

Nutrient Control Design Manual

State of Technology Review Report

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by

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Notice

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Abstract

This EPA document is an interim product in the development of revised design guidance for nitrogen and phosphorus control at municipal WWTPs. This document presents findings from an extensive review of nitrogen and phosphorus control technologies and techniques currently applied and emerging at municipal wastewater treatment plants (WWTP). It includes information on the importance of nutrient removal, the properties and analytical techniques for nitrogen and phosphorus species, and the principles behind biological nitrogen and phosphorus removal and chemical phosphorus precipitation. The report profiles the latest advances in technology to achieve consistently low nutrient levels in plant effluent, including effluent filtration and advanced clarification techniques, along with upto-date research on the removal of emerging microcontaminants such as endocrine-disrupting compounds. Other contemporary issues include how mathematical modeling can improve process design, nutrient removal at small and decentralized treatment systems, and sustainable nutrient recovery.

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Acronyms and Abbreviations

A/O Pho-redox

A2/O 3 Stage Pho-redox AT3 Aeration Tank 3

AOB Ammonia Oxidizing Bacteria
ASM Activated Sludge Model

BABE Bio-Augmentation Batch Enhanced

BAF Biological Aerated Filter

BAR Bio-Augmentation Regeneration/Reaeration

BCFS Biological Chemical Phosphorus and Nitrogen Removal bDON Biodegradable Fraction of Dissolved Organic Nitrogen

BHRC Ballasted High Rate Clarification Processes

BNR Biological Nutrient Removal BOD Biochemical Oxygen Demand

BOD₅ Biochemical Oxygen Demand (5-day)
BPR Biological Phosphorus Removal
COD Chemical Oxygen Demand

CWA Clean Water Act

CWSRF Clean Water State Revolving Fund

CSO Combined Sewer Overflow
DAF Dissolved Air Flotation
DO Dissolved Oxygen

DON Dissolved Organic Nitrogen

 $\begin{array}{ccc} E_1 & & Estrone \\ E_2 & & 17 \ \text{β-estradiol} \end{array}$

EBPR Enhanced Biological Phosphorus Removal

EDC Endocrine Disrupting Chemicals
EDTA Ethylene Diamine Tetraacetic Acid

 EE_2 17 α -ethynylestradiol

EPA U.S. Environmental Protection Agency

FFS Fixed-film Systems

FWPCA Federal Water Pollution Control Act

FWS Free Water Surface

GAO Glycogen Accumulating Organism HRSD Hampton Roads Sanitation District

HRT Hydraulic Retention Time

iDON Inert Dissolved Organic Nitrogen

ISF Intermittent Sand Filter

IWA International Water Association

JHB Johannesburg

MAUREEN Mainstream Autotrophic Recycle Enhanced N-removal

MBR Membrane Bioreactor
MBBR Moving-Bed Biofilm Reactor
MGD Million Gallons per Day
MLE Modified Ludzack Ettinger

MUCT Modified University of Capetown

N Nitrogen

NOAA National Oceanic and Atmospheric Administration

NOB Nitrite Oxidizing Bacteria

NPDES National Pollutant Discharge Elimination System

NTT Nitrogen Trading Tool

ORD EPA Office of Research and Development

ORP Oxidation Reduction Potential
OWASA Orange Water and Sewer Authority
OWM EPA Office of Wastewater Management

P Phosphorus

PAH Polycyclic Aromatic Hydrocarbons
PAO Phosphate Accumulating Organism

PHA Polyhydroxyalkanoates
PHB Poly-B-hydroxy-butyrate
PHV Poly-hydroxy valerate

POTW Publicly Owned Treatment Works

PPCPs Pharmaceuticals and Personal Care Products

RAS Return Activated Sludge
RBC Rotating Biological Contactor

rbCOD Readily Biodegradable Chemical Oxygen Demand

rDON Recalcitrant Dissolved Organic Nitrogen

RO Reverse Osmosis

RSF Recirculating Sand Filters
SAV Submerged Aquatic Vegetation
SBR Sequencing Batch Reactors

SHARON Single Reactor High-activity Ammonia Removal Over Nitrite

SND Simultaneous Nitrification-Denitrification

SRT Solids Retention Time
SSO Sanitary Sewer Overflow

STAC Chesapeake Bay Program Scientific and Technical Advisory

Committee

SWIS Subsurface Wastewater Infiltration System

TDS Total Dissolved Solids
TKN Total Kjeldahl Nitrogen
TMDL Total Maximum Daily Loads

TN Total Nitrogen
TP Total Phosphorus
TSS Total Suspended Solids

TUDP Bio-P Model of the Delft University of Technology

UCT University of Capetown

USDA U.S. Department of Agriculture

USGS U.S. Geological Survey
VIP Virginia Initiative Plant
VFA Volatile Fatty Acids
VSS Volatile Suspended Solids
WAS Waste Activated Sludge

