occurrence in wastewater treatment plants

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent U Activity	Effluent U Activity	Stabilized Sludge U Activity	RF	Reference	Comments
Royersford Waste Water Treatment Facility, Royersford, PA	Primary and secondary treatment; anaerobic digestion; 2-stage biofiltration	10/85	Nuclear Laundry ^a	1.0 Bq/L ^b	0.04 Bq/L	5.2 Bq/L	NR	U.S. NRC Inspection Report No. 030-20934/85-04 1986a	a. Waste water from laundering of contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge; measured ^{233/234} U
		12/85		NM ^b	0.04 Bq/L	4.4 Bq/L			b. From licensee's discharge tanks
		10/85	Nuclear Laundry ^a	0.12 Bq/L ^{b,c}	0.07 Bq/L ^b	0.2 Bq/L ^b	NR	U.S. NRC Inspection Report No. 030-20934/85-04 1986a	a. Waste water from laundering of contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge
		12/85		NM	0.01 Bq/L ^b	1.9 Bq/L ^b			b. Measured ²³⁵ U
Springfield Regional Waste Water Treatment Plant, Springfield, MA	Bio. act. sludge process	2/86	Nuclear laundry ^a	0.3 Bq/L ^{b,d}	0.01 Bq/L ^d	1.7 Bq/L ^d	NR	U.S. NRC Inspection Report No. 030-04632/86-01 1986c	a. Waste water from laundering of contaminated items is filtered and pumped to temporary holding tank, where it is again filtered and stored in tanks until discharge; measured ²³⁵ U
		10/85		NM	ND	4.8 Bq/L ^d			b. Measured ²³⁸ U
		1990	NR ^a	NM	NM	0.3-2.8 Bq/kg w wt ^b	NR	City of Oak Ridge 1990 Land Application Report	a. Measured ²³⁵ U
		1990	NR ^a	NM	NM	2.3-11 Bq/kg w wt ^b	NR	City of Oak Ridge 1990 Land Application Report	a. Measured ²³⁸ U
Oak Ridge Waste Water Treatment Plant, Oak Ridge, TN	Primary and secondary treatment; anaerobic digestion	1990	NR ^a	NM	NM	0.3-2.8 Bq/kg w wt ^b	NR	City of Oak Ridge 1990 Land Application Report	a. Measured ²³⁵ U
		1990	NR ^a	NM	NM	2.3-11 Bq/kg w wt ^b	NR	City of Oak Ridge 1990 Land Application Report	a. Measured ²³⁸ U
Oak Ridge Waste Water Treatment Plant, Oak Ridge, TN	Primary and secondary treatment; anaerobic digestion	1990	NR ^a	NM	NM	0.3-2.8 Bq/kg w wt ^b	NR	City of Oak Ridge 1990 Land Application Report	a. Measured ²³⁵ U
		1990	NR ^a	NM	NM	2.3-11 Bq/kg w wt ^b	NR	City of Oak Ridge 1990 Land Application Report	a. Measured ²³⁸ U

Table 4.11. (contd)

WWTP Location	WWTP Processes	Sampling Period	Licensee Inputs	Influent U Activity	Effluent U Activity	Stabilized Sludge U Activity	RF	Reference	Comments
Oak Ridge Waste Water Treatment Plant, Oak Ridge, TN	Primary and secondary treatment; anaerobic digestion	12/86-5/88 6/88-6/89	NM	NM	NM	110 mg U/kg sludge 300 mg U/kg sludge	NR	Boston et al. 1990	Only maximum concentrations reported; study primarily looked at radionuclide movement in soils from sludge application; measured total U

ND = Not detected
 NM = Not measured
 NR = Not reported
 RF = Reconcentration Factor

4 Radionuclide Geochemistry

conditions, while the U(V) aqueous species (UO_2^+) readily disproportionates to U(IV) and UO_2^{2+} . In aqueous systems, the U(IV) species will not be present to any great degree as a result of precipitation. These precipitates are probably uraninite (UO_2) or some higher O/U solids ratio with an O/U ratio between 2.3 and 2.7 (Maynard 1983 as reported by Bruno et al. 1991). The average uranium concentrations in natural waters under reducing conditions are between 3 and 30 ppb (Bruno et al. 1991); this is consistent with equilibrium concentrations supported by $\text{UO}_2(\text{s})$ (Bruno et al. 1988). In the absence of any complexing agents, U(IV) is expected to hydrolyze to form mononuclear hydroxo complexes, such as $\text{U}(\text{OH})_n^{4-n}$ (Langmuir 1978). It has been suggested that complexation of (IV) actinides form stable complexes with natural organic humic and fulvic acids (log K 12-16; Allard and Persson as reported by Birch and Bachofen 1990); hence U(IV) could form stable organic complexes, increasing the solubility of the U(IV). In general, (IV) actinides species form stronger organic complexes than do the (VI) actinides species (Birch and Bachofen 1990).

Aqueous uranyl tends to form strong complexes with inorganic O-containing ligands such as hydroxide, carbonate, and phosphate. Aqueous UO_2^{2+} hydrolyzes to form a number of aqueous hydroxo complexes including UO_2OH^+ , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$, and $\text{UO}_2(\text{OH})_3^-$. In aqueous systems equilibrated with air or higher pCO_2 waters at near neutral to high pH, the carbonate complexes [UO_2CO_3^0 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$] will dominate, but at lower pH the hydrolysis species will dominate as $\text{CO}_2(\text{g})$ solubility in water decreases. Under the pH conditions typically observed in WWTPs (near neutral), the concentration of the UO_2^{2+} uncomplexed uranyl species are expected to be insignificant (Carroll and Bruno 1991; Grenthe 1992). Phosphate- UO_2^{2+} complexes ($\text{UO}_2\text{HPO}_4^0$, UO_2PO_4^-) could be important in aqueous systems with a pH between six and nine when the total concentration ratio $(\text{PO}_4^{3-})_T/(\text{CO}_3^{2-})_T$ is greater than 10^{-1} (Sandino and Bruno 1992; Langmuir 1978). Complexes of SO_4^{2-} , F, and possibly Cl^- , are potentially important U(VI) species where concentrations of these ions are high. However, their stability is considerably less than the carbanato and phosphato complexes (Grenthe 1992).

Complexation of UO_2^{2+} by dissolved fulvic acid has been suggested to facilitate U transport to and in groundwaters (Bonotto 1989). The stability of a U(VI)-humic acid aqueous complex has been determined to be at least 10^3 greater than that of a Ca^{2+} -humic complex (Shanbhag 1979 as reported by Idiz et al. 1986). In an organic-rich environment like a WWTP, even with the considerable difference in Ca to U concentrations, U complexation could be significant. Other than this information, little is known definitively about aqueous U(VI)-humic acid (or fulvic acid) complexation. However, the carbonate complexes discussed before are very competitive ligands above pH 6. In fact, Shanbhag and Choppin (1981) concluded that the humic acid complexes with uranyl would not be of importance in sea water because of the significant presence of bicarbonate and carbonate at pH 8. Likewise, solutions of Na-bicarbonate-carbonate at pH 7 to 10 proved to be very effective at leaching U(VI) out of Holocene peat (Zielinski and Meier 1988), suggesting a U(VI)-carbanato complex competes well with humic substances. In a study of purified Pettit peat bog humic acid, Idiz et al. (1986) found the adsorption of UO_2^{2+} increased as pH increased until about five and then decreased as a result of the formation of the carbonate complexes.

4.10.3 Precipitation and Coprecipitation

Because of the presence of organic and inorganic ligands, it is not believed that precipitation or coprecipitation of a solid phase will control the solubility of U(VI) in WWTPs. However, if reduction of U(VI) to U(IV) occurs, precipitation of UO_2 is conceivable. Reduction has been suggested to be the result of 1) reduction of U(VI) by organic matter itself, 2) indirect reduction by hydrogen sulfide, and 3) microbial reduction of U(VI) (Andreyev and Chumachenko 1964; Disnar and Trichet 1983; Lovley et al. 1991). Regardless of mechanism, the product of reduction has been observed to be uraninite (UO_2). This mechanism would likely occur in the sewer lines prior to arrival at the WWTP or in the anaerobic digestion process.

4.10.4 Sorption to Organic and Inorganic Solid Phases

Early studies by Szalay (1964) demonstrated that peat-derived humic acid could concentrate U by a factor of

about 10,000 times over the associated waters. In studies of UO_2^{2+} movement through peat columns, measured K_d values were observed to range from 700 to 18,600 L/kg. Competition for exchange or complexation sites associated with particulate organic matter by Ca^{2+} or other macroelement species (such as Mg, Na, K) should not be significant, if the U(VI)-humic acid complex determined for dissolved materials is indicative of the particulate-U(VI) stability. As with dissolved organic matter complexation, however, competition from carbonate may diminish the effectiveness of particulate organic matter to sequester U from solution.

Formation of complexes between U(VI) and organic ligands, such as humic and fulvic particulates, has been studied most frequently because of interest in ore-forming environments. At ambient temperatures ($\sim 25^\circ\text{C}$), U is adsorbed to humic substances through rapid ion exchange and complexation processes with carboxylic and other acidic functional groups without reduction to the U(IV) species (Idiz et al. 1986; Boggs et al. 1985; Shanbhag and Choppin 1981; Nash et al. 1981; Borovec et al. 1979; Szalay 1964). It has been suggested that U(VI) adsorbed (or fixed) to organic matter may undergo reduction to U(IV) followed by precipitation of UO_2 (Andreyev and Chumachenko 1964; Disnar and Trichet 1983). In studies with lignite, however, the uranyl species formed a stable complex with the lignite without subsequent reduction; reduction occurred only at elevated temperatures (Nakashima et al. 1984). However, organic matter does have the capacity to act as a reductant, most notably because of the presence of quinone, sulfone,

and reduced metal porphyrin (tetrapyrroles) moieties (Macalady et al. 1986).

Uranium sorption to iron oxides and smectite clay has been shown to be extensive in the absence of CO_3^{2-} (Kent et al. 1988; Hsi and Langmuir 1985; Ames et al. 1982; McKinley et al. 1994), but in the presence of CO_3^{2-} and organic complexants sorption was shown to be substantially reduced or severely inhibited (Bond et al. 1991; Hsi and Langmuir 1985; Kent et al. 1988; Ames et al. 1982). The importance of U(VI) sorption to inorganic solid phases, such as clays and iron oxides, may be minor because of the limited quantity of these materials and because of the presence of particulate organic matter and dissolved carbonate. The exception to this conclusion would be in the physical-chemical treatment processes where substantial quantities of FeCl_3 or alum are added as flocculating agents.

Overall, it is difficult to elucidate the chemical mechanisms that would dictate removal efficiencies as high as those calculated in Section 4.10.1 for the Royersford, Oak Ridge, and Springfield WWTP. Clearly, the importance of aqueous complexation, organic matter sorption, and oxidation state cannot be underestimated. At present, no information is available on the chemical form of U entering WWTPs or on its potential species interconversions through the treatment processes. This type of information is crucial to understanding the geochemistry of U in a wastewater treatment setting. The available empirical data suggest that U partitions readily to sludge phases in WWTP processes.

5 Radionuclide Mass Balance and Removal Efficiencies in Selected WWTPs: Case Histories

5.1 Introduction

Releasing radioactive materials into sanitary sewer systems is a practice that has been regulated by the NRC since 1957. Since that time, there have been a number of documented cases where radioactive materials have been concentrated in wastewater treatment sludge (see Chapter 4). To understand and quantify the concentration of radionuclides in sewage sludge, the NRC identified several WWTPs to be used as case studies of radioactive materials released to sanitary sewer systems and the potential concentration of these materials in the processed sludge.

The WWTPs selected for the present study are in Oak Ridge, TN; Erwin, TN; and Cleveland, OH (Southerly Plant). The two Tennessee plants were selected because of the likelihood of radioactive materials being released from NRC licensees to the sanitary sewer systems. The Cleveland site was selected because of a reported occurrence of ^{60}Co associated with incinerated sludge ash. The Southerly Plant is part of the NEORS. Because data were available for the NEORS Westerly and Easterly WWTPs, they were also included. The Oak Ridge, Southerly, and Easterly WWTPs employ primary treatment and suspended-growth biologically activated sludge for secondary treatment: Erwin uses primary treatment and rotating biological contactors for secondary treatment while the Westerly WWTP uses an enhanced primary physical-chemical process and tertiary polishing of primary effluent. The normal operating capacities are 1.9, 4.7, 50, 155, and 175 million gallons per day (MGD) for the Erwin, Oak Ridge, Westerly, Easterly and Southerly WWTPs, respectively.

While the focus of the present evaluation was to be on ^{60}Co , ^{137}Cs , ^{51}Cr , ^{54}Mn , ^{85}Sr , ^{89}Sr , ^{90}Sr , ^{65}Zn , ^{234}U , ^{235}U , and ^{238}U , none of the WWTPs are routinely analyzed for these nuclides and none monitored for natural or radioactive Sr. The radionuclide discharge records for ^{60}Co , ^{137}Cs , and U

from licensees and sludge analyses at the Oak Ridge WWTP over a several year period were available; similarly, U isotope discharge and sludge data were available for the Erwin WWTP. Beyond these nuclides at these locations, no information was available for the other nuclides of interest. However, because of other regulatory requirements, influent, effluent, and sludge data collected over several years were available for the stable elements Zn and Cr at the NEORS plants and the Oak Ridge WWTP; Mn data were available for a single year at the Easterly and Southerly WWTPs. While the Zn, Cr, and Mn elemental data are not for the specific nuclides of concern, the radionuclides will react chemically like their stable counterparts. Hence, concentration of stable forms will reflect the behavior of the radionuclides for the WWTPs studied. Thus, the data from analyses of concentrations of these metals will be used as a surrogate for the corresponding radionuclides. Nickel data were collected at Oak Ridge, and the NEORS WWTPs as a potential analog for Co.

The present evaluation collected information from selected licensees discharging to sanitary sewer systems and WWTPs including 1) discharged radionuclides and their activities, 2) the chemical form of discharged radionuclides, 3) the volume of the discharges, 4) radionuclide activity in processed sludge, and 5) sludge production. The results are presented in this chapter and include 1) a description of the WWTPs, 2) descriptions of the metal/radionuclide data collected from licensees and WWTPs, 3) calculations of WWTP metal/radionuclide removal efficiencies and mass balances, and 4) conclusions concerning the usefulness of the data collected and calculations performed. All data presented here were obtained from the licensees and WWTPs. Radioactive materials release data were provided by the NRC or Agreement States licensees who maintain records on sewer releases as a result of NRC requirements. Sludge data were provided by the WWTPs or licensees as a result of monitoring programs.

5.2 Oak Ridge, TN, Wastewater Treatment Plant

The Oak Ridge WWTP, located in Oak Ridge, TN, began operations in 1983. This municipal plant was designed to provide primary, secondary, and tertiary treatment for regionally generated wastewater. The treated liquid effluent is discharged to the East Fork Poplar Creek. The water quality of the discharged effluent is regulated by the plant's National Pollution Discharge Elimination System (NPDES) permit, which is authorized by the state of Tennessee. The major effluent water quality characteristics that are monitored and regulated by designated effluent limitations include biological oxygen demand (BOD), ammonia (as N), suspended solids, fecal coliform, dissolved oxygen, total chlorine residual, pH, and lead (Pb). In addition, Cd, Cr, Cu, Ni, and Zn concentrations are determined for the influent and effluent waste streams. The plant was designed to treat an average daily flow of 4.77 MGD and can handle a peak flow rate of 13.46 MGD. A more detailed description and plant schematic, including the liquid and solid flow patterns and residence times, is presented in Appendix A and Figure A.1.

5.2.1 Radionuclide Discharge to Oak Ridge WWTP

The three major nonmedical contributors of radioactive materials to the Oak Ridge WWTP are Manufacturing Sciences Corp., Quadrex, and the Department of Energy's Y-12 Plant. However, for the time span of interest, several other radioactive material licensees were discharging to the sewer system. These licensees have since gone out of business. One such industry, Bechtel National Incorporated's Service Center, discharged ^{60}Co , ^{137}Cs , ^{144}Ce , and ^{106}Ru during the late 1980s. Only 1989 data were available for the Bechtel discharges. These monthly discharge data indicate the radionuclides were released as batch discharges. However, no details on the pretreatment methods of radionuclide chemical form were provided. The Bechtel discharges were included in the totals for 1989, but were ignored for the other years in which no data were available. However, the discharge quantities in 1989 represented about 20 percent of the total quantities of ^{60}Co and ^{137}Cs discharged by Quadrex that year.

Another unquantified source of radionuclides to the Oak Ridge WWTP was the industrial park package plant known as CRIPPP. The sludge from CRIPPP, which is routinely transferred to the WWTP contained low levels of ^{60}Co , ^{137}Cs , and other radionuclides. Inadequate data were available to determine the actual quantities introduced to the Oak Ridge WWTP via the CRIPPP sludge. However, because the concentrations measured were low and the volumes of sludge transferred were extremely small (relative to the total sludge volumes at the WWTP), CRIPPP does not appear to represent a significant source of radionuclides for the period of interest in this study. Therefore, this source was not included in the mass balance calculations presented below. The major contributors of radioactive materials to the Oak Ridge WWTP are Manufacturing Sciences Inc., Quadrex, and the DOE Y-12 Plant.

Manufacturing Sciences Corp. (MSC), whose discharge waste stream is uranium (U) from recycling depleted U, pretreats their waste stream to conform to release limits set by the State of Tennessee. Prior to about 1989 the release limit was 119 mg/L (ppm) and has since been decreased to 0.9 mg/L (ppm). Currently, wastewater is held in a tank where the pH is decreased to < 3 with H_2SO_4 , then the pH is raised to pH 11 by adding excess $\text{Ca}(\text{OH})_2$ to precipitate U, the solid material settles by sedimentation, and the liquid effluent is removed to a second tank. The effluent pH is adjusted to about seven, it is then filtered through a $0.45\text{-}\mu\text{m}$ pore-size filter before discharge to the sewer. Prior to discharge, the solution is sampled and the total U concentration is determined colorimetrically. The total U activity, concentration, and volume of each discharge event is recorded. The oxidation state(s) of the U is not directly determined; however, the pretreatment process suggests that the U (VI) species predominates, and the colorimetric analysis is specific for U(VI). All releases from MSC are batch rather than continuous flow. Discharge volume and activity data for each release event were supplied by MSC for the years 1989 to 1993 and were used in the present study.

Quadrex, whose waste stream is dependent on the material being processed through their chemical decommissioning and recycling process, has discharged isotopes of the elements Cs, Sr, Co, Mn, Fe, Zn, and U. Similar to MSC, Quadrex pretreats all wastes prior to discharge to the Oak Ridge sewer

system. Because both metals and several radionuclides may be present in the wastewaters, a series of steps are taken by Quadrex to assure compliance with state, EPA, and NRC regulations. Acid neutralized wastewater passes through a zeolite exchange system to storage tanks where metals and radioactivity are monitored. This material is then cycled through a series of charcoal and sand filters until contaminants meet release specifications. This wastewater is then stored in a tank until release. At the time of release, wastewater from the final storage tank passes through a 0.45- μm pore-size filter before discharge to the sewer system. While oxidation states of the various metals and radionuclides present are not determined, the chemical pretreatment suggests that nuclides such as Co, Sr, Mn, and Zn are in the divalent form and U is in the hexavalent [U(VI)] form. All wastewater is released to the sewer system as batch discharges. Discharge volume, radionuclide, and activity data for each release event were supplied by Quadrex for the years 1989 to 1993 and were used in the present study.

The Oak Ridge National Laboratories Y-12 plant discharge stream to the Oak Ridge sewer system consists primarily of various nuclides of U. However, Y-12 process waste streams are treated onsite with none of the wastewater going to the Oak Ridge WWTP. It has been suggested that the bulk of the U isotopes introduced to the sewer system from the Y-12 plant area are the result of infiltration from previously contaminated soils into the sewer pipeline, which is old and in disrepair. The Y-12 U contribution to the total U WWTP influent is not well known. This results from the fact that monitoring is performed at four locations: the Y-12 west and east lines, the City Station line, and the Union Valley line (Figure 5.1). At the two Y-12 lines, the flow monitoring data are unreliable and the City Station monitoring point is a combination of U discharges from MSC and Y-12. The Y-12 contribution is therefore determined by subtracting the Union Valley line U contribution (up-gradient from Y-12) from the U contribution from City Station (down-gradient from Y-12). While samples from the City Station monitoring point are flow proportional 24-hour composites, sampling is performed on a one-day-a-week basis. Monitoring at this frequency assumes that flow, discharge volume, and radionuclide activity is uniform, which is highly unlikely. These complications in determining WWTP U input are discussed in

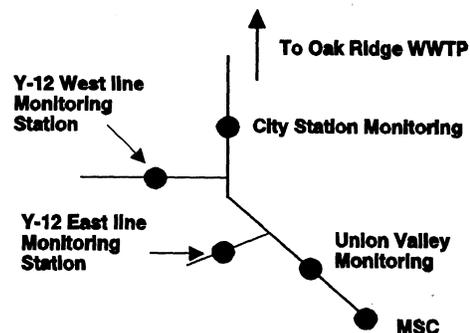


Figure 5.1 Schematic of monitoring stations for determining Y-12 contribution to the Oak Ridge WWTP loading of U

greater detail in conjunction with mass balance calculations and removal efficiencies (Section 5.2.4).

5.2.2 Data Collected from the Oak Ridge WWTP

Daily influent and effluent flows and the corresponding Cr, Ni, and Zn concentrations for the Oak Ridge WWTP over a 23-month period (9/83 through 7/85) were used for metal mass balance and removal efficiency calculations. Daily flows were determined in units of MGD entering the plant in a 24-hour period; effluent was an average of 93 percent of the influent flow. Daily concentrations of metals were determined from samples collected by 24-hour flow proportional samplers at the head of the WWTP after the bar screens, grit tanks, and dechlorination, but prior to discharge. Sample analyses for metals by atomic absorption spectroscopy (AA) were performed at the WWTP after sample acidification with nitric acid to about pH 1 or less and subsequent filtration. For the same 23-month period, data from sludge metal analyses from weekly composite samples of sludge removed from the storage digestors were obtained from the WWTP along with the total quantity of sludge removed from the WWTP per day. The sludge metal content was determined by AA on ashed samples dissolved in nitric acid. From these data, the removal efficiencies and mass balances of Cr, Ni, and Zn were calculated. The removal efficiencies were calculated on a daily basis. However, it was not possible to accurately match metals concentrations as a function of time due to a 105-day lag-time for sludge processing

5 Case Histories

and an irregular sludge removal. The inability to accurately match metal influent removal with sludge metal content required mass balances to be performed on a yearly basis.

Weekly composite sludge samples from the Oak Ridge WWTP, since about 1988, have been analyzed for ^{60}Co , ^{137}Cs , ^{235}U , and ^{238}U by Dr. I. L. Larsen of Environmental Sciences Division, Oak Ridge National Laboratory, as part of a sludge monitoring program instigated by the Oak Ridge WWTP. Analyses of ^{60}Co , ^{137}Cs , and ^{235}U are performed using gamma spectroscopy. The ^{238}U content calculated from the gamma spectra of the ^{238}U progeny, $^{234\text{m}}\text{Pa}$ (γ 1.001 MeV), which is assumed to be in secular equilibrium with ^{238}U . However, at low ^{238}U concentrations the detection limit and error in these calculations are high. Also, Oak Ridge Associated Universities (ORAU) analyzed monthly composite sludge samples for total U by neutron activation analyses, and these analyses were in good agreement with those of Larsen; that is, the standard deviations of the two U determinations overlapped. The monthly composites used by ORAU were made from the weekly samples used in the gamma spectroscopy analysis. Gamma spectroscopy data from 1989 to 1993 were used in mass balance calculations for the above radionuclides.

5.2.3 Mass Balance and Removal Efficiencies for Cr, Ni, and Zn at Oak Ridge WWTP

The daily operational logs provided by the Oak Ridge WWTP for September 1983 through July 1985 were used to obtain data for the following parameters:

- 1) total flow through the WWTP,
- 2) volume of wet sludge removed,
- 3) concentration of acid-soluble Cr, Ni, and Zn in the influent and effluent waste streams,
- 4) weekly average total Cr, Ni, and Zn in sludge, and
- 5) the weekly average percentage of total solids in the final sludge product.

The liquid influent and effluent flow rates were based on data available for the total flow through the WWTP. The total influent volume on a daily basis, F_I (L), is directly related to the daily throughput of the WWTP by

$$F_I = F_T(k) \quad (5.1)$$

where F_T is the total volume through the WWTP in a day (gal) and k is a conversion factor equal to 3.7854 L/gal. Unfortunately, the daily liquid effluent volume for this time frame was not measured. However, data for the monthly average for both influent and effluent flow rates were obtained from this WWTP for 1/91 through 12/93. Since no substantial changes had been made in the WWTP from the earlier time period, the average ratio of influent to effluent flow rates for the latter 24-month time frame (i.e., 0.9237) was used as a conversion factor to calculate the daily effluent volumes using the daily influent volumes for the 9/83 through 7/85 time frame being evaluated. That is, the estimated daily effluent volume, F_E (L), is given by

$$F_E = F_I(0.9237) \quad (5.2)$$

where F_I is the measured daily influent volume calculated by Equation 5.1 and 0.9237 is the proportionality used as a conversion factor.

The metals measured by the Oak Ridge WWTP were Zn, Ni, Cr, Cu, Cd, and Pb. For this evaluation, only Zn, Ni, and Cr (elements which have radionuclides of interest) were used since the other metals were measured at or close to their detection limits, making data interpretation extremely difficult. The data from daily analysis of these three metals in liquid influent, liquid effluent, and weekly sludge analysis were used to calculate the estimated mass of each metal in three different phases: liquid influent, liquid effluent, and sludge. The daily influent metal masses, $M_{M,I}$ (mg), were estimated by

$$M_{M,I} = F_I(C_{M,I}) \quad (5.3)$$

where F_I is the daily influent volume (L) calculated by Equation 5.1 and $C_{M,I}$ is the concentration of metal (M in mg/L) measured in the influent. Similarly, the effluent metal masses, $M_{M,E}$ (mg), were estimated by

$$M_{M,E} = F_E(C_{M,E}) \quad (5.4)$$

where F_E is the daily effluent volume (L) calculated from Equation 5.2, and $C_{M,E}$ is the concentration of metal M (mg/L) measured in the effluent.

The daily operational logs indicated that the sludge was not removed from the WWTP on a daily basis. Therefore, the metal masses in sludge, $M_{M,SL}$ (mg), were calculated on a monthly basis and were estimated by

$$M_{M,SL} = V_{SL}(k)(q)(F_s)(C_{M,SL}) \quad (5.5)$$

where V_{SL} is the monthly volume of sludge removed from the WWTP (gal), k is a conversion factor equal to 3.7854 L/gal, q is the density of the sludge (assumed to be 1 kg/L), F_s is the monthly average ratio of solids to liquid in the sludge sample (by mass), and $C_{M,SL}$ is the concentration of metal M (mg/kg dry solids) in the sludge.

Using the daily metal masses in the influent and effluent volumes calculated from Equations 5.3 and 5.4, the daily removal efficiencies for each of the three metals were calculated for the 23-month time period being evaluated. The removal efficiency for metals, R_M (percent), is given by

$$R_M = \frac{M_{M,I} - M_{M,E}}{M_{M,I}} (100) \quad (5.6)$$

where $M_{M,I}$ is the influent metal mass (kg) calculated by Equation 5.3 and $M_{M,E}$ is the effluent metal mass (kg) calculated by Equation 5.4. Similar calculations were conducted for monthly and yearly average removal efficiencies for the three metals of interest.

Yearly mass balances were calculated from a yearly summation of the influent, effluent, and sludge Cr, Ni, and Zn masses calculated from Equations 5.3, 5.4, and 5.5. That is, the mass balance, MB_M (percent), is given by

$$MB_M = \frac{\sum M_{M,SL} - (\sum M_{M,I} - \sum M_{M,E})}{\sum M_{M,SL}} (100) \quad (5.7)$$

where $\sum M_{M,SL}$ is the annual sludge metal mass (kg), $\sum M_{M,I}$ is the influent metal mass summed over a year (kg), and $\sum M_{M,E}$ is the effluent metal mass summed

over a year (kg). The absolute percentage of MB_M is a measure of how close the metal mass determined from the influent and effluent difference is to that calculated from sludge analyses; the positive or negative value of MB_M is indicative of which mass determination is greatest (i.e., if the percentage is positive more metal is calculated to be in the sludge than can be accounted for by the difference in the influent versus effluent metal masses).

The R_M of Zn from the influent sewage at the Oak Ridge WWTP varied on a daily basis from 7.6 to 100 percent (data not shown). While low R_M values were observed, these were not common; on a daily basis, only eight percent of the calculated Zn R_M values were below 60 percent. As one would expect, the monthly Zn R_M values were far less variable than daily values (Table 5.1). The Zn R_M values varied from 60.8 to 98.1 percent on a monthly basis; this is still, however, a variation of about 40 percent. Similarly, Cr R_M variations on a daily basis ranged from 0 to 100 percent, but low daily values were the exception. More typically, Cr R_M values range between 60 and 100 percent; only 13 percent of the daily R_M values were less than 60 percent. Monthly Cr R_M values are presented in Table 5.2. Unlike Cr and Zn, however, Ni exhibited low R_M values even though variations from 0 to 100 percent removal were observed. Fully 60 percent of the daily Ni R_M values were less than 50 percent. The monthly R_M averages reflect the low values typically observed for Ni (Table 5.3). For comparison, Oliver and Cosgrove (1974) observed an average Ni R_M value of 16 percent during a four-week study conducted at a full scale biologically activated-sludge plant. Removals for Zn and Cr during this same study were 77 percent and 79 percent, respectively. Similarly, Aulenbach et al. (1987) reported Zn and Cr R_M values ranging from 39 to 62 percent and 72 to 90 percent, respectively.

The residence time of the aqueous phase wastewater in the WWTP is about 16 hours (Appendix A; Table A.1). Because of this short time frame, the lag from influent to effluent does not greatly impact the calculation of the R_M . The lag or residence time for the solid phase waste from entry into the plant to disposal as sludge is typically 105 days, but does vary depending on its residence time in the storage digester (this can be 0 to 32 days). This variable lag time

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Table 5.1 The Oak Ridge WWTP influent, effluent, and sludge Zn mass and the Zn removal efficiency on a monthly basis for 23 months

Month	Influent Metal ^(a) (kg)	Effluent Metal ^(b) (kg)	Inf.-Eff. Metal ^(c) (kg)	Removal Efficiency ^(d) (%)	Sludge Metal ^(e) (kg)
9/83	34.2	4.8	29.4	84	19.5
10/83	115.4	7.9	107.5	89	NA ^(f)
11/83	58.6	11.5	47.1	74	NA ^(f)
12/83	160.2	15.1	145.1	70	53.8
1/84	96.1	13.9	82.2	76	44.9
2/84	148.5	11.7	136.8	86	25.0
3/84	80.1	9.1	71.0	84	73.8
4/84	50.2	11.7	38.5	73	47.9
5/84	63.6	19.5	44.1	59	89.7
6/84	69.0	8.4	60.6	87	125.3
7/84	53.8	15.4	38.4	75	68.0
8/84	71.0	3.9	67.1	94	69.7
9/84	107.3	11.5	95.7	84	113.1
10/84	158.9	17.2	141.8	84	51.0
11/84	72.1	15.2	56.9	68	76.7
12/84	44.7	3.9	40.8	89	63.3
1/85	81.6	1.2	80.4	98	19.4
2/85	84.7	26.2	58.5	50	16.7
3/85	77.1	11.1	66.0	81	85.7
4/85	55.7	10.3	45.4	81	99.0
5/85	49.0	8.9	40.1	61	95.7
6/85	48.7	7.9	40.8	83	89.7
7/85	49.6	5.7	43.9	85	66.2
TOTAL	1830.1	252.0	1578.1		1394.1

(a) Calculated according to Equation 5.3.

(b) Calculated according to Equation 5.4.

(c) Difference between the influent and effluent metal mass.

(d) Monthly average value based on daily RM values calculated according to Equation 5.6.

(e) Calculated according to Equation 5.5.

(f) NA = No sludge removed during that period.

Table 5.2 The Oak Ridge WWTP influent, effluent, and sludge Cr mass and the Cr removal efficiency on a monthly basis for 23 months

Month	Influent Metal ^(a) (kg)	Effluent Metal ^(b) (kg)	Inf.-Eff. Metal ^(c) (kg)	Removal Efficiency ^(d) (%)	Sludge Metal ^(e) (kg)
9/83	12.1	0.8	11.3	90	3.7
10/83	47.4	1.2	46.2	91	NA ^(f)
11/83	17.4	2.7	14.7	76	NA ^(f)
12/83	15.1	2.9	12.2	75	18.1
1/84	9.2	1.3	7.9	88	16.0
2/84	24.7	1.2	23.5	93	8.8
3/84	9.2	1.2	8.0	87	22.4
4/84	7.6	1.7	5.9	82	14.0
5/84	10.9	3.5	7.4	74	22.3
6/84	17.0	0.9	16.1	96	28.4
7/84	14.6	4.9	9.7	70	14.7
8/84	24.6	1.2	23.4	96	16.5
9/84	22.1	1.5	20.6	93	30.6
10/84	32.5	2.4	30.1	89	14.9
11/84	15.3	2.1	13.2	84	21.4
12/84	5.6	2.0	3.6	60	17.3
1/85	12.7	1.9	10.8	83	5.0
2/85	7.1	5.0	2.1	78	4.6
3/85	5.6	0.7	4.9	90	20.3
4/85	6.9	2.8	4.1	54	17.9
5/85	4.6	2.8	1.8	74	15.2
6/85	8.0	2.5	5.5	56	12.6
7/85	4.9	1.9	3.0	77	9.9
TOTAL	335.1	49.1	283.3		334.6

(a) Calculated according to Equation 5.3.

(b) Calculated according to Equation 5.4.

(c) Difference between the influent and effluent metal mass.

(d) Monthly average value based on daily RM values calculated according to Equation 5.6.

(e) Calculated according to Equation 5.5.

(f) NA = No sludge removed during that period.

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Table 5.3 The Oak Ridge WWTP influent, effluent, and sludge Ni mass and the Ni removal efficiency on a monthly basis for 23 months

Month	Influent Metal ^(a) (kg)	Effluent Metal ^(b) (kg)	Inf.-Eff. Metal ^(c) (kg)	Removal Efficiency ^(d) (%)	Sludge Metal ^(e) (kg)
9/83	7.0	7.0	4.0	45	2.4
10/83	16.2	7.0	9.0	36	NA ^(f)
11/83	7.8	10.1	1.5	20	NA ^(f)
12/83	10.6	8.3	3.5	35	7.2
1/84	7.7	7.3	2.2	36	5.2
2/84	11.3	7.4	5.1	39	2.4
3/84	8.5	7.7	1.4	19	6.3
4/84	4.6	4.5	0.8	27	3.5
5/84	6.8	6.4	1.9	39	5.3
6/84	7.3	5.2	2.8	47	6.2
7/84	6.5	5.6	2.4	47	2.9
8/84	7.6	4.4	2.9	51	2.8
9/84	12.4	4.6	7.6	50	3.8
10/84	13.4	12.4	1.7	26	1.9
11/84	7.1	6.6	1.9	30	3.0
12/84	4.8	2.7	2.2	59	3.2
1/85	4.7	2.7	1.2	46	1.1
2/85	8.3	5.5	3.8	53	0.8
3/85	8.1	6.0	2.1	30	3.9
4/85	5.9	3.8	1.8	47	3.9
5/85	5.4	3.0	2.5	63	3.8
6/85	5.8	4.6	1.7	34	2.7
7/85	8.5	5.6	3.3	41	2.5
TOTAL	186.3	138.4	67.2		74.8

(a) Calculated according to Equation 5.3.

(b) Calculated according to Equation 5.4.

(c) Difference between the influent and effluent metal mass.

(d) Monthly average value based on daily RM values calculated according to Equation 5.6.

(e) Calculated according to Equation 5.5.

(f) NA = No sludge removed during that period.

makes it difficult to calculate a mass balance over short time periods with confidence. This is evidenced by the variation in the percentage of metal (i.e., Cr, Ni, and Zn) accounted for in the sludge (calculated by Equation 5.7). As Tables 5.4 through 5.6 show, the shorter the time period used to calculate the mass balance the less likely metal sludge content is going to reflect the influent-effluent difference mass. However, if a 12-month period is used, a more accurate mass balance is obtained; the mass balance for a 12-month period was within 17 percent for the metals discussed here.

5.2.4 Mass Balance of ^{60}Co , ^{137}Cs , and U at Oak Ridge WWTP

From discussions with the discharging licensees and examination of their discharge records, the activities of ^{60}Co , ^{137}Cs , and total U discharged yearly to the Oak Ridge sanitary sewer system from 1989 to 1993 were calculated (Table 5.7).

Table 5.4 The Oak Ridge WWTP influent, effluent, and sludge Zn mass and Zn removal efficiency and mass balance on a yearly basis over 23 months

Time Period	Influent Metal ^(a) (kg)	Effluent Metal ^(a) (kg)	Inf-Eff. Metal ^(a) (kg)	Removal Efficiency (%)	Sludge Metal (kg)	Zn Mass Balance (%)
9/83-12/85	368.4	39.3	329.1	89.3	73.3	-342.8
1/84-12/84	1015.3	141.4	873.9	86.1	848.4	-3.0
1/85-7/85	446.4	71.3	375.1	84.0	472.4	20.6
9/83-7/85	1830.1	252.0	1578.1		1394.1	-12.9

(a) Based on sum of monthly data presented in Table 5.1 for the time period noted.

Table 5.5 The Oak Ridge WWTP influent, effluent, and sludge Cr mass and Cr removal efficiency and mass balance on a yearly basis over 23 months

Time Period	Influent Metal ^(a) (kg)	Effluent Metal ^(a) (kg)	Inf-Eff. Metal ^(a) (kg)	Removal Efficiency (%)	Sludge Metal (kg)	Cr Mass Balance (%)
9/83-12/83	92.0	7.6	84.4	91.7	21.8	-3275.1
1/84-12/84	193.3	23.9	169.4	87.6	227.3	-27.4
1/85-7/85	49.8	17.6	32.2	64.7	85.5	63.7
9/83-7/85	335.1	49.1	286.0		334.6	17.0

(a) Based on sum of monthly data presented in Table 5.2 for the time period noted.

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Table 5.6 The Oak Ridge WWTP influent, effluent, and sludge Ni mass and Ni removal efficiency and mass balance on a yearly basis over 23 months

Time Period	Influent Metal ^(a) (kg)	Effluent Metal ^(a) (kg)	Inf-Eff. Metal ^(a) (kg)	Removal Efficiency (%)	Sludge Metal (kg)	Ni Mass Balance (%)
9/83-12/83	41.6	32.4	9.2	22.1	9.6	-87.4
1/84-12/84	98.0	74.8	23.2	23.6	46.6	29.4
1/85-7/85	46.7	31.2	15.5	33.2	18.6	12.2
9/83-7/85	186.3	138.4	47.9		74.8	10.1

(a) Based on sum of monthly data presented in Table 5.3 for the time period noted.

Table 5.7 Activities of ⁶⁰Co, ¹³⁷Cs, and total U released to the Oak Ridge Sanitary Sewer System from 1989 to 1993

Year	Radionuclides		
	⁶⁰ Co (Bq)	¹³⁷ Cs (Bq)	Total U ^(a) (Bq)
1989	1.8E+07	6.1E+05	2.7E+08
1990	4.9E+07	5.9E+06	6.8E+07
1991	3.2E+07	8.9E+06	3.9E+07
1992	2.9E+07	4.9E+06	3.0E+07
1993	4.3E+06	5.0E+06	1.2E+07
Total	1.3E+08	2.5E+07	4.2E+08

(a) This does not include Y-12 discharge.

Quadrex was the primary source of ⁶⁰Co and ¹³⁷Cs during this time frame; Bechtel National Incorporated's Service Center discharged small quantities of each radionuclide during the late 1980s (that is, 87.3 and 3.2 μCi for 1989). The largest contributor of total U was MSC, but their discharge decreased continually from 1989 to 1993 which reflects both a change in pretreatment and a cutback in production. The amount of total U released from 1989 to 1993 shown in Table 5.7 does not reflect the discharges from DOE Y-12 plant (as discussed in Section 5.2.1).

Total activities of ⁶⁰Co, ¹³⁷Cs, and total U in sludge from 1989 to 1993 were determined on a yearly basis (Table 5.8). The percentages of the released radionuclides accounted for in the sludge (mass balance) were calculated on a yearly basis as [(sludge activity/release activity)x100] for the years 1989 to 1993 (Table 5.9). However, this calculation implicitly assumes an R_M of 100 percent. The accountability of released ⁶⁰Co, ¹³⁷Cs, and total U varied considerably by year. Often, the data and subsequent calculations resulted in greater than 100 percent of the radionuclide being accounted for; that is, more radionuclide was found in the sludge than had been released. The exception to this was ⁶⁰Co in 1991 and 1992 when only 47.9 and 29.4 percent of the ⁶⁰Co released, respectively, could be accounted for in the sludge. The 1992 sludge data, however, are slightly biased in that only January to November (i.e., 10 months) is accounted for in the sludge removed from the WWTP.

With the exception of 1989 and 1990, the Cs mass balances might be seen as reasonable since there is less than a factor of two variation between that released and that determined to be in the sludge. However, the R_M for Cs in the Oak Ridge WWTP has not been taken into account in these calculations. During a radio-tracer study conducted at this WWTP, Stetar et al. (1993) determined the Cs R_M to be approximately 12 percent. Considering this R_M, the mass of Cs discharged would have to have been as much as an

Table 5.8 Activities of ^{60}Co , ^{137}Cs , ^{235}U , ^{238}U , and total U found in the Oak Ridge WWTP sludge from 1989 to 1993

Year	^{60}Cs	^{137}Cs	^{235}U	^{238}U	U(Total)
1989	3.2E+07	1.5E+07	8.6E+06	2.6E+08	2.7E+08
1990	5.2E+07	4.1E+07	2.1E+07	1.2E+08	1.4E+08
1991	1.5E+07	1.7E+07	7.5E+06	1.4E+08	1.4E+08
1992 ^(a)	8.4E+06	5.3E+06	7.2E+06	1.2E+08	1.2E+08
1993	6.9E+06	7.9E+06	7.6E+06	1.4E+08	1.5E+08
Total	1.1E+08	8.7E+07	5.2E+07	7.8E+08	8.3E+08

(a) Data only available through October 1992.

Table 5.9 Mass balance^(a) for ^{60}Co , ^{137}Cs , and total U for 1989 to 1993

Year	^{60}Co (%)	^{137}Cs (%)	Total U ^(a) (%)
1989	177.2	2492.4	98.6
1990	107.5	695.1	200.8
1991	47.9	196.5	368.6
1992	29.4	108.1	444.9
1993	159.7	157.0	1221.2

(a) Calculated as sludge activity/released activity)x100.

order of magnitude greater than that reported in Table 5.7 in order to account for the Cs R_M and the amount of Cs found in the sludge (Table 5.8). A similar discrepancy exists for the ^{60}Co mass balance for 1989, 1990, and 1993 in that the Co R_M for the Oak Ridge WWTP is about 30 percent (Stetar et al. 1993). Based on this R_M and the amount of Co observed in the sludge, the reported discharges for these years appear to have been significantly underestimated. However, for 1991 and 1992, incorporation of the R_M into the mass balance calculations results in very reasonable mass balances for Co. If, over the five-year span (1989-1993), all the released and sludge ^{60}Co activity is summed and a five-year mass balance is determined, 87 percent of the released ^{60}Co is accounted for in the sludge; considering that ^{60}Co has

an R_M of about 30 percent, the five-year mass balance is very reasonable. Cesium-137 on the other hand, exhibits a five-year mass balance of 342 percent.