WEF Water Environment Federation

WERF Water Environment Research Foundation

WQS Water Quality Standard

WWTP Wastewater Treatment Plant

Acknowledgements

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1. Introduction

1.1 Purpose

This document presents findings from an extensive state-of-the-technology review of nitrogen and phosphorus control technologies and techniques currently applied and emerging at municipal wastewater treatment plants (WWTP). It includes a description of technologies and identifies key design and operational issues. Because the majority of WWTPs in the United States are equipped with secondary biological treatment, the focus of this report is on process and technology modifications/additions for nutrient removal at existing WWTPs, rather than on new treatment plant design. Emerging issues such as nutrient removal through decentralized treatment, sustainable technologies, and co-removal of emerging contaminants are also discussed.

EPA is publishing this document which is an interim product in the development of revised design guidance for nitrogen and phosphorus control at municipal WWTPs. While the results of the state-of-the-technology review and the technical reference list presented herein will be the basis for the revised design guidance manual, which is scheduled to be published in the Fall of 2009, the Agency is publishing this document at this time to provide this most current technical information in a timely manner.

1.2 Methodology

The project team began the report with an in-depth literature review using a variety of sources including: EPA resources across offices and regions, peer-reviewed journals such as *Water Research* and *Environmental Science and Technology*, meeting presentations and workshops, engineering texts, international reports, government publications, and internet searches. Industry publications such as *Water Environment & Technology* and the Water Environment Research Federation reports were also reviewed. Wastewater treatment experts on the team provided guidance on the sources for the literature review including unpublished information on current research projects in key areas. Based on the results of the in-depth literature review, the team identified key findings and prepared technical summaries for inclusion in this report.

1.3 Organization of the Report

This report is organized into 11 technical chapters as follows:

- Chapter 2. Need for Nitrogen and Phosphorus Removal at Wastewater Treatment
 Plants reviews the status of wastewater treatment in the U.S., the impairment of
 waterways by excessive nutrients, government and industry initiatives to reduce
 nutrient pollution, and the barriers to implementation of such initiatives.
- Chapter 3. Nutrient Constituents in Wastewater and Measurement Methods describes the forms of nitrogen and phosphorus found in wastewater and the analytical techniques used to characterize and measure them.
- Chapter 4. Phosphorus Removal by Chemical Addition discusses the principles behind chemical precipitation, the types of chemicals used, where they are added in the process train, and traditional and advanced solids separation techniques. The chapter

also reviews additional design and operational issues as well as how the choice of chemical impacts sludge handling.

- Chapter 5. Biological Nitrogen Removal examines the principles behind the process, current and emerging process configurations, key design and operational issues such as carbon sources and temperature effects, and potential impacts on sludge handling.
- Chapter 6. Biological Phosphorus Removal and Combination Processes discusses the principles behind biological treatment to remove phosphorus and treatment configurations that can remove both phosphorus and nitrogen from wastewater. The chapter provides descriptions of several processes, provides guidance on how to choose among them, and reviews operational and design considerations including the COD:P ratio, retention time, and temperature.
- Chapter 7. Effluent Filtration discusses types of filters that can be added as a tertiary treatment process to WWTPs and summarizes design and operating principles.
- Chapter 8. Mathematical Modeling explains the need for models in designing nutrient removal processes and examines available models including their input and calibration requirements.
- Chapter 9. Nutrient Removal for Small Communities and Decentralized Wastewater
 Treatment Systems discusses the latest treatment options for on-site wastewater
 treatment systems and clustered development systems.
- Chapter 10. Sustainable Nutrient Recovery highlights efforts to develop low-cost and low-energy technologies to make nutrient removal more efficient, including urine separation technology and resource recovery from sludge.
- Chapter 11. Co-removal of Emerging Contaminants discusses how some advanced technologies to remove nitrogen (N) and phosphorus (P) can achieve the additional benefits of removing some microcontaminants, including endocrine disrupting compounds (EDCs) and pharmaceuticals from wastewater.

The References section at the end of the document provides the full, alphabetized list of technical references reviewed in the development of this report.

2. Need for Nitrogen and Phosphorus Removal at Wastewater Treatment Plants

The purpose of this chapter is to provide an overview of the major factors driving decisions to enhance nutrient removal at WWTPs. Section 2.1 characterizes the industry based on U.S. Environmental Protection Agency (EPA) survey information. Section 2.2 describes the negative impacts of nutrient enrichment, highlighting the history of water quality changes in key regions of the country. EPA and State initiatives to reduce nutrient pollution from wastewater treatment discharges are summarized in Section 2.3, followed by a discussion of key industry initiatives in Section 2.4. Lastly, Section 2.5 highlights several barriers to enhancing nutrient removal at wastewater plants.