Because of the sampling location and methodology (as discussed in Section 5.2.2), the U discharge from the Y-12 plant is difficult to consider. Therefore, it was not part of the calculations that went into Tables 5.7-5.9. This is undoubtedly part of the reason that the total U mass balance is poor and gets worse as this MSC U discharges decrease. The mass balance over the five-year time span of this evaluation shows about 200 percent of the released U accounted for in the sludge. As with the other radionuclides, U does not exhibit an R_M of 100 percent; based on data determined during a five-day study of the Oak Ridge WWTP influent and effluent U concentrations, an average R_M of 64 percent was calculated (Duke et al. 1991; Table 5.10). The incorporation of the R_M into the calculations tends to further exacerbate the imbalance between the release and sludge data.

Based on the data collected and calculations performed, more U is being introduced into the Oak Ridge sanitary sewer system than can be accounted for by licensee records. The major question concerning the Y-12 release and its impact on the U mass balance at the Oak Ridge WWTP still remains. Using the 1991 Y-12 measurements at City Station as the total U source for the WWTP (these measurements should reflect the U contributions of Y-12 and MSC) and comparing them with the U 1991 sludge mass, a mass balance calculation was performed (L. Stetar, unpublished data). This mass balance showed that there was significantly (a factor of 2 to 4) more U in

Table 5.10 Uranium flow through the Oak Ridge WWTP over a five-day period and the calculated R_M (after Duke et al. 1991)

Influent (mg/L)	Effluent (mg/L)	R_M (%)
0.004	0.002	50
0.006	0.003	50
0.003	0.001	67
0.005	0.002	60
0.007	0.001	86
Average 0.005	0.002	64

the sludge than could be accounted for based on the quantities determined as a combined source at City Station; this conclusion was reached even though a R_M of 100 percent was assumed. Clearly, data are not available to determine an accurate U mass balance for the Oak Ridge sanitary sewer system.

5.3 Erwin, TN, Wastewater Treatment Plant

The Erwin WWTP was put into operation in 1962 to provide primary treatment and chlorination of regionally generated wastewater. In response to the 1972 Clean Water Act, the plant was retrofitted in 1988 to provide secondary treatment. The resulting improvements included rotating biological contactors, secondary clarifiers, a new heated anaerobic digester, and a new chlorine contact tank. Thus, the Erwin WWTP currently provides primary and secondary treatment for a design wastewater flow of 1.9 MGD and a peak flow of 5.6 MGD. The plant receives wastewater generated by residents of Erwin and several local industrial facilities including Nuclear Fuel Services, which is the sole source of radioactive discharges to the WWTP. A more detailed description and plant schematic, including the liquid and solid flow patterns and residence times, is presented in Appendix A and Figure A.2.

5.3.1 Radionuclide Discharge to the Erwin WWTP

Nuclear Fuel Services (NFS) is the sole radioactive material licensee discharging to the Erwin WWTP and discharges ^{234}U , ^{235}U , and ^{238}U to the sanitary sewer system. Starting in 1986, NFS began reducing the number of potentially radioactive waste streams that discharged to the Erwin sewer system, including the laundry (removed 12/86) and laboratory drains (removed 9/87). In addition, flow rates (and hence volumes of discharge) were simply estimates by NFS prior to 1987. A proportional sampler was installed in 1987 to collect samples and measure flow. Between 9/87 and 6/92, NFS had a nonvariable source (that is, no discharge streams were removed or added) and flow measurements. In conjunction with these activities, the WWTP used only primary treatment until 5/88 when it added a secondary treatment process (rotating drum).

Because the Erwin WWTP used only primary treatment, discharge data and U sludge analysis were obtained from NFS for 12/87 to 4/88 to coincide with sludge mass data from the WWTP. The choice of this time frame was based on 1) a steady discharge from NFS, 2) flow and sludge analyses data from NFS, and 3) primary sludge masses from the Erwin WWTP. In addition, discharge and sludge analyses data from NFS and sludge masses from the WWTP were obtained for 6/89 to 1/92. During this time, the WWTP used primary and secondary treatment processes. While the plant does take daily influent and effluent samples, via proportional samplers, metals analyses are done on an infrequent basis. Therefore, the only data from the Erwin WWTP used for this project are data related to total U discharge and sludge content. No total U influent or effluent data were available for this plant; therefore, NFS total U discharge and sludge analyses and the WWTP sludge mass data were used for mass balance calculations. The State of Tennessee does have a sludge monitoring program in place. However, monthly analyses are performed on only a single grab sample; ^{235}U is determined only once each month, and total U is determined only once a year. In addition, difficulties in converting the State of Tennessee's total U data from pCi/L wastewater back to Bq/g sludge limited the usefulness of these data to that of a confirmational role. NFS sludge data determined ^{234}U , ^{235}U , and ^{238}U isotopes and, hence, these data were used for sludge U content.

Several concerns with the data obtained for the Erwin WWTPs mass balance exist. First, all the sludge analyses were from a single monthly grab sample from the drying beds at the plant. No effort was made to obtain a sample from each bed or for each mass of sludge removed for disposal. Therefore, in a given month, the total mass of sludge removed for disposal is assumed to have the same concentration of total U as that drying bed where the sludge grab sample was taken. Secondly, the total U activity discharge data obtained for the 6/89 to 1/92 time frame are monthly arithmetic averages, not flow proportional values. In conjunction with this, the flow data supplied by the WWTP were monthly total volumes. In addition to these data concerns and their impact on the calculated mass balances, national security concerns prevented us from obtaining information on the chemical form of the U discharged (i.e., oxidation state), the process producing the U, or any pretreatment processes prior to discharge.

5.3.2 Mass Balance of U at Erwin WWTP

The mass balances of U for the Erwin WWTP were determined in the same manner as the Oak Ridge site; that is, as $[(\text{sludge activity}/\text{release activity}) \times 100]$. The discharge of U to Erwin's sanitary sewer lines during 12/87 to 5/88 were always greater than that calculated to be in the sludge (Table 5.11). Hence, the percentage accounted for in the sludge was considerably less than 100 percent; the observed percentage differed for each of the three U isotopes. Since the R_M for total U for the Oak Ridge WWTP was estimated to be about 64 percent (Table 5.10), the Erwin WWTP R_M for U would be expected to be less than that because only primary treatment was used during the time period evaluated. In fact, the average mass balance for the three U isotopes (33.5 percent) seems to be a reasonable R_M for primary treatment at the Erwin WWTP. However, there is no mechanistic reason for the mass balances of the three U isotopes to be so different. The reason(s) for this disparity may be the result of too short a sampling period, low levels of ^{235}U and ^{238}U , or the manner in which the sludge was sampled. Consequently, the usefulness of these values (even for ^{234}U which does not suffer from low concentrations) is questionable.

The mass balance of ^{234}U , ^{235}U , ^{238}U for the Erwin WWTP from 6/89 through 12/91 suffers from the

same data flaws as the previous time period. During the period used in these mass balance calculations, the WWTP used primary and secondary treatment (section 5.3.1). The mass balance values for all three U isotopes for 1989 are from 6-month period and the low values are believed to be a reflection of the short time period used to collect data for this calculation (Table 5.12). Comparing the 1989 mass balance value to the following year(s) and total values tends to corroborate the assumption that the discrepancy associated with the 1989 values (and by inference the 12/87 to 5/88 values) results from the short evaluation period. Assuming an R_M of 100 percent, ^{234}U sludge content is significantly greater than that released and would be even greater if a more realistic R_M (~50 to 60 percent, based on the Oak Ridge five-day study) were taken into account. The disparity in the R_M for the three isotopes is as perplexing as for the 12/87 to 5/88 period discussed above. Similarly, the usefulness of this data for the Erwin WWTP is questionable.

5.4 Northeast Ohio Regional Sewer District (NEORS) Treatment Plants

The NEORS was created in 1972 to assume the operation and management of wastewater collection, treatment, and disposal facilities for the Cleveland metropolitan area. The NEORS serves a 295 square-mile area and more than one million people. Three major WWTPs are in operation: the Westerly, Easterly, and Southerly WWTPs. Several other WWTPs currently in use will be decommissioned in the near future. In conjunction with the operation of the three WWTPs, the NEORS operates a very sophisticated laboratory designed to perform the analyses and testing of the chemical, biological, and toxicological monitoring needs of the sewer district.

The Westerly WWTP serves approximately 112,000 people in Cleveland and several surrounding suburbs. The treatment plant was constructed in 1974 to provide physical/chemical primary treatment, pressurized multimedial filters, and carbon columns to handle an increasing volume of wastewater, including an increasing number of industrial facility discharges.

Table 5.11 Uranium-234, ²³⁵U, ²³⁸U mass balance for Erwin, TN, WWTP from 12/87 to 5/88

Nuclide	Discharge (Bq)	Sludge (Bq)	U Mass Balance (%)
²³⁴ U	9.7E+07	1.1E+07	11.0
²³⁵ U	9.2E+06	3.4E+06	37.2
²³⁸ U	4.3E+06	2.2E+06	52.4

Table 5.12 Uranium-234U mass balance for Erwin, TN, WWTP from 6/89 through 12/91 and ²³⁵U, ²³⁸U mass balance from 6/89 through 12/90

Isotope	Year	Discharge (Bg)	Sludge (Bq)	U Mass Balance (%)
²³⁴ U	1989	2.0E+08	9.9E+07	49.5
	1990	2.1E+08	2.4E+08	116.7
	1991	<u>1.9E+08</u>	<u>3.8E+08</u>	<u>205.4</u>
	Total	5.9E+08	7.2E+08	121.7
²³⁵ U	1989	2.0E+07	4.7E+06	23.8
	1990	<u>3.6E+06</u>	<u>5.5E+06</u>	<u>150.8</u>
	Total	2.3E+07	1.0E+07	43.7
²³⁸ U	1989	1.5E+07	5.0E+06	33.7
	1990	<u>6.8E+06</u>	<u>1.0E+07</u>	<u>155.0</u>
	Total	2.2E+07	1.5E+07	71.8

Physical/chemical treatment, as opposed to conventional secondary (biological) treatment, was implemented because the Westerly Site could not accommodate the large facilities required for biological treatment processes. Presently, the carbon columns are not in use because of operational/mechanical failures and poor treatment performance. Hence, the Westerly Plant currently provides primary treatment, enhanced by chemical additives, and advanced treatment using the multimedia pressure filters. The plant was designed to treat an average daily flow rate of 50 MGD and a peak flow rate of 100 MGD. The Westerly Plant is located on the shore of Lake Erie west of the mouth of the Cuyahoga River. All of the plant's treated wastewater effluent is discharged into Lake Erie. A complete description and plant schematic, including flow schemes and

residence times, are presented in Appendix A and Figure A.3a and b.

The Easterly WWTP currently serves over 500,000 people in Cleveland and surrounding suburbs. Currently, the Easterly Plant provides primary-treatment and biologically activated-secondary treatment with a design capacity of 155 MGD and a peak capacity of 380 MGD for storm water flow. The sludge produced by this plant is pumped via pipeline to the head works of the Southerly Plant; hence, no sludge data are available. A complete description and plant schematic of the Easterly Plant illustrating flow schemes and residence times are presented in Appendix A and Figure A.4.

The Southerly WWTP is the largest and most complicated of the three major wastewater treatment

plants operated by the NEORSD. The Southerly Plant serves approximately 529,000 residents in the City of Cleveland as well as several adjacent suburbs. Currently, the Southerly Plant provides primary, secondary (two-stage biological process), and tertiary treatment. The plant is designed to completely treat 175 MGD. The plant can treat an additional 225 MGD of storm water flow in the primary, second-stage biological, and tertiary treatment processes. The plant can also treat an additional 335 MGD of storm water flow in the primary treatment stage only. Hence, the peak plant capacity with combined wastewater and storm water flow is 735 MGD. All of the plant's treated wastewater effluent is discharged to the Cuyahoga River. A complete description and plant schematic, including the liquid and solid flow patterns and residence times, are presented in Appendix A and Figures A.5a through A.5d.

5.4.1 Data Collected from the NEORSD

The Westerly, Easterly, and Southerly WWTPs sample the respective influent and effluent streams daily via a 24-hour flow proportional sampler. Influent flows at each of the Westerly and Easterly WWTPs are determined after all interceptor streams are mixed and grit removed; the Southerly Plant influent flow is measured for two streams (24-hour flow proportional samples are collected at each). Effluent volume at each of the plants is approximately equal to the total influent volume. Wastewater samples are sent to the NEORSD laboratory for analyses. Influent and effluent Cr, Ni, and Zn analyses are performed on acidified (nitric acid), filtered samples by inductively coupled argon plasma atomic emission spectroscopy (ICP). The sample preparation is very similar to that performed by Oak Ridge except ICP is used for metal quantification rather than AA; in both cases, the metals concentration is given as "total soluble metals." In addition, samples of sludge cake (sludge prior to incineration) from the Westerly and Southerly Plants are analyzed for total metals content. The samples of known mass and water content are ashed, the ash dissolved in nitric acid, filtered, and concentrations determined by ICP.

Monthly influent flow volumes, sludge masses, and metals (Cr, Ni, and Zn) concentrations in the influent,

effluent, and sludge were provided by the Westerly and Southerly WWTPs. With the exception of sludge metals concentrations, similar data were available for the Easterly WWTP (where the sludge from the Easterly WWTP is pumped via pipeline to the headworks of the Southerly Plant). Monthly averages for the Westerly and Easterly WWTPs from 1990 to 1993 were used to calculate metal (Cr, Ni, and Zn) removal efficiencies; mass balances for these metals from 1990 to 1993 were calculated for the Westerly WWTP. Calculations were performed in the same manner as those for the Oak Ridge WWTP (Section 5.2.3). Because of the complexity and size of the Southerly WWTP, total influent metals concentrations are difficult to determine because six interceptors come together to make up the total flow into the plant, and the samples for metals determinations are not taken until after the grit removal tanks and after the flow is divided into two flow paths that use different sets of primary settling tanks. Therefore, only 1993 Southerly data were used in removal efficiency and mass balance calculations. These data included 1) the volumes of flow from each of these two paths and their corresponding metals concentrations, 2) the total effluent volume and metals concentrations, and 3) the sludge cake mass and metal concentrations. In addition, total and soluble metals (Cd, Cu, and Zn) determinations were performed at the Southerly Plant for influent and effluent materials during a 32-day period from 11/28/89 to 1/8/90. For this 32-day study, the soluble component was operationally defined as the concentration in solution after filtration through a 0.45 μm pore-size filter; the sampling and analysis were performed by an independent contractor.

5.4.2 Mass Balance and R_M Calculations for Cr, Ni, and Zn at the NEORSD

The Westerly WWTP offered the most complete data of the three NEORSD WWTPs and provided an opportunity to study a nonbiological, chemical-physical plant. The Easterly WWTP is essentially a larger version of the Oak Ridge WWTP; a mass balance of Cr, Ni, and Zn at the Easterly Plant was not possible as the sludge produced at this WWTP is pumped to the head works of the Southerly Plant without metals being determined. The Southerly WWTP is a very complex biologically based treatment facility; this complexity arises as the result of its size, multiple interceptors,

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and the number of cycled waste streams (see Appendix Figures A.5a-d).

The mass balances of Cr, Ni, and Zn for 1990 through 1993 for the Westerly WWTP are reasonable; that is, the metals concentrations that were removed over the years (as determined from influent - effluent masses) agree fairly well with that found in the sludge (Table 5.13). For a given year, the greatest discrepancy in mass balance was about 50 percent (for Zn, 1993); that is, about twice as much Zn was in the sludge compared to that removed from the influent. When the mass balance is determined over a four-year time-span, much of the yearly variability is removed.

These same three metals were tracked for a 23-month period at the Oak Ridge WWTP (Tables 5.4-5.6) and the mass balances demonstrated a similar trend over time. With longer time-spans, the metal accounted for in the sludge tended toward closer agreement with the (influent-effluent) determination. While the total mass balances for the three metals are comparable for the two WWTPs, Oak Ridge mass balances tended, overall, to be better (-12.9, 17, and 10.1 percent for Zn, Cr, and Ni, respectively, for Oak Ridge). This may be a reflection of the Oak Ridge calculations being performed using daily influent/effluent concentrations as opposed to the monthly averages used for the Westerly Plant calculations. However, the Ni calculations for the Westerly WWTP are even better than the Oak Ridge mass balance values and tend to obfuscate any conclusions of plant-to-plant comparisons with respect to monthly averages versus daily logs.

Mass balances for the Southerly WWTP for 1993 are not much different than that observed for the Westerly and Oak Ridge WWTPs for a given year (Table 5.14). While only a single year's worth of data were available for the Southerly Plant, the results from the Oak Ridge and Westerly WWTPs would suggest that if multiple year data were available, mass balances at the Southerly Plant would tend to improve.

The monthly R_M percentages for Zn, Cr, and Ni, determined for the three NEORS D WWTPs (data not shown) from averaged monthly influent and effluent data, are not very different from each other or from that calculated for the Oak Ridge WWTP (Tables 5.1-5.3). As noted for the Oak Ridge

calculations, monthly averages tend to smooth out the variation observed on a daily basis. For instance, the daily Zn R_M ranged between 24.6 and 92.8 percent during a 32 day period of late 1989 and early 1990 at the Southerly WWTP, which is very close to that observed for the Oak Ridge WWTP. As can be seen from Table 5.15, the Zn high - low range for monthly R_M values for the Southerly WWTP is not nearly so variable as the daily values, and the R_M range for a given metal is similar across the four WWTPs.

Daily influent and effluent total and soluble Zn concentrations were tracked for a 32-day period at the Southerly WWTP; soluble Zn, in the context of this study, is operationally defined as the Zn concentration that is not removed by filtration by a 0.45- μ m pore size filter. Figure 5.2 shows that the daily Zn influent concentration varies greatly but the effluent concentration is relatively constant (with the exception of days 23 and 26), and hence, the Zn R_M varies tremendously over the 32-day period. The dissolved influent Zn concentration plotted in Figure 5.2 is observed to track the total effluent concentration fairly well suggesting that dissolved Zn is not readily removed from the aqueous phase. Similar results have been observed for Cu and Cd at the Southerly WWTP and for Cd at the Easterly WWTP.

The removal of metals (and related radionuclides) from influent wastewaters at WWTPs is believed to be the result of both chemical and physical mechanisms (see Chapter 3). However, the data shown in Figure 5.2 would suggest that the overriding factor in this removal is the distribution of a metal between the settleable solids and aqueous phases, and that metals associated with settleable solids are removed but dissolved metals are not. In other words, removal of metals and radionuclides is largely dependent on the efficiency of solids removal at a given WWTP. If the distribution of a metal between these two phases and the solids removal were constant over a wide range of metal concentrations, then the R_M would be fairly constant and could be considered a concentration factor; however, this does not appear to be the case at the Southerly and Easterly WWTPs. Similar conclusions were reported by Patterson et al. (1984) in an investigation of metals removal in combined treatment systems. Essentially, Patterson et al. found that removal of metals across treatment systems [i.e., primary and secondary (activated sludge) treatment] was directly related to the distribution of the metal

Table 5.13 Mass balance of Cr, Ni, and Zn during 1990 through 1993 at the Westerly WWTP

Year	Metal	Inf.-Eff. Metal ^(a) (kg)	Sludge Metal ^(b) (kg)	Metal Mass Balance ^(c) (%)
1990	Zn	22703.7	30794.1	26.3
	Cr	4648.5	6897.5	32.6
	Ni	1352.5	1246.9	-8.5
1991	Zn	29031.9	30620.8	5.2
	Cr	6358.4	7663.8	17.0
	Ni	1050.8	1068.6	1.7
1992	Zn	23514.5	32673.8	28.0
	Cr	5568.6	7480.2	25.6
	Ni	1772.8	1223.0	-45.0
1993	Zn	20321.4	40266.8	49.5
	Cr	6585.2	9451.9	30.3
	Ni	466.7	895.4	47.9
total	Zn	95571.5	13455.5	28.87
	Cr	23160.8	3143.4	26.46
	Ni	4642.8	4433.9	-4.71

(a) The difference between the influent mass calculated using Equation 5.3 and the effluent mass calculated using Equation 5.4.

(b) Calculated according to Equation 5.5

(c) Calculated according to Equation 5.7.

Table 5.14 Mass balance of Cr, Ni, and Zn during 1990 through 1993 at the Southerly WWTP

Metals	Inf.-Eff. Metal ^(a) (kg)	Sludge ^(b) (kg)	Metal Mass Balance ^(c) (%)
Zn	90591.2	73366.0	-23.48
Cr	20241.1	17204.9	-17.65
Mn	45162.1	27408.1	-64.78
Ni	8157.6	5991.9	-36.1

(a) The difference between the influent mass calculated using equation 5.3 and the effluent mass calculated using Equation 5.4.

(b) Calculated according to Equation 5.5

(c) Calculated according to Equation 5.7.

between the aqueous and solid phases and the performance of the clarifiers for solids separation.

While the removal of suspended solids is clearly related to removal of metals (Chapter 4), the conclusions drawn here for Figure 5.2 and by Patterson et al. (1984) are as yet unsubstantiated at other WWTPs. For instance, Stetar et al. (1993) showed that approximately 30 percent of Co was removed in the Oak Ridge WWTP, but only 10 percent of original influent Co was associated with suspended solids. These data suggest that as much as 90 percent of the Co was dissolved and about 20 percent of this fraction was removed. Also, other studies have shown that solids removal is not the sole source of metal removal (see Chapter 4).

5.5 Summary of the Case Histories

Metals/radionuclides removal efficiencies calculated for the WWTPs and discussed in this evaluation vary greatly day to day. Monthly average R_M values, however, are less variable (as one would expect), appear to be very similar between the WWTPs studied, and those based on the monthly averaged R_M values yield mass balances as good as those based on daily R_M values. This would suggest that the average metal R_M may be useful as a reconcentration factor.

The usefulness of R_M values in determining the ability of radionuclides to concentrate in the solid phase sludge is, however, questionable since radionuclides are pulsed discharges. That is, radionuclide R_M values for different wastewater treatment processes of WWTPs are not known, nor are their daily or monthly fluctuations.

Mass balance calculations for the metals Cr, Ni, and Zn were shown to be reasonable. However, this resulted from our being able to balance the removal to sludge (based on influent - effluent concentrations) with that found in the sludge. Even with this level of data completeness, short-term balances were often poor; as the time span over which the mass balance was based increased, the mass balance became more accurate. This time dependence results from the difference in residence times for sludge versus that for the aqueous phase. Since these lag times are not constant, it is essentially impossible to relate sludge metal masses to particular daily events of influent metal removal masses.

Ideally, the mass of radionuclide discharged by a licensee(s) should be greater than the mass of radionuclide determined in the sludge and be a function of the radionuclide's ability to associate with the sludge; that is, a reconcentration factor. This was clearly not the case for the WWTPs studied. Mass balance calculations for radionuclides based on licensee discharge data and WWTP sludge data were not shown to be robust. Generally, the release data grossly underestimated what was found in the sludge. In the case of the Erwin WWTP, the major causes for this underestimating were 1) data available for the licensee(s) were monthly arithmetic averages of discharge concentrations and total volume discharged (these data were not flow proportional) and 2) the sludge analyses were performed on a single monthly grab sample. It seems likely that any agreement between the discharge and sludge mass balance determined from the above data would be fortuitous. Even when the release data are available on a daily basis (as for Co and Cs at Oak Ridge) and reliable sludge information is available, only limited success is achieved, as evidenced by the mass balance of Co for the Oak Ridge WWTP; yearly mass balance calculations showed that between 1.7 times and 0.29 times

Table 5.15 Comparison of $R_{M(a)}$ ranges for Zn, Cr, and Ni at four WWTPs

Metal	Westerly ^(b)		Easterly ^(b)		Southerly ^(c)		Oak Ridge ^(d)	
	hi, %	lo, %	hi, %	lo, %	hi, %	lo, %	hi, %	lo, %
Zn	95.5	66.0	86.4	42.1	95.2	83.3	98.1	49.6
Cr	97.3	60.1	98.5	71.1	95.9	89.9	96.3	53.8
Ni	91.9	17.5	74.8	16.7	70.8	39.3	63.2	19.2

- (a) R_M values calculated according to Equation 5.6.
 (b) Range in R_M values from a 4-year period from averaged monthly data.
 (c) Range in R_M values from a 1-year period from averaged monthly data.
 (d) Range in R_M values from a 23-month period from averaged monthly data (Section 5.2.4).

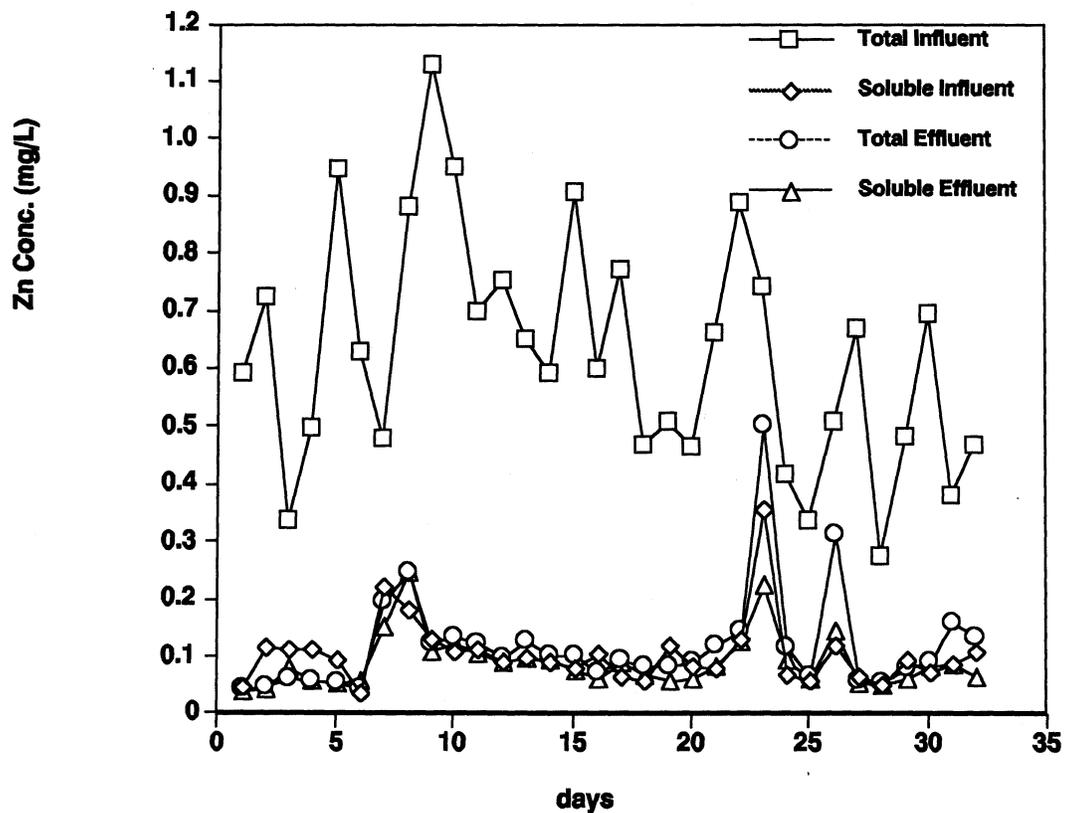


Figure 5.2 Variation of Southerly WWTP Zn influence concentration over time in comparison to dissolved (soluble) influent and effluent Zn concentration and total effluent concentration

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the ^{60}Co released was found in the sludge during a 5-year period. The only time a balance was obtained was when a single mass balance encompassing all five years was performed. This balance was within a factor of two to three of what would be calculated based on the $\text{Co } R_M$ value. On the other hand, the Cs mass balance for the same time period greatly underestimated Cs sludge content, even assuming a 100 percent removal efficiency.

These disparities in mass balance values between licensee discharge and sludge content are centered around one major fact, the data used in this study were collected to address regulatory concerns not to perform quantitative mass balances. The U mass balance for Oak Ridge is a good example of this point. The monitoring data of the DOE Y-12 Plant discharge was reasonable enough to determine that discharge to the Oak Ridge sanitary sewer systems was well below DOE guidelines (and for that matter below NRC guidelines), but was almost useless in attempting a U mass balance. One of the problems with using only licensee discharge data is that nonpoint discharge (that is, release to sewers from

background sources, etc.) cannot be taken into account; this could explain some of the overestimation with U and Cs mass balance at the Oak Ridge WWTP. Also, little is known about the quantity of material lost in the sewer line during transport to the WWTP and this may impact the amount of a given radionuclide observed at the headworks of a WWTP. For regulatory purposes, a single monthly grab sample may be sufficient, but for mass balance calculations a more reasonable sampling technique and schedule is needed. Each of the sites used for radionuclide mass balance (Oak Ridge and Erwin) suffered from one or more of these problems. Oak Ridge had excellent sludge sampling and analysis but lacked sufficient influent data. Erwin lacked adequate sludge sampling for the purposes of these evaluations, as well as influent data. If the licensee data collected at Oak Ridge for U, Co, and Cs were backed up by data similar to that obtained for Zn, Ni, and Cr (that is, influent/effluent data), a clearer picture of radionuclide behavior in WWTPs and associated sewer lines could be drawn.

6 Mechanisms and Modeling of the Reconcentration of Radionuclides in Sewage Sludge

6.1 Introduction

Discharge of radionuclides to municipal sewer systems is allowed and regulated by the NRC in accordance with 10 CFR 20.2003 (January 1994), or by agreement states in accordance with state regulations. Prior to the 1994 revision of 10 CFR 20, discharge of radionuclides to municipal sewer systems had resulted in a number of cases of sludge contamination at WWTPs (Chapter 4). Even with radioactive particulate release restrictions now present in 10 CFR 20.2003, it is not clear if current regulations (if properly observed) are adequate to prevent future occurrences of potentially harmful buildup of radionuclides in sewage sludge because dissolved radionuclide behavior in WWTPs is poorly understood.

Originally, our modeling of the reconcentration of radionuclides in sewage sludge was planned to evaluate WWTP data collected in Chapter 5 with respect to 1) the processes in which reconcentration of radionuclides occurred, 2) the chemical/physical forms of each radionuclide and how these forms affect reconcentration, 3) a mechanistic-based reconcentration pathway for the radionuclides (or surrogate compounds), and 4) calculation of a theoretical concentration factor. In addition, wastewater treatment processes (in use or contemplated) which could reconcentrate dissolved radionuclides were to be identified. As can be seen from Chapter 5, the data generated was not sufficient to accomplish the above evaluation. A detailed literature review was performed with particular attention given to models used to predict metal/radionuclide behavior in WWTPs. A number of models designed to evaluate trace metal behavior in WWTPs or particular WWTP processes were identified. To evaluate the effectiveness of these models on a full scale WWTP, input data from the WWTP case studies (Chapter 5) were considered as possible input for the models. It was determined that none of these case studies contained all the data necessary to test the models. To address this problem, the NEORS D agreed to

collect data at their Easterly WWTP to be used for model testing.

A detailed description of the models evaluated for predicting the behavior of metals/radionuclides in WWTPs is given in Section 6.2. Some discussion of the mechanistic details of these models is provided along with input data requirements and discussion concerning the availability of the required input data for these models. The data collected at the NEORS D Easterly Plant which were used in the model assessment are described in Section 6.3. Results and discussion of the modeling efforts are presented in Section 6.4. In addition, the usefulness of this information with regards to the intended goal of predicting radionuclide behavior in WWTPs and its general applicability to other WWTPs are discussed. Conclusions are summarized in Section 6.5.

6.2 Modeling Approaches to Determine Radionuclide/Metal Removal Efficiencies of Wastewater Treatment Plants

Wastewater treatment plants employ a combination of physical, chemical, and biological processes to remove suspended and floatable material, biodegradable organic matter, nutrients, and pathogenic microorganisms (Chapter 2). In recent years, the treatment objectives of these facilities have increased to include removal of metals, and many man-made organic contaminants. Inputs of these hazardous materials to WWTPs and increases in the removal efficiency have resulted in an increased potential for sewage sludge to attain high concentrations of hazardous materials. This increased efficiency for removing hazardous materials has resulted in the removal of radionuclides discharged to WWTPs.

6 Mechanisms and Modeling

Predicting the reconcentration of metals and radionuclides in WWTPs is challenging because of the number and complexity of physicochemical and biochemical reactions occurring in these systems. The present lack of information characterizing the solid and dissolved phases and how they interact with radionuclides precludes any rigorous modeling efforts. Especially lacking is an understanding of the number and nature of the binding sites and how these sites change as a function of time and type of wastewater treatment process. Since essential information is lacking for a mechanistic model to be created, available models generally rely on empirically derived constants. Typically, these empirical models use fitting parameters determined under a specific set of conditions, often in a laboratory-simulated WWTP or a pilot scale plant. Because these conditions can vary greatly between WWTPs and within a WWTP (for example, temperature, suspended solids concentrations, etc.), the general applicability of these models is in question. The predictive capability of the empirical approach is expected to diminish as conditions deviate from those under which the empirical model was determined. In addition, there is no way to predict the magnitude of the error to be expected when operating and chemical conditions deviate from those under which the empirically derived model parameters were determined.

All the models reviewed in this section were designed specifically for predicting the behavior of toxic metals (typically Cd, Cr, Pb, Zn, Ni, etc.) in WWTPs. None of the models uncovered during the literature search specifically addressed radionuclide behavior; however, many of the toxic metals are chemically identical to their radioactive counterparts, while others can serve as analogs. For example, the chemical behavior of ^{51}Cr and ^{65}Zn will be identical to Cr and Zn in a WWTP and Ni is likely to behave as an analog for ^{60}Co . In addition, the same physical/chemical processes are operative for both toxic metals and radionuclides. As a result, models useful for predicting toxic metal behavior will also be useful for predicting radionuclide behavior, when the appropriate input data for any particular radionuclide are available. The models discussed below can be placed in one of two general categories: process models and time-series analysis models. Process models couple a dissolved/solids distribution component to a solids removal component to predict

the effect of each unit process or the entire WWTP on the dissolved and solid-bound metal concentrations (Patterson et al. 1984; Monteith et al. 1993; Imai and Gloyna 1991; Imai 1988). There are several approaches to describing the dissolved/solids distribution component (Section 6.2.1), whereas the solids removal is determined directly by measurement of solids concentration at various locations in the process. The time-series analysis models define the distribution of metals between the solids and dissolved phases by regression analysis (Melcer et al. 1989). Typically, influent and effluent metal concentration data are used as the input for these models and adjustable parameters are used to fit the data to a regression line.

6.2.1 Dissolved/Solids Distribution Models

There are several approaches to describing the partitioning of metals between wastewater solids and the aqueous phase. The mechanisms governing this process have been described, in general, in Section 3.3.3. Some empirical approaches presently being used to model dissolved/solids distribution are presented below.

6.2.1.1 Distribution Coefficient and Langmuir Isotherm Models

Perhaps the simplest approach for modeling the equilibrium distribution of metals and radionuclides between the dissolved phase and the particulate phase is the distribution coefficient (K_d , typical units are L/kg) approach (Section 3.3.3):

$$K_d = \frac{S}{M_D} = \frac{\sum [\text{solid species}]}{\sum [\text{dissolved species}]} \quad (6.1)$$

where S is the solid phase metal concentration (typical units are $\mu\text{g}/\text{kg}$) and M_D is the dissolved phase metal concentration (typical units are $\mu\text{g}/\text{L}$). This empirical parameter is a ratio of all possible solid species over all dissolved species. The solid species include species formed by 1) surface complexation, 2) physical adsorption, 3) ion-exchange, and 4) precipitation. The dissolved species include 1) free metal; 2) inorganic complexes formed with such anions as hydroxide, carbonate, etc.; 3) dissolved organic complexes; and in some cases 4) complexes formed

with colloidal particles. For the K_d approach to be applicable, the adsorption isotherm (plot of concentration of metal on the solid phase versus the dissolved metal concentration, with all other variables remaining constant) must be linear. The distribution coefficient approach is generally applicable when the solids exhibit low adsorption densities for the metal.

As the adsorption density increases and the surface sites become saturated, the adsorption isotherms often begin to flatten out (become non-linear). When non-linear isotherm behavior is observed, the Langmuir isotherm model is often used (see Gould and Genetelli 1978; Riffaldi et al. 1983; Bell et al. 1989; Nielson et al. 1984):

$$S = \frac{bX_m M_D}{1 + bM_D} \quad (6.2)$$

where b is a constant related to the energy of adsorption and X_m is the maximum adsorbed concentration of the adsorbate on the solid. Like the distribution coefficient, the Langmuir approach is empirical; however, this model does assume some type of surface adsorption mechanism is operative and the number of surface sites is finite.

The general applicability of these empirical metal distribution models in the context of predicting metal behavior in WWTPs remains uncertain. Successful application of this empirical approach would, in general, require that 1) the reactions go to equilibrium (are fast relative to the unit process residence times), 2) the reactions are reversible, and 3) the chemical environment in each wastewater unit process is uniform in space and time such that the assumed metals distribution between the particulate and dissolved phases remains constant. At this point, the degree to which these conditions exist is poorly understood. Few studies have thoroughly examined the rates of metal adsorption onto sewage particles and even fewer studies have determined the reversibility of the adsorption process or the rates of desorption (for example, Martin et al. 1985; Chen et al. 1974; Patterson et al. 1984; Nelson et al. 1981; Cheng et al. 1975). We have not identified any work which has examined the rate of metal complex formation with dissolved sewage materials. Thorough characterization of sewage materials in adsorption

studies is very rare and, as a result, comparison of data from different studies is problematic.

The effect of variable input to WWTPs on the empirical modeling approach is also unknown. For example, large variations in the concentrations of metals in the influent of WWTPs as a function of time have been documented (Melcer et al. 1989; Nielsen and Hrudey 1983; Oliver and Cosgrove 1974). In two of these studies (Nielsen and Hrudey 1983; Oliver and Cosgrove 1974) both the total and dissolved metals were measured as a function of time and removal efficiencies were determined. Because other variables such as total suspended solids (TSS) or volatile suspended solids (VSS) were not measured, it is not possible to determine if variable metal concentration inputs result in variable distribution coefficients or even if variable distribution coefficients might be expected as a result of increased complexation with dissolved constituents such as DOC (Equation 6.1).

From these observations, it is clear that to establish the applicability and limitations of the empirical approach, a number of sewage treatment plants should be systematically studied in detail. A better knowledge of the mechanistic details governing the interactions between the metals/radionuclides and the suspended solids is also required to determine if the simplifying assumptions made in the empirical modeling approach are valid.

6.2.1.2 Conditional Stability Constants

Several researchers have measured conditional stability constants for metal association with dissolved and solid components in biologically activated sludge (Cheng et al. 1975; Nelson et al. 1981; Fistoe and Nelson 1983; Martin et al. 1985). In these studies, the equilibrium reaction for the complexation of dissolved free metals (M) and dissolved organic ligands (L) in the biologically activated sludge are assumed to occur as follows:



where ML_x is the complex species. The conditional stability constant corresponding to this reaction (K_L) is defined as

6 Mechanisms and Modeling

$$K_L = \frac{[M L_x]}{[M] [L]^x} \quad (6.4)$$

where [] indicate concentration. Equilibrium adsorption of metals onto the biologically activated-sludge solids (S) is expressed as



The corresponding conditional stability constant for the metal-sludge complex or surface complexation constant (K_s) is

$$K_s = \frac{[MS]}{[M] [S]} \quad (6.6)$$

where [S] is the free surface site concentration of the solids and [MS] is the concentration of the total metal bound to the sludge. If these equations are assumed to be applicable to the system at hand, the algebraic combination of Equations 6.4 and 6.6 along with equations to describe inorganic speciation would permit the determination of metal distribution between the solid and dissolved phases.

Conditional stability constants are accurate only under chemical conditions similar to those in which the constants were created. For example, the conditional stability constants determined by Cheng et al. (1975) with a laboratory scale biologically activated-sludge process using "ground dog food" as substrate are not necessarily universally applicable for all treatment plants or for biologically activated sludge of different composition. Other researchers have attempted to broaden the useful range of conditional stability constants by creating an adjustable constant; that is, the constant would vary as a function of some other wastewater constituent (Nelson et al. 1981; Fristoe and Nelson 1983; Martin et al. 1985). Often the stability constant will be fit to a linear regression equation with the dependent variable being a wastewater property such as pH. Nelson et al. (1981) and Fristoe and Nelson (1983) adjusted conditional stability constants to wastewater pH and sludge age. Martin et al. (1985) provided a modification to the conditional stability constants for surface complexes to include the effect of pH directly into the surface complexation model.

Although conditional stability constants are widely used to describe interactions of metals with both surface and dissolved constituents in sewage sludge and they are effective under the conditions they were determined, their general use for complex mixtures has been suggested to be inappropriate (Perdue 1989; MacCardy and Perdue 1991). As is the case for humic substances, sewage sludge is a very complex mixture of organic materials (Almendros et al. 1991; Garcia et al. 1992; Boyd and Sommers 1990). For solutions containing complex mixtures of organic ligands, metals at low concentration will be bound by the strongest binding sites, giving an apparent stability constant which is relatively large. As the concentration of metal increases relative to the ligand concentration, binding must occur at increasingly weaker sites, yielding apparent stability constants which are smaller than those determined at lower metal concentrations. In other words, stability constants determined for a mixture of complex ligands are not really constant at all, but a function of the metal to ligand ratio. As a result, Equations 6.4 and 6.6 will not effectively describe the complexity of the metal interactions occurring in sewage treatment systems under variable conditions. This is especially true when the metal to ligand or metal to solid ratio is varied significantly from that used in determining the value of the constant experimentally.

6.2.2 Process Models

Determining the dissolved/solids distribution of metals provides only part of the necessary information for modeling metal/radionuclide reconcentration in the sewage treatment systems. Operational characteristics of the treatment plant, such as solids removal efficiency (for each unit process), must also be included to effectively model the behavior of metals in sewage treatment processes. A number of researchers have combined the distribution coefficient or conditional stability constant approach with factors to account for suspended solids removal to develop a model to predict metal behavior in WWTPs (Patterson et al. 1984; Monteith et al. 1993; Imai and Gloyna 1991; Imai 1988). In practice, solids removal efficiency values for these models are rarely calculated from first principles. Instead, they are determined by direct measurements of the concentration of solids in the influent and effluent of a unit process. Three process models are briefly described below.

6.2.2.1 Patterson et al. Models

Patterson et al. (1984) proposed four entirely-empirical models to describe the distribution of metals between solid and dissolved phases in a pilot treatment plant. The four models had similar conceptual approaches based on a series of batch and pilot scale experiments, but differed primarily in regards to their simplifying assumptions and the number of wastewater characteristics accounted for in the model. The pilot plant consisted of a primary settling unit, a secondary biologically activated-sludge unit, a secondary clarifier, and a chlorination unit. These researchers determined that the amount of metals in the solid phase (fraction of metals that could not pass through a 0.45- μm filter) was strongly correlated to the total metal concentration in suspension and the concentration of volatile suspended solids (VSS, solid fraction retained by a 0.45- μm filter that could be volatilized at 600°C), while being poorly correlated to the concentration of dissolved organic matter. The most robust and accurate model, Model 3, can be used to determine the distribution of metals between the solid and dissolved phases of raw sewage, primary effluent, activated sludge, and secondary effluent. Model 3 is presented in Equation 6.7:

$$M_T \times \frac{VSS}{M_S} = A(VSS) + B \quad (6.7)$$

where M_T is the total metal concentration ($\mu\text{g L}^{-1}$), M_S is the solid bound metal concentration ($\mu\text{g L}^{-1}$), A and B are fitting parameters, and VSS is the volatile suspended solids concentration. Typically, M_T and VSS are input parameters and M_S is the output. The fitted parameters not only vary between metals but also between process liquids.

Model 4 is a simplified version of Model 3 and was developed for application where total suspended solids concentrations are high. This model can predict M_T with somewhat less accuracy than Model 3, but its only input requirement is total metal concentration. This model is presented in Equation 6.8:

$$M_T = A \times M_S + B \quad (6.8)$$

Model 4 is simplified such that A and B are the adjustable parameters used to fit M_T and M_S to a linear relationship. Model 2 accounts for soluble organic carbon (SOC):

$$M_T \left[\frac{VSS}{M_S} \right] = A(VSS) + B(SOC) + C \quad (6.9)$$

where A, B, and C are adjustable parameters. Model 1 accounts for SOC and hydrogen ion (H^+) activity:

$$M_T \left[\frac{VSS}{M_S} \right] = A(VSS) + B(SOC) + C(\text{H}^+) + D \quad (6.10)$$

where A, B, C, and D are adjustable parameters.

Patterson et al. determined that no additional accuracy in model prediction was obtained by accounting for SOC or hydrogen ion activity and therefore dismissed Models 1 and 2 as unnecessarily complicated. It should be noted that these models were developed from data obtained from a pilot scale WWTP. Model 3 was evaluated for its ability to predict metal reconcentration at the NEORS Easterly Plant and these results will be presented in Sections 6.3 and 6.4.

6.2.2.2 TOXCHEM Model

The TOXCHEM (Monteith et al. 1993) model is similar in many respects to the Patterson et al. models. One important difference is that TOXCHEM not only accounts for sorption of metals to VSS but also for metal precipitation from solution. Adsorption reactions are modeled using the distribution coefficient (K_d) approach.

The total metal removed is assumed to be associated with suspended solids removed in the primary and secondary settlers. Contrary to the authors' claim, the model is in fact highly empirical. Both the adsorption and solubility determinations were empirically derived from pilot plant test data. Several potentially significant variables such as DOC and pH were not considered in their analyses. In addition, the partition coefficients used in the model were determined by curve fitting pilot plant test data. These coefficients were significantly different from those determined in batch tests, yet no explanation for this discrepancy was

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The major advancement of TOXCHEM over the Patterson et al. models, is that it does provide some means to account for precipitation to occur in the modeled system. In pilot plant studies in which metals were added to the influent, precipitation was found to be significant. It is unclear, however, if precipitation in full scale treatment plants is a significant mechanism. For example, influent concentrations of Cu, Ni, Pb, and Zn in the full scale treatment plant studied (Burlington Skyway Plant) were generally lower than the solubilities determined in filtered solutions of primary and secondary effluent. Influent Cr concentrations were very close to the solubility limits determined in the filtered primary and secondary effluent. Aluminum was the only metal which had an influent concentration significantly above its solubility determined in filtered primary and secondary effluent. In regards to radionuclide reconcentration in WWTPs, it is unlikely that ^{234}U , ^{235}U , ^{238}U , ^{60}Co , or ^{137}Cs would attain concentrations high enough to precipitate as a pure phase solid (Chapter 3). As a result, there is no significant advantage to using the TOXCHEM model over the Patterson et al. model.

6.2.2.3 CRAS Model

The CRAS model is a semi-equilibrium model used to predict the behavior of Cr(III) in the biologically activated-sludge process under steady state conditions (Imai and Gloyna 1991; Imai 1988). This model has the best fundamental basis of all the models reviewed. It is based on three principles: chemical equilibria, steady state, and mass balance. Conditional stability constants are used to describe adsorption, soluble organic complexation, and intracellular microbial uptake. Precipitation of Cr(III) and oxidation to Cr(VI) were not included in the model because these reactions were believed to be unimportant (Imai and Gloyna 1990; Imai 1988). Chemical input parameters used by the model include total Cr(III) concentration, free Cr(III) concentration, hydrolyzed Cr(III) concentration, VSS, TSS, SOC concentration, and organic complexation capacity. Process input parameters used by the model include reactor volume, influent flow rate, wastage flow rate, hydraulic retention time, and sludge age.

Some important refinements have been made to the model since it was first issued (Imai and Gloyna 1993). Comparison of model predictions with

experimental results revealed that the CRAS model was capable of predicting the total chromium (TCr) and dissolved chromium (DCr) concentrations when the TCr concentrations were on the increase, but the model underestimated the TCr and overestimated the DCr as the TCr decreased. The causes of the deviations were believed to include a hysteresis effect (slower metal desorption than adsorption from the solid phase) and irreversible removal of Cr by intracellular uptake. A refined version of the model (Imai and Gloyna 1993) accounts for these effects, resulting in greater predictive capabilities. The new version also provides the option to account for sludge age and pH.

Some potential problems exist with the CRAS model. It requires physicochemical data that are not readily available and are costly to obtain (especially if done correctly). These data include conditional stability constants to describe adsorption, soluble organic complexation, and intracellular uptake. In addition to these difficulties, there are problems with the use of stability constants to describe Cr(III) complexation with the complex mixture of organic binding sites in sewage, as was indicated in Section 6.2.1.2. Iron(III) coprecipitation treatment was used in an attempt to validate the amount of organically complexed Cr(III) predicted by the model using the measured stability constants. In this treatment it was assumed that free and hydrolyzed Cr(III) were coprecipitated and organically complexed chromium remained in solution. The effectiveness of this procedure is untested. For example, it is well known that dissolved organic carbon (both free and metal complexes) adsorb to iron oxides (see Zachara et al. 1994). In addition, if free and hydrolyzed Cr(III) are removed from solution, Cr-organic complexes will dissociate to reestablish equilibrium. As a result, it is not believed that the agreement between model predictions and this measurement is a true validation. Another problem with the CRAS model is that it has a very narrow scope. It is applicable only for biologically activated-sludge unit processes and only for Cr(III). Finally, the model has not been fully verified. It was developed and tested only with data from a laboratory scale reactor.

Despite the problems discussed above in regard to some of the details of the CRAS model, the general approach taken in this model is superior to all the other modeling approaches reviewed. For example, more sophisticated approaches for describing metal

complexation with complex mixtures of ligands such as the stability function approach (MacCarthy and Perdue 1991) could be incorporated into the CRAS model. In addition, CRAS could easily be extended to other sewage treatment processes beyond the biologically activated-sludge process. Finally, further studies could be conducted to determine the input parameters, required for the model, for any radionuclide or metal of interest.

6.2.3 Time-Series Analysis Model

Another approach which has been used to model the dynamic behavior of trace contaminants in sewage treatment plants is time-series analysis (Melcer et al. 1989). In this approach, a statistical model was constructed to correlate influent and effluent concentrations of contaminants. The only input parameters used to construct the model are the influent and effluent concentrations of the contaminants of interest. The constants used in this model have no physical meaning, they are simply mathematical fitting parameters. As a result, the usefulness of this model is highly uncertain. Its predictive capabilities would continually decrease as chemical, biological, and physical conditions of WWTPs increasingly deviate from those used to create the constants. Some of the operational parameters and conditions which could potentially affect contaminant removal efficiencies of sewage treatment plants include plant design, flow rate, influent suspended solids concentration, influent metal concentration, pH, alkalinity, major ion chemistry, COD, sludge volume index, sludge age, suspended solids removal, mixed liquor suspended-solids concentration, settling time, temperature, concentration of extracellular polymers and other complexing agents, and individual contaminant chemistry. Because none of these variables were considered in the statistical study, any effect that these variables might have on the contaminant removal efficiency within the sewage treatment plant was essentially ignored. Unfortunately, the model was not verified using data from another WWTP.

6.3 Easterly Wastewater Treatment Plant Data

Wastewater treatment plant data were collected over a seven-day period by the NEORSD at their Easterly Plant to test the usefulness of available models for predicting metals removal with data which could be obtained relatively easily. The following parameters were measured: TSS, VSS, volatile dissolved solids (VDS, 0.45 μ filtrate), DOC, total metals (M_T , acid digested) and dissolved metals (M_D , 0.45 μ filtrate). The TSS, VSS, and VDS measurements were performed according to standard methods. The DOC was measured using a Dohrmann DC-80 carbon analyzer. The metals studied were measured by ICP. All measurements, except the DOC measurements, were performed by the NEORSD Analytical Services. Sub-samples were sent to Pacific Northwest Laboratory (PNL) for DOC analysis. Figure 6.1 is a flow diagram of the Easterly WWTP. Included are the major unit processes, residence times, and locations of the sampling points. Sample collection points were numbered 1 through 7 as follows: #1—raw sewage, #2—primary effluent, #3—aeration tank mixed liquor, #4—secondary clarifier, #5—chlorine contact tank effluent, #6—primary sludge, and #7—secondary sludge. Samples were collected every day for seven days. Sampling points #1, #2, #4, and #5 were collected with hourly automatic sample collectors to obtain flow proportional composite samples over a 24-hour period. Sample points #3, #6, and #7 were taken as grab samples every four hours. Results of the four-hour grab samples were "compositized" by weighting each sample according to the flow rate. In general, the weighting factors were not substantially different from one, because the flow rate did not vary substantially from the average during the course of the sampling period.

During the course of the study, effluent flow rates at the Easterly Plant varied between 302 and 135 MGD. An average of 2000 gallons per day of pickle liquor was routinely added to the waste stream prior to the primary clarifier. Pickle liquor is a sulfuric-acid-based solution derived from the pickling process at steel mills and contains approximately 50,000 mg/L iron, 100 mg/L zinc, 100 mg/L chromium, 25 mg/L nickel, and 3 mg/L copper. This solution is intended to act as a coagulant. Although adding this solution does not significantly increase the total metal

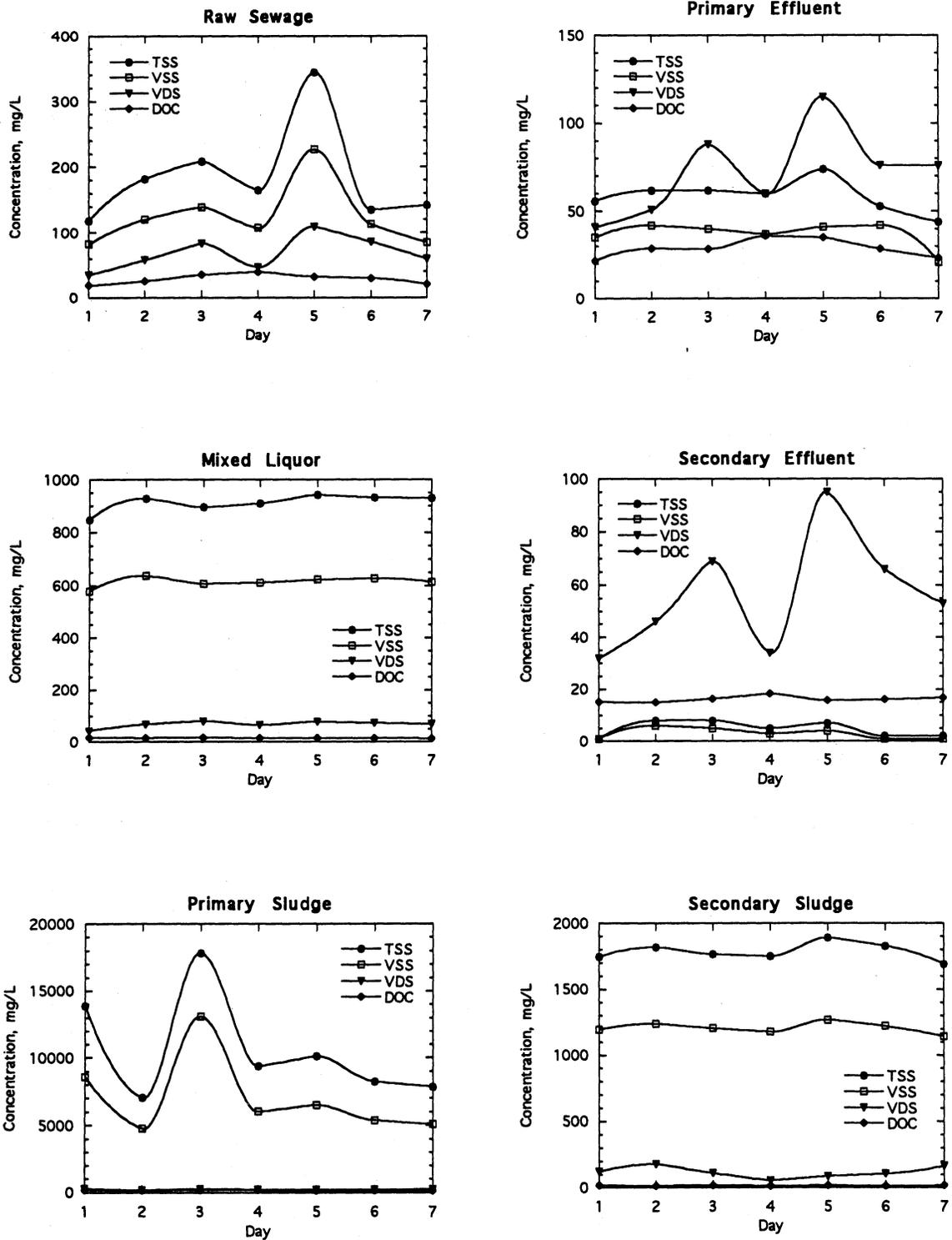


Figure 6.2 24-hour composite concentrations for TSS, VSS, VDS, and DOC in the various process streams of the Easterly Wastewater Treatment Plant as a function of sampling day

concentrations above raw influent levels, it may impact the chemical dynamics within the primary clarifier through the precipitation of iron hydroxides.

The TSS, VSS, VDS, and DOC measurements results for raw sewage, primary effluent, mixed liquor, secondary effluent, primary sludge, and secondary sludge are presented in Figure 6.2. The data for the chlorine contact tank effluent are not included because changes in the effluent chemistry resulting from the chlorination process are not relevant to the study at hand. The lines drawn between the points are interpolations and do not represent a fit by a model. As would be expected, VSS concentrations are generally lower than TSS. These two parameters appear to be well correlated, suggesting that VSS is a major portion of TSS. The DOC concentrations are lower than VDS concentrations and are not well correlated. This may be caused by a significant CO_2 component to VDS resulting from oxidation of organic material in the sewage.

Total concentrations of the six metals analyzed in the raw sewage, primary effluent, and secondary effluent are shown in Figure 6.3. Similar plots for the primary sludge, secondary sludge, and mixed liquor are shown in Figure 6.4. In general, the total metal concentrations appear to be correlated to the TSS and VSS concentrations, suggesting that the major portion of the total metal is associated with the suspended solid phase. A notable exception to this generalization is nickel, which is known to be much less strongly associated with the solid phase than the other metals (Cheng et al. 1975; Monteith et al. 1993). One final observation is that the total metal concentrations in the primary sludge are not well correlated with the TSS/VSS ratio. This could be related to additions of pickle liquor to the process stream prior to its entering the primary clarifier.

Dissolved concentrations of the six metals in the raw sewage, primary effluent, and secondary effluent are shown in Figure 6.5. Similar plots for the primary sludge, secondary sludge, and mixed liquor are shown in Figure 6.6. If we confine our attention to the dissolved metals concentrations in the raw sewage, primary effluent, mixed liquor, and secondary effluent it becomes apparent that each of the metals pass through the treatment process at relatively constant concentrations, suggesting that the dissolved metal concentrations in the raw sewage equal the final

effluent concentrations for these metals. Deviations from this trend are observed in the primary sludge for iron, nickel, and zinc and in the secondary sludge for copper. The high dissolved iron concentration in the primary sludge probably results from the addition of pickle liquor prior to the primary clarifier. Elevated nickel and zinc concentrations in the primary sludge are likely to be the result of lower surface binding of these metals relative to the other metals examined in this study (low K_d values, see later discussion in Section 6.4). The cause of the elevated copper concentrations in the secondary sludge is unknown; however, copper tends to form stronger complexes relative to other divalent transition metals with amino acids (Martell and Smith 1974) known to occur in sewage sludge (Almendros et al. 1991). If elevated levels of dissolved amino acids occur in the secondary sludge, this could explain the elevated dissolved copper concentrations.

6.4 Model Results

The metal concentration data collected at the Easterly Plant (Section 6.3) was modeled using the Patterson et al. Model (1983; Equation 6.7) and the Distribution Coefficient Model (Equation 6.1). The Patterson et al. Model was selected for its simplicity, limited data input requirements, and reported good predictive capabilities. Of the four metals distribution models presented by Patterson et al., Model 3 was reported to have the greatest predictive ability and was therefore used in this study. Equation 6.7 and the fitted parameters, A and B, determined by Patterson et al. for raw sewage, primary treatment effluent, secondary treatment mixed liquor (biologically activated sludge), and the secondary treatment effluent were used in the calculations conducted for this report. These values vary for each metal and process liquid.

As a result of the empirical nature of these models, application of both the Patterson et al. and K_d approaches requires that 1) the reactions go to equilibrium (are fast relative to the unit process residence times), 2) the reactions are reversible, and 3) the chemical environment in each wastewater unit process is uniform in space and time. Previous studies have indicated that adsorption of metals onto sewage sludge is relatively rapid, with the major portion of metal adsorption occurring within 15 minutes, but with an

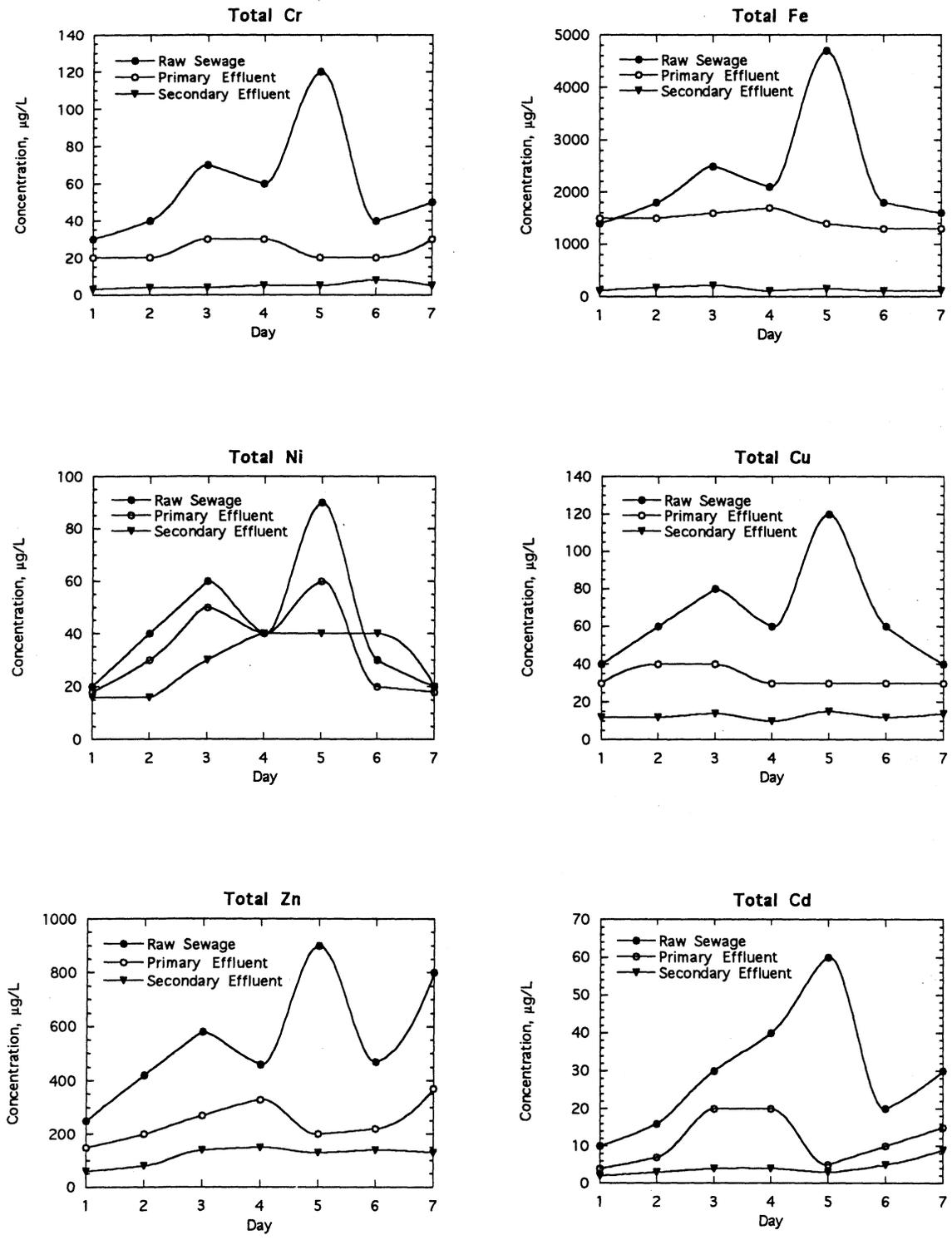


Figure 6.3 Total metal concentrations in the raw sewage, primary effluent, and secondary effluent of the Easterly Wastewater Treatment Plant as a function of sampling day

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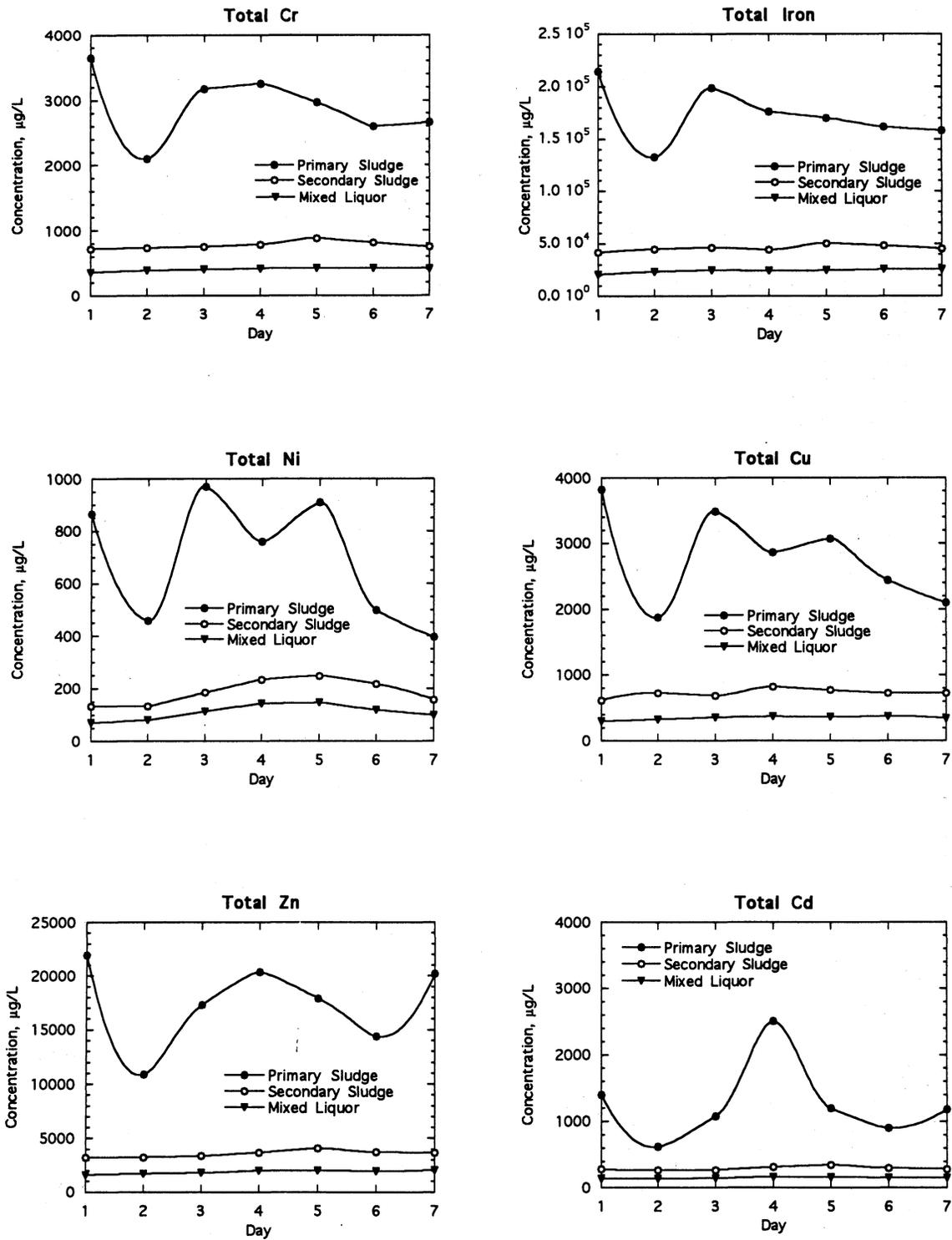


Figure 6.4 Total metal concentrations in the primary sludge, secondary sludge, and mixed liquor of the Easterly Wastewater Treatment Plant as a function of sampling day

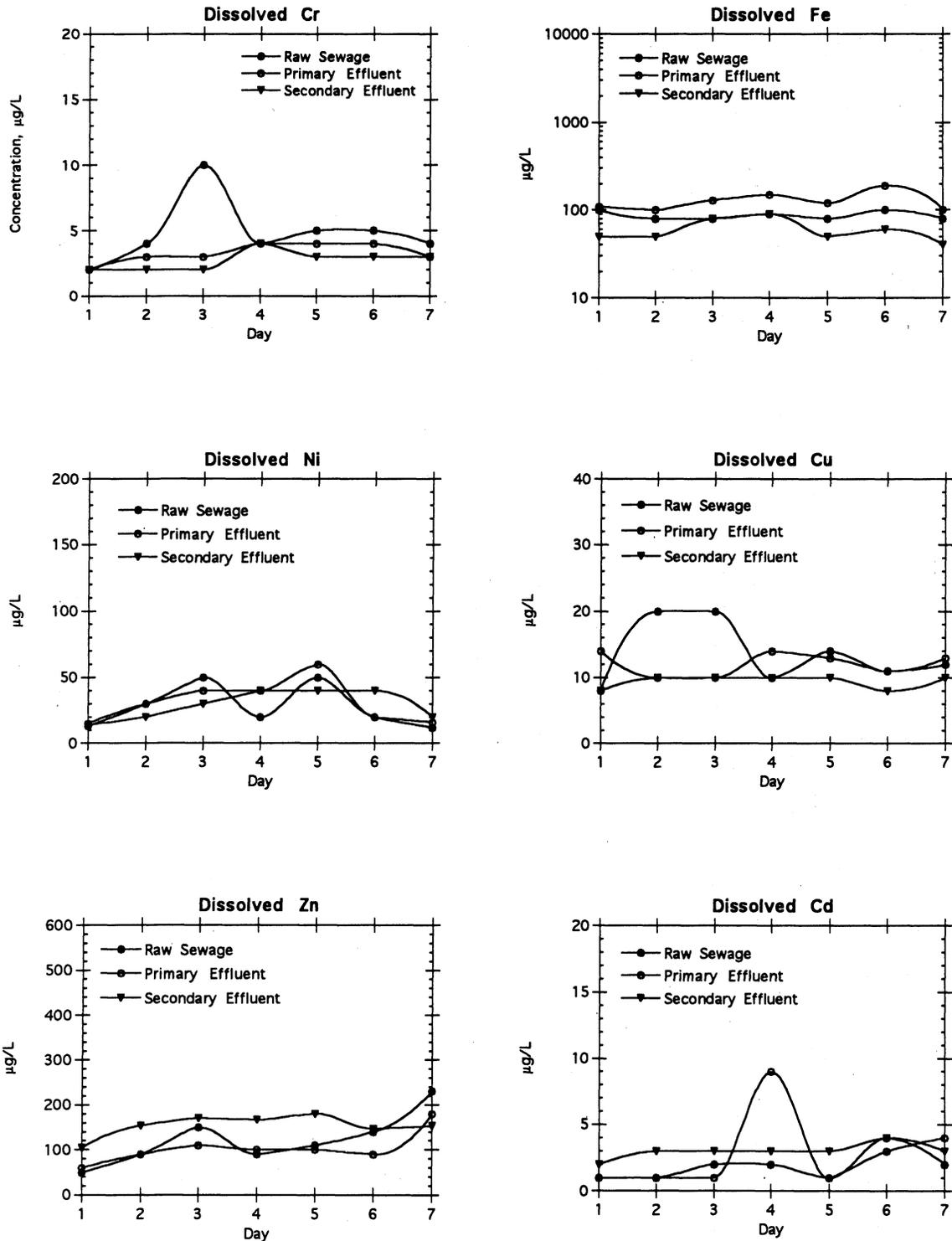


Figure 6.5 Dissolved metal concentrations in the raw sewage, primary effluent, and secondary effluent of the Easterly Wastewater Treatment Plant as a function of sampling day

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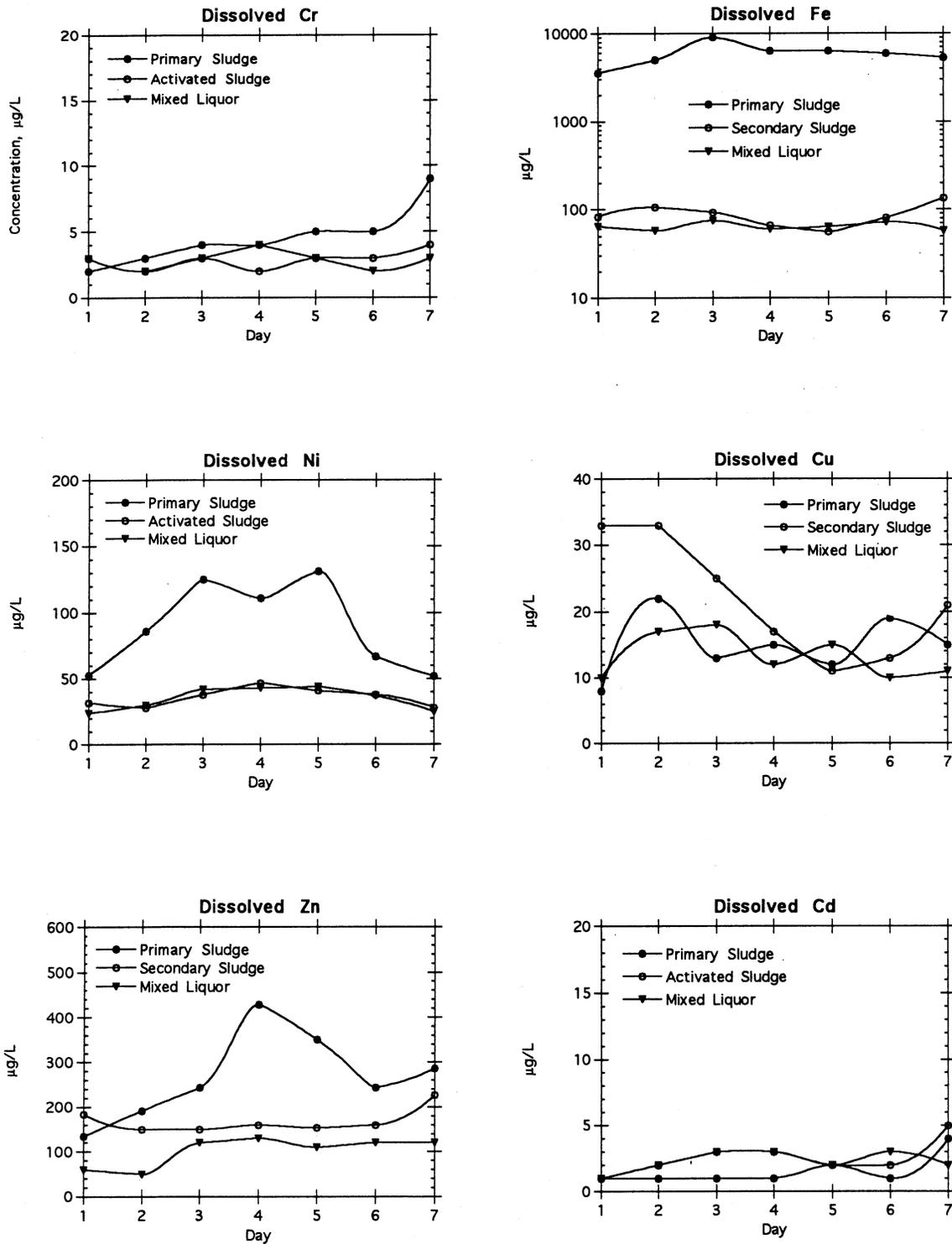


Figure 6.6 Dissolved metal concentrations in the primary sludge, secondary sludge, and mixed liquor of the Easterly Wastewater Treatment Plant as a function of sampling day

additional small amount of adsorption occurring for hours (Patterson et al. 1984; Cheng et al. 1975). A lack of chemical homogeneity in wastewater systems could potentially compromise the usefulness of this approach. Variations in the WWTP chemical environment occur as a result of variable influent chemistry as a function of time and non-uniform mixing in the WWTP. With these limitations in mind, we elected to also apply the K_d approach to WWTPs because it has had some success describing complex geological systems (Van Genuchten 1980). Perhaps just as important, the required input parameters for this model can be easily measured at WWTPs. Although the model is quite similar to the Patterson et al. Model (Equation 6.7), it uses one less adjustable fitting parameter. This will be discussed in more detail in Section 6.5.

The classical K_d equation (Equation 6.1) was rewritten so that the concentration of metal associated with the solid phase, M_S , could be calculated from the total metal concentration, M_T , and total suspended solids concentration in the wastewater stream (the concentration of solids in a suspension $>0.45\mu\text{m}$, in units of mg/L). These input requirements are similar to the Patterson et al. Model (VSS and M_T). The rewritten K_d equation used in our model was

$$M_S = \frac{M_T}{1 + \frac{1}{TSS \times K_d \times 10^{-6}}} \quad (6.11)$$

This form of the equation was chosen so that the output, M_S , could be compared with that of the Patterson et al. Model. The K_d values used in Equation 6.11 in units of L/kg , were determined from the Easterly Plant data using Equation 6.12:

$$K_d = \frac{M_T - M_D}{TSS} \times 10^6 \quad (6.12)$$

where M_D is the dissolved metal concentration (μg metal/L), operationally defined as the metal concentration that passed through a $0.45\text{-}\mu\text{m}$ filter.

6.4.1 Results from the Patterson et al. Model

The metal concentrations associated with the solid phase (M_S) predicted by the Patterson et al. Model were generally well correlated to actual measured values (Figures 6.7 and 6.8). All measured M_S [$M_T - M_D = M_S$] values that were determined to be at or below the detection limit, ≤ 1 , were plotted as being equal to 1. Almost all the correlation coefficients describing the relationship between predicted and measured M_S values were significant at the 5% level ($r_{\text{critical}}, P \leq 0.05 = 0.514$). The strongest correlations existed in the mixed liquor where the metals and solids concentrations were greatest. The weakest correlations existed in the secondary effluent where metals and solids concentrations were often low and the range of these values was also narrow. The low correlation coefficients in the secondary effluent are likely more reflective of the limitations of the data than of the model itself. The correlation coefficients for Ni were consistently the lowest among the metals investigated. The poor Ni correlations may indicate that processes other than sorption to the solid phase, such as DOC complexation, may be influencing Ni fractionation in the wastewater stream. The poor correlations between these two values could also be the result of the total Ni concentration in each of these process liquids being quite low, near the ICP detection limit for Ni.

The above correlations generally indicate that the predicted and measured M_S values are closely related. They do not provide any estimate of the precision of the predictive capability of the model. Such an estimate was calculated as follows:

$$\text{Error}(\%) = \left| \frac{M_{S,\text{Measured}} - M_{S,\text{Predicted}}}{M_{S,\text{Measured}}} \right| \times 100 \quad (6.13)$$

where $M_{S,\text{Measured}}$ and $M_{S,\text{Predicted}}$ represent the concentrations of the solid bound metals actually measured and predicted by the model. The absolute amount of the percent differences between $M_{S,\text{Measured}}$ and $M_{S,\text{Predicted}}$ was calculated in Equation 6.13 to compensate for the offsetting effects that negative and positive differences would have on averages of error values (Table 6.1).

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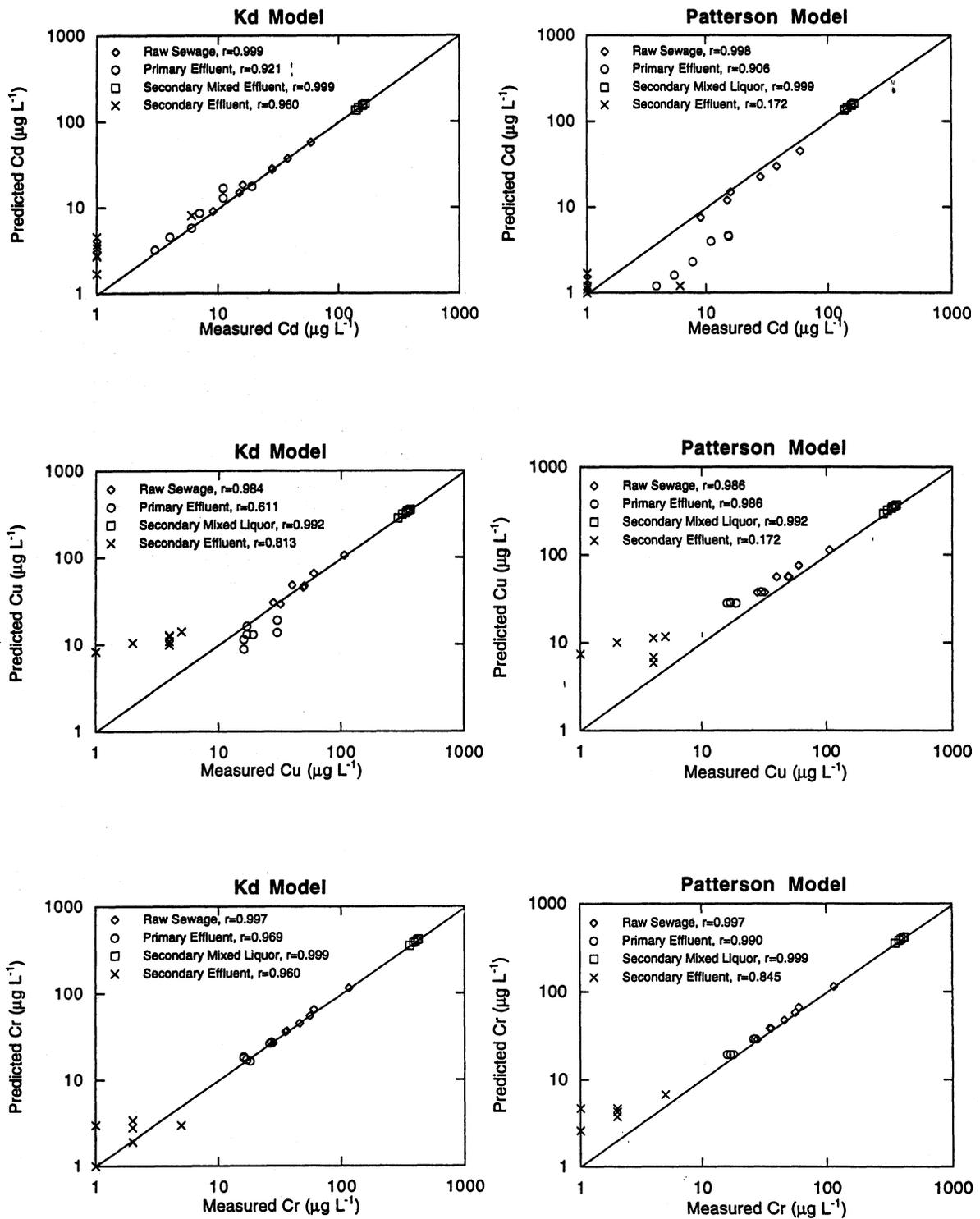


Figure 6.7 Predicted Cd, Cr, and Cu solid-phase concentrations, M_S , from the Patterson et al. and K_d Models versus measured solid-phase concentrations. Diagonal lines in each plot indicate perfect agreement between measured and predicted M_S values.

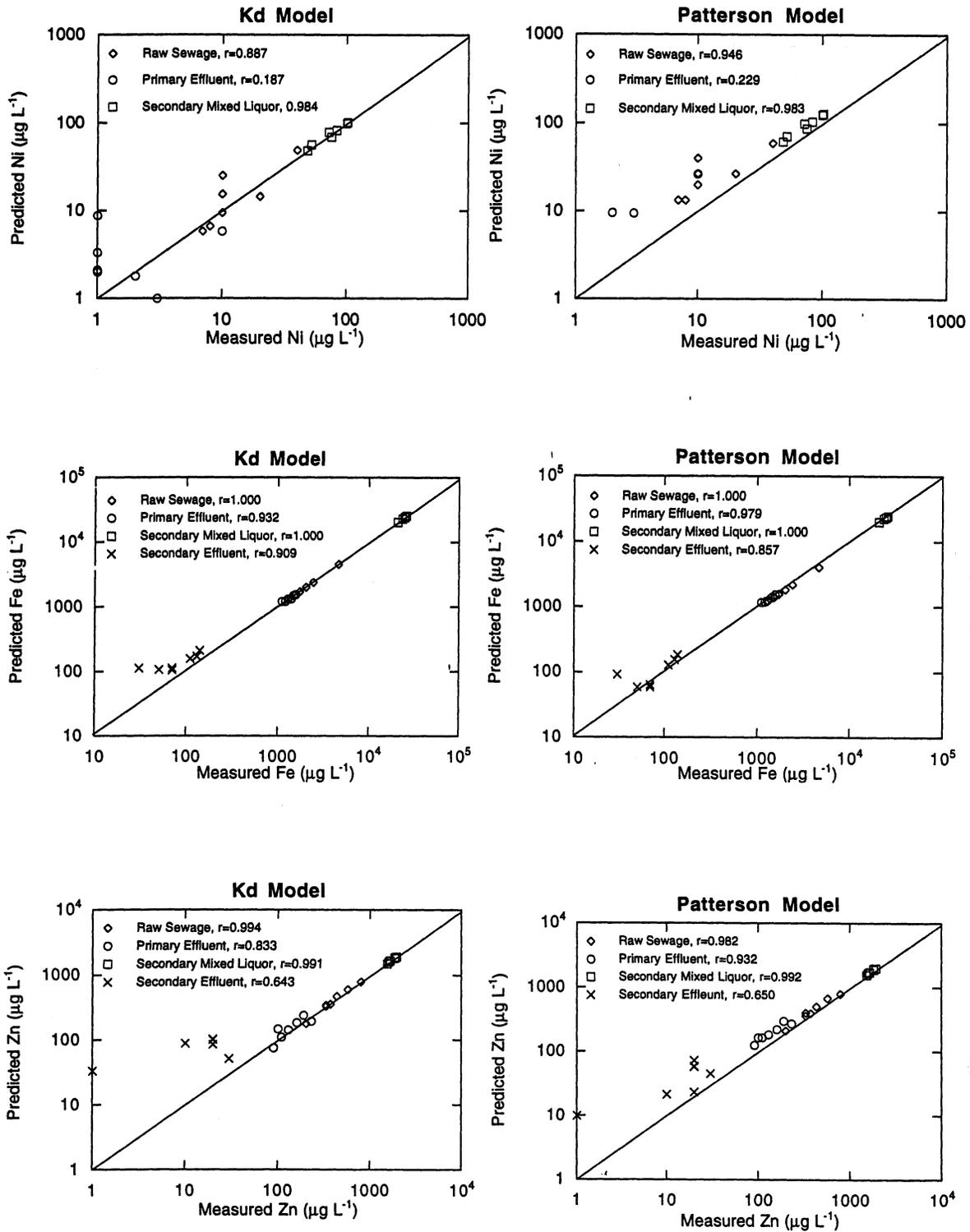


Figure 6.8 Predicted Ni, Fe, and Zn solid-phase concentrations from the Patterson et al. and K_d Models versus measured solid-phase concentrations. Diagonal lines in each plot indicate perfect agreement between measured and predicted M_S values.