2.1 Status of Wastewater Treatment in the U.S.

The 1972 Amendments to the Federal Water Pollution Control Act (FWPCA)(Public Law 92-500), also known as the Clean Water Act (CWA), established the foundation for wastewater discharge control in the U.S. The CWA's primary objective is to "restore and maintain the chemical, physical, and biological integrity of the Nation's waters." The CWA established a program to ensure clean water by requiring permits that limit the amount of pollutants discharged by all municipal and industrial dischargers into receiving waters. Discharges are regulated under the National Pollutant Discharge Elimination System (NPDES) permit program. As of 2004, there were 16,583 municipal wastewater utilities [also known as Publicly Owned Treatment Works (POTWs)] regulated under the CWA, serving approximately 75 percent of the Nation's population (U.S. Public Health Service and USEPA, 2008) with the remaining population served by septic or other onsite systems.

Wastewater treatment has generally been defined as containing one or more of the following four processes: (1) preliminary, (2) primary, (3) secondary, and (4) advanced - also known as tertiary treatment. Preliminary treatment consists of grit removal, which removes dense inert particles and screening to remove rags and other large debris. Primary treatment involves gravity settling tanks to remove settleable solids, including settleable organic solids. The performance of primary settling tanks can be enhanced by adding chemicals to capture and flocculate smaller solid particles for removal and to precipitate phosphorus. Secondary treatment follows primary treatment in most plants and employs biological processes to remove colloidal and soluble organic matter. Effluent disinfection is usually included in the definition of secondary treatment.

EPA classifies advanced treatment as "a level of treatment that is more stringent than secondary or produces a significant reduction in conventional, non-conventional, or toxic pollutants present in the wastewater" (U.S. Public Health Service and USEPA, 2008). Other technical references subdivide advanced treatment, using the terms "secondary with nutrient removal" when nitrogen, phosphorus, or both are removed and "tertiary removal" to refer to additional reduction in solids by filters or microfilters (Tchobanoglous et al, 2003). Effluent filtration and nutrient removal are the most common advanced treatment processes.

The CWA requires that all municipal wastewater treatment plant discharges meet a minimum of secondary treatment. Based on data from the 2004 Clean Watersheds Needs Survey, 16,543 municipal WWTPs (99.8 percent of plants in the country) meet the minimum secondary wastewater treatment requirements. Of those that provide at least secondary treatment, approximately 44 percent provide some kind of advanced treatment (U.S. Public Health Service and USEPA, 2008). Figure 2-1 shows how secondary and advanced wastewater treatment have been implemented since 1940 and also provides

projected treatment for 2024. Note that "No Discharge" refers to systems that do not discharge treated wastewater to the Nation's waterways and dispose of wastewater via methods such as industrial reuse, irrigation, or evaporation.

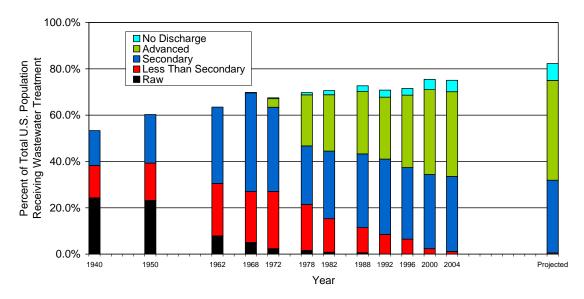


Figure 2-1. Population served by POTWs nationwide for select years between 1940 and 2004 and projected to 2024 (if all needs are met), organized by wastewater treatment type.

Source: U.S. Public Health Service and USEPA Clean Watersheds Needs Surveys 2004 Report to Congress (U.S. Public Health Service and USEPA, 2008).

2.2 Nutrient Impairment of U.S. Waterways

The harmful effects of eutrophication due to excessive nitrogen and phosphorus concentrations in the aquatic environment have been well documented. Algae and phytoplankton growth can be accelerated by higher concentrations of nutrients as they can obtain sufficient carbon for growth from carbon dioxide. In addition to stimulating eutrophication, nitrogen in the form of ammonia can exert a direct demand on dissolved oxygen (DO) and can be toxic to aquatic life. Even if a treatment plant converts ammonia to nitrate by a biological nitrification process, the resultant nitrate can stimulate algae and phytoplankton growth. Phosphorus also contributes to the growth of algae. Either nitrogen or phosphorus can be the limiting nutrient depending on the characteristics of the receiving water. Nitrogen is typically limiting in estuarine and marine systems and phosphorus in fresh water systems.

According to the 2007 report *Effects of Nutrient Enrichment in the Nation's Estuaries: A Decade of Change*, increased nutrient loadings promote a progression of symptoms beginning with excessive growth of phytoplankton and macroalgae to the point where grazers cannot control growth (Bricker et al., 2007). These blooms may be problematic, potentially lasting for months at a time and blocking sunlight to light-dependent submerged aquatic vegetation (SAV). In addition to increased growth, changes in naturally occurring ratios of nutrients may also affect which species dominate, potentially leading to nuisance/toxic algal blooms. These blooms may also lead to other more serious symptoms that affect biota, such as low DO and loss of SAV. Once water column nutrients have been depleted by phytoplankton and macroalgae and these blooms die, the bacteria decomposing the algae then consume oxygen, making it less available to surrounding aerobic aquatic life. Consequently, fish and invertebrate kills may occur due to hypoxia and anoxia, conditions of low to no DO. Eutrophic conditions may also cause risks to human health, resulting from consumption of shellfish contaminated with algal

toxins or direct exposure to waterborne toxins. Eutrophication can also create problems if the water is used as a source of drinking water. Chemicals used to disinfect drinking water will react with organic compounds in source water to form disinfection byproducts, which are potential carcinogens and are regulated by EPA.

Advanced eutrophic conditions can lead to "dead zones" with limited aquatic life, which describes the hypoxia condition that exists in the Northern Gulf of Mexico. A recent U.S. Geological Survey (USGS) report titled *Differences in Phosphorus and Nitrogen Delivery to the Gulf of Mexico from the Mississippi River Basin* documents the contribution of nitrogen and phosphorus from agricultural and non-agricultural sources in the Mississippi River basin (Alexander et al., 2008). On June 16, 2008 the joint federal-state Mississippi River/Gulf of Mexico Watershed Nutrient Task Force released its *2008 Action Plan for Reducing, Mitigating, and Controlling Hypoxia in the Northern Gulf of Mexico and Improving Water Quality in the Mississippi River Basin,* which builds upon its 2001 plan by incorporating emerging issues, innovative approaches, and the latest science, including findings from EPA's Science Advisory Board. Improvements include more accountability through an Annual Operating Plan, better tracking of progress, state and federal nutrient reduction strategies, and a plan to increase awareness of the problem and implementation of solutions (USEPA, 2008b).

Nutrient pollution has also caused significant problems in the Chesapeake Bay. Elevated levels of both nitrogen and phosphorus are the main cause of poor water quality and loss of aquatic habitats in the Bay. Significant algae blooms on the water surface block the sun's rays from reaching underwater bay grasses. Without sunlight, bay grasses cannot grow and provide critical food and habitat for blue crabs, waterfowl, and juvenile fish. The Chesapeake Bay Program estimates that 22 percent of the phosphorus loading and 19 percent of the nitrogen loading in the Bay comes from municipal and industrial wastewater facilities (Chesapeake Bay Program, 2008).

The first national attention to nutrient contamination occurred in the Great Lakes. In the 1960s Lake Erie was declared "dead" when excessive nutrients in the Lake fostered excessive algae blooms that covered beaches and killed off native aquatic species due to oxygen depletion. At that time, phosphorus was the primary nutrient of concern due to the advent of phosphate detergents and inorganic fertilizers. With the enactment of the CWA and the Great Lakes Water Quality Agreement in 1972, a concerted effort was undertaken to reduce pollutant loadings, including phosphorus in the Lake. Although the health of the Lake improved dramatically, in recent years, there has been renewed attention to the re-emergence of a "dead" zone in Lake Erie, again due to nutrient loadings. Recent studies by scientists and the National Oceanic and Atmospheric Administration (NOAA) have also hypothesized a relationship between excessive nutrients in the Lake and the presence of two aquatic invasive species – the zebra mussel and the quagga mussel (Vanderploeg et al., 2008).

Development and population increases in the Long Island Sound Watershed have resulted in a significant increase in nitrogen loading to the Sound. The increased nitrogen loads have stimulated plant growth, increased the amount of organic matter settling to the benthic zone, lowered DO levels, and changed habitats. The primary concerns in the Sound include hypoxia, the loss of sea grass, and alterations in the food web. Management efforts are currently underway to reduce nitrogen pollution by more than half with a focus on upgrading WWTPs with new technologies and removing nitrogen by reducing polluted run-off through best management practices on farms and suburban areas (Long Island Sound Study, 2004).

The above represent four examples of impaired large water bodies impacted by nutrient loadings. There are more than 80 additional estuaries and bays, and thousands of rivers, streams, and lakes that are also impacted by nutrients in the U.S. In fact, all but one state and two territories have

CWA section 303(d) listed¹ water body impairments for nutrient pollution. Collectively, states have listed over 10,000 nutrient and nutrient–related impairments.

Climate change may also be a significant influence on the development of future eutrophic symptoms. According to the report *Effects of Nutrient Enrichment in the Nation's Estuaries: A Decade of Change*, the factors associated with climate change that are expected to have the greatest impacts on coastal eutrophication are:

- Increased temperatures
- Sea level rise
- · Changes in precipitation and freshwater runoff

Increased temperatures will have several effects on coastal eutrophication. Most coastal species are adapted to a specific range of temperatures. Increases in water temperatures may lead to expanded ranges of undesirable species. Higher temperatures may also lead to increased algal growth and longer growing seasons, potentially increasing problems associated with excessive algal growth and nuisance/toxic blooms. Additionally, warmer waters hold less DO, therefore potentially exacerbating hypoxia. Temperature-related stratification of the water column may also worsen, having a further negative effect on DO levels.