Table 6.1 Predicted solid-bound metal concentrations, M_S , from the Patterson et al. Model (Equation 6.5) and measured solid-bound metal concentrations^(a)

Process Liquid	Value	Metal					
		Cd	Cr	Cu	Fe	Ni	Zn
Raw Sewage	Measured (mg L ⁻¹)	28	54	52	2,184	15	431
	Predicted (mg L ⁻¹)	22 ^(b)	56	62 ^(b)	1,976 ^(b)	29 ^(b)	481 ^(b)
	Error (%) ^(c)	18±6	5±4	22±12	9±2	115±119	12±8
Primary Effluent	Measured (mg L ⁻¹)	9	21	21	1,343	2	144
	Predicted (mg L ⁻¹)	9	24	31 ^(b)	1,335	18 ^(b)	207 ^(b)
	Error (%)	12±14	13±6	55±23	2±2	253±114	46±16
Mixed Liquor	Measured (mg L ⁻¹)	152	401	334	24,143	76	1,739
	Predicted (mg L ⁻¹)	151	403	345 ^(b)	23,522 ^(b)	96 ^(b)	1,843
	Error (%)	1±0	1±0	3±1	3±0	28±8	6±1
Secondary Effluent	Measured (mg L ⁻¹)	1	2	3	86	^(d)	17
	Predicted (mg L ⁻¹)	2 ^(b)	4 ^(b)	8 ^(b)	107 ^(b)	^(d)	42 ^(b)
	Error (%)	52±27	142±107	149±125	46±72	^(d)	141±95

(a) Each value represents a mean of seven values.

(b) A significant difference ($P \leq 0.05$) between measured and predicted means as determined by the Paired Two-Sample for Means t-Test.

(c) Mean ± standard deviation. Error calculated by Equation 6.9.

(d) No detectable Ni associated with solid phase of secondary effluent.

The percent error of the Patterson et al. Model was generally quite low in the raw sewage, primary effluent, and secondary mixed liquor (Table 6.1). The secondary effluent consistently had the highest percent errors. The asterisks in Table 6.1 indicate a significant difference ($P \leq 0.05$) between the means of the seven pairs of predicted and measured values. The statistical analysis used to determine significant differences between means was the Paired Two-Sample for Means t-Test (Netter and Wasserman 1974). Based on this statistical test, 66% of the predicted values were significantly different from the measured values. The Patterson et al. Model was more successful at predicting M_S levels of Fe, Cd, and Cr than for Cu, Ni, and Zn. The model was more successful at predicting M_S levels in the raw sewage, primary effluent, and mixed liquor than in the secondary effluent. These results reflect those of the regression analysis (correlation coefficients, Figures 6.7 and 6.8) and percent error values presented in Table 6.1. For any given metal, it also appeared that the model was more successful at

predicting M_S levels in process liquids of greater M_T and M_S levels. The overall average error for each of the process liquids determined with all the metals is as follows: mixed liquor < raw sewage < primary effluent < secondary effluent. This ranking correlates with M_T and M_S levels in these process liquids.

6.4.2 Results from the K_d Model

K_d values calculated using Equation 6.12 and the metal concentration data presented in Figures 6.3 through 6.6 are presented in Table 6.2. A ranking of the K_d values generated from the Easterly Plant data is as follows: Fe > Cr > Cd > Cu > Zn > Ni (Table 6.2). This ranking is similar to that presented by Lester (1987a and b) for metal removal efficiencies, except Cu was located between Fe and Cr in the ranking sequence (Tables 3.4 and 3.5). In general, the K_d values for a given metal did not vary greatly between process liquids, thereby making the average value for the six process liquids a reasonable estimate of metal partitioning between the solid and dissolved

Table 6.2. Averages and standard deviations^(a) of Distribution Coefficient (K_d ; $L\ kg^{-1} \times 10^{-3}$)^(b) for six metals in process liquids at the Easterly Wastewater Treatment Plant over a seven-day period

Site		K_d					
		Cd	Cu	Cr	Fe	Ni	Zn
Raw Sewage	AVG	92	23	69	134	3.4	21
	STD	44	9.4	29	19	1.8	6.6
Primary Effluent	AVG	91	10	120	191	1.5	25
	STD	98	17	53	55	1.9	7.6
Mixed Liquor	AVG	75	29	162	412	2.4	13
	STD	21	7.3	35	40	0.4	2.2
Secondary Effluent	AVG	176	157	295	517	17	40
	STD	366	178	286	463	56	30
Primary Sludge	AVG	103	20	71	3.0	0.7	7.0
	STD	76	8.2	26	1.0	0.2	2.7
Secondary Sludge	AVG	76	22	156	312	2.3	12
	STD	40	10	26	94	0.3	1.7
Overall ^(c)		112	58	192	287	8.2	22
		153	90	135	255	30	20

(a) $N=7$

(b) K_d values were calculated using Equation 6.12.

(c) Mean value for all processes and materials on a daily basis.

phases. Somewhat higher K_d values were calculated for the secondary effluent; however, these values also have a higher degree of error associated with them.

The M_T and TSS data from the Easterly Plant were entered into the K_d Model (Equation 6.11) and M_s was calculated for comparison with the measured values ($M_T - M_s$). The resulting correlation coefficients and percent errors were calculated and are shown in Table 6.3. Because this same data was used to create the K_d Model constants, the resulting error between predicted and actual data is more a qualitative measure of the variability of the data and errors resulting from the chemical-analytical method (measurements of M_T and M_D) and cannot be used to validate the predictive capabilities of the model itself. Therefore, based on mathematical rather than chemical or physical considerations, these data show that the K_d Model will have a greater ability to predict Easterly Plant data than the Patterson et al. Model. In order to conduct an objective comparison between

the two models, a set of data developed independently of both the Patterson et al. and the Easterly Plant study would be required.

All the correlation coefficients describing the linear relationship between the predicted values from the K_d Model and the actual values (except Ni/primary effluent data) were significant at the 5% level of certainty ($r_{critical}, P \leq 0.05 = 0.514$) (Figure 6.6 and 6.7). The correlation coefficients of the K_d Model were about the same or slightly higher than those for the Patterson et al. Model. The K_d Model generally had higher correlation coefficients in the secondary effluent than the Patterson et al. Model.

The percent errors of the K_d Model followed nearly identical trends as those observed for the Patterson et al. Model; that is, there were generally higher errors associated with the secondary effluent than the other process liquids and with Ni than with the other metals. As expected, the percent errors of the K_d Model were

Table 6.3. Predicted solid-bound metal concentrations, M_S , from the K_d Model (Equation 6.7) and measured solid-bound metal concentrations^(a)

Process Liquid	Value	Metal					
		Cd	Cr	Cu	Fe	Ni	Zn
Raw Sewage	Measured (mg L ⁻¹)	28	54	52	2,184	15	431
	Predicted (mg L ⁻¹)	28	54	53	2,185	18	440
	Error (%) ^(b)	3±5	3±6	9±3	0±0	42±46	5±4
Primary Effluent	Measured (mg L ⁻¹)	9	21	21	1,343	2	144
	Predicted (mg L ⁻¹)	10	22	14 ^(d)	1,362	4	157
	Error (%)	18±17	6±16	32±7	4±3	25±24	19±15
Mixed Liquor	Measured (mg L ⁻¹)	152	401	334	24,143	76	1,739
	Predicted (mg L ⁻¹)	152	401	335	24,143	76	1,743
	Error (%)	0±0	0±1	1±0	0±0	4±4	1±1
Secondary Effluent	Measured (mg L ⁻¹)	1	2	3	86	(c)	17
	Predicted (mg L ⁻¹)	2	3	5 ^(d)	98 ^(d)	(c)	18
	Error (%)	78±44	61±63	45±64	45±64	(c)	37±22

(a) Each value represents a mean of seven values.

(b) Mean ± standard deviation. Error calculated by Equation 6.9.

(c) No detectable Ni associated with solid phase of secondary effluent.

(d) A significant difference ($P \leq 0.05$) between measured and predicted means as determined by the Paired Two-Sample for Means t-Test.

generally appreciably less than those of the Patterson et al. Model. Based on the Paired Two-Sample for Means t-Test, only 13% of the K_d Model's predicted values differed from the measured values (Table 6.3). The model was more successful at predicting the M_S levels of Cd, Cr, Cu, Fe, and Zn than those of Ni.

The diagonal lines in each plot in Figures 6.6 and 6.7 indicate a perfect agreement between measured and predicted M_S values. A trend consistent with both models is that the coordinates tended to deviate more away from the diagonal line as the concentration of measured metal decreased. In most cases, the models tended to over-estimate M_S at the lower M_S levels. The models tended to be most successful at predicting Cr, Fe, and Zn and less successful at predicting Cu, Cd, and Ni.

Because of the completely empirical nature of the Patterson et al. Model, it was not expected to be as successful as it was for predicting the metals concentrations on the solids. However, after closer

inspection of the two models it became apparent that they were actually very similar. The K_d model in the present nomenclature is

$$K_d = \frac{M_S}{\frac{TSS}{M_D}} \quad (6.14)$$

In order to evaluate the differences between the Patterson et al. Model and the K_d Model, Equation 6.14 can be rearranged using the equality $M_D = M_T - M_S$ to obtain Equation 6.15.

$$M_T \times \frac{TSS}{M_S} = TSS + \frac{1}{K_d} \quad (6.15)$$

Patterson et al. have shown that there is a strong correlation between TSS and VSS for all process liquids. The average VSS/TSS ratio was shown to range from 0.65 in the secondary effluent to 0.73 in

the raw sewage. If it is assumed that the equality $TSS = C \times VSS$ holds, Equation 6.15 can be rearranged in order to obtain Equation 6.16:

$$M_T \times \frac{VSS}{M_S} = VSS + \frac{1}{C \times K_d} \quad (6.16)$$

By comparing Equation 6.16 to Equation 6.7, we can see that these two equations are similar. If B is taken to be equal to $1/(C \times K_d)$, the only difference between the two equations is that Equation 6.7 has an additional fitting parameter, A. If A is set equal to 1, the equations would be mathematically identical. The values of A determined by Patterson et al. through regression analysis ranged from 0.96 to 2.69 for the various metals in the various process liquids, with most of the values being clustered near 1.

6.5 Conclusions

A review of modeling efforts to describe the behavior of metals in WWTPs suggests that metals removal is directly related to the dissolved/particulate distribution of each metal in the raw sewage and mixed liquor (aerobic digestion liquor) and the removal efficiency of suspended solids (and associated metals) in the primary and secondary clarifiers. Metals which are most strongly associated with suspended solids are removed most effectively within WWTPs, while the suspended solids removal efficiency of a WWTP governs the overall metal removal efficiency.

Results of the modeling effort conducted in this work indicate that the potential for successful application of the process model approach, in which measurements of the suspended solids removal efficiencies are combined with an empirical metals distribution model, appears to have some promise for predicting metal/radionuclide reconcentration in sewage sludge at WWTPs. If further work can verify that this modeling approach is generally applicable for all or most WWTPs, then this approach could provide a basis for predicting the behavior of radioactive contamination in sewage sludge.

The process model tested in this study was developed by Patterson et al. This simple model combines the use of empirical descriptions of the distribution of metals between the solid and liquid phases with measurements of VSS removal efficiencies to determine metal removal efficiencies in WWTPs. If the metal/radionuclide distribution parameters are known, the concentration of metal/radionuclides in the sludge can be determined from the total metal/radionuclide concentrations and VSS concentrations in the WWTP influent and the VSS removal efficiencies in the primary and secondary clarifiers. Further analyses suggest that a simple K_d approach to describe the distribution of metal/radionuclides would be just as effective as the approach taken by Patterson et al., but would require one less fitting parameter. To apply the empirical process modeling approach to radionuclides, radionuclide specific K_d values are required. These parameters must be determined experimentally.

Although the results of our limited study indicate that empirical models hold some promise for successfully predicting metal/radionuclide behavior in WWTPs in some instances, their general applicability remains uncertain. Successful application of the empirical approach requires, in general, that 1) the reactions go to equilibrium (are fast relative to the unit process residence times), 2) the reactions are reversible, 3) the chemical environment in each wastewater unit process is uniform in space and time such that the assumed metals distribution between the solid and liquid phases remains constant, and 4) all of these conditions remain consistent for each WWTP to which the model is applied. At this point, the degree to which these conditions are universally and consistently applicable is unclear because only the Easterly Plant case was studied and the degree to which the previously mentioned conditions are true is poorly understood. To determine the limitations of the approach, a number of sewage treatment plants should be systematically studied in detail. A better knowledge of the mechanistic details governing the interactions between the metals/radionuclides and the suspended solids is also required to determine if the simplifying assumptions made in the empirical modeling approach are valid.

6 Mechanisms and Modeling

While the above empirical approach may prove to be adequate for specific sewage treatment processes (that is, microbial processes versus chemical/physical processes), a more rigorous and scientifically credible technique such as the approach used in the CRAS Model would prove more viable. Because CRAS is based on fundamental mechanistic principles, it has the capability to be universally applicable for all

WWTPs under widely varying conditions. This is because the input data are mechanistically based and are able to account for the effects of changing chemical and physical conditions. However, because the required data for the radionuclides of interest are not currently available, use of this approach is not possible at this time.

7 Conclusions

The objectives of this study were to 1) assess whether radioactive materials that are released to sanitary sewer systems undergo significant reconcentration within the WWTPs and 2) determine the physical and/or chemical processes that may result in their reconcentration within the WWTPs. The results of this study were intended to assist us in developing strategies for assessing whether the NRC sanitary sewer disposal regulations are needed. This one-year study attempted to address these objectives by collecting information and data from the open literature, NRC reports, EPA surveys, licensees that discharge radioactive materials to sanitary sewer systems, and WWTPs that are impacted by these discharges.

A review of the literature clearly demonstrated that radioactive materials discharged to sanitary sewer systems are reconcentrated in sludge produced as a result of wastewater treatment (Chapters 3 and 4). Reconcentration can be described as a two-stage process. Initial reconcentration occurs as a result of primary and/or secondary treatment (Chapter 2) where physical/chemical processes remove radioactive materials from sewage as the sewage is changed to sludge. Secondary reconcentration, a purely physical phenomenon, occurs as a result of sludge handling techniques (that is, anaerobic digestion, dewatering, stabilization, incineration). Reconcentration of radioactive materials occurs by reduction of the solids to solution ratio; that is, increasing the density of the solid phase without loss of radioactive material. The sludge incineration process is by far the greatest reconcentration step since the mass of the sludge is greatly reduced as a result of water removal and combustion.

The degree to which a given radionuclide is reconcentrated during the initial phase depends on 1) the partitioning of the radionuclide between the suspended solids and the aqueous (dissolved) phase, 2) the concentration of suspended solids, 3) the suspended solids removal efficiency, 4) the degree to which the

dissolved radionuclide is partitioned to solids during primary and secondary treatment, and 5) the wastewater treatment processes used. Underlying these five points are fundamental physical/chemical processes including 1) aqueous and solid phase complexation of radionuclides, 2) microbial and/or chemical additive (that is, inorganic coagulants) adsorption and absorption of radionuclides, and 3) chemical speciation (including oxidation-reduction). Quantitatively, these processes are dictated by 1) the chemical composition of the suspended solids and dissolved species (organic and inorganic), 2) the chemical form (and changes in form) of the radionuclide during wastewater treatment, and 3) the wastewater treatment processes.

Currently, 10 CFR 20.2003 states that "Disposal by release into sanitary sewerage may occur if the material is readily soluble (or is readily dispersible biological material) in water...". Because of the difficulty in determining or defining solubility, NRC has suggested that licensees calculate or determine the solubility product (K_{sp} ; discussed in Section 3.3) for their discharge, or if this is not possible, utilize filtration as an operational definition for determining if suspended radioactive material is present in the waste stream (NRC 1994). At present, filtration by a 0.45- μm pore-size filter is often utilized. However, neither of these techniques guarantee that reconcentration during wastewater treatment will not occur.

Assuming similar wastewater and treatment conditions, reconcentration is dictated by the partitioning of radioactive materials between the aqueous and settleable solid phases. For instance, essentially all the dissolved ^{241}Am and ^{232}Th entering a WWTP would likely partition to the solid phase. Conversely, little of the dissolved ^{131}I and $^{99\text{m}}\text{Tc}$ would likely partition to the solid phase. Thus, there is a much greater likelihood that ^{241}Am and ^{232}Th would reconcentrate in sewage sludge than ^{131}I and $^{99\text{m}}\text{Tc}$. In this example, another important parameter controlling radionuclide reconcentration in sewage sludge is the half-life of the radionuclide. Although $^{99\text{m}}\text{Tc}$ and ^{131}I may constitute

7 Conclusions

over 90 percent of the radioactivity in many wastewater streams, their very short half-lives (nine hours and eight days, respectively; Table 4.1) greatly reduce their presence as a function of time. Americium-131, ^{232}Th , and ^{238}U have very long half-lives (greater than 400 years) and their presence will not diminish appreciably as a function of time.

Reconcentration of metals/radionuclides not associated with suspended solids (dissolved) is unlikely to occur during primary treatment. For example, removal efficiencies for the truly soluble Co species (free metal or complex) are < 1 percent during primary treatment (Section 4.4). Reconcentration during secondary treatment has been suggested to occur depending on the metal/radionuclide and the secondary treatment process and conditions, but neither the mechanism(s) or unit process(s) involved are understood in a quantitative manner.

There are no studies in the open literature specifically evaluating the effects of different unit processes on radionuclide reconcentration. Qualitatively it may be inferred from existing models (Chapter 6) and metal reconcentration studies (Chapters 3, 4, and 5) that radionuclide reconcentration is affected by the type of unit process in a WWTP. There is a dearth of specific quantitative information, however, on the effectiveness of different processes to reconcentrate dissolved and settleable solid-associated radioactive materials. For instance, suspended- and attached-growth (Section 2.3) secondary treatment processes may differ considerably in their reconcentration abilities. In addition, little information concerning tertiary treatment processes (Section 2.4) and reconcentration of radionuclides was found in the literature and none of the WWTPs investigated used tertiary treatment for toxic compound removal.

To understand and quantify the reconcentration of radionuclides in sewage sludge, the NRC identified several WWTPs to be used as case studies of radioactive materials released to sanitary sewer systems and the concentration of these materials in processed sewage sludge (Chapter 5). Quantitative mass balance and process analysis of WWTP unit operations and processes were attempted. The hypotheses behind these investigations were twofold: 1) the most easily determined factor for metals removal is the removal efficiency of an entire plant (the difference between influent and effluent masses

divided by the influent mass), and hence, this removal efficiency potentially could be used as a metal reconcentration factor; and 2) for radionuclides, where often only licensee discharge and total activity in the sludge was known, mass balance calculations could yield an effective estimate of a reconcentration factor. The latter hypothesis was based on the belief that, ideally, the mass of radionuclide discharged by a licensee(s) should be greater than the mass of radionuclide determined in the sludge and be a function of the radionuclide's propensity to associate with the sludge (that is, a reconcentration factor).

Metal removal efficiencies calculated for the WWTPs discussed in the present study vary greatly day to day. Yearly average removal efficiencies for Zn, Cr, and Ni appear to be very similar across the WWTPs studied; hence, average values may be useful as rough estimates of overall reconcentration factors for contaminants present on a daily basis. Still, the usefulness of removal efficiencies in determining the ability of radionuclides to reconcentrate is questioned because radionuclides are typically discharged intermittently and it is unclear how this would affect an averaged removal efficiency.

Mass balance calculations for the metals Cr, Ni, and Zn were shown to be very reasonable. However, this resulted from our being able to balance the removal to sludge (based on influent-effluent concentrations) with that found in the sludge. Even with this level of data completeness, short-term balances were often poor; as the time span over which the balance was performed increased, the mass balance became more accurate. This time dependence results from the difference in residence times for sludge versus the aqueous phase in WWTPs. Since this lag time is not constant, it is essentially impossible to relate sludge metal masses to particular daily events of influent metal removal masses.

Mass balance calculations for radionuclides based on licensee discharge data and WWTP sludge data were not shown to be reliable. Generally, the release data grossly underestimated what was found in the sludge. It was uncommon to find any agreement between the licensee(s) discharge and sludge mass balance. These disparities between licensee discharge and sludge content are centered around the fact that the data used in this study were collected to address regulatory concerns, not to perform mass balance calculations.

The U mass balance for Oak Ridge is a good example of this point. The monitoring data of Y-12 discharge were reasonable enough to determine that discharge to the Oak Ridge sanitary sewer systems were well below DOE guidelines (and for that matter below NRC guidelines), but were almost useless in attempting a U mass balance. Another problem associated with using only licensee discharge data is that nonpoint discharge (that is, release to sewers from background sources) can not be taken into account. Also, little is known about the quantity of material lost in the sewer line during transport to the WWTP and this may impact the amount of a radionuclide observed at the headworks of a WWTP. For regulatory purposes, a single monthly grab sample may be sufficient, but more sophisticated sampling techniques and procedures are needed to address the objectives of this study. If the licensee data collected at Oak Ridge for U, Co, and Cs were backed up by data similar to that obtained for Zn, Ni, and Cr (that is, influent/effluent data), a clearer picture of radionuclide behavior in WWTPs and associated sewer lines could be drawn.

Unfortunately, there is very limited data currently available or collected during WWTP investigations (Chapter 5) that could be used to make generic quantitative calculations of the potential for radionuclide reconcentration. It is clear, however, that information garnered from studying licensee radionuclide discharge records and sludge composition will not yield sufficient data to address the concern of radionuclide reconcentration in a quantitative manner for an entire WWTP, let alone specific unit processes.

Although the results of our limited modeling study indicate that empirical models hold some promise for successfully predicting metal/radionuclide behavior in WWTPs in some instances, their general applicability remains uncertain (Chapter 6). To determine the limitations of the approach, a number of sewage

treatment plants should be systematically studied in detail. A better knowledge of the mechanistic details governing the interactions between the metals/radionuclides and the suspended solids is also required to judge if the simplifying assumptions made in the empirical modeling approach are valid. If further work can verify that this modeling approach is generally applicable for all or most WWTPs, then this approach could provide a basis for regulatory rule making designed to control radioactive contamination in sewage sludge.

While the above empirical approach may prove to be adequate for specific sewage treatment processes (that is, microbial versus chemical/physical processes), a more rigorous and scientifically credible approach would be one based on fundamental mechanistic principles. This approach would be universally applicable for all WWTPs under widely varying conditions because the input data would be mechanistically based and capable of accounting for changing chemical and physical conditions. However, because the required data for the radionuclides of interest are not currently available, use of this approach is not possible at this time.

With the data and models currently available, it is not possible to quantitatively determine the physical and chemical processes that cause reconcentration or to calculate, *a priori*, reconcentration factors for specific WWTP unit processes or WWTPs in general. Clearly, the partitioning between the aqueous and solid phase and the removal of settleable solids play a dominant roll. Further, the effect of multiple licensees discharging to a single WWTP cannot be assessed using the currently available information. Therefore, the available data are not sufficient, in our opinion, to assess the adequacy of 10 CFR 202.003 in preventing occurrences of radionuclide concentrations in sewage sludge at levels which present undue risk to the public; nor is the available data sufficient to suggest strategies for changing 10 CFR 20.2003.

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Appendix A

Comparative Calculational and Perspective Tool

A.1 Background

In 1992 NUREG/CR-5814 was published. This report contained the results of a generic radiation pathway and exposure scenario study to examine the potential radiological hazard to the public resulting from exposure to radionuclides in sewage sludge during its treatment and disposal (Kennedy et al. 1992). The radiation exposure pathways used were the routes through which individuals may be exposed to radiation or radioactive materials as a result of radionuclides discharged into a sanitary sewer system. A collection of exposure pathways was used to construct eleven credible scenarios that were designed to be conceptual representations of patterns of human activity (actions, events, or lifestyles) associated with different sewer system operations and sludge treatment and disposal activities that result in radiation exposures to selected individuals or groups of individuals. The scenarios, assumptions, and parameter values for that generic study were selected in a manner to produce prudently conservative (not worst-case) estimates of individual radiation doses.

The authors of the 1992 generic sewer study recognized that, even though extensive data was not available, radionuclides could be reconcentrated in a WWTP anywhere for 0 to 100 percent. However, the generic nature of that study precluded the consideration of key items, such as partitioning of the various radionuclides between the sludge and liquid effluent phases during sewage treatment. As a result, it was assumed in that study that 100 percent of the released radionuclide activity 1) reached the WWTP, 2) remained associated with the sludge solids, and 3) was contained in the liquid effluent of the WWTP. The authors recognized that this approach of accounting for the total activity inventory in both sludge and liquid effluent would likely provide overestimates of the potential doses.

From this study, two major points were recognized:

1) little if any data exists for determining the

percentage of the discharged radionuclides that reach the headworks of a WWTP, and 2) radionuclide reconcentration in sludge generated at WWTPs is not an all-or-none phenomenon for most, if not all, radionuclides. For example, Stetar et al. 1993 have shown that approximately 30 percent of radiocobalt (as ^{58}Co) that enters the Oak Ridge WWTP will ultimately be partitioned with the sludge solids. As shown in Chapters 4 and 5, most radionuclides reconcentrate in WWTPs from 0 to 100 percent depending on the radionuclide and the chemical environment of the various WWTP processes used. In some cases, greater than 100 percent of the activity discharged may be observed in the sludge, presumably due to influx of the radionuclide from natural sources or from contaminated soil surrounding sewer lines.

A.2 Calculational Tool Description

At the request of the NRC, PNL developed a calculational and perspective tool, based on the models and assumptions used in NUREG/CR-5814, which is to serve as an aid to rapid understanding of the relationship between the amount of various radionuclides released by a NRC licensee into a sanitary sewer system and the magnitude of potential exposures that may be received by an individual. The calculational and perspective tool, called *SEWRDOSE* (Version 1.1), is presented as a spreadsheet application developed using the commercial software package, "Quattro Pro for Windows" (Version 5.0). Six of the original eleven scenarios (scenarios 2, 3, 4, 5, 7, and 9) from NUREG/CR-5814 were chosen for inclusion in the tool. These scenarios describe activities and exposure pathways for calculation of potential radiation doses for the following: a WWTP sludge process operator, a member of the public involved in activities around the river used for the WWTP liquid effluent discharge, a WWTP incinerator operator, a member of the public exposed to sludge incinerator effluent to the air, a member of the public involved in sludge application to agricultural soil, and

Appendix A

a landfill equipment operator at a landfill that receives sludge or sludge incinerator ash. The radionuclides chosen by the NRC for inclusion in the tool were: ^{241}Am , ^{60}Co , ^{54}Mn , ^{90}Sr , ^{131}I , ^{137}Cs , ^{192}Ir , ^{228}Th , and ^{238}U .

The same default parameter values used in NUREG/CR-5814 were used as the default parameter values in the SEWRDOSE tool. These default parameter values, as well as the range of values considered in NUREG/CR-5814 are shown in Figure A.1, which is the input page for SEWRDOSE. As in NUREG/CR-5814, the SEWRDOSE tool uses the assumptions that discharged radionuclide activity 1) reaches the WWTP, 2) remains associated with the sludge solids, and 3) is contained in the liquid effluent of the WWTP. The doses resulting from use of the SEWRDOSE tool will be the same as those reported in NUREG/CR-5814 (Kennedy et al. 1992) when the default parameter values are used. Any of the parameter values shown on the input page can be changed by the user and will result in changes in the reported potential doses from exposure incurred in the various exposure scenarios.

In the SEWRDOSE tool, the potential doses resulting from calculations using the user-selected parameter values are presented in several different ways. First, for each radionuclide considered, a flow diagram of the resulting doses for each of the six scenarios is presented. As shown in Figure A.2 using ^{60}Co as the example, a $3.7\text{E}+07$ Bq/y (1 Ci/y) release into the sanitary sewer system, would potentially result in a dose of 3.6 mSv/Y (360 mrem/y) to a WWTP sludge process operator (Scenario #2). Similar to the generic study (Kennedy et al. 1992), the SEWRDOSE tool was developed using the assumptions that 100 percent of the released radionuclide activity 1) reached the WWTP, 2) remained associated with the sludge solids, and 3) was contained in the liquid effluent of the WWTP. The potential doses resulting from a $3.7\text{E}+07$ Bq/y (1 Ci/y) release of ^{60}Co for the remaining scenarios, numbers 3, 4, 5, 7, and 9, are also depicted on the flow diagrams (Figure A.2).

The resulting doses are also presented in several different tabular formats. The first (Figure A.3) format shows the resulting doses, by scenario, for each of the nine radionuclides. For comparison, the doses are shown for calculations using the default

input parameter values and those using the user-selected input values. The second (Figure A.4) format presents the doses for each exposure pathway for the six scenarios and nine radionuclides when the user-selected input parameter values were used in the calculations. The last tabular format used (Figure A.5) presents a summary of the doses for each exposure pathway for the six scenarios, segregated by radionuclide. As mentioned above, the resulting doses will be the same as those reported in NUREG/CR-5814 (Kennedy et al. 1992) when the default parameter values are used.

The SEWRDOSE tool also provides a summary of equations and conversions (multipliers) used to obtain the various doses. The equations are those performed within the spreadsheet to calculate the values for radioactivity inventory, environmental media concentrations, and effective external and internal exposure times, using the results presented in NUREG/CR-5814 as a starting point. The calculations performed in the SEWRDOSE tool by no means replace the complex calculational methods used in NUREG/CR-5814, which are described in detail in Section A.3.

A.2.1 Example Calculation Using the SEWRDOSE Tool

As an example of how the SEWRDOSE tool can be used, discharge of ^{60}Co for the year 1990 at the Oak Ridge WWTP is used to calculate potential radiation doses for the various scenarios. This WWTP does not incinerate the sludge generated during treatment; thus, Scenarios 4, 5, and 9 do not apply in this example. As mentioned above, the generic nature of the 1992 NUREG/CR-5814 study precluded the use of specific information regarding radionuclide reconcentration during wastewater treatment. Thus, the SEWRDOSE tool, which was developed using the same assumptions as in NUREG/CR-5814, assumes that 100 percent of discharged radionuclides will remain associated with the sludge and 100 percent will also be contained in the liquid effluent. This approach for accounting for the total activity inventory in both sludge and liquid effluent may overestimate the potential doses resulting from the various exposure scenarios.

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— INPUT PAGE —

MAIN MENU

User input required for parameters listed below. Use scroll bars/arrow keys to see rest of page.

The highlighted "user input" values shown below are those that will be used in the dose calculations.

As a new value is entered, the resulting doses are reflected in both the flow diagrams and the summary tables.

		DEFAULTS	RANGE*	USER INPUT	PARAMETER
GENERAL	Activity Release Rate (Ci/yr):	1.0	—	1.0E+00	REL
	Pre-WWTP Holdup Fraction:	0.0	0 - 1	0.0	PSHF
	Capacity of the WWTP (MG/d):	5.0	1 - 50	5.0	STPCAP
	Sludge Production Rate (lb/MG):	2064	1650 - 4780	2064	SPRL
	Dry-to-Wet Fraction:	0.3	0.1 - 0.4	0.30	DWF
SCENARIO #2 STP Worker	Decay Time within Scenario #2 (d):	3.0	3 - 50	3.0	DTIM2
	External Exposure Time in Scenario #2:	1500	500 - 1750	1500	EET2
	Internal Exposure Time in Scenario #2:	1500	500 - 1750	1500	IET2
	Respirable Fraction in Scenario #2:	0.2	0 - 1	0.2	SRF2
SCENARIO #3 River Discharge	Decay Time within Scenario #3 (d):	0.3	0.3 - 1	0.30	DTIM3
	River Flow Rate (cubic m/sec):	100	20 - 3000	100	RIVFLO
	Fraction of WWTP Effluent to River:	1.0	0 - 1	1.0	FTR
	External Exposure Time in Scenario #3:	1800	100 - 4400	1800	EET3
	Internal Exposure Time in Scenario #3:	1800	100 - 4400	1800	IET3
	Respirable Fraction in Scenario #3:	0.2	0 - 1	0.2	SRF3
SCENARIO #4 Incinerator Worker	Decay Time within Scenario #4 (d):	3.0	3 - 50+	3.0	DTIM4
	Incin. Reduction Fract.(lb ash/lb sludge):	0.3	0.23 - 0.35	0.3	INCRF
	Fraction of WWTP Effluent to Sludge:	1.0	0 - 1	1.0	FTS
	External Exposure Time in Scenario #4:	1000	100 - 2000	1000	EET4
	Internal Exposure Time in Scenario #4:	1000	100 - 2000	1000	IET4
SCENARIO #5 Incinerator Air Effluent	Respirable Fraction in Scenario #4:	0.5	0 - 1	0.5	SRF4
	Decay Time within Scenario #5 (d):	3.0	3 - 60+	3.0	DTIM5
	External Exposure Time in Scenario #5:	1800	100 - 4000	1800	EET5
	Internal Exposure Time in Scenario #5:	1800	100 - 4000	1800	IET5
	Respirable Fraction in Scenario #5:	1.0	0 - 1	1.0	SRF5
	Fraction of Incin. Product as Air Effluent:				(RNRELI)
	Am-241	0.005	0 - 1	0.005	RNRELa
	Co-60	0.005	0 - 1	0.005	RNRELb
	Mn-54	0.005	0 - 1	0.005	RNRELc
	Sr-90	0.005	0 - 1	0.005	RNRELd
	I-131	0.100	0 - 1	0.100	RNRELe
	Cs-137	0.005	0 - 1	0.005	RNRELf
	Ir-192	0.005	0 - 1	0.005	RNRELg
	Th-228	0.005	0 - 1	0.005	RNRELh
U-238	0.005	0 - 1	0.005	RNRELk	

Figure A.1 Input page from the SEWRDOSE calculational tool

-- INPUT PAGE (cont.)--

SCENARIO #7	Decay Time within Scenario #7 (d):	12.0	0 - 50	12.0	DTIM7
Sludge Applied to	Sludge Land Application Rate (Mg/ha):	15.0	2 - 35	15.0	SLAR
Agricultural Soil	External Exposure Time in Scenario #7:	2000	500 - 2000	2000	EET7
	Internal Exposure Time in Scenario #7:	2000	500 - 2000	2000	IET7
	Respirable Fraction in Scenario #7:	0.2	0 - 1	0.2	SRF7
SCENARIO #9	Decay Time within Scenario #9 (d):	3.5	2 - 20	3.5	DTIM9
Landfill of	Fraction of Ash as Dry:	0.9	0.8 - 0.99	0.9	DRYASH
Incinerator Ash	Landfill Dilution Factor:	0.1	0.001 - 1	0.1	LFDF
	External Exposure Time in Scenario #9:	1000	100 - 2000	1000	EET9
	Internal Exposure Time in Scenario #9:	1000	100 - 2000	1000	IET9
	Respirable Fraction in Scenario #9:	0.2	0 - 1	0.2	SRF9

*(Range of values considered in NUREG/CR-5814 [Kennedy, et al. 1992])

Figure A.1 (contd)

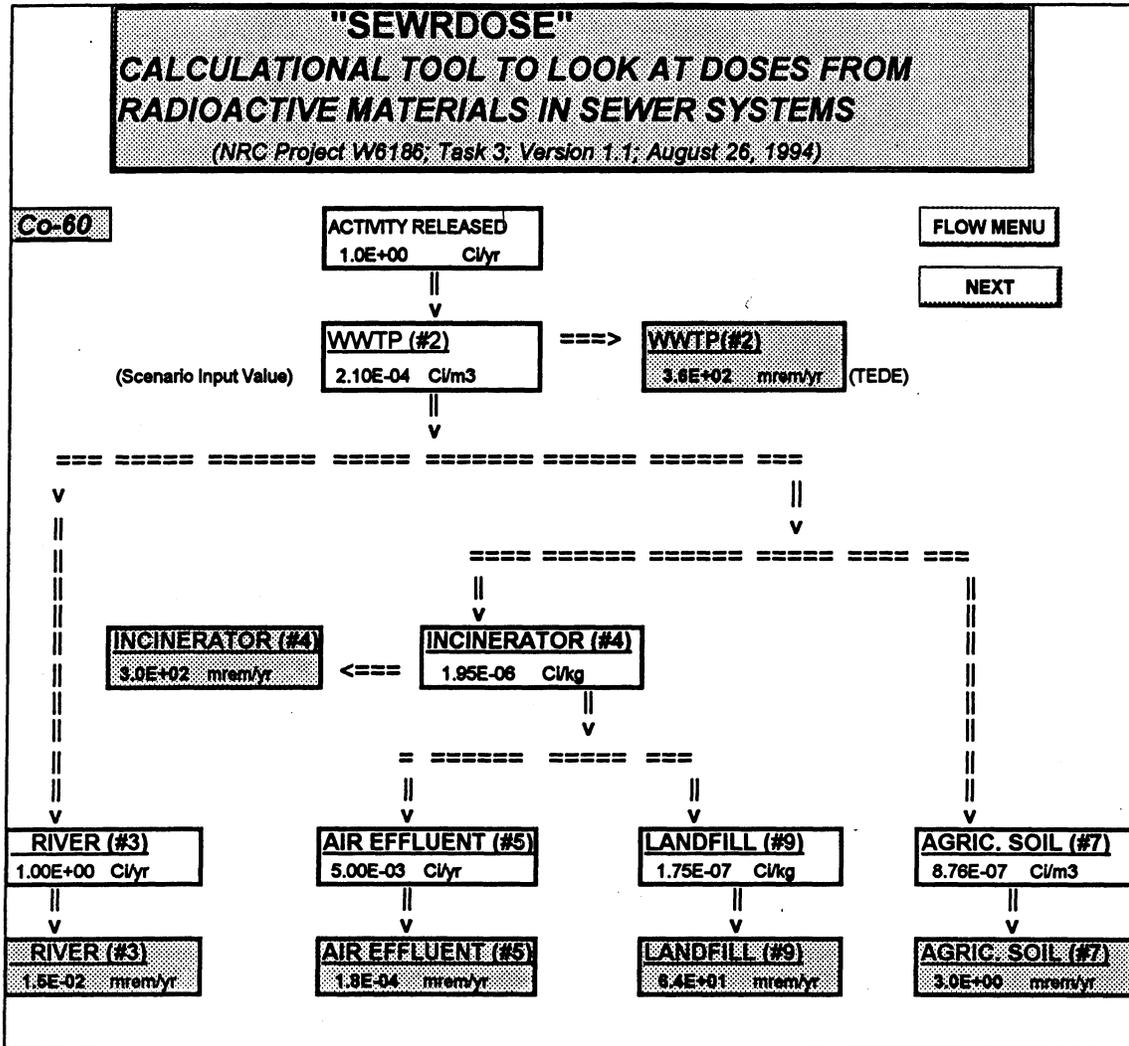


Figure A.2 Flow diagram for doses for six different scenarios calculated for ⁶⁰Co using the SEWRDOSE calculational tool

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SUMMARY OF DOSES, BY SCENARIO, RESULTING FROM PARAMETER VALUES CHANGES
(For listing of parameter values used, return to input page)

MAIN MENU

SMY MENU

DOSES PER 1 Ci/Yr RELEASE RATE (TEDE, mrem/yr)

NUCLIDE	DOSES PER 1 Ci/Yr RELEASE RATE (TEDE, mrem/yr)								
	SCENARIO #2	SCENARIO #3	SCENARIO #4	SCENARIO #5	SCENARIO #7	SCENARIO #9	SCENARIO #9	SCENARIO #9	SCENARIO #9
Am-241	1.9E+01	9.6E-01	3.4E+02	2.7E-01	5.5E-01	3.1E+00	3.1E+00	3.1E+00	3.1E+00
Co-60	3.8E+02	1.5E-02	3.0E+02	1.8E-04	3.0E+00	6.4E+01	6.4E+01	6.4E+01	6.4E+01
Mn-54	1.1E+02	3.3E-03	9.8E+01	1.8E-05	1.1E+00	2.1E+01	2.1E+01	2.1E+01	2.1E+01
Si-90	2.3E-02	3.0E-02	1.6E-01	1.2E-04	1.7E+01	4.3E-03	4.3E-03	4.3E-03	4.3E-03
I-131	3.9E+01	8.5E-03	3.6E+01	3.4E-04	3.0E-01	7.3E+00	7.3E+00	7.3E+00	7.3E+00
Cs-137	8.0E+01	1.6E+00	7.1E+01	3.1E-05	7.6E-01	1.5E+01	1.5E+01	1.5E+01	1.5E+01
Ir-192	1.2E+02	1.2E-03	1.1E+02	2.2E-05	1.0E+00	2.2E+01	2.2E+01	2.2E+01	2.2E+01
Th228	1.3E+01	1.8E-01	2.5E+02	2.0E-01	1.8E-01	2.2E+00	2.2E+00	2.2E+00	2.2E+00
U238	4.8E+00	5.3E-03	9.2E+01	7.5E-02	2.5E-02	6.1E-01	6.1E-01	6.1E-01	6.1E-01

DOSES FOR NEW PARAMETER VALUES CHOSEN (TEDE, mrem/yr)

(See INPUT PAGE for parameter values used)