Climate change models predict increased melting of polar icecaps and changes in precipitation patterns, leading to sea level rise and changes in water balance and circulation patterns in coastal systems. Sea level rise will gradually inundate coastal lands, causing increased erosion and sediment delivery to water bodies, and potentially flooding wetlands. The increased sediment load and subsequent turbidity increase may cause SAV loss. The positive feedback between increased erosion and algal growth (as erosion increases, sediment associated nutrients also increase, stimulating growth) may also increase turbidity. The loss of wetlands, which act as nutrient sinks, will further increase nutrient delivery to estuaries.

Another report titled Aquatic Ecosystems and Global Climate Change – Potential Impacts on Inland Freshwater and Coastal Wetland Ecosystems in the United States notes that climate change of the magnitude projected for the U.S. over the next 100 years will cause significant changes to temperature regimes and precipitation patterns across the U.S. (Poff et al., 2002). Such alterations in climate pose serious risks for inland freshwater ecosystems (lakes, streams, rivers, wetlands) and coastal wetlands, and may adversely affect numerous critical services provided to human populations.

These conclusions indicate climate change is a significant threat to the species composition and function of aquatic ecosystems in the U.S. However, critical uncertainties exist regarding the manner in which specific species and whole ecosystems will respond to climate change. These arise both from uncertainties about how regional climate will change and how complex ecological systems will respond. Indeed, as climate change alters ecosystem productivity and species composition, many unforeseen ecological changes are expected that may threaten the goods and services that these systems provide to humans.

¹ Required by Section 303(d) of the CWA, the 303(d) list is a list of state's water bodies that do not meet or are not expected to meet applicable Water Quality Standards with technology-based controls alone.

2.3 Federal and State Initiatives to Reduce Nutrient Pollution

2.3.1 NPDES Permitting

Established by the FWPCA Amendment of 1972, EPA's NPDES permit program has been the primary mechanism for controlling pollution from point sources. Point sources are discrete conveyances such as pipes or man-made ditches. Individual homes that are connected to a municipal system, use a septic system, or do not have a surface discharge do not need an NPDES permit; however, POTWs and other facilities must obtain permits if they discharge directly to surface waters.

NPDES permits for wastewater discharges contain, among other information, effluent limits for "conventional" pollutants such as biochemical oxygen demand (BOD), total suspended solids (TSS), and pH as well as limits for specific toxicants including various organic and inorganic chemicals. Permits may also include effluent limits for "non-conventional" pollutants such as nitrogen and phosphorus. Effluent limits can be technology-based and/or water-quality based. EPA has established technology-based, secondary treatment effluent limits for BOD as 5-day biochemical oxygen demand (BOD₅), TSS, and pH. Water-quality based effluent limits are set if the technology-based limits are not sufficient to maintain the water quality standards (WQS) of the receiving water.

Federal and State regulations related to WQSs and Total Maximum Daily Loads (TMDLs) are expected to drive down NPDES effluent limits for nitrogen and phosphorus. WQS define the goals for a water body by designating its uses, setting criteria to protect those uses, and establishing provisions to protect water bodies from pollutants. Criteria can be narrative or numeric. Regulatory agencies can adopt *nutrient criteria* to protect a water body against nutrient over-enrichment and eutrophication caused by nitrogen and phosphorus. In June 1998, EPA issued a *National Strategy for the Development of Regional Nutrient Criteria*. This was followed by publication of recommended nutrient criteria for most streams and lakes in 2001. In a January 9, 2001 *Federal Register* notice, EPA recommended that states and other regulatory agencies develop a nutrient criteria plan to outline their process for adopting such nutrient criteria (*Federal Register*, 2001). As of May 2007, only a handful of States and Territories had adopted nutrient criteria for nitrogen and phosphorus (USEPA, 2007a), although many have made progress in criteria development. In a memo dated May 25, 2007, EPA encouraged all regulatory agencies to "...accelerate their efforts and give priority to adopting numeric nutrient standards or numeric translators for narrative standards for all waters in States and Territories that contribute nutrient loadings to our waterways" (USEPA, 2007b).

CWA Section 303(d) requires states to develop TMDLs for water bodies on the 303(d) list of impaired waters. A TMDL is a calculation of the maximum amount of a pollutant a water body can receive and still meet WQS. TMDLs serve as a tool for implementing WQS. The TMDL targets or endpoints represent a number where the applicable WQS and designated uses (e.g., such as public water supply, contact recreation, and the propagation and growth of aquatic life) are achieved and maintained in the water body of concern. TMDLs identify the level of pollutant control necessary to meet WQS and support the designated uses of a water body. Once a TMDL is set, the total load is allocated among all existing sources. The allocation is divided into two portions - a load allocation representing natural and non-point sources and a waste load allocation representing NPDES permitted point source discharges. In many regions, water bodies have a poor ability to assimilate nutrients or water bodies are already impaired from past pollution and the water body cannot handle large loads of additional nutrients. In these cases, TMDLs may require nutrient permit levels to be even lower than what might be allowed otherwise by nutrient criteria.

2.3.2 Water Quality Trading

Water quality trading is a market-based approach to improve and preserve water quality. Trading can provide greater efficiency in achieving water quality goals by allowing one source to meet its regulatory obligations by using pollutant reductions created by another source that has lower pollution control costs. For example, under a water quality trading program, a POTW could comply with discharge requirements by paying distributed sources to reduce their discharges by a certain amount. The use of geographically-based trading ratios provides an economic incentive, encouraging action toward the most cost effective and environmentally beneficial projects.

EPA issued a Water Quality Trading Policy in 2003 to provide guidance to States and Tribes on how trading can occur under the CWA and its implementing regulations. The policy discusses CWA requirements that are relevant to water quality trading including: requirements to obtain permits, antibacksliding provisions, development of WQSs including an antidegradation policy, NPDES permit regulations, TMDLs and water quality management plans. EPA also developed a number of tools and guidance documents to assist states, permitted facilities, non-point sources, and stakeholders involved in the development of trading programs (www.epa.gov/owow/watershed/trading.htm). Recently, the U.S. Department of Agriculture (USDA) National Resources Conservation Service released a Nitrogen Trading Tool (NTT) prototype for calculating nitrogen credits based on the Nitrogen Loss and Environmental Assessment Package Model (Gross et al., 2008).

Water quality trading programs have been successfully implemented in several states and individual watersheds across the county. For example, nitrogen pollution from point sources into the Long Island Sound was reduced by nearly 25 percent using an innovative Nitrogen Credit Trading Program. In Connecticut, the program was implemented among 79 sewage treatment plants in the state. Through the Nitrogen Credit Exchange, established in 2002, the Connecticut program has a goal of reducing nitrogen discharges by 58.5 percent by 2014.

A recent American Society of Civil Engineers journal article points out, however, that regulatory frameworks for water quality trading programs have yet to be adopted by the majority of States. Barriers to adopting such programs include uncertainty in: (1) the mechanisms for determining appropriate credits and ratios between point sources and distributed sources; and (2) approaches to ensure that promised reductions actually occur (Landers, 2008).

2.3.3 Technology Evaluation and Guidance

In addition to regulatory and policy initiatives, EPA helps control nutrients through the development and dissemination of technical information. For example, EPA's Office of Wastewater Management (OWM) has developed a number of technology fact sheets on secondary and advanced biological treatment (USEPA, 1999b; 1999c). OWM has also published several technology reports including *Emerging Technologies for Wastewater Treatment and In-Plant Wet Weather Management* (USEPA, 2008a). This technology guide, published in February 2008, is designed to help municipal wastewater treatment system owners and operators find information on emerging wastewater treatment and in-plant wet weather management. OWM is also finalizing a document titled *Municipal Nutrient Removal Technologies Reference Document*. Although still in draft, volume 1 of the Technical Report is designed to provide performance and cost information to wastewater facilities on nutrient removal.

Recently, EPA Region 10 initiated a project to evaluate municipal WWTPs that have demonstrated exemplary phosphorus removal through their treatment processes. In April 2007, the

Region published a report titled, *Advanced Wastewater Treatment to Achieve Low Concentration of Phosphorus* (EPA Region 10, 2007).

In 1975, EPA's Office of Research and Development (ORD) published its first technology design guidance for nitrogen removal: *Process Design Manual for Nitrogen Control*. The manual was updated in 1993 and focused on biological/mechanical processes that were finding widespread application for nitrification and nitrogen removal at that time. The development of guidance for phosphorus removal followed a similar schedule, with ORD publishing the document, *Process Design Manual for Phosphorus Removal*, in 1971. In 1976, the manual was updated to include design guidance for phosphorus removal using mineral addition and lime addition. In 1987, EPA published two technical documents to address phosphorus control: (1) an update to the 1976 *Process Design Manual for Phosphorus Removal*, and (2) a handbook titled, *Handbook – Retrofitting POTWs for Phosphorus Removal in the Chesapeake Bay Drainage Basin*. The primary goal of this project was to obtain and share information about the technology, performance, and costs of applying advanced wastewater treatment for phosphorus removal. EPA is currently revising these materials to provide updated, state-of-the technology design guidance for both nitrogen and phosphorus control at municipal WWTPs. This State of Technology Report is an interim publication in the development of these design guidance documents.