NUCLIDE	DOSES FOR NEW PARAMETER VALUES CHOSEN (TEDE, mrem/yr)								
	SCENARIO #2	SCENARIO #3	SCENARIO #4	SCENARIO #5	SCENARIO #7	SCENARIO #9	SCENARIO #9	SCENARIO #9	SCENARIO #9
Am-241	1.9E+01	9.6E-01	3.4E+02	2.7E-01	5.5E-01	3.1E+00	3.1E+00	3.1E+00	3.1E+00
Co-60	3.8E+02	1.5E-02	3.0E+02	1.8E-04	3.0E+00	6.4E+01	6.4E+01	6.4E+01	6.4E+01
Mn-54	1.1E+02	3.3E-03	9.8E+01	1.8E-05	1.1E+00	2.1E+01	2.1E+01	2.1E+01	2.1E+01
Si-90	2.3E-02	3.0E-02	1.6E-01	1.2E-04	1.7E+01	4.3E-03	4.3E-03	4.3E-03	4.3E-03
I-131	3.9E+01	8.5E-03	3.6E+01	3.4E-04	3.0E-01	7.3E+00	7.3E+00	7.3E+00	7.3E+00
Cs-137	8.0E+01	1.6E+00	7.1E+01	3.1E-05	7.6E-01	1.5E+01	1.5E+01	1.5E+01	1.5E+01
Ir-192	1.2E+02	1.2E-03	1.1E+02	2.2E-05	1.0E+00	2.2E+01	2.2E+01	2.2E+01	2.2E+01
Th228	1.3E+01	1.8E-01	2.5E+02	2.0E-01	1.8E-01	2.2E+00	2.2E+00	2.2E+00	2.2E+00
U238	4.8E+00	5.3E-03	9.2E+01	7.5E-02	2.5E-02	6.1E-01	6.1E-01	6.1E-01	6.1E-01

Figure A.3 From the SEWRDOSE calculational tool, a summary page of radiation doses, separated by scenario

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SUMMARY OF DOSES, BY EXPOSURE PATHWAY, RESULTING FROM PARAMETER VALUES CHANGES

SCENARIO-> NUCLIDE	#2 INHAL. DOSE	#3 INHAL. DOSE	#4 INHAL. DOSE	#5 INHAL. DOSE	#7 INHAL. DOSE	#9 INHAL. DOSE	MAIN MENU
Am-241	1.8E+01	1.7E-05	3.4E+02	2.7E-01	6.5E-02	3.0E+00	
Co-60	8.1E-03	0.0E+00	1.6E-01	1.2E-04	3.0E-05	1.4E-03	
Mn-54	2.5E-04	0.0E+00	4.9E-03	3.9E-06	9.3E-07	4.4E-05	
Sr-90	8.6E-03	0.0E+00	1.6E-01	1.2E-04	3.0E-05	1.4E-03	
I-131	9.6E-04	0.0E+00	1.9E-02	2.9E-04	1.6E-06	1.6E-04	
Cs-137	1.1E-03	0.0E+00	2.1E-02	1.7E-05	4.1E-06	1.9E-04	
Ir-192	1.0E-03	0.0E+00	2.0E-02	1.6E-05	3.6E-06	1.7E-04	
Th228	1.3E+01	1.0E-05	2.5E+02	2.0E-01	4.5E-02	2.2E+00	
U238	4.8E+00	4.5E-06	9.2E+01	7.5E-02	1.8E-02	8.1E-01	

SCENARIO-> NUCLIDE	#2 INGEST. DOSE	#3 INGEST. DOSE	#4 INGEST. DOSE	#5 INGEST. DOSE	#7 INGEST. DOSE	#9 INGEST. DOSE	SMY MENU
Am-241	0.0E+00	9.6E-01	0.0E+00	0.0E+00	4.8E-01	0.0E+00	
Co-60	0.0E+00	1.2E-02	0.0E+00	0.0E+00	6.2E-02	0.0E+00	
Mn-54	0.0E+00	2.6E-03	0.0E+00	0.0E+00	1.2E-01	0.0E+00	
Sr-90	0.0E+00	3.0E-02	0.0E+00	0.0E+00	1.7E+01	0.0E+00	
I-131	0.0E+00	8.5E-03	0.0E+00	0.0E+00	1.4E-01	0.0E+00	
Cs-137	0.0E+00	1.6E+00	0.0E+00	0.0E+00	6.5E-02	0.0E+00	
Ir-192	0.0E+00	9.0E-04	0.0E+00	0.0E+00	2.8E-02	0.0E+00	
Th228	0.0E+00	1.8E-01	0.0E+00	0.0E+00	1.4E-01	0.0E+00	
U238	0.0E+00	5.3E-03	0.0E+00	0.0E+00	7.2E-03	0.0E+00	

SCENARIO-> NUCLIDE	#2 EXT'L DOSE	#3 EXT'L DOSE	#4 EXT'L DOSE	#5 EXT'L DOSE	#7 EXT'L DOSE	#9 EXT'L DOSE
Am-241	5.4E-01	5.5E-06	5.3E-01	1.1E-07	5.2E-03	1.2E-01
Co-60	3.6E+02	2.9E-03	3.0E+02	5.8E-05	2.9E+00	6.4E+01
Mn-54	1.1E+02	7.1E-04	9.8E+01	1.4E-05	9.4E-01	2.1E+01
Sr-90	1.4E-02	7.8E-06	1.3E-03	1.5E-07	1.3E-04	2.9E-03
I-131	3.9E+01	1.7E-05	3.6E+01	4.6E-05	1.6E-01	7.3E+00
Cs-137	8.0E+01	7.3E-04	7.1E+01	1.4E-05	6.9E-01	1.5E+01
Ir-192	1.2E+02	3.2E-04	1.1E+02	6.1E-06	9.8E-01	2.2E+01
Th228	1.3E-01	1.7E-03	1.3E-01	3.2E-05	1.2E-03	2.7E-03
U238	2.9E-03	2.6E-05	3.2E-03	5.2E-07	3.2E-05	6.9E-04

SCENARIO-> NUCLIDE	#2 TEDE (mrem/yr)	#3 TEDE (mrem/yr)	#4 TEDE (mrem/yr)	#5 TEDE (mrem/yr)	#7 TEDE (mrem/yr)	#9 TEDE (mrem/yr)
Am-241	1.9E+01	9.6E-01	3.4E+02	2.7E-01	5.5E-01	3.1E+00
Co-60	3.6E+02	1.5E-02	3.0E+02	1.8E-04	3.0E+00	6.4E+01
Mn-54	3.6E+02	3.3E-03	9.8E+01	1.8E-05	1.1E+00	2.1E+01
Sr-90	2.3E-02	3.0E-02	1.6E-01	1.2E-04	1.7E+01	4.3E-03
I-131	3.9E+01	8.5E-03	3.6E+01	3.4E-04	3.0E-01	7.3E+00
Cs-137	8.0E+01	1.6E+00	7.1E+01	3.1E-05	7.6E-01	1.5E+01
Ir-192	1.2E+02	1.2E-03	1.1E+02	2.2E-05	1.0E+00	2.2E+01
Th228	1.3E+01	1.8E-01	2.5E+02	2.0E-01	1.9E-01	2.2E+00
U238	4.8E+00	5.3E-03	9.2E+01	7.5E-02	2.5E-02	8.1E-01

Figure A.4 From the SEWRDOSE calculational tool, a summary page of radiation doses, separated by exposure pathway

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(NRC Project W6186, Task 3, Version 1.1; August 26, 1994)

SUMMARY OF DOSES, BY RADIONUCLIDE, RESULTING FROM PARAMETER VALUES CHANGES

MAIN MENU SMY MENU

Nuclide	DOSES PER 1 Ci/yr RELEASE RATE (mrem/yr)									DOSES FOR NEW PARAMETER VALUES CHOSEN (mrem/yr)								
	Scenario	INHALATIO	INGESTION	EXTERNAL	TEDE	Scenario	INHALATIO	INGESTIO	EXTERNA	TEDE	Scenario	INHALATIO	INGESTIO	EXTERNA	TEDE			
Co-60	#2	8.1E-03	0.0E+00	3.80E+02	3.8E+02	#2	8.1E-03	0.0E+00	0.0E+00	3.8E+02	3.8E+02	3.8E+02	3.8E+02	3.8E+02	3.8E+02			
Co-60	#3	0.0E+00	1.2E-02	2.90E-03	1.8E-02	#3	0.0E+00	1.2E-02	1.2E-02	2.9E-03	2.9E-03	1.8E-02	1.8E-02	1.8E-02	1.8E-02			
Co-60	#4	1.6E-01	0.0E+00	3.00E+02	3.0E+02	#4	1.6E-01	0.0E+00	0.0E+00	3.0E+02	3.0E+02	3.0E+02	3.0E+02	3.0E+02	3.0E+02			
Co-60	#5	1.2E-04	0.0E+00	6.60E-05	1.8E-04	#5	1.2E-04	0.0E+00	0.0E+00	6.6E-05	6.6E-05	1.8E-04	1.8E-04	1.8E-04	1.8E-04			
Co-60	#7	3.0E-05	6.2E-02	2.90E+00	3.0E+00	#7	3.0E-05	6.2E-02	6.2E-02	2.9E+00	2.9E+00	3.0E+00	3.0E+00	3.0E+00	3.0E+00			
Co-60	#9	1.4E-03	0.0E+00	6.40E+01	6.4E+01	#9	1.4E-03	0.0E+00	0.0E+00	6.4E+01	6.4E+01	6.4E+01	6.4E+01	6.4E+01	6.4E+01			

(See INPUT PAGE for parameter values used)

Figure A.5 From the SEWRDOSE calculational tool, a summary page of radiation doses, separated by exposure pathway for ⁶⁰Co

The parameter values used for this example calculation (Figure A.6) were from information obtained from the Oak Ridge WWTP. The 1990 annual discharge rate of ^{60}Co to the Oak Ridge WWTP was reported to be $4.9\text{E}+07$ Bq/y or $1.3\text{E}-03$ Ci/y (Table 5.7). The output of the WWTP was taken to be 5.9 MGD. The dry-to-wet fraction was taken as 0.04, which was the annual average of the percent solids measured in the sludge prior to removal from the WWTP. The flow rate of the river into which liquid effluents are discharged was taken to be 0.03 cubic m/s (1 cubic ft/s) at low flow. The potential doses for the various exposure scenarios resulting from using these assumptions are shown in a flow diagram (Figure A.7) and a summary table (Figure A.8).

A.3 Calculational Methods Used in NUREG/CR-5814

NUREG/CR-5814, entitled *Evaluation of Exposure Pathways to Man from Disposal of Radioactive Materials Into Sanitary Sewer Systems* (Kennedy et al. 1992), presents potential doses to sewage treatment plant (STP) workers and affected members of the public that may have interactions with sewage sludge, STP liquid effluent, sewage incinerator air emissions, or ash from incinerated sewage sludge after radioactive materials are disposed of in a sanitary sewer system. Potential radiation doses related to these interactions were calculated using the GENII software system (Napier et al. 1988a and b) using scenarios designed to describe these interactions.

The equations presented here are abstracted from Chapter 4, "Mathematical Representations" in *GENII - The Hanford Environmental Radiation Dosimetry Software System, Volume 1: Conceptual Representation* (Napier et al. 1988a). Equations used from the GENII manual are referenced by equation number and document page number.

A.3.1 Calculation Methods

The models of exposure pathways in the GENII software system that were used to estimate potential doses to individuals from various exposure pathways

are presented below. The exposure scenarios are of two basic types: far-field and near-field. These are defined in the GENII documentation (Napier et al. 1988a, p. 2.1) as follows:

A far-field scenario is defined as one that determines the impact into a wide environment, such as releases from a stack to individuals or populations downwind. In a near-field scenario, the focus is on the doses an individual could receive at a particular location as a result of initial contamination or external sources, i.e., buried waste or contaminated soil.

Two scenarios in the 1992 generic sewer study are considered far-field scenarios. These are the STP Liquid Effluent Scenario (#3) and the Sludge Incinerator Effluent Scenario (#5). All other scenarios are near-field; that is, the contamination is localized in areas containing sludge or residue (ash) from incineration of sludge. Input concentrations used in the GENII dose calculations are addressed in Section A.3.2. For the far-field scenarios, transport of contaminants is described below. Note that the units expressed in the equations may differ from those in the input files since the GENII code performs unit conversions prior to the calculation of results.

A.3.1.1 Transport Calculations and Environmental Accumulation

The models for transport of contaminants by air and water and accumulation in the soil implemented in the GENII software system are described in the following sections. Note that the equation number and page number from the GENII manual are presented beside the equation number, where applicable.

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— INPUT PAGE —

MAIN MENU

User input required for parameters listed below. Use scroll bars/arrow keys to see rest of page.

The highlighted "user input" values shown below are those that will be used in the dose calculations.

As a new value is entered, the resulting doses are reflected in both the flow diagrams and the summary tables.

		DEFAULTS	RANGE*	USER INPUT	PARAMETER
GENERAL	Activity Release Rate (Ci/yr):	1.0	—	1.3E-03	REL
	Pre-WWTP Holdup Fraction:	0.0	0 - 1	0.0	PSHF
	Capacity of the WWTP (MG/d):	5.0	1 - 50	5.9	STPCAP
	Sludge Production Rate (lb/MG):	2064	1650 - 4780	580	SPRL
	Dry-to-Wet Fraction:	0.3	0.1 - 0.4	0.04	DWF
SCENARIO #2	Decay Time within Scenario #2 (d):	3.0	3 - 50	50.0	DTIM2
STP Worker	External Exposure Time in Scenario #2:	1500	500 - 1750	1750	EET2
	Internal Exposure Time in Scenario #2:	1500	500 - 1750	1750	IET2
	Respirable Fraction in Scenario #2:	0.2	0 - 1	0.2	SRF2
SCENARIO #3	Decay Time within Scenario #3 (d):	0.3	0.3 - 1	0.25	DTIM3
River Discharge	River Flow Rate (cubic m/sec):	100	20 - 3000	1	RIVFLO
	Fraction of WWTP Effluent to River:	1.0	0 - 1	0.0	FTR
	External Exposure Time in Scenario #3:	1800	100 - 4400	1800	EET3
	Internal Exposure Time in Scenario #3:	1800	100 - 4400	1800	IET3
	Respirable Fraction in Scenario #3:	0.2	0 - 1	0.2	SRF3
SCENARIO #4	Decay Time within Scenario #4 (d):	3.0	3 - 50+	0.0	DTIM4
Incinerator Worker	Incin. Reduction Fract.(lb ash/lb sludge):	0.3	0.23 - 0.35	0.0	INCRF
	Fraction of WWTP Effluent to Sludge:	1.0	0 - 1	0.0	FTS
	External Exposure Time in Scenario #4:	1000	100 - 2000	0	EET4
	Internal Exposure Time in Scenario #4:	1000	100 - 2000	0	IET4
	Respirable Fraction in Scenario #4:	0.5	0 - 1	0.0	SRF4
SCENARIO #5	Decay Time within Scenario #5 (d):	3.0	3 - 60+	0.0	DTIM5
Incinerator Air Effluent	External Exposure Time in Scenario #5:	1800	100 - 4000	0	EET5
	Internal Exposure Time in Scenario #5:	1800	100 - 4000	0	IET5
	Respirable Fraction in Scenario #5:	1.0	0 - 1	0.0	SRF5
	Fraction of Incin. Product as Air Effluent:				(RNRELi)
	Am-241	0.005	0 - 1	0.005	RNRELa
	Co-60	0.005	0 - 1	0.005	RNRELb
	Mn-54	0.005	0 - 1	0.005	RNRELc
	Sr-90	0.005	0 - 1	0.005	RNRELd
	I-131	0.100	0 - 1	0.100	RNRELe
	Cs-137	0.005	0 - 1	0.005	RNRELf
	Ir-192	0.005	0 - 1	0.005	RNRELg
	Th-228	0.005	0 - 1	0.005	RNRELh
	U-238	0.005	0 - 1	0.005	RNRELk

Figure A.6 Input page from the SEWRDOSE calculational tool showing assumptions based on the discharge of ^{60}Co to the Oak Ridge WWTP in 1990

--- INPUT PAGE (cont.)---

SCENARIO #7	Decay Time within Scenario #7 (d):	12.0	0 - 50	12.0	DTIM7
Sludge Applied †	Sludge Land Application Rate (Mg/ha):	15.0	2 - 35	15.0	SLAR
Agricultural Soil	External Exposure Time in Scenario #7:	2000	500 - 2000	2000	EET7
	Internal Exposure Time in Scenario #7:	2000	500 - 2000	2000	IET7
	Respirable Fraction in Scenario #7:	0.2	0 - 1	0.2	SRF7
SCENARIO #9	Decay Time within Scenario #9 (d):	3.5	2 - 20	0.0	DTIM9
Landfill of	Fraction of Ash as Dry:	0.9	0.8 - 0.99	0.0	DRYASH
Incinerator Ash	Landfill Dilution Factor:	0.1	0.001 - 1	0.0	LFDF
	External Exposure Time in Scenario #9:	1000	100 - 2000	0	EET9
	Internal Exposure Time in Scenario #9:	1000	100 - 2000	0	IET9
	Respirable Fraction in Scenario #9:	0.2	0 - 1	0.0	SRF9

* (Range of values considered in NUREG/CR-5814 [Kennedy, et al. 1992])

Figure A.6 (contd)

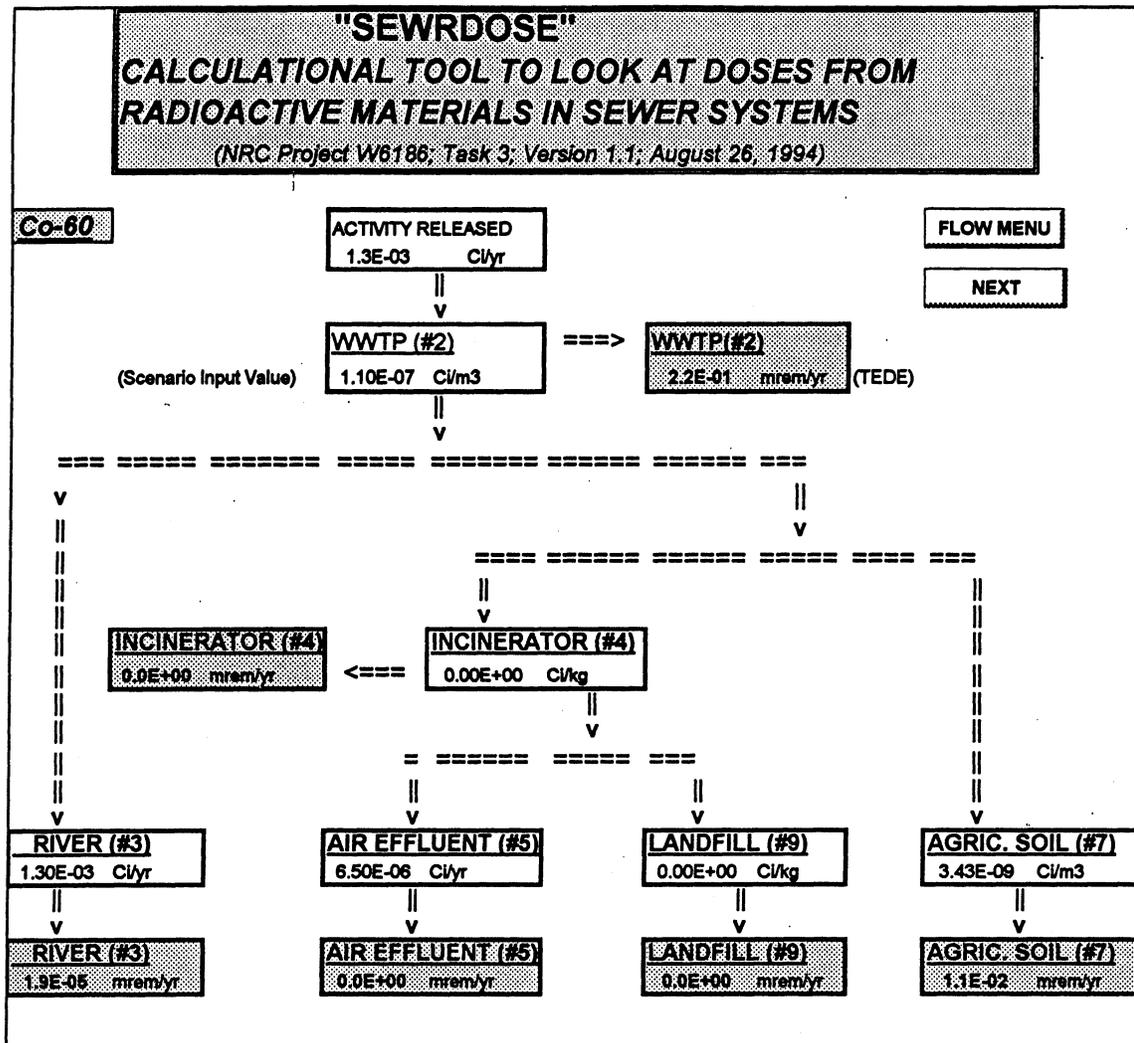


Figure A.7 Flow diagram for doses for six different scenarios calculated from the 1990 ⁶⁰Co discharge to the Oak Ridge WWTP ⁶⁰Co using the SEWRDOSE calculational tool

**"SEWRDOSE"
CALCULATIONAL TOOL TO LOOK AT DOSES FROM
RADIOACTIVE MATERIALS IN SEWER SYSTEMS**

(NRC Project W6186, Task 3, Version 1.1, August 26, 1984)

SUMMARY OF DOSES, BY RADIONUCLIDE, RESULTING FROM PARAMETER VALUES CHANGES

MAIN MENU SBY MENU

Co-60		DOSES PER 1 Ci/YR RELEASE RATE (mrem/yr) Co-60										DOSES FOR NEW PARAMETER VALUES CHOSEN (mrem/yr)			
		<i>(See INPUT PAGE for parameter values used)</i>													
Nuclide	Scenario	INHALATIO	INGESTION	EXTERNAL	TEDE	Scenario	INHALATIO	INGESTIO	EXTERNA	TEDE	Scenario	INHALATIO	INGESTIO	EXTERNA	TEDE
Co-60	#2	8.1E-03	0.0E+00	3.80E+02	3.6E+02	#2	4.9E-06	0.0E+00	2.2E-01	2.2E-01	#2	4.9E-06	0.0E+00	2.2E-01	2.2E-01
Co-60	#3	0.0E+00	1.2E-02	2.90E-03	1.6E-02	#3	0.0E+00	1.8E-05	3.8E-06	1.9E-06	#3	0.0E+00	1.8E-05	3.8E-06	1.9E-06
Co-60	#4	1.6E-01	0.0E+00	3.00E+02	3.0E+02	#4	0.0E+00	0.0E+00	0.0E+00	0.0E+00	#4	0.0E+00	0.0E+00	0.0E+00	0.0E+00
Co-60	#5	1.2E-04	0.0E+00	5.80E-05	1.8E-04	#5	0.0E+00	0.0E+00	0.0E+00	0.0E+00	#5	0.0E+00	0.0E+00	0.0E+00	0.0E+00
Co-60	#7	3.0E-05	6.2E-02	2.90E+00	3.0E+00	#7	1.2E-07	0.0E+00	1.1E-02	1.1E-02	#7	1.2E-07	0.0E+00	1.1E-02	1.1E-02
Co-60	#9	1.4E-03	0.0E+00	6.40E+01	6.4E+01	#9	0.0E+00	0.0E+00	0.0E+00	0.0E+00	#9	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Figure A.8 From the SEWRDOSE calculational tool, a summary page of radiation doses, separated by exposure pathway for ⁶⁰Co discharged to the Oak Ridge WWTP in 1990

Appendix A

Atmospheric Dispersion. In the Sludge Incinerator Effluent Scenario (#5), the annual average dispersion factor ($\bar{\chi}/Q'$) at the exposure location (assumed to be $1E-06 \text{ sec/m}^3$) is used. When a precalculated value is input, no decay correction during transport is made by GENII. The average air concentration is

$$\bar{\chi} = Q \bar{\chi}/Q' \quad (\text{A.1})$$

where $\bar{\chi}$ = the average air concentration (Ci/m^3)
 Q = the release rate of the contaminant (Ci/sec)
 $\bar{\chi}/Q'$ = long-term normalized time-integrated air concentration (sec/m^3).

The ground surface contamination of radionuclide i from atmospheric deposition is given by

$$Cs_i = \bar{\chi} v_{d_i} t \quad (\text{A.2})$$

(Eq. 4.3.27, p. 4.38)

where Cs_i = the surface contamination of radionuclide i (Ci/m^2)
 $\bar{\chi}$ = the average air concentration (Ci/m^3)
 v_{d_i} = the deposition velocity (m/sec) of radionuclide i
 t = the time period for which the average concentration was computed (sec).

The deposition velocity is a constant of proportionality between surface contamination rate and the concentration of contaminants in air. For noble gases, a deposition velocity of zero is used; for most particulates, a deposition velocity of 0.001 m/sec is used; and for iodines, a deposition velocity of 0.01 m/sec is used. (The symbols for the various parameters in Equation A.2 have been modified slightly from those used in PNL-6584 for clarity.)

Surface Water Transport. In the STP Liquid Effluent Scenario (#3), a surface water transport model is used. The dilution volume is equivalent to the river flow rate. The water concentration is calculated as follows

$$Cw_i = \frac{Q'w_i}{RV} \quad (\text{A.3})$$

(Eq. 4.5.2, p. 4.54)

where Cw_i = the concentration of radionuclide i in surface water (Ci/L)
 $Q'w_i$ = the release rate of radionuclide i to the surface water body (Ci/sec)
 RV = the river flow rate, or dilution volume for the receiving water body representative of the usage location (L/sec).

This concentration is used with all exposure pathways associated with contaminated water usage.

Soil Contamination Models. Soil contamination models in GENII include deposition and removal from surface soils. Contaminants accumulate via deposition from the atmosphere and irrigation and are removed by chain decay from each soil compartment and by leaching into deeper soils.

For the air deposition pathway, the deposition rate is calculated using the air concentration and an average deposition velocity as follows:

$$Du_i = Ca_i v_{d_i} \quad (\text{A.4})$$

(Eq. 4.6.1, p. 4.57)

where Du_i = deposition rate ($\text{Ci/m}^2\text{-sec}$)
 Ca_i = average air concentration of radionuclide i (Ci/m^3)

and other term(s) as previously defined.

For the water pathways, the deposition rate is calculated from the irrigation rate and water concentration as

$$Du_i = 25.4 Cw_i I / (2.592 \cdot 10^6 \text{ MY}) \quad (\text{A.5})$$

(Eq. 4.6.2, p. 4.57)

where 25.4 = number of liters in 1 in. applied over 1 m^2
 I = irrigation water application rate (in./y)
 $2.592 \cdot 10^6$ = units conversion factor (sec/mo)
 MY = number of mo/y that irrigation occurs.

and other term(s) as previously defined.

Removal from the surface soils through leaching into deeper soils is treated by means of a soil removal rate constant, λ_{wi} , which is a correction for long-term leaching out of the surface soil rooting and resuspension zones (Napier et al. 1988a, p. 4.58).

A.3.1.2 Inhalation Dose

The dose from inhalation may be calculated either from a near-field exposure to respirable dust, or from exposure to a plume downwind of an emission source. In a near-field exposure, the dose from inhalation is based on the concentration in air of respirable particulate matter (aerodynamic diameter 10 μm or less). The use of respirators or other breathing protection may be represented by a reduction in the effective airborne dust concentration or by reduction in the exposure time (effective exposure time may be a fraction of the actual exposure duration).

For an individual working in proximity to contaminated sludge or ash, the dose from inhalation of dust is given by

$$\text{Dinh}_i = 3.15 \cdot 10^7 B C_a f \text{Dh}_i \quad (\text{A.6})$$

(Eq. 4.7.1a, p. 4.63)

where

- Dinh_i = individual dose from inhalation (rem/y) [Dn_i in document]
- $3.15 \cdot 10^7$ = the number of seconds in a year
- B = ventilation (breathing) rate for exposed individuals (m^3/sec)
- f = fraction of year exposed to inhalation (dimensionless)
- Dh_i = inhalation dose conversion factor for radionuclide i (rem per Ci inhaled)

and other term(s) as previously defined.

For particulate mass loading, the concentration of radionuclide i in the air is the product of soil concentration and dust loading, as follows:

$$C_a = C_d C_i \quad (\text{A.7})$$

where C_d = airborne dust concentration in respirable particles (kg/m^3)

C_i = concentration of radionuclide i in the airborne dust (Ci/kg)

and other term(s) as previously defined.

For an individual residing downwind of an emission source, dose from the inhalation of contaminants is given by

$$\text{Dinh}_i = 3.15 \cdot 10^7 B Q' \bar{x}/Q' \text{Dh}_i \quad (\text{A.8})$$

(Eq. 4.7.1b, p. 4.63)

where Q' = average release rate of radionuclide i (Ci/sec)

and other term(s) as previously defined.

A.3.1.3 Ingestion Dose

Ingestion is assumed to occur through the food chain. (Inadvertent ingestion of contaminated materials by transfer of loosely bound contamination on surfaces from hands to the mouth was not considered in this study.) The general equation for estimating the committed dose for the ingestion pathway is given by

$$\text{Ding}_i = \sum_j U_j C_{i,j} \text{Dg}_i \quad (\text{A.9})$$

where

- Ding_i = the committed effective dose equivalent from one year's intake of radionuclide i by ingestion (rem)
- U_j = consumption rate food product type j (kg/y)
- $C_{i,j}$ = concentration of radionuclide i in food type j (Ci/kg)
- Dg_i = the ingestion dose conversion factor (rem/Ci ingested).

Note that in the calculational tool developed as part of the current study, the ingestion parameters have been lumped together since the dose calculations performed for the study were not designed to specifically evaluate the impact of each parameter related to ingestion. In the absence of other information, the original doses and consumption parameters presented in the 1992 generic sewer study (Kennedy et al. 1992) can be

Appendix A

scaled up or down only as a single unit. "What if"-type estimates for ingestion dose can be made by applying a single value to scale the group of ingestion dose parameter values up or down.

However, for completeness, the general form of the equations used to calculate ingestion doses in the NUREG/CR-5814 study are presented below for drinking water, aquatic foods, crop ingestion from direct deposition on leaves and from root uptake, and animal product ingestion from contaminate feed and from animal ingestion of contaminated water. The concentration of radionuclides in either air or water is assumed to be the starting point for the environmental transport analysis. The calculation of the concentration of each radionuclide in each food type (fish, crops, and animal products) is quite complex. Equations given here pertain to chronic exposures.

The total ingestion dose, D_{ing} , is the sum of the components from water (D_w), aquatic foods (D_a), vegetables (D_v), and animal products (D_m)

$$D_{ing_i} = D_{w_i} + D_{a_i} + D_{v_i} + D_{m_i} \quad (A.10)$$

Drinking Water. The concentration of contaminants in drinking water is addressed above under "Surface Water Transport." The dose to an individual using a contaminated domestic water supply (river water) is calculated as follows

$$D_{w_i} = U_w C_{w_i} T_{f_i} \exp(-\lambda_i t_p) D_{g_i} \quad (A.11)$$

(Eq. 4.7.4a, p. 4.65)

where

- D_{w_i} = individual dose from water ingestion for radionuclide i (rem/y)
- U_w = annual water-intake rate for an individual (L/y)
- C_{w_i} = water concentration of radionuclide i (Ci/L)
- T_{f_i} = water treatment purification factor, fraction of contaminant remaining after treatment for radionuclide i (dimensionless)
- λ_i = radiological decay constant for radionuclide i (sec^{-1})
- t_p = time of transit through the water distribution system (sec)

D_{g_i} = ingestion dose conversion factor for radionuclide i (rem per Ci ingested).

Aquatic Foods. The dose from ingestion of contaminated fish is as follows

$$D_{a_i} = U_f C_{w_i} B_{if} \exp(-\lambda_i t_p) D_{g_i} \quad (A.12)$$

(Eq. 4.7.5a, p. 4.66)

where

- D_{a_i} = individual dose from aquatic food ingestion for radionuclide i (rem)
- U_f = consumption rate of fish, for individuals (kg/d)
- B_{if} = bioaccumulation factor for fish (L/kg)
- t_p = time for decay from food harvest to consumption (sec)

and other term(s) as previously defined. (This equation is simplified to refer to fish rather than for four types of aquatic foods presented in the GENII documentation (Napier et al. 1988a).

Crop Ingestion. Irrigating with contaminated water or direct deposition of airborne contaminants onto plants can contaminate agricultural crops, as noted under "Soil Contamination Models."

For direct deposition onto leaves

$$C_{l_{ip}} = D_{u_i} T_{v_p} r [1 - \exp(-\lambda_e t_{ep})] \exp(-\lambda_i t_{hp}) / (\lambda_e Y_p) \quad (A.13)$$

(Eq. 4.7.6, p. 4.67)

where

- $C_{l_{ip}}$ = concentration of radionuclide i in the vegetable for pathway p (leafy, root, grain, or fruit) from deposition onto leaves (Ci/kg)
- D_{u_i} = deposition rate from air or water onto farmlands ($\text{Ci}/\text{m}^2/\text{sec}$)
- T_{v_p} = translocation factor from plant surfaces to edible parts of the plant (dimensionless), currently assumed at 1.0 for leafy vegetables and forage crops, and 0.1 for all other vegetation
- r = fraction of initial deposition retained on the plant (dimensionless), [discussed below]

- λ_{e_i} = effective weathering and decay constant (sec^{-1})
 t_{e_p} = duration of the growing period for plant type p (sec)
 th_p = time between harvest and consumption for the vegetable type (sec)
 Y_p = yield of crop type p (kg/m^2).

For the root uptake pathway from air deposition

$$C_{r_{ip}} = [Cd_i R_{p2} + (Cs_i/P + Cb_i) R_{p1}] Bv_{ip} \exp(-\lambda_i th_p) \quad (\text{A.14})$$

(Eq. 4.7.7, p. 4.67)

where

- $C_{r_{ip}}$ = plant concentration from uptake through roots for radionuclide I and plant type p (Ci/kg)
 Cd_i = deep soil concentration for radionuclide i (Ci/kg), [discussed below]
 Cs_i = area soil concentration from air deposition for radionuclide i (Ci/m^2)
 Cb_i = residual soil concentration from previous years' deposition of radionuclide i (Ci/kg)
 P = effective soil density in the plow layer (kg/m^2)
 Bv_{ip} = soil-to-plant transfer factor for radionuclide i (dimensionless) and plant type p
 R_{p1} = root penetration factor for surface soil (dimensionless)
 R_{p2} = root penetration factor for deep soil (dimensionless).

and other term(s) as previously defined.

The root penetration factor is included for cases where the contamination is not uniform with soil depth. The factor allows a simple correction based on the fraction of the plant root system that is in contaminated soil.

The total plant concentration is the sum of the contributions from direct deposition and soil uptake, as follows:

$$C_{ip} = Cl_{ip} + Cr_{ip} \quad (\text{A.15})$$

(Eq. 4.7.8 p. 4.68)

where C_{ip} is the concentration of radionuclide i in crop type p at the time of consumption (Ci/kg).

The dose from ingestion of four types of agricultural crops is estimated from plant concentrations and the average consumption rates, as follows:

$$Dv_i = \sum_{p=1}^4 U_p C_{ip} Dg_i \quad (\text{A.16})$$

(Eq. 4.7.9, p. 4.69)

where

- Dv_i = the dose from consumption of contaminated crops (rem/y)
 U_p = consumption rate of crops (leafy, root, grain, or fruit) (kg/y)

and other term(s) as previously defined.

The interception fraction, r , for a given vegetation type is a factor that accounts for the fact that not all of the material deposited within an area will end up on vegetation surfaces. A default value of 0.25 is used for deposition by irrigation. Empirical relationships between biomass and interception fraction are used. The formulations for atmospheric deposition tend to estimate higher concentrations than did previous techniques.

Animal Product Ingestion. The animal product concentration resulting from animal ingestion of contaminated feed is calculated as follows:

$$Cf_{im} = C_{ip} F_{mi} f Qf \exp(-\lambda_i th_m) \quad (\text{A.17})$$

(Eq. 4.7.11, p. 4.70)

where Cf_{im} = concentration of radionuclide i in animal product m, from animal ingestion of contaminated feed (Ci/L for milk and Ci/kg for meat)

C_{ip} = concentration of radionuclide i in feed crop p, used by the animal (Ci/kg)

F_{mi} = transfer coefficient that relates daily intake rate by an animal to the concentration in an edible animal product (Ci/L milk per Ci/day for milk and Ci/kg meat per Ci/day for meat)

f = fraction of animal feed that is contaminated (dimensionless)

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Q_f = consumption rate of feed by the animal (kg/d)
 th_m = holdup time between harvest or slaughter and consumption for the animal product (sec).

and other term(s) as previously defined.

The contribution from animal ingestion of contaminated water is calculated as follows:

$$C_{w_{im}} = C_{w_i} F_{mi} f_w Q_w \exp(-\lambda_i th_m) \quad (\text{A.18})$$

(Eq. 4.7.12, p. 4.71)

where

$C_{w_{im}}$ = concentration of radionuclide i in an animal product m , from animal ingestion of water (Ci/kg for meat and Ci/L for milk)
 f_w = fraction of animal water that is contaminated (dimensionless)
 Q_w = consumption rate of water by the animal (L/d)

and other term(s) as previously defined. Default values of the animal consumption rates used in the GENII code are given in the default values file, DEFAULT.IN. A listing of this file is given in Figure A.9.

The total concentration in the animal product is the sum of the contributions from feed and water intake:

$$C_{im} = C_{w_{im}} + C_{f_{im}} \quad (\text{A.19})$$

(Eq. 4.7.13 p. 4.72)

where C_{im} is the concentration of radionuclide i in animal product m (Ci/kg for meat and eggs, Ci/L for milk).

The individual dose is calculated from the animal product concentration and the consumption rate of the products as follows:

$$D_{mi} = \sum_{m=1}^4 U_m C_{im} Dg_i \quad (\text{A.20})$$

(Eq. 4.7.14, p. 4.72)

where D_{mi} = the individual dose for radionuclide i from ingestion of animal product m (rem)

U_m = average daily consumption rate of animal product m (L/d for milk and kg/d for meat)

and other term(s) as previously defined. The summation is over the four animal product types: meat, milk, poultry, and eggs.

A.3.1.4 External Dose

External dose is a function of the radionuclide contaminant activity and the geometry used to model the interaction with the contaminant. For the scenarios included in NUREG/CR-5814, it was assumed that individuals could receive external exposure from radionuclides in several different ways: localized concentrations of the contaminated product, soil or air via the air transport pathway, aquatic recreational activities, or soil contaminated by irrigation water from surface water transport pathways.

External exposure to radionuclides may be from contaminated air or soil via the air transport pathway, aquatic recreational activities, or from contaminated soil due to irrigation for surface water transport pathways.

Contaminated Ground. For exposure to contaminated ground, with the external dose factors based on an infinite plane, the external dose from penetrating radiation is given by

$$Dx_i = ts Cs_i Ds_i \quad (\text{A.21})$$

(Eq. 4.7.24, p. 4.84)

where

Dx_i = annual effective dose equivalent to an individual from exposure to contaminated ground for radionuclide i (rem)
 ts = time of exposure to contaminated ground (h).
 Ds_i = the effective dose equivalent from a source contaminated with unit concentration of radionuclide i , based on infinite plane or geometry and shielding specific to the scenario, rem/h per Ci/m^2 .

INVENTORY PARAMETERS		
0.037, 3.7E4, 3.7E7, 3.7E10, 1.0	NVU	Source input conversion
1.0, 0.15, 224.0	SVU	Soil source conversion
ENVIRONMENTAL PARAMETERS		
0.008	ABSHUM	Absolute humidity (kg/m ³)
2	PRCNTI	Air dispersion conserv. flag
0.001	DPVRES	Deposition vel./resuspension
1.0E-9	LEAFRS	Leaf resuspension factor
2.0,2.0,3.0,0.8,0.8,0.8,1.0,0.8,1.0,1.5	BIOMAS	BIOMA2 Biomass (kg/m ²)
0.25	DEPFR2	Interception frac./irrigate
15.0	SURCM	Depth of surface soil (cm)
224.0	SLDN	Surface soil density (kg/m ²)
1.5E3	SSLDN	Soil density (kg/m ³)
True	HARVST	Harvest removal considered?
410.0	SOLING	Soil ingested (mg/da)
14.0	WTIM	Weathering time (da)
1.0, 0.1, 0.1, 0.1	TRANS	Translocation, plants
0.1, 0.1, 0.1, 0.1, 1.0, 1.0	TRANSA	Translocation, animal food
68.0, 0.12, 55.0, 0.12, 68.0, 55.0	CONSUM	Animal Consumption (kg/da)
50.0, 0.3, 60., 0.3	DWATER	Animal drinking water (L/da)
0.0, 0.8, 1.0, 0.8	FRACUT	Acute fresh forage by season
0.2, 0.3, 0.5, 1.0	SHORWI	Shore width factors
0.02	INGWAT	Swim water ingested (L/hr)
25295.0	TCWS	H ₂ O/sed. transfer (L/m ² /yr)
0.4, 5.0, 4.0	YELDBT	BIOT: Veg. prod. (kg/m ² /yr)
9.41E-4, 2*7.48E-4	TOTEXC	BIOT: Excavation (m ² /m ³ -yr)
1.0, 0.81, 0.19, 0.02, 0.008, 0.002,	EXCAV	BIOT: Frac. soil brought to
1.0, 0.9, 0.096, 0.006, 0.0005, 0.0005,		surface from within the
1.0, 0.9, 0.096, 0.006, 0.0005, 0.0005		waste by animal excavation
270.0	RINH	Chronic breathing (cm ³ /sec)
330.0	RINHA	Acute breathing (cm ³ /sec)
10	NDIST	Number of distances
805.0, 2414.0, 4023.0, 5632.0, 7241.0,		
12068.0, 24135.0, 40255.0, 56315.0,		
72405.0	X	JF/chi/Q/pop grid dist. (m)
0.1, 0.25, 6*0.18, 2*0.2	DRYFAC, DRYFA2	dry/wet ratio
METABOLIC PARAMETERS		
0.5, 50.0, 500.0		XDIV
0.5, 0.5, 0.95, 0.05, 0.8, 0.0, 0.0, 0.2, 0.0,		ADJ
0.1, 0.9, 0.5, 0.5, 0.15, 0.4, 0.4, 0.05, 0.0,		
0.01, 0.99, 0.01, 0.99, 0.05, 0.4, 0.4, 0.135, 0.015		
DOSE PARAMETERS		
0.25, 0.15, 0.12, 0.12, 0.03, 0.03, 5*0.06	WT	Weighting factors
2.0	SI2I	Semi-infinite/inf

Figure A.9 GENII Hanford-Specific Default Parameter Values for NUREG/CR-5814 GENII Default Parameter Values (28-Mar-90 RAP)

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Aquatic Recreational Activities. For water pathways, the recreational dose is

$$De_i = (0.5 tb + ts) Cw_i Db_i + tf Cd_i W Ds_i \quad (A.22)$$

(Eq. 4.7.21, p. 4.82)

where

- De_i = dose to an individual from external exposure for radionuclide i , from aquatic recreational activities (rem)
- tb = time spent by an individual in boating (h) (the 0.5 multiplier indicates the dose factor of half that for swimming)
- ts = time spent by an individual swimming (h)
- tf = time spent by an individual fishing or in shoreline activities (h)
- Db_i = external dose conversion factor for radionuclide i , for immersion in water (rem/h per Ci/L)
- Cd_i = sediment concentration of radionuclide i , deposited on shoreline from contaminated water (Ci/m²)
- W = shore width factor to correct for finite size of shoreline (dimensionless)
- Ds_i = external dose conversion factor for exposure to a contaminated plane of radionuclide i (rem/h per Ci/m²)

and other term(s) as previously defined.