2.4 Industry Initiatives – The Nutrient Removal Challenge Program

In early 2007, The Water Environment Research Foundation (WERF) created a *Nutrient Removal Challenge* program the goals of which are to:

- Identify, assess, and make recommendations for improvement of sustainable wastewater nutrient removal technologies
- Provide information to help agencies meet various receiving water body requirements and other wastewater treatment goals (e.g., climate change, sustainability, cost-effectiveness, reliability)
- Research to inform regulatory decision making and help practitioners comply with increasingly high levels of nitrogen and phosphorus removal with a focus on improving plant performance

This multi-year program will be funded for 5 years with WERF and external funds anticipated to total \$8-10 million. This research effort will:

- Promote collaborative efforts and engage stakeholders
- Increase technology understanding, explore Limits of Technology (LOT), and reduce costs
- Provide sound scientific information to support regulators, wastewater treatment plant owners and operators, and other stakeholders
- Leverage WERF research dollars to maximize program contributions and impacts

As part of the Nutrient Challenge's kick-off activities, a WERF Nutrient Research Stakeholder Workshop was held on March 7 and 8, 2007 in Baltimore, MD, to further refine the Challenge's research needs and to seek funding partners and collaborators. The facilitated workshop drew almost 100 participants representing all of the key stakeholder groups in the industry. A total of 25 priority areas were identified, many of them similar to those identified in a similar workshop conducted by WERF in 2006. Generally, these projects fall within the identified top-priority research areas of:

• Characterization of effluent organic nitrogen

- Accuracy of analytical measurement techniques for low concentrations of phosphorus
- Alternative carbon sources for denitrification

WERF will also be developing a *Nutrient Compendium*, a comprehensive, living document that describes the current knowledge of regulatory and technological nutrient removal issues. The document will describe the key knowledge areas affecting nutrient removal to very low levels and identifies knowledge gaps related to nutrient removal. Seven topics have been selected as the top priority. These are:

- Effluent dissolved organic nitrogen
- Alternative carbon sources
- Regulatory issues for low-level nitrogen and phosphorus
- Operations
- Biological treatment processes for achieving low nitrogen and phosphorus effluent levels
- Low phosphorus concentration measurements
- Tertiary phosphorus removal

2.5 Barriers to Implementing Nutrient Removal

There are a number of barriers that may impact forward progress in implementing nutrient removal processes and achieving reductions in aquatic ecosystems beyond that which is currently being achieved, including:

- Costs
- Limitations on physical expansion
- State resources
- Increased carbon footprint
- Advanced operations and control

Nutrient removal comes at a cost to municipal wastewater treatment facilities and their ratepayers. Although funding from the Clean Water State Revolving Fund (CWSRF) is available, it is not sufficient to address the myriad of CWA-related infrastructure needs (U.S. Public Health Service and USEPA, 2008).

A second factor affecting the cost of nutrient removal at wastewater facilities is limitations on physical expansion of wastewater treatment facilities. Some plants are located in urban areas and do not have any way to obtain the physical space necessary to expand. Space limitations can severely limit the type of approaches that can be used to reduce nutrients.

In some cases, States are struggling to find the resources to develop WQSs to address nutrient criteria. Although EPA has developed numerous tools and guidance documents, further technical assistance may be needed to ensure effective forward progress in this area.

Two potentially negative environmental impacts of employing advanced technologies to remove nutrients from wastewater are the increase in the carbon footprint and quantity of biosolids requiring disposal. The increased carbon footprint will result not only from the nitrogen removal process but also from the increased energy usage necessary to power the technology needed to achieve the proposed nutrient reduction levels. For utilities in states such as California where greenhouse gas reduction requirements are on the horizon, increased emissions due to higher energy usage and nitrogen removal

are cause for serious concern. Higher energy usage may also translate into increased emissions of airborne nutrients in the form of increased nitrogen oxide emissions.

Operation of biological processes for nitrogen and phosphorus removal requires advanced knowledge for successful and consistent removal to low effluent levels. The level of process control is much greater than for BOD_5 and TSS removal. In addition, these processes are susceptible to wet weather, cold weather, and inhibitory substances entering the plants. Plant influent characteristics vary considerably from one community to another and must be taken into account in the design and operation of nutrient removal facilities in terms of its impacts on tank volumes and chemical requirements.

Despite the challenges associated with nutrient removal, new research and information are steadily becoming available. EPA and industry initiatives discussed earlier in this chapter will continue to help disseminate this information to wastewater professionals to provide them with the latest information on nutrient removal strategies.

3. Nutrient Constituents in Wastewater and Measurement Methods

This chapter provides an overview of the sources, forms, and measurement methods for nitrogen and phosphorus in wastewater.