The average sediment concentration is given by:

$$Cd_i = 100 T_i C_{wi} [1 - \exp(-\lambda_i T_b)] \quad (A.23)$$

(Eq. 4.7.22a, p. 4.82)

- where T_b = length of time the sediment is exposed to the contaminated water (d)
- T_i = physical half-life of the radionuclide (d)
- 100 = transfer constant from water to sediment (L/m²/d).

Specific Geometries. In most instances, the external dose is based on contaminated ground and is represented as an infinite plane. A simple geometric model of dose rate reduction for small surface areas from the ONSITE/MAXI1 program (Napier et al. 1984, pp. 2.20, 2.23) is provided in GENII (Napier et al. 1988b, p. 3.15). A correction factor is applied for contaminated areas smaller than 1250 m². Specific sets of external dose conversion factors for the geometry and shielding are used for three scenarios in the NUREG/CR-5814 study. The dose conversion factors were generated with EXTDF, the adaptation of ISOSHL (Engel et al. 1966) incorporated into the GENII software system. For the STP Worker scenario, the geometry is represented as an infinite slab, 1 meter thick, with 2 meters between the source and the worker. The technique employed to use a customized dose factor library with GENII is described in Section A.3.4.

Air Submersion. Persons submersed in a plume of airborne material will receive radiation exposure from gamma and x-rays emitted external to the body. For chronic releases, the air submersion dose is calculated as follows:

$$Dl_i = Q_i' (\bar{\chi}/Q') DFs_i \quad (A.24)$$

(Eq. 4.4.2, p. 4.42)

where

- Dl_i = individual dose from external exposure to the plume for radionuclide i (rem)
- Q_i' = annual average release rate of radionuclide i (Ci/year)
- $\bar{\chi}/Q'$ = chronic release atmospheric dispersion factor at the exposure location (sec/m³)
- DFs_i = submersion dose factor precalculated from EXTDF program for radionuclide i (rem per Ci - sec/m³).

The preceding equation can be adapted to calculate the submersion dose from the airborne dust loading, as described for inhalation dose above.

The total external dose, D_{ext} , is the sum of the contributions from ground, aquatic recreations, and submersion:

$$\text{Dext}_i = \text{Dx}_i + \text{De}_i + \text{Dl}_i \quad (\text{A.25})$$

A.3.1.5 Total Dose

The total dose from all exposure pathways is the sum of the components, from inhalation, ingestion, and external doses:

$$\text{Dttl}_i = \text{Dinh}_i + \text{Ding}_i + \text{Dext}_i \quad (\text{A.26})$$

where Dttl_i is the total dose from all pathways (rem/y) and other term(s) are as previously defined.

A.3.2 Input Concentrations for Exposure Scenarios Used in NUREG/CR-5814

For a unit input of a radionuclide into a sanitary sewer system, the concentration of each radionuclide in sewage sludge is dependent upon the amount of sludge generated by the STP. The amount of sludge generated (or dilution) is dependent on the size of the STP and the amount of sludge generated per unit throughput of the STP system. The base case STP size and sludge generation assumptions for the generic sewer study as described in NUREG/CR-5814 (Kennedy et al. 1992) were a STP capacity of 5 MGD and a generation of 938 kg (2064 lb) dry sludge per MGD, which amount to 4690 kg (10320 lb) dry sludge per day (U.S. Environmental Protection Agency 1979 pp. 11-31).

Table A.1 lists the system parameters used to determine concentrations resulting from a unit input (that is, $3.7\text{E}+10$ Bq/y or 1 Ci/y) of a radionuclide to an STP for the scenarios and media considered in the NUREG/CR-5814 study.

Table A.2 (modified from Table A.16 of NUREG/CR-5814) shows the equations used to derive sludge and ash concentrations. Table A.3 shows the origin of the source term that was used as GENII (Napier et al. 1988a) input for each scenario (modified from Table A.15 of NUREG/CR-5814). This conversion was necessitated by the fact that the GENII code will only allow input values in certain units. Table A.4 (Table A.17 from NUREG/CR-5814) lists concentrations of various contaminated environmental media used in the study, based on $3.7\text{E}+10$ Bq/y or 1 Ci/y released to a 5 MGD STP, and the equations used to obtain those values.

A.3.3 Parameter Values Used in NUREG/CR-5914

The user has the option of changing most parameters used in GENII (Napier et al. 1988). Parameters which are routinely changed are located in the formatted GENII input files. Tables A.5 and A.6 present comparisons of input parameters used in the NUREG/CR-5814 study with GENII's Hanford-specific Maximally Exposed Individual (MEI) and average individual defaults and Hanford-specific ranges. Table A.5 presents this information for the scenarios which include food pathways, namely, for the STP Effluent (River, Downstream, Scenario #3), Sludge Incinerator (Downwind, Scenario #5), and Agricultural Application of Sludge (Scenario #7). Input parameters for the STP Operator, Incinerator Operator, and Landfill Equipment Operator Scenarios (#2, #4, and #9) are listed in Table A.6.

In Tables A.5 and A.6, the columns headed "MEI," "Ave," "Min," and "Max" show list default Hanford values used for the MEI, the Average Individual, and the minimum and maximum Hanford-specific values accepted by "Apprentice" (the GENII input file pre-processor). The final column gives a brief description of the parameter.

An unabridged list of GENII default values and ranges is shown in Table A.7.

Parameters not included in the input file because they are changed infrequently are read from the file DEFAULT.IN. This file includes such information as soil density, weathering half-time, translocation factor, and animal feed consumption rates. This file may be edited to change the parameter values.^(a) Figure A.9 is a listing of the GENII file, DEFAULT.IN.

(a) Another default parameter file may be substituted by changing the name of the file corresponding to DEFAULT.IN in FILRNAME.DAT.

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Table A.1 Parameters Affecting Concentrations

Scenario	Medium	Parameters Affecting Concentrations
STP Operator (#2)	Wet Sludge	STP Capacity (MGD) Unit Sludge Protection (lb dry sludge/MGD) Dry/Wet ratio Sludge Density (kg/m ³)
STP Liquid Effluent (#3)	Effluent Water to River	Radionuclide-specific removal River flow rate
Incin. Operator/Ash Handler (#4)	Dry Ash	STP Capacity (MGD) Unit Sludge Production (lb dry sludge/MGD) Mass reduction on incineration (mass residue/mass sludge) Radionuclide-specific stack emissions & Ash retention
Sludge Incin. Effluent (#5)	Air	Incinerator sludge throughput (if not a unit radionuclide calculation) Radionuclide-specific stack emissions
Incin. Ash Truck Driver (#6)	Wet Ash	Parameters for #4, Dry ash, above, plus, Wet/Dry ratio
Sludge Agricultural Soil Application (#7)	Sludge/soil	Parameters for #2, Wet sludge, above Application Rate Mg/ha
Sludge Nonagricultural Application (#8)	Sludge/soil	Parameters for #2, Wet sludge, above Application Rate Mg/ha
Landfill Operator (#9)	Wet Ash	Parameters for #4, Dry ash, above Wet/Dry ratio Fraction contaminated (dilution)

Table A.2 Derivation of Sludge and Ash Concentrations (modified from NUREG/CR-5814 Table A.16)

Parameter	Value	Units	Calculation or Reference
Activity Released	1.0	Ci/y	Maximum allowed in 10 CFR 20
	5.0	Ci/y ^3H	Maximum allowed in 10 CFR 20
STP Capacity	5.0	MGD	EPA 1979
Unit Sludge Production	2064	lb dry sl/MGD	EPA 1979
Sludge (dry) Density	1.6	g/cm ³	_____
Sludge (wet) Density	1.2	g/cm ³	_____
Ash Density	1.6	g/cm ³	_____
Sludge solid Fraction (wet)	0.3	-	_____
Sludge Incinerator Residue Fraction	0.3	-	(.23-.35 EPA 1979, p. 11-39 0.3-0.6 EPA 1986 p. 3-3)
Sludge Production	1.7E+06	kg/y	2064 lb/MGD x 5 MGD x 365 day/y x 1 kg /2.2 lb
Ash Production	5.1E+05	kg/y	2064 lb/MGD x 5 MGD x 365 day/y x 1 kg/2.2 lb x 0.3 lb ash/lb sludge = Sludge Production x sludge incin. residue fraction
Ash mass concentration	1.9E-06	Ci/kg	1 Ci/5.1 E+5 kg Ash = Activity released/Ash production
Ash volume concentration	3.1E-03	Ci/m ³	1.95E-6 Ci/kg x 1.6E+3 kg/m ³ = Ash mass concentration x ash density
Sludge (dry) mass concentration	5.8E-07	Ci/kg	1 Ci/y x 1 y/1.7E+6 kg sludge = Activity released/sludge production
Sludge (dry) volume concentration	9.3E-04	Ci/m ³	5.8E-7 Ci/kg x 1.6E+3 kg/m ³ = Sludge mass concentration x sludge density
Sludge (wet) mass concentration	1.7E-07	Ci/kg	5.8E-7 Ci/kg x 0.3 (solids) = Sludge (dry) mass concentration x sludge (wet) solids fraction
Sludge (wet) volume conc.	2.1E-04	Ci/m ³	1.7E-7 Ci/kg x 1.2E+3 kg/m ³ = Sludge (wet) mass concentration x sludge (wet) density

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Table A.3 Calculation of source term (GENII input) for each scenario (from NUREG/CR-5814, Table A.15)

Number	Scenario Description	GENII Source Term	Medium	Calculation of GENII Input
1	Sewer System Inspector	varies Ci/m ³	Waste Water	0.01 * 10 CFR 20 Table II, Column 2
2	STP Operator	2.1E-04 Ci/m ³	Wet Sludge	1 Ci/y/(2064 lb dry sludge/MGD x 5 MGD x 365 day/y x 1 kg/ 2.2 lb x 0.3 (dry/wet) x 1.2E+3 kg/m ³)
3	STP Liquid Effluent	1.0E+00 Ci/y	to River	1 Ci/y (5 Ci 3H)
4	Sludge Incinerator Operator	2.0E-06 Ci/kg	Dry Ash	1 Ci/y/(2064 lb/MGD x 5 MGD x 365 day/y x 1 kg/ 2.2 lb x 0.3 lb ash/lb sludge) (0.1 x 5 = 0.5 Ci 3H; 0.25 Ci 14C)
5	Sludge Incinerator Effluent	5.0E-03 Ci/y	to Air	1 Ci/y x RF Where RF = 0.005 with the following exceptions: 5 Ci 3H x 0.9 = 4.5 Ci 3H; 0.75 14C; 0.1 P, S, I; 0.01 Cl, Tc, Ru
6	Incinerator Ash Disposal Truck Driver	2.8E-03 Ci/m ³	Wet Ash	1 Ci/(2064 lb/MGD x 5 MGD x 365 day/y x 1 kg/2.2 lb x 0.3 lb ash/lb sludge) x 1600 kg/m ³ x 0.9 (dry/wet wt)
7	Sludge Agricultural Soil Application	8.8E-07 Ci/m ²	Sludge/soil	1 Ci/(2064 lb dry sludge/MGD x 5 MGD x 365 day/y x 1 kg/2.2 lb) x 15 Mg/ha 1E+3 kg/Mg x 1 ha/1E+4 m ²
8	Sludge Nonagricultural Soil Application	5.8E-06 Ci/m ²	Sludge/soil	1 Ci/(2064 lb dry sludge/MGD x 5 MGD x 365 day/y x 1 kg/2.2 lb) x 100 Mg/ha 1E+3 kg/Mg x 1 ha/1E+4 m ²
9	Landfill Operator	1.8E-07 Ci/kg	Wet Ash	1 Ci/(2064 lb/MGD x 5 MGD x 365 day/y x 1 kg/2.2 lb x 0.3 lb ash/lb sludge) x 0.9 (dry fraction) x 0.1 ^(a) exceptions: 5 Ci x 0.1 = 0.5 Ci 3H; 1 Ci x 0.25 = 0.25 Ci 14C

(a) Dilution factor: 0.1 multiplied by source term to account for non-dedicated landfill.

Table A.4 Concentrations of contaminated environmental media based on 1 Ci/year released to 5 MGD sewage treatment plant (from NUREG/CR-5814, Table A.17)

Number	Scenario	Environmental Concentration	Medium	Calculation
1	Sewer System Inspector	0.01 x 10CFR20	Waste Water	0.01 x 10CFR20 Appendix B Table II Column 2
2	STP Operator	2.1E-4 Ci/m ³	Wet Sludge	1 Ci/y / 1.7E6 kg dry sludge x 0.3 (dry/wet) x 1.2E+3 kg/m ³
3	STP Liquid Effluent	0.32 pCi/l	River Water	1 Ci/y / (100 m ³ /sec x 3.16E+7 sec/y) x 1E+9 pCi/l / Ci/m ³
4	Sludge Incinerator Operator	2 nCi/g	Dry Ash	1 Ci/5.1E+5 kg/y ash x RF (H3, C14) x E+6 nCi/g / Ci/kg
5	Sludge Incinerator Effluent	3.2E-5 pCi/l	Air	1 Ci/y x RF x 1E-6 Sec/m ³ x y/3.16E+7 sec x E+9 pCi/l / Ci/m ³
6	Incinerator Ash Disposal Truck Driver	1.8 nCi/g	Wet Ash	1 Ci/5.1E+5 kg Ash x 1E+6 nCi/g / Ci/kg x 0.9 (dry/wet wt)
7	Sludge Agricultural Soil Application	3.7 pCi/g	Sludge/soil	1 Ci/y / 1.7E+6 kg Sludge x 15 Mg/ha x 1E+3 kg/Mg x 1ha/1E+4 m ² x m ² /240 kg ^(a)
8	Sludge Nonagricultural Soil Application	24 pCi/g	Sludge/soil	1 Ci/y / 1.7E+6 kg Sludge x 100 Mg/ha x 1E+3 kg/Mg x 1ha/1E+4 m ² x m ² /240 kg
9	Landfill Operator	180 pCi/g	Wet Ash	1 Ci/5.1E+5 kg x .9 (dry fraction) x E+9 pCi/g / Ci/m ³ x 0.1 ^(b)

(a) The conversion factor 240 kg/m² soil is for a 15 cm depth, with a density of 1600 kg/m³.

(b) The 0.1 dilution factor accounts for a non-dedicated landfill; 10 % of the contents is Incinerator ash.

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Table A.5 Comparison of sewer study input parameters with GENII Hanford-specific defaults and ranges for scenarios with food pathways

#3	#5	#7	MEI	Ave	Min	Max	Description
River	Air	Agric.	TRANSPORT				
N/A	1E-6	N/A	0.0	0.0	0.0	1.0	Chi/Q value (sec/m ³):
River	Air	Agric.	SURFACE WATER TRANSPORT				
100.	N/A	N/A	3.0E+3	3.0E+3	0.0	1.0E+6	Average river flow rate (m ³ /s):
0.	N/A	N/A	0.0	0.0	0.0	1.0E+3	Transit time to irrigation withdrawal location (hr):
River	Air	Agric.	EXPOSURE: EXTERNAL				
0	1800	500	8766.0	8766.0	0.0	8766.0	Individual annual exposure time to plume (hr):
1800	1800	500	4380.0	2920.0	0.0	8766.0	Individual annual exposure time to soil contamination (hr):
10.	N/A	N/A	100.0	10.0	0.0	1000.0	Individual annual exposure time while swimming (hr):
5.	"	"	100.0	5.0	0.0	8766.0	Individual annual exposure time while boating (hr):
17.	"	"	500.0	17.0	0.0	1000.0	Individual annual exposure time from shoreline activities (hr):
1	"	"	1	1	1	4	Shoreline type (1-river, 2-lake, 3-ocean, 4-tidal basin):
1.	"	"	8.0	13.0	0.0	1000.0	Transit time for release to reach aquatic recreation area (hr):
T	"	"	T				External Ground Exposure: Is irrigation with contaminated water considered?
30.	"	"	40.0	40.0	0.0	100.0	External Ground Exposure: irrigation water application rate (in/irrigation season):
6.	"	"	6	6	0	12	External Ground Exposure: duration of irrigation (mo/yr):

#3	#5	#7	MEI	Ave	Min	Max	Description
River	Air	Agric.	EXPOSURE: INHALATION				
360 ^(a)	3990.	400 ^(b)	8766.0	8766.0	0.0	8766.0	Individual annual inhalation exposure (hr):
1	0	1	0	0	0	2	Resuspension (0-not considered, 1-use Mass Loading model, 2-use Anspaugh model):
1.0E-4	N/A	1.0E-4	1.0E-4	1.0E-4	1.0E-9	1.0E-2	Mass loading factor (g/m ³):
River	Air	Agric.	AQUATIC FOODS / DRINKING WATER				
N/A ^(c)	N/A	N/A	T				Is drinking water treated?
0.	"	"	730.0	440.0	0.0	1.0E+3	Per capita drinking water consumption rate (L/yr):
0.	"	"	0.0	0.0	0.0	1000.0	Fish - Transit time for release to reach harvest area (hr):
1.	"	"	1.0	1.0	0.0	1.0E+3	Fish - Holdup between harvest and consumption (da):
6.9	"	"	40.	6.9	0.0	1.0E+2	Fish - Per capita consumption rate (kg/yr):
River	Air	Agric.	TERRESTRIAL FOOD CROPS & CONSUMPTION				
14	1	1	1.0	14.0	0.0	365.0	Leafy Vegetables - Holdup between harvest and consumption (da):
4.9	4.9	4.9	30.0	15.0	0.0	200.0	Leafy Vegetables - Per capita consumption rate (kg/yr):
14	14	14	5.0	14.0	0.0	365.0	Other Vegetables - Holdup between harvest and consumption (da):
45.5	45.5	45.5	220.0	140.0	0.0	300.0	Other Vegetables - Per capita consumption rate (kg/yr):
14	14	14	5.0	14.0	0.0	365.0	Fruit - Holdup between harvest and consumption (da):
21.	21.	21.	330.0	64.0	0.0	500.0	Fruit - Per capita consumption rate (kg/yr):
180	180	180	180.0	180.0	0.0	365.0	Cereals - Holdup between harvest and consumption (da):
23.5	23.5	23.5	80.0	72.0	0.0	300.0	Cereal and bread - Per capita consumption rate (kg/yr):

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#3	#5	#7	MEI	Ave	Min	Max	Description
River	Air	Agric.	ANIMAL PRODUCTS & CONSUMPTION				
20	20	N/A	15.0	34.0	0.0	365.0	Meat (beef and pork) - Holdup between harvest and consumption(da):
47.5	47.5	"	80.0	70.0	0.0	200.0	Meat (beef and pork) - Per capita consumption rate (kg/yr):
34	4	"	1.0	34.0	0.0	365.0	Poultry- Holdup between harvest and consumption (da):
0	0	"	18.0	8.5	0.0	50.0	Poultry - Per capita consumption rate (kg/yr):
2.0	2.0	"	1.0	4.0	0.0	365.0	Milk- Holdup between harvest and consumption (da):
55.	55.	"	270.0	230.0	0.0	1000.0	Milk - Per capita consumption rate (kg/yr):
18	18	"	1.0	18.0	0.0	365.0	Eggs - Holdup between harvest and consumption (da):
0	0	"	30.0	20.0	0.0	100.0	Eggs - Per capita consumption rate (kg/yr):

- (a) Equivalent Inhalation Hours: 360 hr = 1800 hr x 0.2 respirable fraction.
- (b) Equivalent Inhalation Hours: 400 hr = 2000 hr x 0.2 respirable fraction.
- (c) No drinking water intake downstream from STP discharge.

Table A.6 Comparison of sewer study input parameters with GENII Hanford-specific defaults and ranges for worker exposure scenarios

#2	#4	#9	MEI	Ave	Min	Max	Description
STP OP	INCIN	LFILL	EXPOSURE: EXTERNAL				
0	0	0	8766.0	8766.0	0.0	8766.0	Individual annual exposure time to plume (hr):
1500	100 ^(a)	250 ^(b)	4380.0	2920.0	0.0	8766.0	Individual annual exposure time to soil contamination (hr):
STP OP	INCIN	LFILL	EXPOSURE: INHALATION				
300 ^(c)	400 ^(d)	100 ^(e)	8766.0	8766.0	0.0	8766.0	Individual annual inhalation exposure (hr):
1	1	1	0	0	0	2	Resuspension (0-not considered, 1-use Mass Loading model, 2-use Anspaugh model):
1.0E-3	1.0E-3	4.0E-4	1.0E-4	1.0E-4	1.0E-9	1.0E-2	Mass loading factor (g/m ³):

(a) Effective External Hours: 100 hr = 1000 hr exposed x 0.1 shielding factor.

(b) Effective External Hours: 250 hr = 1000 hr x 0.25 shielding factor.

(c) Effective Inhalation Hours: 300 hr = 1500 hr x 0.2 respirable fraction.

(d) Effective Inhalation Hours: 500 hr = 1000 hr x 0.5 respiratory protection factor.

(e) Effective Inhalation Hours: 200 hr = 1000 hr x 0.2 respirable fraction.

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Table A.7 Unabridged list of GENII Hanford-Specific Input Parameters, Default Values, and Ranges used in NUREG/CR-5814

MEI	Ave	Min	Max	Description
TIME				
1	1	0	70	Intake ends after ___ years:
50	50	0	70	Dose calculations end after ___ years:
1	1	0	70	Release ends after ___ years:
0	0	0	1000	There were ___ years of air deposition prior to the beginning of the intake period:
0	0	0	1000	There were ___ years of irrigation deposition prior to the beginning of the intake period:
NEAR-FIELD SCENARIOS				
0	0	0	1000	The inventory was disposed ___ years prior to the beginning of the intake period:
0	0	0	1000	Loss of institutional control occurred ___ years prior to the intake period:
1.0	1.0	0.0	1.0	Fraction of roots in surface soil, (top 15 cm layer):
0.0	0.0	0.0	1.0	Fraction of roots in deep soil:
0.0	0.0	0.0	1.0	Manual redistribution; deep soil/surface soil dilution factor:
F				Is source area less than 1250 m ² (Y/N)?
1250.0	1250.0	0.0	1250.0	Source area for external dose modification factor (m ²):
AIR TRANSPORT				
1	1	0	3	XOQOPT
0.0	0.0	0.0	1.0	Chi/Q value (sec/m ³):
0.0	0.0	0.0	1.0	E/Q value (sec/m ³):
0.0	0.0	0.0	10.0	Population-weighted Chi/Q value (person sec/m ³):
1	1	1	16	Maximum individual is located in sector index (1 = South):
1000.	1000.	100.0	100000	Maximum individual is located ___ meters from release point:
T				Do you wish to calculate chi/q grid from joint frequency data(Y/N)?
F				Is this an elevated release (Y/N) ?
T				Effective stack height (Y/N) ?
100.0	100.0	0.0	1000.0	Stack height (m):
1.0	1.0	0.0	5000.0	Stack flow (m ³ /s):
5.0	5.0	0.001	30.0	Stack radius (m):
100.0	100.0	0.0	300.0	Effluent temperature (degrees Celsius):
100.0	100.0	0.0	5000.0	Building cross-sectional (vertical) area (m):
10.0	10.0	0.0	100.0	Building height (m):
F				Use building wake model (Y/N):
1	1	1	16	Which down-wind sector (1 = South):

MEI	Ave	Min	Max	Description
SURFACE WATER TRANSPORT				
1.0	1.0	0.0	1.0	Surface water mixing ratio:
3.0E+3	3.0E+3	0.0	1.0E+6	Average river flow rate (m ³ /s):
100.0	100.0	0.0	1.0E+2	Average water flow rate (m/s):
1	1	0	3	MIXFLG
0.0	0.0	0.0	1.0E+3	Transit time to irrigation withdrawal location (hr):
0.0	0.0	0.0	1.0E+4	Rate of effluent discharge to receiving water body (m ³ /s):
0.0	0.0	0.0	1.0E+4	Longshore distance from release point to usage location (m):
0.0	0.0	0.0	1.0E+4	Offshore distance to water intake (m):
0.0	0.0	0.0	1.0E+3	Average water depth in surface water body (m):
0.0	0.0	0.0	1.0E+3	Average river width (m):
0.0	0.0	0.0	1.0E+2	Depth of effluent discharge point to surface water (m):
WASTE FORM AVAILABILITY				
0.0	0.0	1.0E-20	1.0E+3	Waste form / package half life (yr):
0.0	0.0	0.0	1.0E+2	Waste / contaminated soil thickness (m):
0.0	0.0	0.0	1.0E+3	Depth of soil overburden (m):
BIOTIC TRANSPORT OF BURIED SOURCE				
T				Do you wish to consider biotic transport during inventory decay/buildup period (Y/N):
T				Do you wish to consider biotic transport during intake period (Y/N):
1	1	1	3	Pre-intake site condition (1- Arid non-agricultural, 2- Humid non-agricultural, 3- agricultural):
FAR-FIELD - POPULATION				
1	1	1	2	POPOPT
1.0	1.0	1.0	5.0E+6	Total population:
1.0	1.0	1.0E-12	10.0	Population-weighted E/Q value:
INVENTORY				
1	1	1	3	Surface soil source units (1-m ² , 2-m ³ , 3-kg):
EXTERNAL EXPOSURE				
8766.0	8766.0	0.0	8766.0	Individual annual exposure time to plume (hr):
4380.0	2920.0	0.0	8766.0	Individual annual exposure time to soil contamination (hr):
100.0	10.0	0.0	1000.0	Individual annual exposure time while swimming (hr):
100.0	5.0	0.0	8766.0	Individual annual exposure time while boating (hr):
500.0	17.0	0.0	1000.0	Individual annual exposure time from shoreline activities (hr):
1	1	1	4	Shoreline type (1-river, 2-lake, 3-ocean, 4-tidal basin):
8.0	13.0	0.0	1000.0	Transit time for release to reach aquatic recreation area (hr):
T				External Ground Exposure: Is irrigation with contaminated water considered?
1	1	1	2	External Ground Exposure: irrigation water source (1-ground water, 2-surface water):
40.0	40.0	0.0	100.0	External Ground Exposure: irrigation water application rate (in/irrigation season):
6	6	0	12	External Ground Exposure: duration of irrigation (mo/yr):

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MEI	Ave	Min	Max	Description
1.0	1.0	0.0	1.0	Fraction of plume passage time spent in plume:
INHALATION				
8766.0	8766.0	0.0	8766.0	Individual annual inhalation exposure (hr):
0	0	0	2	Resuspension (0-not considered, 1-use Mass Loading model, 2-use Anspaugh model):
1.0E-4	1.0E-4	1.0E-9	1.0E-2	Mass loading factor (g/m ³):
1.0	1.0	0.0	15.0	Top soil available for resuspension (cm):
INGESTION POPULATION				
1	1	0	3	FOQOPT
0.0	0.0	1.0E-12	1.0	Food-weighted Chi/Q value (sec/m ³):
0	0	0	5.0E+6	Population ingesting aquatic foods, 0 defaults to total population (person):
0	0	0	5.0E+6	Population ingesting drinking water, 0 defaults to total population (person):
F				Do you wish to consider dose from contaminated food exported out of the region?
DRINKING WATER				
1	1	1	2	Drinking water source (1-ground water, 2-surface water):
T				Is drinking water treated?
1.0	1.0	0.0	10.0	Holdup/transit time of drinking water (da):
730.0	440.0	0.0	1.0E+3	Per capita drinking water consumption rate (L/yr):
AQUATIC FOODS				
F				Are aquatic foods harvested from salt water (default is fresh water)?
F				Do you wish to consider uncontaminated food imported into the region?
0.0	0.0	0.0	1000.0	Fish - Transit time for release to reach harvest area (hr):
15000.	15000.	0.0	1.0E+6	Fish - Total production (kg/yr):
1.0	1.0	0.0	1.0E+3	Fish - Holdup between harvest and consumption (da):
40.	6.9	0.0	1.0E+2	Fish - Per capita consumption rate (kg/yr):
0.0	0.0	0.0	1000.0	Mollusc - Transit time for release to reach harvest area (hr):
0.0	0.0	0.0	1.0E+6	Mollusc - Total production (kg/yr):
0.0	0.0	0.0	1.0E+3	Mollusc - Holdup between harvest and consumption (da):
6.9	0.0	0.0	1.0E+2	Mollusc - Per capita consumption rate (kg/yr):
0.0	0.0	0.0	1000.0	Crustacea - Transit time for release to reach harvest area (hr):
0.0	0.0	0.0	1.0E+6	Crustacea - Total production (kg/yr):
0.0	0.0	0.0	1.0E+3	Crustacea - Holdup between harvest and consumption (da):
6.9	0.0	0.0	1.0E+2	Crustacea - Per capita consumption rate (kg/yr):
0.0	0.0	0.0	1000.0	Aquatic plants - Transit time for release to reach harvest area (hr):
0.0	0.0	0.0	1.0E+6	Aquatic plants - Total production (kg/yr):
0.0	0.0	0.0	1.0E+3	Aquatic plants - Holdup between harvest and consumption (da):
6.9	0.0	0.0	1.0E+2	Aquatic plants - Per capita consumption rate (kg/yr):

MEI	Ave	Min	Max	Description
TERRESTRIAL FOODS				
90.0	90.0	1.0	365.0	Leafy vegetables - Growing time (da):
2	2	0	2	Leafy vegetables - Irrigation source (0-none, 1-ground water, 2-surface water):
35.0	35.0	0.0	100.0	Leafy vegetables - Irrigation rate (in/irrigation season):
6.0	6.0	0.0	12.0	Leafy Vegetables - Irrigation duration (mo/yr):
1.5	1.5	0.0	10.0	Leafy vegetables - Yield (kg/m ²):
0.0	0.0	0.0	1.0E+8	Leafy Vegetables - Total production (kg/yr):
1.0	14.0	0.0	365.0	Leafy Vegetables - Holdup between harvest and consumption (da):
30.0	15.0	0.0	200.0	Leafy Vegetables - Per capita consumption rate (kg/yr):
90.0	90.0	1.0	365.0	Other vegetables - Growing time (da):
2	2	0	2	Other vegetables - Irrigation source (0-none, 1-ground water, 2-surface water):
40.0	40.0	0.0	100.0	Other vegetables - Irrigation rate (in/irrigation season):
6.0	6.0	0.0	12.0	Other Vegetables - Irrigation duration (mo/yr):
4.0	4.0	0.0	10.0	Other vegetables - Yield (kg/m ²):
0.0	0.0	0.0	1.0E+8	Other Vegetables - Total production (kg/yr):
5.0	14.0	0.0	365.0	Other Vegetables - Holdup between harvest and consumption (da):
220.0	140.0	0.0	300.0	Other Vegetables - Per capita consumption rate (kg/yr):
90.0	90.0	1.0	365.0	Fruit - Growing time (da):
2	2	0	2	Fruit - Irrigation source (0-none, 1-ground water, 2-surface water):
35.0	35.0	0.0	100.0	Fruit - Irrigation rate (in/irrigation season):
6.0	6.0	0.0	12.0	Fruit - Irrigation duration (mo/yr):
2.0	2.0	0.0	10.0	Fruit - Yield (kg/m ²):
0.0	0.0	0.0	1.0E+8	Fruit - Total production (kg/yr):
5.0	14.0	0.0	365.0	Fruit - Holdup between harvest and consumption (da):
330.0	64.0	0.0	500.0	Fruit - Per capita consumption rate (kg/yr):
90.0	90.0	1.0	365.0	Cereals - Growing time (da):
0	0	0	2	Cereals - Irrigation source (0-none, 1-ground water, 2-surface water):
0.0	0.0	0.0	100.0	Cereals - Irrigation rate (in/irrigation season):
0.0	0.0	0.0	12.0	Cereals - Irrigation duration (mo/yr):
0.8	0.8	0.0	10.0	Cereals - Yield (kg/m ²):
0.0	0.0	0.0	1.0E+8	Cereals - Total production (kg/yr):
180.0	180.0	0.0	365.0	Cereals - Holdup between harvest and consumption (da):
80.0	72.0	0.0	300.0	Cereal and bread - Per capita consumption rate (kg/yr):

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MEI	Ave	Min	Max	Description
ANIMAL FOOD PRODUCTS				
15.0	34.0	0.0	365.0	Meat (beef and pork) - Holdup between harvest and consumption (da):
80.0	70.0	0.0	200.0	Meat (beef and pork) - Per capita consumption rate (kg/yr):
0.0	0.0	0.0	1.0E+8	Meat (beef and pork) - Total production (kg/yr):
1.0	1.0	0.0	1.0	Meat - Fraction of animal drinking water that is contaminated:
0.25	0.25	0.0	1.0	Meat - Fraction of animal diet consisting of contaminated grain:
90.0	90.0	1.0	365.0	Meat - Grain growing time (da):
0	0	0	2	Meat - Grain irrigation source (0-none, 1-ground water, 2-surface water):
35.0	35.0	0.0	100.0	Meat - Grain irrigation rate (in/irrigation season):
6.0	6.0	0.0	12.0	Meat - Grain irrigation duration (mo/yr):
0.8	0.8	0.0	10.0	Meat - Grain yield (kg/m ²):
180.0	180.0	0.0	365.0	Meat - Storage time for grain (da):
0.75	0.75	0.0	1.0	Meat - Fraction of animal diet consisting of contaminated hay:
45.0	45.0	1.0	365.0	Meat - Hay growing time (da):
2	2	0	2	Meat - Hay irrigation source (0-none, 1-ground water, 2-surface water):
47.0	47.0	0.0	100.0	Meat - Hay irrigation rate (in/irrigation season):
6.0	6.0	0.0	12.0	Meat - Hay irrigation duration (mo/yr):
2.0	2.0	0.0	10.0	Meat - Hay yield (kg/m ²):
100.0	100.0	0.0	365.0	Meat - Storage time for hay (da):
1.0	34.0	0.0	365.0	Poultry- Holdup between harvest and consumption (da):
18.0	8.5	0.0	50.0	Poultry - Per capita consumption rate (kg/yr):
0.0	0.0	0.0	1.0E+6	Poultry - Total production (kg/yr):
1.0	1.0	0.0	1.0	Poultry - Fraction of drinking water that is contaminated:
1.0	1.0	0.0	1.0	Poultry - Fraction of animal diet consisting of contaminated grain:
90.0	90.0	1.0	365.0	Poultry - Grain growing time (da):
0	0	0	2	Poultry - Grain irrigation source (0-none, 1-ground water, 2-surface water):
0.0	0.0	0.0	100.0	Poultry - Grain irrigation rate (in/irrigation season):
0.0	0.0	0.0	12.0	Poultry - Grain irrigation duration (mo/yr):
0.8	0.8	0.0	10.0	Poultry - Grain yield (kg/m ²):
180.0	180.0	0.0	365.0	Poultry - Storage time for grain (da):

MEI	Ave	Min	Max	Description
1.0	4.0	0.0	365.0	Milk- Holdup between harvest and consumption (da):
270.0	230.0	0.0	1000.0	Milk - Per capita consumption rate (kg/yr):
0.0	0.0	0.0	1.0E+8	Milk - Total production (kg/yr):
1.0	1.0	0.0	1.0	Milk cow - Fraction of drinking water that is contaminated:
0.25	0.25	0.0	1.0	Milk cow - Fraction of animal diet consisting of contaminated hay:
45.0	45.0	1.0	365.0	Milk cow - Hay growing time (da):
2	2	0	2	Milk cow - Hay irrigation source (0-none, 1-ground water, 2-surface water):
47.0	47.0	0.0	200.0	Milk cow - Hay irrigation rate (in/irrigation season):
6.0	6.0	0.0	12.0	Milk cow - Hay irrigation duration (mo/yr):
2.0	2.0	0.0	10.0	Milk cow - Hay yield (kg/m ²):
100.0	100.0	0.0	365.0	Milk cow - Storage time for hay (da):
0.75	0.75	0.0	1.0	Milk cow - Fraction of animal diet consisting of contaminated fresh forage:
30.0	30.0	1.0	365.0	Milk cow - Fresh forage growing time (da):
2	2	0	2	Milk cow - Fresh forage irrigation source (0-none, 1-ground water, 2-surface water):
47.0	47.0	0.0	100.0	Milk cow - Fresh forage irrigation rate (in/irrigation season):
6.0	6.0	0.0	12.0	Milk cow - Fresh forage irrigation duration (mo/yr):
1.5	1.5	0.0	10.0	Milk cow - Fresh forage yield (kg/m ²):
0.0	0.0	0.0	365.0	Milk cow - Storage time for fresh forage (da):
1.0	18.0	0.0	365.0	Eggs - Holdup between harvest and consumption (da):
30.0	20.0	0.0	100.0	Eggs - Per capita consumption rate (kg/yr):
0.0	0.0	0.0	1.0E+8	Eggs - Total production (kg/yr):
1.0	1.0	0.0	1.0	Laying hen - Fraction of drinking water that is contaminated:
1.0	1.0	0.0	1.0	Laying hen - Fraction of animal diet consisting of contaminated grain:
90.0	90.0	1.0	365.0	Laying hen - Grain growing time (da):
0	0	0	2	Laying hen - Grain irrigation source (0-none, 1-ground water, 2-surface water):
0.0	0.0	0.0	100.0	Laying hen - Grain irrigation rate (in/irrigation season):
0.0	0.0	0.0	12.0	Laying hen - Grain irrigation duration (mo/yr):
0.8	0.8	0.0	10.0	Laying hen - Grain yield (kg/m ²):
180.0	180.0	0.0	365.0	Laying hen - Storage time for grain (da):

A.3.4 External Dose Factor Libraries Used in NUREG/CR-5814

A customized dose factor library may be used in a GENII (Napier et al. 1988a and b) calculation by substituting a modified library for the standard external dose factor library. Such a dose factor library was developed to perform dose calculations in NUREG/CR-5814 for the Sewer Inspector Scenario (#1), STP Sludge Process Operator Scenario (#2), and Ash Truck Driver Scenarios (#6). The technique used to substitute a modified set of dose factors is described in this section. In brief, the steps are as follows: 1) create dose factors for a specific geometry using the GENII module, EXTDF, which is an updated version of the radionuclide shielding code, ISOSHL (Engel et al. 1966); 2) make a special external dose factor library, using results of the EXTDF calculations; 3) run GENII accessing the special library; and, if necessary, 4) perform separate computer runs for pathways involving surface contamination.

A.3.4.1 EXTDF Calculations

The EXTDF module of the GENII software system was used to calculate external dose factors for three scenarios in the sewer study document. The EXTDF calculates a dose factor for each radionuclide in the GENII libraries from a description of the geometry and shielding associated with a given radioactive source. For the NUREG/CR-5814 study, a customized external dose factor library was created using the specialized dose factor lists in place of the dose factors for buried waste at three depths, as described in the following section.

A.3.4.2 External Dose Factor Library GRDFX

The standard library external dose factor library, GRDF.DAT, is described in the GENII documentation (p. 2.30 of Vol. 2). This file contains dose

factors for air immersion, water surface, soil surface, and deep soil or buried waste with 15 cm, 0.5 m, and 1.0 m of clean overburden.

A specialized external dose factor library is created and substituted for the standard library. In the new dose factor library (GRDFX.DAT), the three new lists of external dose factors are inserted into the three columns which normally correspond to buried waste. Figure A.10 shows the title lines and pertinent excerpts from the GRDF.DAT and GRDFX.DAT files.

A.3.4.3 Accessing GRDFX

GENII assigns each external file a unique logical unit number. These assignments are stored in the file "FILENAME.DAT," shown in Figure A.11. The user may assign different files by modifying FILENAME.DAT. The revised external dose factor library is accessed by substituting "GRDFX.DAT" for "GRDF.DAT" in FILENAME.DAT. In this case, logical unit number 10 corresponds to GRDFX.DAT in a sewer project subdirectory.

In the input files for the three 1992 generic sewer study scenarios, the source inventory is treated as deep soil or buried waste. The depth of soil overburden, 0.15 m, 0.5 m, or 1.0 m, is used merely as a pointer in order to access the correct list of dose factors to be used for each scenario.

A.3.4.4 Surface Contamination Pathways

Since the program works as though the waste is "buried," additional GENII runs are necessary to calculate doses from internal exposure pathways from surface contamination. Results from the external and internal exposure are then summed to obtain the total dose (TEDE).

 External Dose Factors for GENII in person Sv/yr per Bq/n (8-May-90 RAP)

n	Air Submersion m3	Water Surface L	Soil Surface "m3"	Buried 0.15 m m3	Buried 0.5 m m3	Buried 1.0m m3
H 3	1.95E-16	2.86E-16	1.04E-20	0.00E+00	0.00E+00	0.00E+00
BE7	1.01E-07	1.39E-07	5.39E-11	4.97E-12	2.77E-14	1.94E-17
BE10	4.21E-10	5.88E-10	1.30E-13	1.66E-15	1.95E-18	5.66E-22
C 14	1.41E-11	2.02E-11	2.23E-15	8.89E-19	3.86E-24	3.56E-31
N 13	1.93E-06	2.66E-06	1.03E-09	9.53E-11	5.30E-13	3.72E-16

 Modified External Dose Factors for GENII Sv/yr per Bq/m3 (8-Aug-90)

n	Air Submersion m3	Water Surface L	Soil Surface "m3"	STP WKR 0.15 m m3	ASH TRANS 0.5 m m3	SEWER MAINT 1.0 m m3
H 3	1.95E-16	2.86E-16	1.04E-20	6.56E-21	0.00E+00	1.18E-19
BE7	1.01E-07	1.39E-07	5.39E-11	5.77E-11	1.87E-12	1.24E-11
BE10	4.21E-10	5.88E-10	1.30E-13	1.27E-13	1.29E-15	5.99E-14
C 14	1.41E-11	2.02E-11	2.23E-15	2.10E-15	3.32E-19	2.70E-15
N 13	1.93E-06	2.66E-06	1.03E-09	1.11E-09	3.58E-11	2.37E-10

Figure A.10 Headings and excerpts from external dose factor libraries GRDF.DAT and GRDFX.DAT

Appendix A

2	\GENII\RMDLIB.DAT
3	\GENII\METADATA.DAT
4	\GENII\RMDBYELE.DAT
5	\GENII\GENII.IN
6	\GENII\GENII.OUT
7	\GENII\WORK.BUF
8	\GENII\FTRANS.DAT
9	\GENII\BIOAC1.DAT
10	\SEWER2\2\GRDFX.DAT
11	\GENII\ENV.IN
12	\GENII\DOSSUM.DAT
13	\GENII\ENV.OUT
14	\GENII\DOSE.OUT
15	\GENII\INTDF.OUT
16	\GENII\CDEINC.OUT
17	\GENII\DITTY.OUT
18	\GENII\INTDF.IN
19	\GENII\DITTYQA.OUT
20	\GENII\CDE.OUT
21	\GENII\MEDIA.OUT
22	\GENII\DEFAULT.IN
23	\GENII\JOINTFRE.IN
24	\GENII\CHIQ.IN
25	\GENII\PLUMDRF.DAT
26	\GENII\ENERGY.DAT
27	\GENII\POP.IN
28	\GENII\GENII2.OUT
29	
30	\GENII\DSFCT30.DAT
31	\GENII\WATREL.IN
32	\GENII\AIRREL.IN
33	\GENII\DITTY.IN
34	\GENII\SOLIB.DAT
35	\GENII\EXTDF.IN
36	\GENII\EXTDF.OUT
37	\GENII\DOSINC.OUT
38	\GENII\GAMEN.DAT
39	\GENII\DOSEQA.OUT
40	\GENII\DOSINC.DAT
41	\GENII\SEE.IN
42	\GENII\FOODPROD.IN
43	
44	\GENII\SEERPT.OUT
45	\GENII\SEE1.DAT
46	\GENII\SEE2.DAT
47	\GENII\SEE3.DAT
48	
49	\GENII\WORK2.BUF
50	\GENII\WORK3.BUF

Figure A.11 GENII file FILENAME.DAT

Appendix B

Wastewater Treatment Plants Waste Stream Descriptions

B.1 Oak Ridge Plant Waste Streams Description

The Oak Ridge WWTP, located in Oak Ridge, TN, began operations in 1983. This municipal plant was designed to provide primary, secondary, and tertiary treatment for regionally generated wastewater. The treated liquid effluent is discharged into East Fork Poplar Creek. The water quality of the discharged effluent is regulated by the plant's National Pollution Discharge Elimination System (NPDES), authorized by the state of Tennessee. The major effluent water quality characteristics that are monitored and regulated by designated effluent limitations include biological oxygen demand (BOD), ammonia (as N), suspended solids, fecal coliform, dissolved oxygen, total chlorine residual, pH, and lead (Pb). In addition, cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and zinc (Zn) are determined for the influent and effluent waste streams. The plant was designed to treat an average daily flow of 4.67 MGD and can handle a peak flow rate of 13.36 MGD.

The first treatment stage, primary treatment, consists of two bar screens (Section 2.2.1.1), two grit tanks (Section 2.2.1.3), and two primary settling tanks (Section 2.2.2). Secondary treatment consists of two aeration tanks (Section 2.3.1.1) and two final (secondary) settling tanks. The final settling tank effluent is discharged to the tertiary treatment stage of the plant which consists of four granular medium filters (Section 2.4.1.1). The filter effluent is then chlorinated and dechlorinated in two chlorination chambers (Section 2.3.2.4). The disinfected wastewater then flows down a cascading ladder for post aeration and is discharged to East Fork Poplar Creek (Figure B.1).

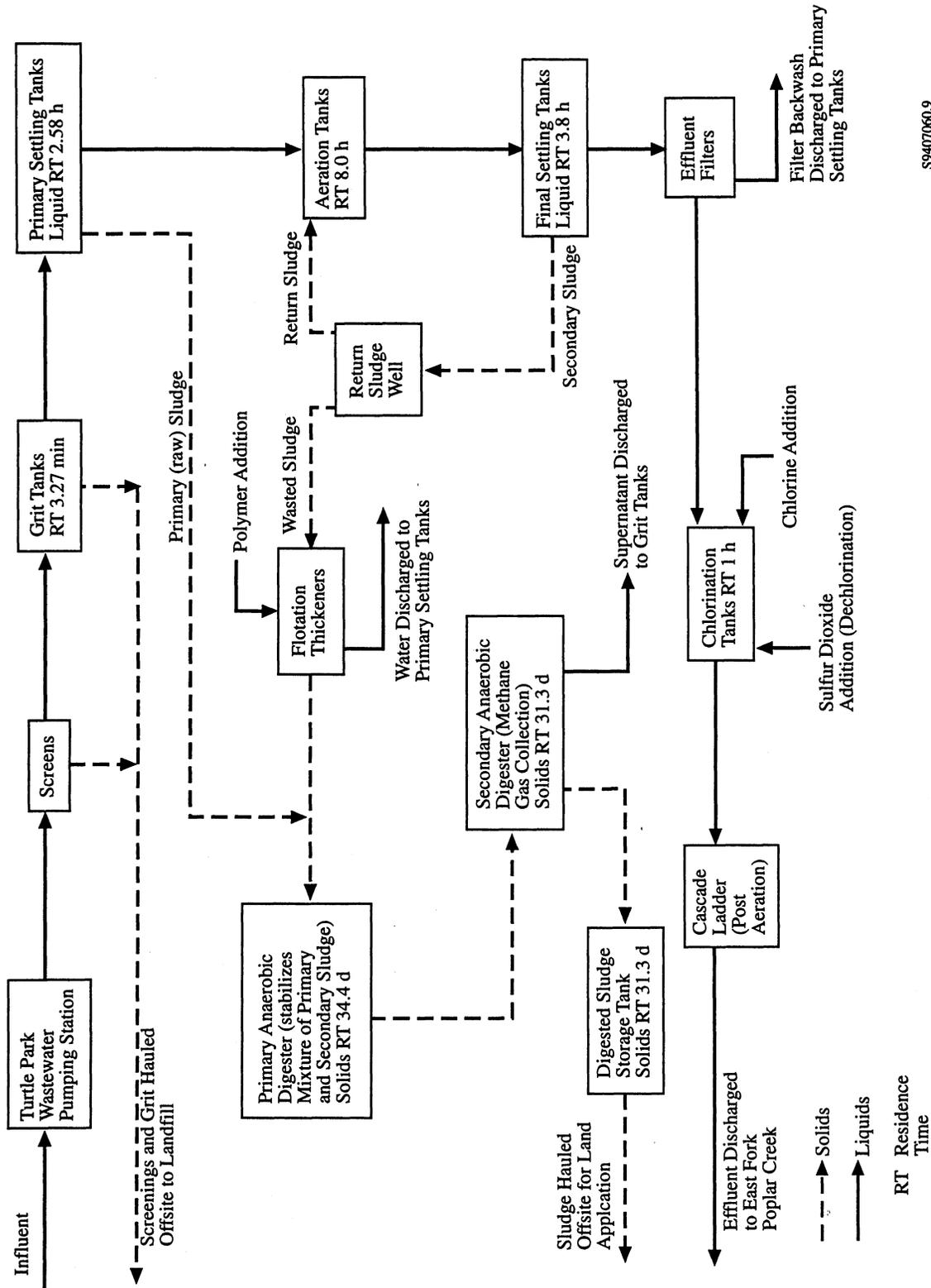
The influent wastewater contains both liquid and solids (primarily organic). The liquid residence time in plant (from the time it enters the bar screens until it

is discharged to East Fork Poplar Creek) is approximately 16 hours (Table B.1). The solids and liquid are pass through the bar screens and grit tanks where large objects and grit are removed from the bulk wastewater. The screenings and grit are collected into a hopper and hauled offsite to a sanitary landfill. The remaining liquid and organic solids then enter the primary settling tanks where the majority of the settleable organic solids (approximately 60 percent) and floating material (for example, oil and grease) are separated and removed. The solids removed from the primary settling tanks are designated primary (raw) sludge.

Table B.1 Oak Ridge Wastewater Treatment Plant liquid residence time based on a wastewater design flow = 4.67 MGD

Unit Operation	Residence Time (hours)
Screens	0
Grit Tanks	0.06
Primary Settling Tanks	2.6
Aeration Tanks	8
Final Settling Tanks	3.8
Dual-Medium Filters	0.5
Chlorination Tanks	0.95
Total Hours = 15.9	

The liquid effluent from the primary settling tanks is discharged to the aeration tanks where the wastewater is treated biologically using the suspended growth



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Figure B.1 Oak Ridge Wastewater Treatment Plant flow diagram and residence times

activated-sludge process. The aeration tanks contain an optimum population (for example, approximately 2500 mg/L suspended solids) of aerobic microorganisms (for example, heterotrophic bacteria) that assimilate the incoming organic matter (that is, the organic suspended solids that are not removed by the primary settling tanks). Air is supplied to the tanks via air diffusers located along the bottom of each tank. The resulting microorganism growth, designated "biologically activated sludge," produces a settleable organic solid which is separated from the bulk wastewater in the final settling tanks. Any remaining suspended organic solids in the final settling tank effluent are removed in the final filters. The wastewater is evenly distributed to four dual-media filters that are operated in a down-flow mode. Each filter consists of an open-top rectangular basin containing a layer of anthracite on top of a layer of sand which overlies a bottom layer of gravel. The wastewater flows downward through the anthracite and sand, adsorbing the remaining suspended solids. The polished wastewater exits the filters through the gravel underdrain layer and is discharged to the chlorination chambers. A concentrated chlorine (Cl_2)/water solution is added to the wastewater just upstream of the chlorination chambers. The chlorine contact time (that is, liquid residence time in a chamber) is approximately one hour (Table B.1). Prior to discharge, a concentrated sulfur dioxide (SO_2) solution is added to the disinfected wastewater for dechlorination. The wastewater is then post aerated, via a cascading ladder, to increase the dissolved oxygen level before it is discharged to the East Fork Poplar Creek. The required discharged wastewater pH range is six to nine. In 1993, the annual average pH above and below the effluent point of discharge in the East Fork Poplar Creek was 7.9 and 7.8, respectively.

There are two solids streams generated in the plant: primary sludge and secondary (waste-activated) sludge (Figure B.1). The residence times (from the time the wastewater enters the plant until the sludge is hauled from the storage digester) are approximately 97 days and 106 days for the primary and secondary sludge, respectively (Tables B.2 and B.3). In the primary settling tanks, the primary sludge is separated from the bulk wastewater and pumped to the primary digesters (Figure B.1). In the final settling tanks, the secondary sludge is separated from the bulk wastewater and pumped to the return sludge well. The return sludge well is a holding facility where the

Table B.2 Oak Ridge Wastewater Treatment Plant primary sludge residence time based on a wastewater design flow = 4.67 MGD

Unit Operation	Residence Time (days)
Screens	0
Grit Tanks	0.002
Primary Settling Tanks	0.33 ^(a)
Primary Anaerobic Digesters	34.4
Secondary Anaerobic Digester	31.3
Storage Digester	31.3
Total Days = 97.3	

(a) The settled primary sludge from the primary settling tanks is collected in a hopper and pump to the primary digesters three times per 24-hour period. The pumping duration is approximately one hour. Therefore, it was assumed that the sludge retention time in the primary settling tanks (that is, in the hopper) was one third of 24 hours (0.33 days).

majority (approximately 97 percent) of the collected secondary (biologically activated) sludge is recycled back to the aeration tanks to maintain the optimum (approximately 2500 mg/L) population of biological solids for the activated-sludge process. Hence, the majority of the secondary sludge flows in a recycle loop between the aeration tanks, final settling tanks, and the return sludge well.

The average length of time the biologically activated sludge is recycled, designated the mean cell residence time, is approximately eight hours (Table B.3). The portion of secondary sludge not recycled to the aeration tanks (that is, waste-activated sludge) is discharged to the dissolved-air flotation sludge thickener. The object of the thickener is to dewater the sludge before it is sent to the primary digesters. Dewatering is achieved by floating the solids upward where they are separated, via skimmers, from the remaining wastewater. Solids flotation is enhanced by

Table B.3 Oak Ridge Wastewater Treatment Plant secondary design flow sludge residence time based on a wastewater design flow = 4.67 MGD

Unit Operation	Residence Time (days)
Screens	0
Grit Tanks	0.002
Primary Settling Tanks	0.33 ^(a)
Mean Cell Residence Time ^(b)	8.22 ^(c)
Flotation Thickener	0.25 ^(d)
Primary Anaerobic Digesters	34.4
Secondary Anaerobic Digester	31.3
Storage Digester	31.3
Total Days = 105.5	

- (a) The settled primary sludge from the primary settling tanks is collected in a hopper and pump to the primary digesters three times per 24-hour period. The pumping duration is approximately one hour. Therefore, it was assumed that the sludge retention time in the primary settling tanks (that is, in the hopper) was one third of 24 hours (0.33 days).
- (b) Includes the aeration tanks, final settling tanks, and the return sludge well.
- (c) Based on average month mean cell residence times from 1993.
- (d) Based on an average thickener operation time.

introducing dissolved air, under pressure, into the sludge stream. The resulting air bubbles attach to solids, thereby increasing their buoyancy. A cationic organic polymer (Section 3.2.1.2) is added to the sludge thickener feed to promote flocculation (that is, solids aggregation) enhancing the thickening process. Currently, the plant uses a high molecular weight (> 10⁷ g/mol) polymer. The polymer is injected into the sludge feed as a concentrated polymer/water

solution to provide an average polymer sludge feed concentration of 2500 ppm. The thickened secondary sludge is then discharged to the primary digesters.

Both the primary and thickened secondary sludge streams are mixed and discharged into two primary anaerobic digesters. The objective of the anaerobic digesters is to stabilize the sludge. The purpose of stabilization is to reduce pathogens in the sludge, eliminate offensive odors, and reduce or eliminate the potential for putrefaction. Anaerobic digestion reduces the sludge (organic matter) to methane and carbon dioxide with minimal production of biomass. The sludge is recycled and heated, using methane-burning boilers, in the digesters for approximately 34 days. During this residence time, complex organic compounds such as sugars, fats, carbohydrates, and proteins are broken down to simple organic materials by groups of bacteria called "acid-formers." Also, methanogenic bacteria use the organic material to produce methane, carbon dioxide, and other gases. A pH of seven is required to promote rapid digestion. The resulting stabilized sludge, generated gas, and liquid in the primary digesters are pumped to the secondary digester. The secondary digester is a storage tank with a gas collection system. The collected methane gas is piped to the boilers as a fuel supply. The liquid (supernatant) is sent to the grit tanks. The digested sludge, which has a secondary digester residence time of approximately 31 days, is pumped to the storage digester. The sludge, on average, remains in the storage digester for 31 days, after which it is pumped into a storage truck and hauled offsite for land application on the Department of Energy's Oak Ridge Reservation. The pH of the stabilized sludge is typically seven with a percent total solids concentration ranging between about three and five percent.

Most of the year, the stabilized sludge is hauled from the storage digester. However, during the dry summer months, when peak sludge land application is conducted, the storage digester is often emptied because it does not contain enough sludge volume to meet the land application demand. Therefore, during peak land application, the sludge is often hauled directly from the secondary digester, which reduces the sludge residence time by 31 days (that is, the time the sludge would have normally remained in the storage digester).

B.2 Erwin Plant Waste Streams Description

The Erwin WWTP was put into operation in 1962 to provide primary treatment, chlorination, and anaerobic sludge digestion of regionally generated wastewater. In response to the 1972 Clean Water Act, the plant was retrofitted in 1988 to provide secondary treatment. The resulting improvements included rotating biological contactors, secondary clarifiers, a new heated anaerobic digester, and a new chlorine contact tank. Thus, the Erwin WWTP currently provides primary and secondary treatment for a design wastewater flow of 1.9 MGD and a peak flow of 5.6 MGD. The plant receives wastewater generated by residents of Erwin and several local industrial facilities including Nuclear Fuel Services—the single source of radioactive discharges to the plant.

The untreated wastewater collected in the sewer system flows to the head of the treatment plant (Figure B.2). The first treatment stage, primary treatment, consists of a bar screen (Section 2.2.1.1), an aerated grit chamber (Section 2.2.1.3), a lift station, and two primary settling tanks (Section 2.2.2). The second treatment stage consists of four rotating biological contactor (RBC) units (Section 2.3.1.2; similar to Figure 2.10) and two secondary clarifiers (Section 2.3.2.4). The secondary clarifier effluent is then discharged to a chlorine contact tank. Once the treated wastewater is disinfected, it is discharged to the Nolichucky River.

The influent wastewater contains both liquid and solids (primarily organic). The liquid residence time in the plant (that is, from the time the wastewater enters the bar screen until it leaves the chlorine contact tank) is approximately seven hours (Table B.4). Both the liquid and solids are passed through a mechanically-cleaned bar screen where large debris are removed from the bulk wastewater and collected in a storage container. The wastewater then continues to the aerated grit tank where high-density solids (for example, sand and gravel) are allowed to settle. The settled grit is collected from the bottom of the tank with mechanically operated buckets and dispensed into a storage container. Both the screenings and grit material are hauled offsite to a sanitary landfill. The wastewater then flows into the

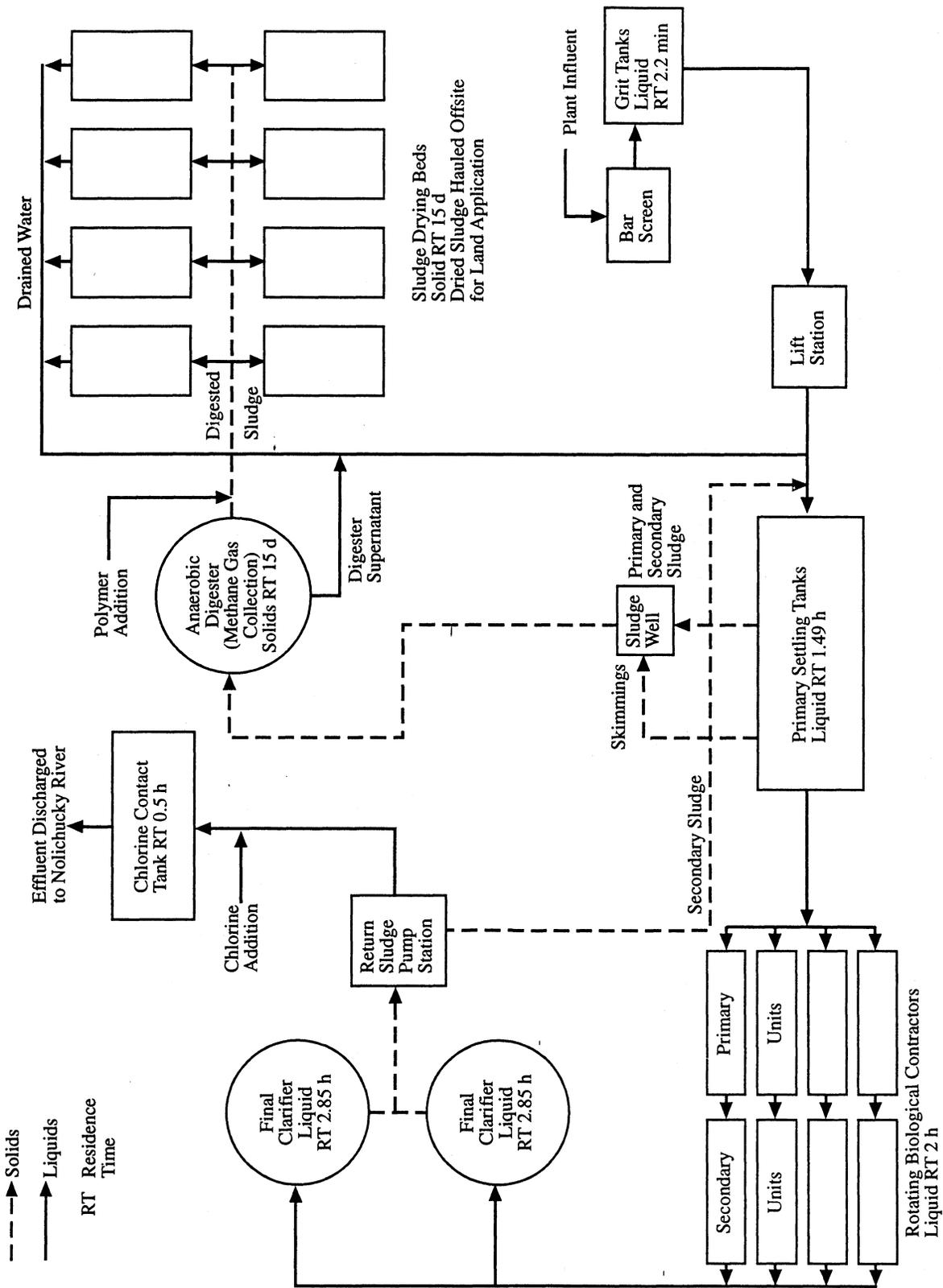
Table B.4 Erwin Wastewater Treatment Plant liquid residence time based on a wastewater design flow = 1.9 MGD

Unit Operation	Residence Time (hours)
Bar Screen	0
Grit Tank	0.04
Primary Settling Tanks	1.49
Rotating Biological Contactors	2
Final Clarifiers	2.9
Chlorine Contact Tank	0.5
Total Hours = 6.9	

lift station wet well (that is, holding tank) where it is pumped to the head of the primary settling tanks.

There are two rectangular primary settling tanks operated in parallel to remove the majority of organic solids (approximately 60 percent of the influent suspended solids and 25 percent of the influent biological oxygen demand) and floating material (for example, oil and grease). Effluent from the primary settling tanks is sent to a distribution structure where the flow is evenly divided into four separate feed streams, one for each RBC unit.

Each RBC unit consists of two RBCs operated in series (Figure B.2). The RBCs use an attached-growth aerobic biological treatment process to reduce the carbonaceous biological oxygen demand exerted by the suspended organic solids in the bulk wastewater that were not removed by the primary settling tanks. Each RBC contains an open-top rectangular concrete basin, a rotating shaft with attached plastic media, and a cover. The wastewater enters one end of the tank where it comes into contact with a series of plastic disks (polyethylene) attached to the rotating shaft. The diameter of the plastic disks is 12 feet and approximately 40 percent of the diameter is immersed in the wastewater. The shaft rotates the disks at a speed of one revolution per minute, perpendicular to the direction of the wastewater flow. A thin film of



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Figure B.2 Erwin Wastewater Treatment Plant flow diagram and residence times

aerobic bacteria becomes attached to the plastic media. The rotating media alternately brings the aerobic bacteria into contact with the organic solids substrate in the wastewater and the oxygen present in the ambient air providing a continuous carbonaceous substrate and oxygen supply for bacterial growth. As the attached film thickens, the outlying portion of the film is removed (sloughed) from the media by the shearing force created between the rotating disks and the wastewater.

The sloughed biological solids remain suspended in the RBC effluent. The RBC effluent is discharged to two final (secondary) clarifiers that are operated in parallel and designed to allow the biological solids (secondary sludge) to settle. The final clarifier effluent is then discharged to the chlorine contact tank where a concentrated Cl_2 /water solution is continuously added to the wastewater via a diffuser. The chlorine contact tank contains four baffles and provides a chlorine contact time (that is, liquid residence time) of approximately 30 min for an average design flow of 1.9 MGD. Finally, the disinfected effluent is transported in a pipeline about a half mile to the Nolichucky River.

Both primary and secondary sludge is removed from the bulk wastewater (Figure B.2). The primary sludge, which is removed from the influent wastewater by the primary settling tanks, has an approximate residence time of 30 days (Table B.5). The secondary sludge, which is removed from the bulk wastewater in the final clarifiers, has an approximate residence time of 31 days (Table B.6). The settled secondary sludge and floating material are removed from the final clarifiers, collected in the return sludge pumping station, and pumped to the head of the primary settling tanks. This return sludge is mixed with the influent wastewater just upstream of the primary settling tanks. Mixing the secondary solids with the influent wastewater improves the settling efficiency of the primary settling tanks. The solids and skimmings removed from the primary settling tanks, a combination of primary and secondary solids, are collected in a sludge well and pumped to the anaerobic digester.

The objective of the anaerobic digester is to stabilize the sludge. The purpose of stabilization is to reduce pathogens in the sludge, eliminate offensive odors, and reduce or eliminate the potential for putrefaction

Table B.5 Erwin Wastewater Treatment Plant primary sludge residence time based on a wastewater design flow = 1.9 MGD

Unit Operation	Residence Time (days)
Bar Screen	0
Grit Tank	0.002
Primary Settling Tanks	0.25 ^(a)
Anaerobic Digester	15
Sludge Drying Beds	15
Total Days = 30.3	

- (a) The settled sludge from the primary settling tanks is collected in hoppers and pumped to the anaerobic digester four times a day. Therefore, it was assumed that the sludge detention time in the primary settling tanks was one fourth of a day.

that is, the decomposition of organic matter). Anaerobic digestion reduces the sludge (organic matter) to methane and carbon dioxide with minimal production of biomass. The sludge is recycled and heated (95°F), using a methane-burning furnace, in the digester for approximately 15 days. During this residence time, complex organic compounds such as sugars, fats, carbohydrates, and proteins are broken down to simple organic materials by groups of bacteria called "acid-formers." Another group of bacteria, called "methane-formers," use the organic material to produce methane, carbon dioxide, and other gases. A pH of seven is required to promote rapid digestion. The collected methane gas is piped to the furnace as a fuel supply. The liquid (supernatant) is sent to the primary settling tanks. The digested sludge is discharged to the sludge drying beds (Section 2.5.6.1). A high molecular weight ($\sim 10^6$ g/mol) cationic polymer is added to the sludge in the discharge pipeline as a thickening agent. The solids concentration of the polymer-treated stabilized sludge is 5 wt%. There are a total of eight sludge drying beds with four beds used for drying on a two-week cycle period. Therefore, the approximate solids residence

Table B.6 Erwin Wastewater Treatment Plant secondary sludge residence time based on a wastewater design flow = 1.9 MGD

Unit Operation	Residence Time (days)
Bar Screen	0
Grit Tank	0.002
Primary Settling Tanks	0.06 ^(a)
Rotating Biological Contactors	0.08
Final Clarifiers	0.25 ^(b)
Primary Settling Tanks	0.25 ^(c)
Anaerobic Digester	15
Sludge Drying Beds	15
Total Days = 30.7	

- (a) The residence time for the secondary solids includes the influent wastewater suspended organic solids that are not removed in the primary settling tanks. Hence, the liquid residence time is used.
- (b) The return sludge is pumped to the primary settling tanks four times a day.
- (c) The primary settling tanks solid residence time. Accounts for the settling of the secondary solids recycled from the final clarifiers.

time in the drying beds is 15 days. Each drying bed contains a layer of sand overlying an underdrain system. The sludge is spread uniformly over the sand layer and entrapped water is either drained through the layer or evaporated. The drained water is collected and sent to the primary settling tanks. The dried sludge, which has an average moisture content of 60 percent, is hauled offsite to local farms for land application.

B.3 Westerly Plant Waste Streams Description

The Westerly WWTP is one of three major wastewater treatment plants operated by the NEORS. The Westerly Plant serves approximately 112,00 people in Cleveland and several surrounding suburbs. The treatment plant was constructed in 1974 to provide physical/chemical primary treatment, pressurized multimediuim filters, and carbon columns to handle an increasing volume of wastewater; including an increasing number of industrial facility discharges. Physical/chemical treatment, as opposed to conventional secondary (biological) treatment, was implemented because the Westerly Plant could not accommodate the large facilities required for biological treatment processes. Also, the potential adverse impacts (for example, bacteria toxicity due to pH fluctuations) caused by large industrial discharges influenced the decision to implement physical/chemical treatment processes.

Presently, the carbon columns are not in use because of operational/mechanical failures and poor treatment performance. Hence, the Westerly Plant currently provides primary treatment, enhanced by chemical additives, and advanced treatment using the multi-medium pressure filters. The plant was designed to treat an average daily flow rate of 50 MGD and a peak flow rate of 100 MGD. The Westerly Plant is located on the shore of Lake Erie west of the mouth of the Cuyahoga River. All the plant's treated wastewater effluent is discharged into Lake Erie. A plant schematic, including flow schemes and residence times, is illustrated in Figure 5.4a and b.

The Westerly WWTP influent flows to the head of the treatment plant via the Westerly Interceptor sewer line. Additional combined sewer wastewater (that is, a combination of storm water and sewage) flows into the plant via the Northwestern Interceptor. The primary treatment includes the headworks, chemical handling and feeding, and the flocculator-clarifiers (Figures B.3a and b). The headworks includes a junction structure, two bar screens (Section 2.2.1.1), four aerated grit tanks (Section 2.2.1.3), and a grit dewatering cyclone. Chemical handling and feeding includes two lime slurry flash mix tanks and two ferric chloride flash mix tanks. There are four flocculator-clarifiers used to settle the primary chemical sludge (Sections 2.2.2 and 2.3.2). The advanced treatment

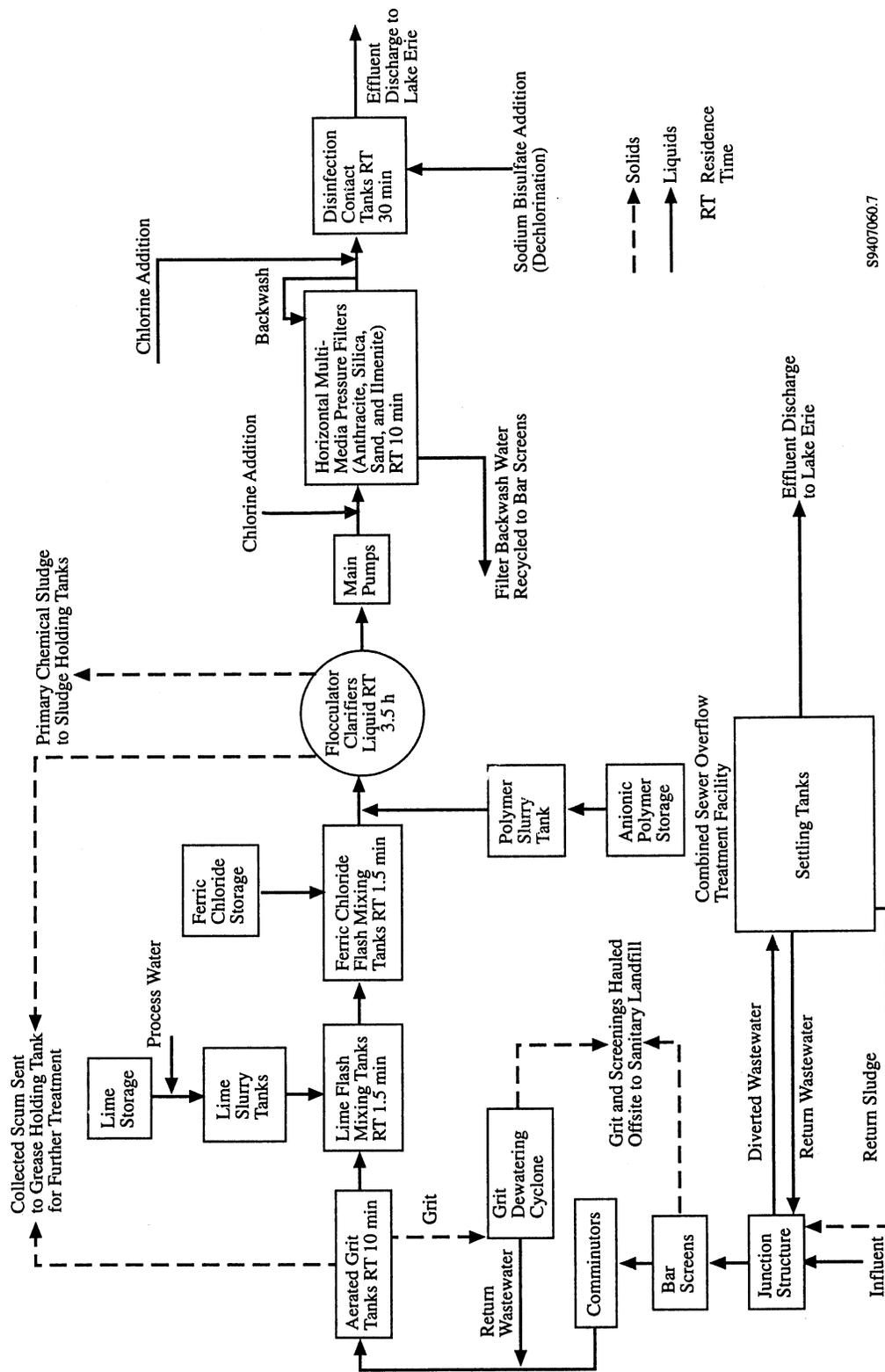


Figure B.3a Westery Wastewater Treatment Plant flow diagram and residence times

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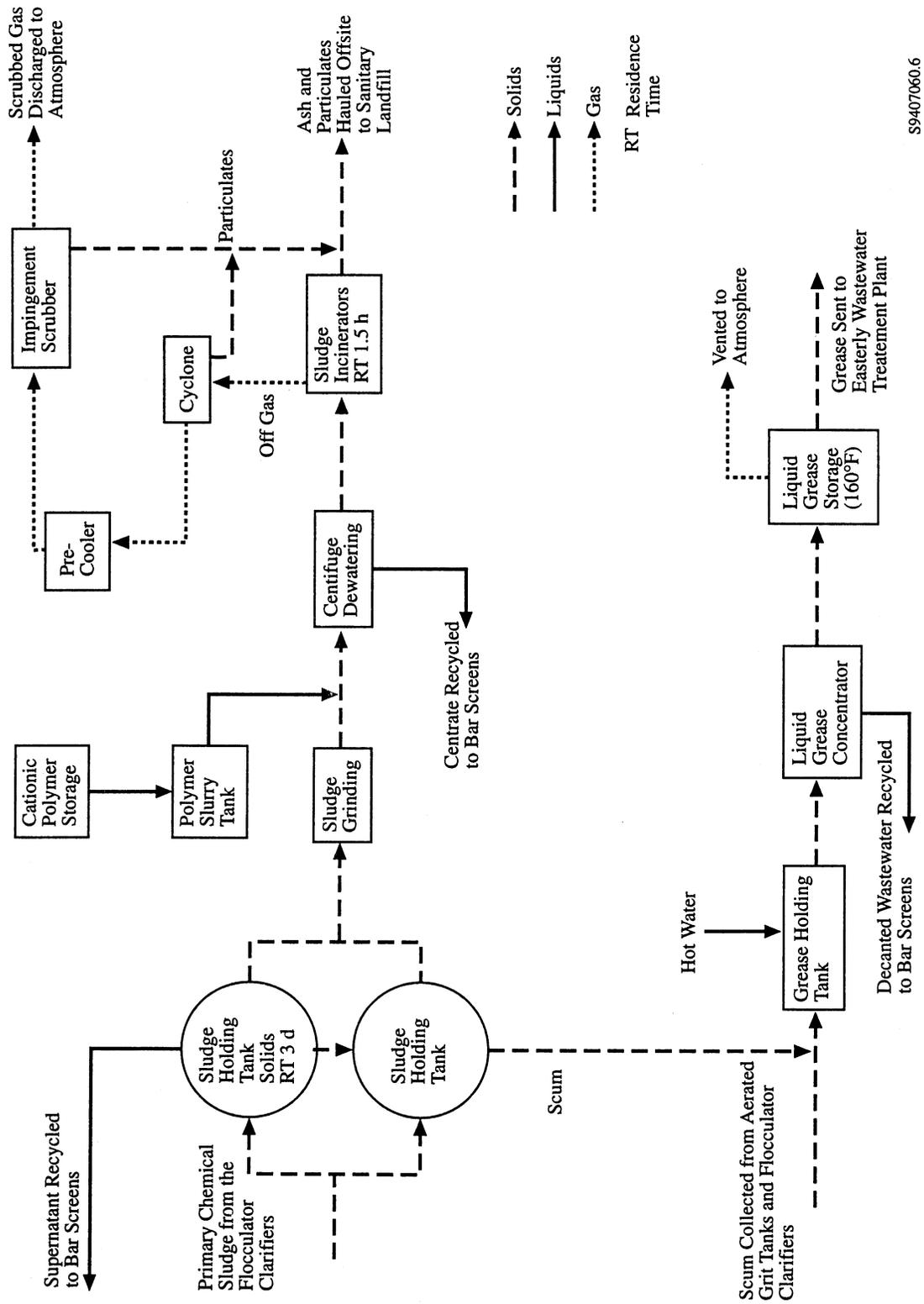


Figure B.3b Westerly Wastewater Treatment Plant flow diagram and residence times

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stage consists of 14 horizontal multimediu pressure filters (Section 2.4.1.1). The filter effluent is disinfected and dechlorinated using four disinfection contact tanks (Section 2.3.2.4). Finally, the disinfected effluent is discharged to Lake Erie. These treatment facilities are designed to handle a dry weather flow rate of 50 MGD. During the rainy season, when the influent daily flow can exceed 50 MGD, the junction structure at the plant headworks is designed to divert the excess wastewater to the plant's combined sewer overflow (CSO) treatment facility. The excess flow is primarily caused by storm water collected in the combined sewer systems that flows into the Northwesterly Interceptor. The CSO treatment facility consists of four rectangular Imhoff settling tanks (that is, the tanks constructed and used in the original Westerly Plant) that are operated in parallel. The liquid effluent is discharged to Lake Erie and the settled solids remain in the bottom of the tanks until the CSO facility is taken off line (that is, the influent flow rate decreases to less than 50 MGD). When the CSO facility is taken off line, the settling tanks contents, both the wastewater and settled sludge, are pumped back to the plant headworks and mixed with the influent wastewater for subsequent primary and advanced treatment.

The influent wastewater contains both liquid and solids (primarily organic). The liquid residence time in the plant (that is, from the time the wastewater enters the bar screens until it is discharged from the disinfection contact tanks), based on an average flow of 30 MGD and only two flocculator-clarifiers in operation, is approximately four hours (Table B.7). When the CSO treatment facility is not in operation, all of the wastewater flow enters the junction structure and flows through two mechanically cleaned bar screens that are operated in parallel. The wastewater then flows through four comminutors where large solids (for example, rags) are cut/ground up into smaller size pieces. The comminuted wastewater flows into four aerated grit chambers, operated in parallel, where high-density solids (for example, sand and gravel) settle. The settled grit is sent to a grit dewatering cyclone and finally, the dewatered grit and collected screenings are combined and hauled offsite to a sanitary landfill. The grit tank effluents flow to the chemical handling and feeding phase of the plant. The Westerly Plant uses chemical additives to provide chemical precipitation treatment and flocculation. The objective of chemical precipitation and flocculation is to facilitate the removal of dissolved

and suspended solids, BOD, and phosphorus, via gravity settling, in the flocculator-clarifiers. Chemical precipitation generates settleable solids in the wastewater that can absorb and entrap both dissolved and suspended solids. Once these solids are formed, a flocculating agent is added to the wastewater to promote aggregation of the solids into larger, more settleable flocs.

Table B.7 Westerly Wastewater Treatment Plant liquid residence time based on an average wastewater flow = 30 MGD

Unit Operation	Residence Time (hours)
Aerated Grit Tanks	0.17
Lime Slurry Flash Mix Tanks	0.03
Ferric Chloride Flash Mix Tanks	0.03
Flocculator-Clarifiers	3.5
Pressure Filters	0.17
Disinfection Contact Tanks	0.5
Total Hours = 4.4	

The chemical precipitation step includes the addition of lime followed by the addition of ferric chloride. Pebble lime, CaO, is stored onsite and mixed with process water in a lime slurry tank. The resulting slurry, which is about three to six percent CaO, is added to the lime slurry flash mix tanks via downcomer pipes positioned approximately one foot above the surface of the wastewater. The two open-top lime slurry flash mix tanks are operated in parallel and each contains a mechanical stir paddle that rapidly mixes the lime slurry with the wastewater. The objective of the lime slurry addition is to prevent the wastewater pH from decreasing below the effluent limit of 6.5. This is a concern because the addition of the ferric chloride solutions increases the acidity of the wastewater and could lower the pH below 6.5 if the lime was not added upstream. The lime-treated wastewater, which has a pH of about 8.4, flows into two open-top ferric chloride flash mix tanks operated

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in parallel. The top of the ferric chloride tanks are positioned several feet below and adjacent to the lime slurry tanks creating a cascading spillway where the ferric chloride is added (as a 28 percent FeCl_3 solution) via a horizontal diffuser pipe located about one foot above the wastewater surface. The mixing regime created by the spillway is used to mix the coagulant with the wastewater.

At pH 8.4, the ferric iron (Fe^{3+}) added to the wastewater readily forms a gelatinous, insoluble hydroxide precipitate, $\text{Fe}(\text{OH})_3$. The easily settleable ferric hydroxide solids adsorb and entrap suspended solids in the wastewater improving the removal efficiency of suspended solids and BOD in the downstream flocculator clarifiers. Ferric iron also reacts with soluble phosphorus in the influent wastewater to form insoluble ferric phosphate (FePO_4) precipitates which enhance the flocculator-clarifiers phosphorus removal efficiency. The target FeCl_3 wastewater dose range is 15 to 30 mg/L. Two large open channels transport the chemically treated wastewater from the ferric chloride flash mix tanks to the flocculator clarifiers. Just downstream from the flash mix tanks, a high molecular weight anionic polymer is added to the wastewater via a horizontal diffuser pipe located about one foot above the water. The solution is mixed with water in a polymer slurry tank and then added to the wastewater. The average anionic polymer wastewater dose is 0.50 mg/L.

The flocculator-clarifiers are large circular settling basins with a flocculating zone located in the upper center section of the basin. The flocculating (that is, slow mixing) zone is generated by a slowly rotating mixer paddle. The wastewater enters the clarifiers at the basin center, is slowly mixed in the flocculating zone which promotes particle-particle aggregation, and then enters a quiescent settling zone where the flocculated solids are allowed to settle. The two flocculator-clarifiers currently in operation achieved an 80 percent suspended solids removal efficiency in 12/93.

The flocculator-clarifier effluent is pumped to the multimedia pressure filters that remove the remaining suspended solids from the bulk wastewater in order to satisfy the plant's effluent suspended solids, BOD, and phosphorus limits. There are a total of 14 filters operated in parallel. Each filter contains a layer of anthracite on top of a layer of sand which overlies a layer of ilmenite (FeTiO_3). Finally, there is a bottom

layer of gravel that provides an underdrain system for the filtered wastewater to exit the filter bed. The filters are operated in a downflow mode at approximately 60 psi. When a filter becomes clogged (indicated by the pressure drop across the bed) it is backwashed by reversing the direction of flow. The backwashing step, which typically requires several bed volumes of filtered wastewater, creates a fluidized filter bed to remove solids collected in the medium layers. The back wash water is collected and recycled back to the bar screens. The filter beds are also surface washed to enhance the cleaning process. Chlorine is added to the pressure filter influent, as a concentrated sodium hypochlorite (NaClO)/water solution, to reduce the potential for bacteria growth in the filter beds. The pressure filter effluent flows to four disinfection contact tanks operated in parallel. The NaClO is used as the disinfecting agent. It is purchased as a concentrated NaClO /water solution (~15 percent NaClO), stored onsite, and fed to the disinfection contact tanks influent via an in-line static mixer. Sodium bisulfite (NaHSO_3) is added to the disinfected wastewater at the tail end of the contact tanks to dechlorinate the plant effluent before it is discharged to Lake Erie.

Two solid streams, the primary chemical sludge collected in the bottom of the flocculator-clarifiers and scum (for example, grease) collected from the aerated grit tanks, flocculator-clarifiers, and sludge holding tanks, are treated at the Westerly Plant (Figures B.3a and b). The primary chemical sludge flows from the flocculator-clarifiers to two sludge holding tanks. These tanks are covered circular settling basins designed to gravity thicken (that is, dewater) the sludge. The gas collected in the headspace of the tanks is discharged to water scrubbers and then vented to the atmosphere. The scum (that is, floating material) is collected and sent to grease handling facilities. The thickened sludge, which has a solids concentration of about four percent, is pumped to two in-line sludge grinders operated in parallel. The ground sludge is then dewatered in a centrifuge to a final solids concentration of 20 percent. A high molecular weight cationic polymer is added to the centrifuge sludge feed to enhance the dewatering/thickening process.

The dewatered sludge cake is sent to one of two multiple hearth incinerators (sludge furnace) where the volatile solids are incinerated (at 840°C) and converted to water and gas. The resulting gas is drawn, via a large induced-draft fan, through a cyclone, pre-cooler,

and impingement scrubber, and then discharged to the atmosphere. The particulates scrubbed from the gas in the cyclone and impingement scrubber are collected with the incinerator ash and sent offsite to a sanitary landfill. The primary chemical sludge residence time in the plant (that is, from the time it enters the bar screens until it leaves the incinerators as ash) is approximately four days (Table B.8).

Table B.8 Westerly Wastewater Treatment Plant sludge residence time based on an average wastewater flow = 30 MGD

Unit Operation	Residence Time (days)
Aerated Grit Tanks	0.007
Lime Slurry Flash Mix Tanks	0.001
Ferric Chloride Flash Mix Tanks	0.001
Flocculator-Clarifiers	1
Sludge Holding Tanks	3
Sludge Incinerators	0.06
Total Days = 4.0	

All of the scum collected in the plant is sent to the grease handling facilities which include a grease holding tank, liquid grease concentrator, and liquid grease storage tank. Hot water is added to the grease holding tank to prevent it from solidifying. The softened grease/water mixture is pumped to the concentrator tank, which is designed to float and skim the grease to separate it from the water. The decanted water is recycled to the bar screens and the concentrated grease is sent to the liquid grease storage tank. This tank is heated to approximately 70°C to prevent solidification during storage. The grease is then hauled offsite to the Easterly WWTP for final treatment.

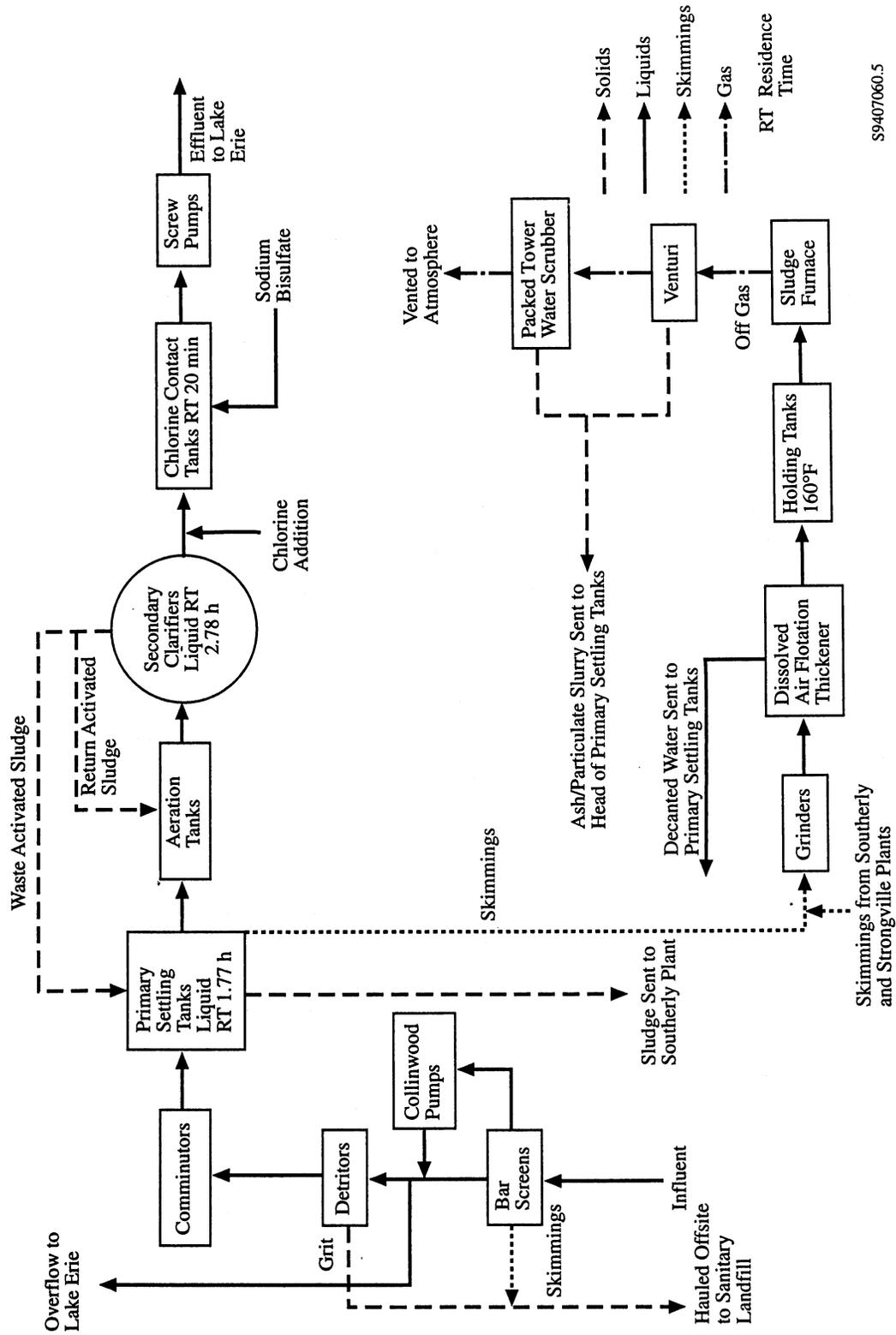
B.4 Easterly Plant Waste Streams Description

The Easterly WWTP currently serves over one half million people in Cleveland and surrounding suburbs. Currently, the Easterly Plant provides primary and biologically activated-sludge secondary treatment with a design capacity of 155 MGD and a peak capacity of 380 MGD for storm water flow. The sludge produced at this WWTP is pumped via pipeline to the Southerly WWTP. A schematic of the Easterly Plant illustrating flow schemes and residence times is shown in Figure B.4.

The influent wastewater flows into the plant headworks via the Easterly, Heights Hilltop, and Collinwood Interceptors. Presently, the average daily influent wastewater flow (dry weather) is 150 MGD. The Easterly Plant's primary treatment stage includes bar screens, detritors, comminutors, and primary settling tanks. The secondary treatment stage includes two aeration tank facilities followed by two secondary clarifier facilities. Finally, the secondary clarifier effluent is disinfected and dechlorinated in chlorine contact tanks and discharged to Lake Erie. In essence, the Easterly WWTP is a larger version of the Oak Ridge WWTP.

The liquid residence time (that is, from the time the wastewater enters the bar screens until it leaves the chlorine contact tanks), based on an average daily flow rate of 150 MGD, is about five hours (Table B.9).

The plant influent enters the bar screens (a total of nine operated in parallel) where large debris is removed from the wastewater. The removed debris (screenings) are collected and hauled offsite to a sanitary landfill. The wastewater from the Easterly and Heights Hilltop Interceptors flows directly to the detritor tanks for grit removal. The Collinwood Interceptor wastewater is pumped to the detritor tanks (Figure B.4). Flow in excess of 380 MGD is diverted to the overflow channel that discharges the overflow to Lake Erie. The detritors, a type of grit tank, remove grit (for example, sand and gravel) from the influent wastewater. The collected grit is hauled offsite to a sanitary landfill and the detritor effluent flows into eight comminutors operated in parallel. The comminutors grind and cut up large solids to enhance solids removal in the primary settling tanks. The comminuted wastewater then flows into 12 rectangular primary settling tanks, operated in parallel.



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Figure B.4 Easterly Wastewater Treatment Plant flow diagram and residence times

Table B.9 Easterly Wastewater Treatment Plant liquid residence time based on an average wastewater flow = 150 MGD

Unit Operation	Residence Time (hours)
Headworks	0.25
Primary Settling Tanks	1.8
Secondary Clarifiers	2.8
Chlorine Contact Tanks	0.35
Total Hours = 5.2	

The primary effluent flows to eight aeration tanks; each tank contains four passes (that is, four baffled compartments). Return activated sludge is recycled from the secondary clarifiers to pass number one and influent wastewater flows into passes two through four. This type of aeration tank flow scheme is called biologically activated-sludge step aeration. The approximate length of time the solids remain in the aeration tank-secondary clarifier recycle loop, designated the "mean cell residence time" (MCRT), is six days. Ceramic dome fine bubble air diffusers are located near the bottom of the aeration tanks in each pass. Air is supplied from large blowers and diffused into the wastewater to provide an oxygen source for aerobic bacteria. The bacteria population (that is, biomass) assimilates the carbonaceous biological oxygen demand (CBOD) present in the wastewater. Suspended organic solids that were not removed upstream in the primary settling tanks are the primary source of CBOD. The approximate concentration of biomass in the aeration tanks, designated the "mixed liquor suspended solids," is 1000 to 1500 mg/L. The resulting bacteria growth, which produces a settleable organic solid, and wastewater mixture flows to the secondary clarifiers.

There are 20 secondary clarifiers (that is, circular settling tanks) operated in parallel that are designed to remove the organic solids generated in the aeration tanks. The clarified wastewater is then disinfected

using four chlorine contact tanks operated in parallel. Sodium hypochlorite (NaClO) is the disinfecting agent currently used. It is added as a concentrated NaClO/water solution (~15 wt% NaClO) to the inlet of the contact tanks. Sodium bisulfite is added to the tail end of the contact tanks to dechlorinate the disinfected wastewater. The outlet of the contact tanks is at a lower elevation than the discharge point in Lake Erie. Therefore, the contact tanks effluent is lifted, via screw pumps, to an elevation above the discharge point. Thus, after the screw pumps, the Plant's effluent flows by gravity into Lake Erie.

The Easterly Plant generates two solid streams consisting of sludge and skimmings (Figure B.4). The sludge, which is a combination of primary and secondary (activated) sludge, and ash from the skimmings furnace, is sent to the Southerly Plant for final treatment and disposal via a pipeline. The residence times for the primary and secondary sludge (that is, from the time the wastewater enters the bar screens until the sludge leaves the plant) are tabulated in Table B.10). The primary sludge consists of the solids removed from the influent wastewater in the primary settling tanks. The secondary sludge consists of the excess (wasted) activated sludge that is removed from the wastewater by the secondary clarifiers but is not recycled back to the aeration tanks. This wasted

Table B.10 Easterly Wastewater Treatment Plant sludge residence time based on an average wastewater flow = 150 MGD

Unit Operation	Residence Time (days)
Headworks	0.01
Primary Settling Tanks	0.13
Primary Sludge Residence Time = 0.14	
Mean Cell Residence Time ^(a)	5.7
Secondary Sludge Residence Time = 5.8	

(a) Includes aeration tanks and secondary clarifiers

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sludge is sent to the influent channel of the primary settling tanks to improve the tanks' solid removal efficiencies. Thus, the solids collected in the bottom of the primary settling tanks are a combination of primary (raw) sludge and excess activated sludge.

The skimmings (that is, primarily grease) collected in the primary settling tanks are sent to the Easterly Plant's skimmings and treatment facilities. These facilities, which include grinders, a dissolved air flotation (DAF) thickener, holding tanks, and a furnace, also receive skimmings from the Southerly and Strongsville Plants. The skimmings are first processed through a series of in-line grinders. The ground skimmings then flow into the DAF thickener which is used to concentrate (dewater) the skimmings stream. Compressed air is mixed in the skimmings stream, under pressure, which then flows into the bottom of an open-top tank. In the tank, the compressed air forms air bubbles that attach to the organic solids increasing their buoyancy. The solids then float to the top of the tank where they are removed by skimmers. The remaining wastewater is sent back to the primary settling tanks and the concentrated skimmings are stored in heated (160°F) holding tanks. The sludge then flows into a fluidized-bed furnace operated at approximately 1450°F. The resulting gas stream, which contains particulates (for example, ash) and water vapor, flows through a venturi scrubber and water scrubber. The particulates removed by the venturi are combined with the spent scrubber water and sent to the primary settling tanks.

B.5 Southerly Plant Waste Streams Description

The Southerly WWTP is the largest and most complicated of three major wastewater treatment plants operated by the NEORS. The Southerly Plant serves approximately 529,000 residents in the Cleveland, as well as several adjacent suburbs. Currently, the Southerly Plant provides primary, secondary (two-stage biological process), and tertiary treatment. The plant is designed to completely treat 175 MGD. The plant can treat an additional 225 MGD of storm water flow in the primary, second-stage biological, and tertiary treatment processes. Finally, the plant can treat an additional 335 MGD of storm water flow in the primary treatment stage only. Hence, the peak plant capacity, with combined

wastewater and storm water flow is 735 MGD. All of the plant's treated wastewater effluent is discharged to the Cuyahoga River. A plant schematic, including the liquid and solid flow patterns and residence times, is illustrated in Figures B.5a through d.

The Southerly Plant wastewater influent flows into the plant headworks via six major sewer interceptors (that is, pipelines). The headworks and primary clarifiers make up the plant's primary treatment stage. The headworks contains junction structures, bar screens, and aerated grit tanks. There are two separate primary clarifier facilities; one contains tank numbers 1 through 10 and the other contains tank numbers 11 through 18. There are two separate biological secondary treatment processes; first stage aeration and second stage aeration. These activated-sludge processes are operated in series and each have separate clarifier facilities. First Stage Aeration removes CBOD and phosphorus from the wastewater. Second Stage Aeration uses biological nitrification to remove ammonia from the wastewater. The Second Stage Aeration effluent flows to the tertiary treatment stage of the plant which consists of 28 dual-media filters. The filter effluent is disinfected in four chlorine contact tanks and then discharged to the Cuyahoga River.

The influent wastewater contains both liquid and solids (primarily organic). The liquid residence time in the plant (that is, from the time it enters the bar screens until it leaves the chlorine contact tanks) is approximately 24 hours (Table B.11) based on an average daily flow of 125 MGD undergoing complete treatment. The wastewater flow enters the junction structures, which combines the flow from the six interceptors, and then passes through one of the seven bar screen and grit tank facilities. The collected screenings and grit are hauled offsite to a sanitary landfill. The grit tank effluent is split and sent to the primary settling tank facilities, which are operated in parallel. Under normal flow conditions (that is, 125 MGD), primary settling tanks 1 through 10 and two of primary settling tanks 11 through 18 are in service. The primary effluent flows to First Stage Aeration where three activated-sludge aeration tanks, with four passes each, are operated in parallel. The aeration tanks' effluent flow is split and sent to two First Stage Aeration primary clarifier facilities that are also operated in parallel. One facility contains six circular settling tanks (clarifiers) and the other contains four rectangular settling tanks. Under normal flow

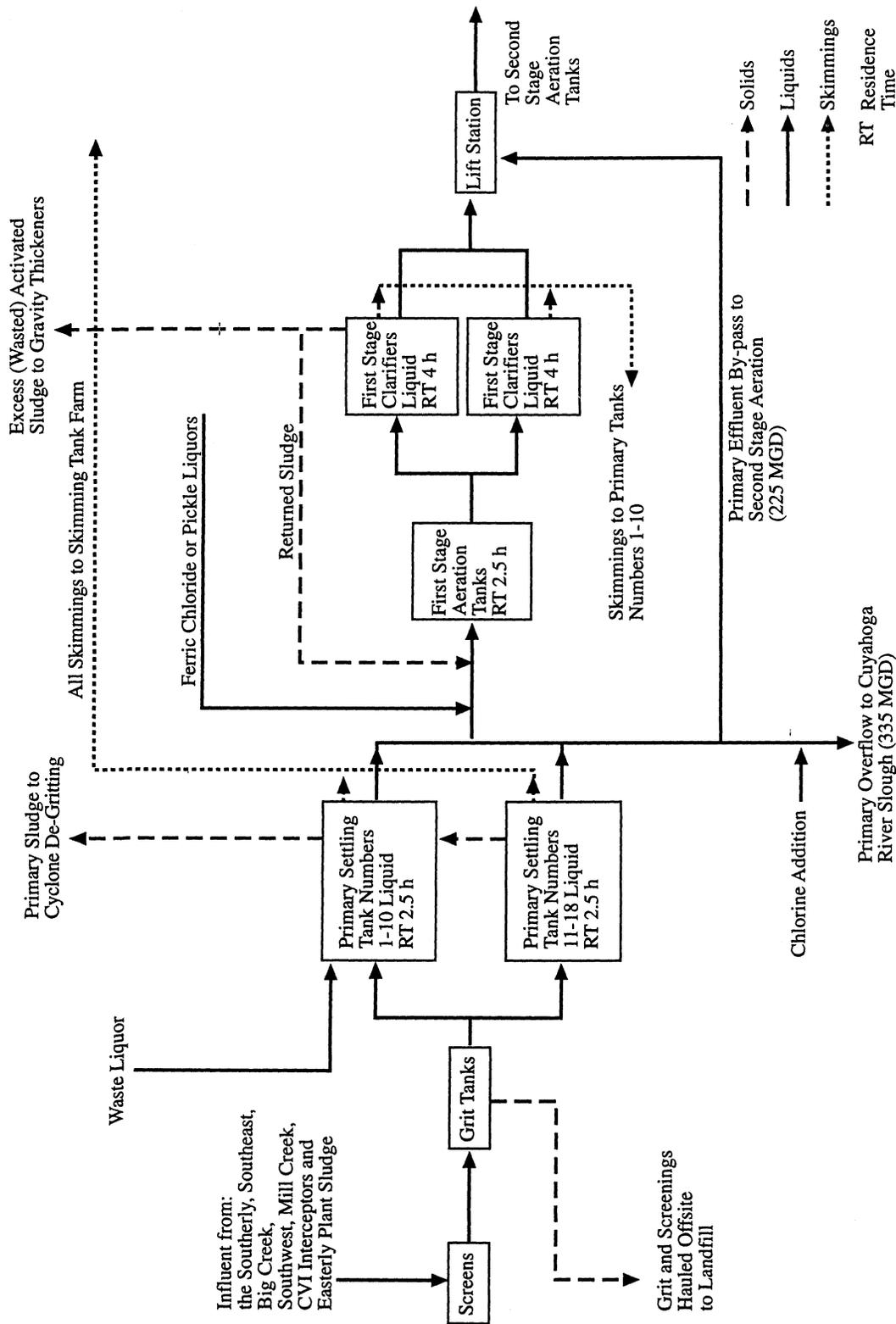
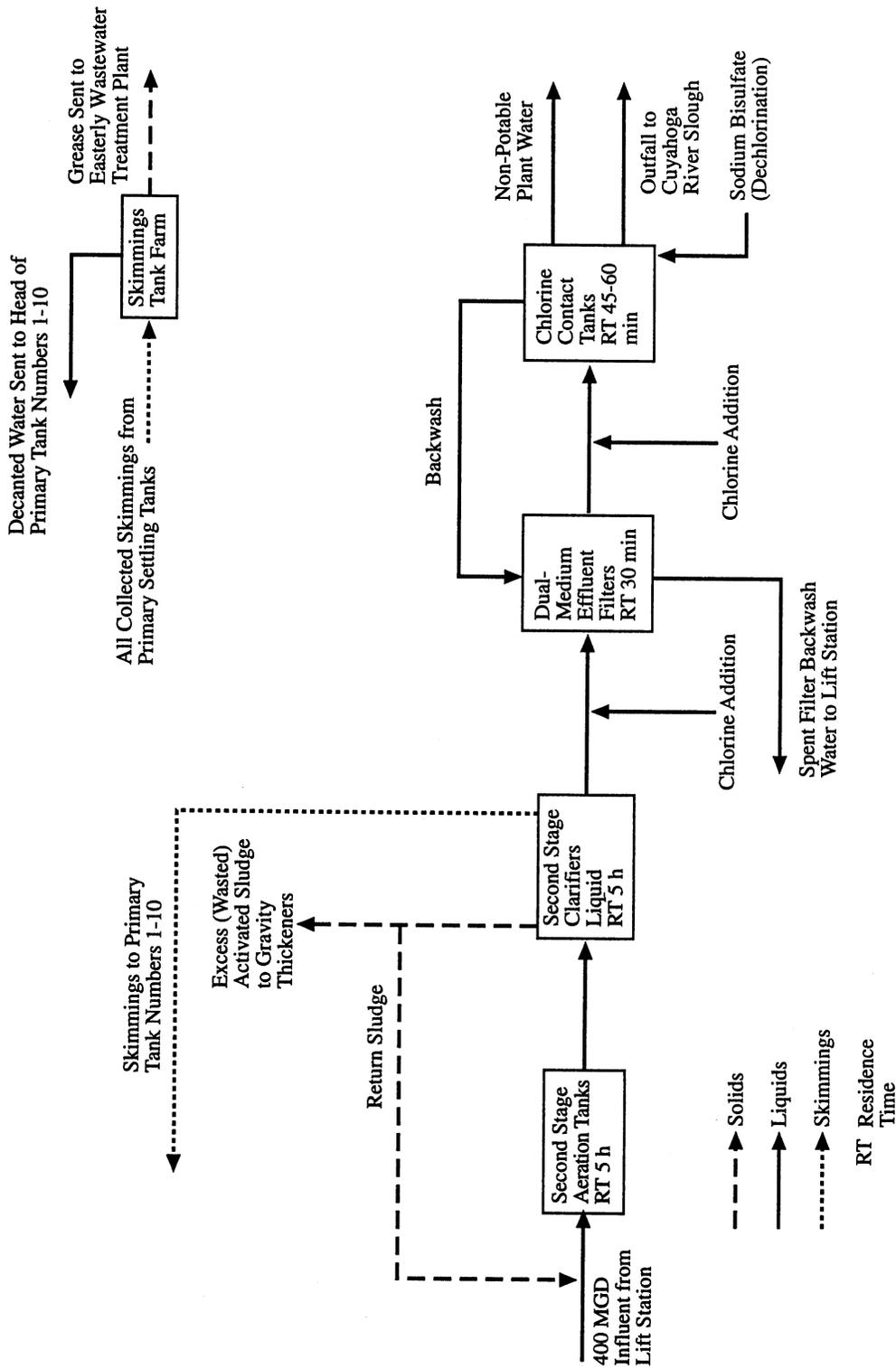


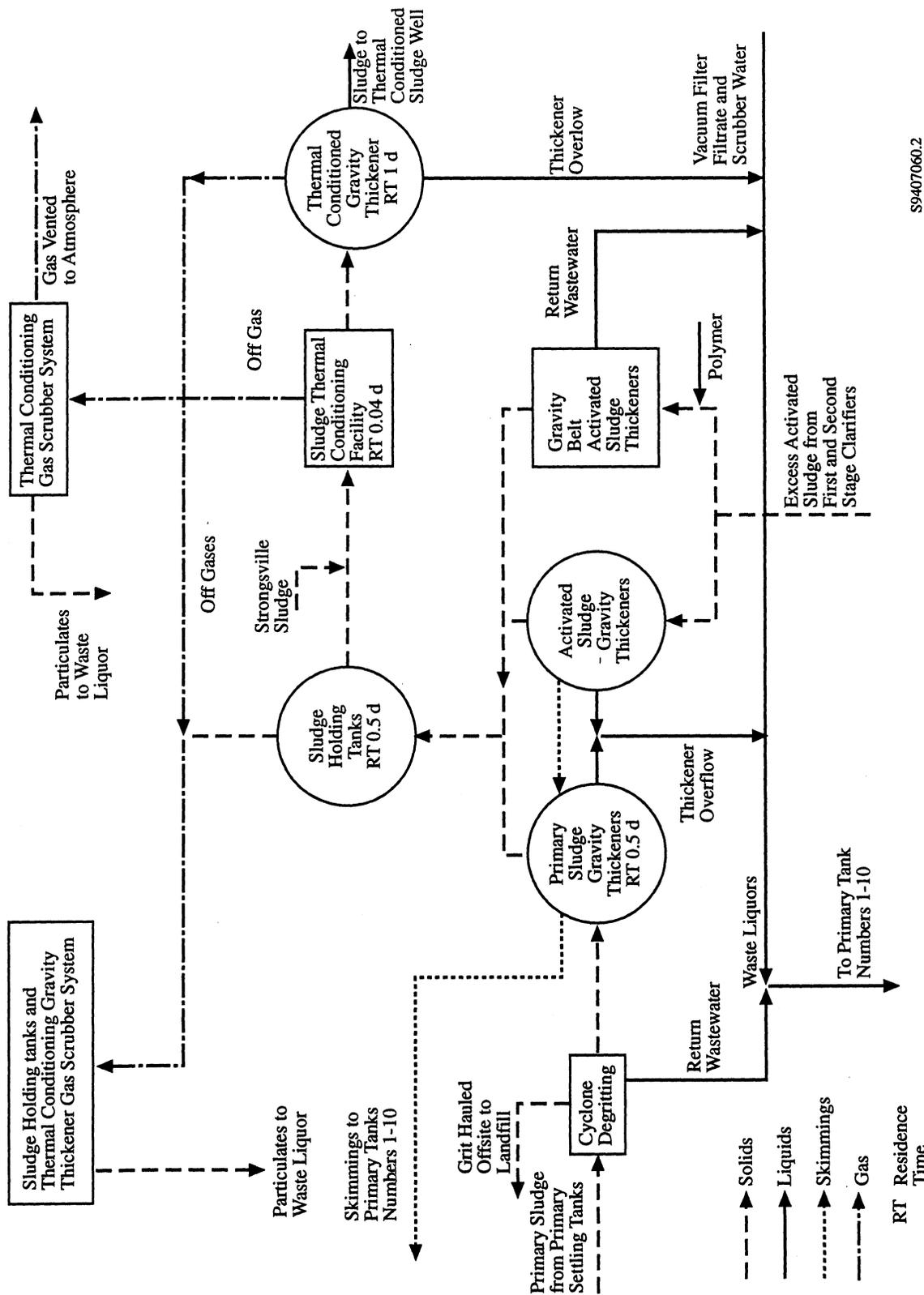
Figure B.5a Southerly Wastewater Treatment Plant flow diagram and residence times

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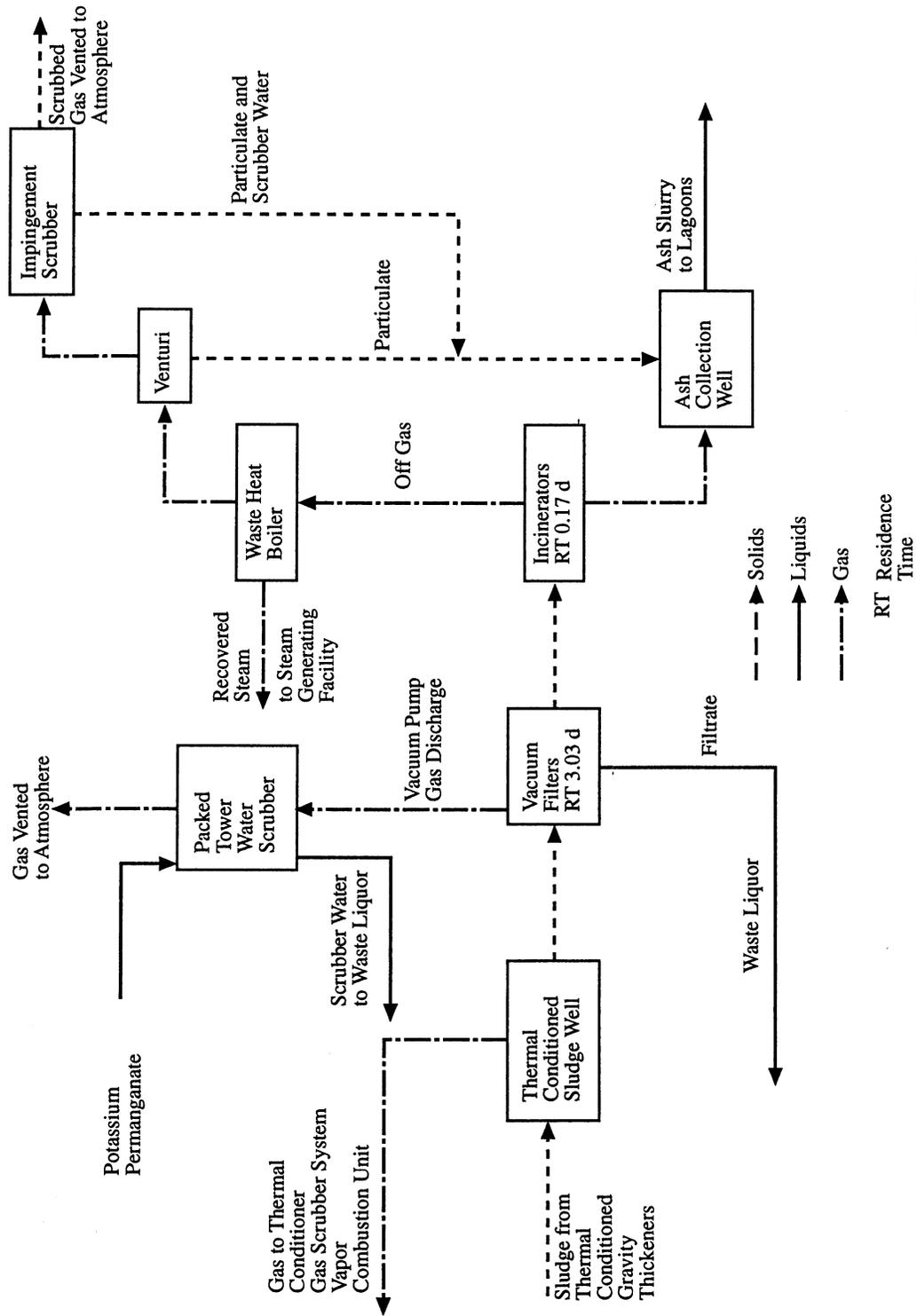
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Figure B.5b Southerly Wastewater Treatment Plant flow diagram and residence times



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Figure B.5c Southernly Wastewater Treatment Plant flow diagram and residence times



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Figure B.5d Southernly Wastewater Treatment Plant flow diagram and residence times

Table B.11 Southerly Wastewater Treatment Plant liquid residence time based on an average wastewater flow = 125 MGD

Unit Operation(s)	Residence Time (hours)
Bar Screens and Grit Tanks	0.033
Primary Settling Tanks ^(a)	2.5
First Stage Aeration ^(b)	2.5
First Stage Clarifiers ^(c)	4
Second Stage Aeration ^(d)	5
Second Stage Clarifiers ^(d)	5
Dual-Medium Filters and Chlorine Contact Tanks	1.5
Channels, Pipelines ^(e)	~3
Total Hours = 23.5	

- (a) Based on tank numbers 1-10 and two of tank numbers 11-18 operating in parallel
- (b) Based on all three tanks operating in parallel
- (c) Based on all ten tanks operating in parallel
- (d) Based on eight out of ten tanks operating in parallel
- (e) Accounts for the liquid residence time in channels and pipelines connecting the unit operations

conditions, all ten settling tanks are in service. Although not typically used, the plant has facilities for adding ferric chloride or pickle liquor to the head of First Stage Aeration to enhance CBOD and phosphorus removal.

The First Stage Aeration clarifier effluent flows into a lift station that pumps the wastewater to the head of the Second Stage Aeration tanks. There are a total of

Table B.12 Southerly Wastewater Treatment Plant primary-sludge residence time based on an average wastewater flow = 125 MGD

Unit Operation(s)	Residence Time (days)
Primary Settling Tanks	0.13
Primary Sludge Gravity Thickeners and Sludge Storage Tanks	1
Thermal Conditioning Reactors	0.04
Thermal Conditioned Sludge Thickeners	1
Vacuum Filters	0.03
Incinerators	0.17
Total Days = 2.4	

ten aeration tanks and each tank has an in-line second stage clarifier bank downstream. Each clarifier bank contains three settling tanks (A, B, and C) in series. Tanks A and B are circular (clarifiers) and Tank C is rectangular. Under normal flow conditions, eight out of the ten aeration tanks and corresponding clarifier banks are operated in parallel. Air is supplied to both the First and Second Stage Aeration tanks via large blowers that feed fine bubble diffusers located on the tank bottoms. The air supplies oxygen to the aerobic bacteria and helps keep the biological solids in suspension (that is, mixed).

The second stage clarifier effluent flows to the dual-media effluent filters. There are a total of 28 filters operated in parallel. Each filter contains a filter bed medium consisting of a layer of anthracite on top of a layer of sand, overlying an underdrain gravel layer. The filter influent is chlorinated (using a concentrated sodium hypochlorite solution) to reduce bacteria growth in the filter beds. The pressure filter effluent flows to four disinfection contact tanks operated in parallel. Sodium hypochlorite is used as the disinfecting agent. It is purchased as a concentrated NaClO/water solution (~15 percent NaClO), stored onsite, and fed to the disinfection contact tanks influent. Sodium bisulfite is added to the disinfected

Table B.13 Southerly Wastewater Treatment Plant first stage excess activated-sludge residence time based on an average wastewater flow = 125 MGD

Unit Operation(s)	Residence Time (days)
Primary Settling Tanks ^(a)	0.10
First Stage MCRT ^(b)	2.1
Excess Activated-Sludge Gravity Thickeners and Sludge Storage Tanks	1
Thermal Conditioning Reactors	0.04
Thermal Conditioned Sludge Thickeners	1
Vacuum Filters	0.08
Incinerators	0.17
Total Days = 4.5	

(a) Liquid residence time

(b) Mean cell residence time; includes First Stage Aeration tanks and clarifiers

wastewater at the tail end of the contact tanks to dechlorinate the plant effluent before discharging it to the Cuyahoga River.

There are three solids streams generated in the plant: primary sludge, secondary (excess activated) sludge, and skimmings (for example, grease). The residence times (that is, from the time the sludge is collected in the settling tanks until the ash leaves the incinerator) for each solids stream are tabulated in Tables B.12 through B.14. The primary sludge collected in the bottom of the primary settling tanks is sent to two cyclone degritters (that is, centrifugal separators) that are operated in parallel. The purpose of the cyclone is to remove grit (for example, sand and gravel) from the sludge to prevent excess wear on plant equipment.

The collected grit is hauled offsite to a sanitary landfill and the recovered wastewater is added to the plant's waste liquor stream. The waste liquor stream flows to the head of primary settling tanks 1

Table B.14 Southerly Wastewater Treatment Plant second stage excess activated-sludge residence time based on an average wastewater flow = 125 MGD

Unit Operation(s)	Residence Time (days)
Primary Settling Tanks ^(a)	0.10
Second Stage MCRT ^(b)	20-70
Excess Activated-Sludge Gravity Thickeners and Sludge Storage Tanks	1
Thermal Conditioning Reactors	0.04
Thermal Conditioned Sludge Thickeners	1
Vacuum Filters	0.08
Incinerators	0.17
Total Days = 22.4-72.4	

(a) Liquid residence time

(b) Mean cell residence time; includes Second Stage Aeration tanks and clarifiers

through 10. The de-gritted primary sludge flows to three covered gravity thickeners (that is, circular settling tanks) where the sludge is allowed to settle and thicken. The gravity thickeners typically achieve a thickened sludge solids concentration of five percent. The thickener overflow (that is, supernatant) is added to the waste liquor stream and the skimmings are sent to the head of primary settling tanks 1 through 10. The skimmings collected in the primary settling tanks are sent to the skimmings tank farm where they are dewatered and stored at 70°C. The recovered wastewater is added to the plant's waste liquor stream and the skimmings are hauled to the Easterly Plant for further treatment.

The excess activated sludge is generated by the First and Second Stage Aeration activated-sludge processes. The First Stage Aeration process uses a population of aerobic bacteria that assimilate CBOD and phosphorus

from the wastewater. The resulting bacteria growth produces large settleable solids that are removed from the bulk wastewater in the first stage clarifiers. The biologically activated sludge is recycled back to the aeration tanks in order to maintain the optimum population of biomass (approximately 2100 mg/L suspended solids in the mixed liquor) in the aeration tanks for maximum CBOD and phosphorus removal. The average MCRT for the biologically activated sludge is 2.1 days. The portion of sludge not recycled back to the aeration tanks (that is, excess biologically activated sludge) is discharged to either a gravity belt thickener and/or the excess activated-sludge gravity thickener tanks. In the Second Stage Aeration process, a different population of aerobic bacteria are used. These bacteria convert ammonia to nitrate in order to meet the plant's ammonia effluent limit. This process has its own biologically activated-sludge recycle loop with a typical MCRT of 20 to 70 days and a mixed liquor suspended solids concentration of 3400 mg/L. The second stage excess activated sludge is also discharged to either a gravity belt thickener and/or an excess activated-sludge gravity thickener tank.

Under normal plant flow conditions (that is, 125 MGD), approximately 25 percent of the total excess activated sludge flow is sent to one of two gravity belt thickeners. A high molecular weight cationic polymer is added to the belt thickener sludge feed to enhance the dewatering process. The sludge flows on top of a belt assembly where water is allowed to drain, by gravity, through the belt dewatering the sludge to a solids concentration of about five percent. The drained wastewater flows into the plant's waste liquor stream. The remaining 75 percent of the excess biologically activated sludge flow is sent to two covered gravity thickeners. These excess sludge gravity thickeners function identically to the primary sludge gravity thickeners and produce a thickened sludge solids concentration of about five percent. The thickener overflow is sent to the waste liquor stream and the skimmings are sent to the head of primary settling tanks number 1 through 10.

Sludge from the primary and excess sludge gravity thickeners and the gravity belt thickeners flows into two sludge holding tanks. The tanks are covered and sealed in order to collect the gas generated by the thickened sludge. This gas stream is passed through a scrubber system and then vented to the atmosphere.

The scrubber system includes a plenum, packed tower water scrubber, a vacuum combustion chamber, and a heat exchanger. The plenum and packed tower remove particulates from the gas stream, which are then added to the plant's waste liquor stream. The vacuum combustion chamber, operated at 790°C, thermally destroys unwanted vapors. The downstream heat exchanger cools the gas and recycles the recovered heat back to the combustion chamber. Finally, the cooled gas is vented to the atmosphere.

Sludge from the sludge holding tanks is sent to the Zimpro wet air oxidation thermal conditioning facility. The Zimpro wet air oxidation process uses an external air supply, heat, and pressure to break down the biological solids in the sludge and increase the efficiency of the downstream sludge-dewatering process. The Southerly Plant has five wet air oxidation reactors that are operated in parallel. Under normal flow conditions, two or three reactors are operated simultaneously. Typical reactor temperatures and pressures are 200°C and 286 psi, respectively. The air and temperature oxidize the organic solids (for example, water-particle conglomerate structures are ruptured and release entrapped water) and the pressure prevents water vaporization in the reactor. The gas stream generated from the Zimpro process is passed through a separate scrubbing system that includes an atmospheric scrubber well, packed tower water scrubber, vacuum combustion chamber (790°C), and heat exchanger. The particulates collected in the atmospheric scrubber well and packed tower are added to the plant's waste liquor stream.

The thermally conditioned sludge is sent to two out of four thermal conditioned gravity thickeners. The thermal conditioned gravity thickeners are covered and sealed for gas collection. The gas stream is combined with the gas collected from the sludge holding tanks, upstream from the Zimpro facility, scrubbed, and vented to the atmosphere (Figure B.5c). The thickener overflow (that is, supernatant) is added to the plant's waste liquor stream. The thickened thermal conditioned sludge, which has a solids concentration of 12 to 15 wt%, flows into the thermal conditioned sludge well where the sludge is briefly stored and then sent to the vacuum filters. The gas collected in the well is sent to the vapor combustion chamber of the Zimpro gas scrubbing system.

There are a total of 12 vacuum filters used as a final sludge dewatering step. Under normal flow

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conditions, eight filters are operating simultaneously. The filters are operated under vacuum to draw water out of the sludge stream through the filter. The filtrate is added to the plant's waste liquor stream. The vacuum pump gas discharge is scrubbed in a separate scrubbing system; a packed tower water scrubber. Potassium permanganate is added to the scrubber water to enhance the removal of target vapors (for example, hydrogen sulfide and mercaptans). The scrubbed gas is then vented to the atmosphere. The resulting sludge filter cake, which is about 45 wt% solids, is sent to the sludge incinerators.

There are four multiple-hearth incinerators operated in parallel at 815°C. Under normal flow conditions, three incinerators are operated simultaneously. The ash produced by the incineration process is collected in an ash collection well and mixed with water. The resulting ash slurry is sent to the ash slurry lagoons, which function as settling ponds. Once the lagoons fill up with settled ash, they are taken out of service and cleaned (that is, the ash is dug out of the lagoon to restore its original capacity). The removed ash is then used as fill material on the plant site. The gas stream generated from the incineration process is scrubbed through the incinerator gas scrubbing system. This system includes a waste heat boiler, venturi scrubber, and impingement scrubber. The waste heat boiler recovers heat generated by the incinerators and produces steam that is sent to the plant's steam generating facility. The recovered heat results in an energy savings of 30 to 40 percent of the total steam generating facility energy requirements.

Particulates removed by the venturi and impingement scrubbers are added to the ash slurry stream. Finally, the scrubbed gas is vented to the atmosphere.

The Southerly Plant receives the sludge generated at the NEORS Easternly and Strongsville Plants. Under normal operating conditions, the Easternly Plant sludge flows into the plant headworks (typically 1.9 to 2.1 MGD with a solids concentration of about 1.1 percent), is combined with the influent wastewater, and then removed from the bulk wastewater in the primary settling tanks. The reason for processing the Easternly sludge in this flow scheme (Figure B.5c) is to treat it in the cyclone degritters along with the primary sludge. Degritting the Easternly Plant sludge minimizes equipment wear in the subsequent solids handling facilities. The plant is designed to send the Easternly Plant sludge directly to the cyclones or store it in a separate gravity thickener. However, under normal flow conditions, these sludge handling options are not practiced. Sludge from the Strongsville Plant is pumped directly into the inlet of the Zimpro wet air oxidation facility. The daily volume of Strongsville Plant sludge processed at the Southerly Plant is so small, compared to the Easternly Plant sludge volume, that degritting is not required. In 1992, about 19.8 wet tons per day of Strongsville Plant sludge, with a solids concentration of 11 percent, were treated at the Southerly Plant. There is a septic sewage dumping station at the Southerly Plant that receives, on average, about 30,000 gallons per day of septic sewage. This small fraction of sewage is added to the influent wastewater at the plant headworks for complete treatment.

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Sewers in Accordance with 10 CFR Part 20

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10. SUPPLEMENTARY NOTES

11. ABSTRACT (200 words or less)

The U.S. Nuclear Regulatory Commission (NRC), in accordance with 10 CFR 20, and agreement states, in accordance with state regulations, regulates the discharge of radioactive materials into sanitary sewer systems. A one-year study was conducted by Pacific Northwest Laboratory (PNL) for the NRC to assess whether radioactive materials that are discharged to sanitary sewer systems undergo significant reconcentration within the wastewater treatment plants (WWTP) and to determine the physical and/or chemical processes that may result in radionuclide reconcentration within the WWTPs. The study objectives were addressed by collecting information and data on wastewater treatment, relevant geochemical processes, and individual radionuclide behavior in WWTPs from the open literature, NRC reports, EPA surveys, and interviews with NRC licensees and staff of WWTPs that may be impacted by these discharges. Radionuclide mass balance and removal efficiencies were calculated for WWTPs at Oak Ridge, TN; and Erwin, TN, but were not shown to be reliable since the licensee release data generally underestimated the mass of radionuclide that was ultimately found in the sludge. This disparity may be due, in part, to the fact that data available for use in this study were collected to address regulatory concerns and not to perform mass balance calculations. A limited modeling study showed some promise for predicting radionuclide behavior in WWTPs, however, the general applicability of using these empirical models remains uncertain. With the data and models currently available, it is not possible to quantitatively determine the physical and chemical processes that cause reconcentration or to calculate, *a priori*, reconcentration factors for specific WWTP unit processes or WWTPs in general.

12. KEY WORDS/DESCRIPTORS (List words or phrases that will assist researchers in locating the report.)

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