3.1 Nitrogen

Nitrogen is an essential nutrient for plants and animals. Approximately 80 percent of the earth's atmosphere is composed of nitrogen and it is a key element of proteins and cells. The major contributors of nitrogen to wastewater are human activities such as food preparation, showering, and waste excretion. The per capita contribution of nitrogen in domestic wastewater is about 1/5th of that for BOD. Total nitrogen in domestic wastewater typically ranges from 20 to 70 mg/L for low to high strength wastewater (Tchobanoglous et al., 2003). Factors affecting concentration include the extent of infiltration and the presence of industries. Influent concentration varies during the day and can vary significantly during rainfall events, as a result of inflow and infiltration to the collection system.

The most common forms of nitrogen in wastewater are:

- Ammonia (NH₃)
- Ammonium ion (NH₄⁺)
- Nitrite (NO₂⁻)
- Nitrate (NO₃⁻)
- Organic nitrogen

Nitrogen in domestic wastewater consists of approximately 60 to 70 percent ammonia-nitrogen and 30 to 40 percent organic nitrogen (Tchobanoglous et al., 2003; Crites and Tchobanoglous, 1998). Most of the ammonia-nitrogen is derived from urea, which breaks down rapidly to ammonia in wastewater influent.

EPA approved methods for measuring ammonia, nitrate, and nitrite concentration use colorimetric techniques. Organic nitrogen is approximated using the standard method for Total Kjeldahl Nitrogen (TKN) (APHA, AWWA, and WEF, 1998). The TKN method has three major steps: (1) digestion to convert organic nitrogen to ammonium sulfate; (2) conversion of ammonium sulfate into condensed ammonia gas through addition of a strong base and boiling; and (3) measurement using colorimetric or titration methods. Because the measured concentration includes ammonia, the ammonia-nitrogen concentration is subtracted from the TKN to determine organic nitrogen. Nitrogen components in wastewater are typically reported on an "as nitrogen" basis so that the total nitrogen concentration can be accounted for as the influent nitrogen components are converted to other nitrogen compounds in wastewater treatment.

WWTPs designed for nitrification and denitrification can remove 80 to 95 percent of inorganic nitrogen, but the removal of organic nitrogen is typically much less efficient (Pehlivanoglu-Mantas and Sedlak, 2006). Domestic wastewater organic nitrogen may be present in particulate, colloidal or dissolved forms and consist of proteins, amino acids, aliphatic N compounds, refractory natural compounds in drinking water (e.g. humic substances), or synthetic compounds (e.g. ethylene diamine

tetraacetic acid (EDTA)). Organic nitrogen may be released in secondary treatment by microorganisms either through metabolism or upon death and lysis. Some nitrogen may be contained in recondensation products. Hydrolysis of particulate and colloidal material by microorganisms releases some organic nitrogen as dissolved, biodegradable compounds. Amino acids are readily degraded during secondary biological treatment, with 90 to 98 percent removal in activated sludge systems and 76 to 96 percent removal in trickling filters. However, other forms of organic nitrogen may be more persistent in wastewater treatment processes.

The importance of organic nitrogen has increased as effluent limits on nitrogen have become more stringent. With more impaired waterways from nutrient loads, effluent limits for total nitrogen (TN) concentrations of 3.0 mg/L or less are becoming more common. The dissolved organic nitrogen (DON) concentration in the effluent from biological nutrient removal treatment facilities was found to range from 0.50 to 1.50 mg/L in 80 percent of 188 plants reported by Pagilla (STAC-WERF, 2007) and values as high as 2.5 mg/L were observed. Thus, for systems without effluent filtration or membrane bioreactors (MBRs) that are trying to meet a TN treatment goal of 3.0 mg/L, the effluent DON contribution can easily be 20 to 50 percent of the total effluent nitrogen concentration, compared to only about 10 percent for conventional treatment (Pehlivanoglu-Mantas and Sedlak, 2004).

The chemical composition of DON in wastewater effluents is not completely understood. Sedlak (2007) has suggested that only about 20 percent of the DON has been identified as free and combined amino acids, EDTA, and other trace nitrogen compounds. About 45 percent may be unidentified low molecular weight compounds and the other 35 percent as unidentified high molecular weight compounds containing humic acids and amides. Similar results were found by Khan (2007). Early work by Parkin and McCarty (1981) suggested that 40 to 60 percent of effluent DON is non-bioavailable. The non-bioavailable portion is also referred to as recalcitrant DON (rDON).

To address these and other water quality issues associated with DON, WERF has identified DON as a high priority research area. In September 2007, the Chesapeake Bay Program Scientific and Technical Advisory Committee (STAC) and WERF co-hosted a workshop titled "Establishing a Research Agenda for Assessing the Bioavailability of Wastewater-Derived Organic Nitrogen in Treatment Systems and Receiving Waters." The event brought together leaders in the field to discuss the composition, bioavailability, measurement, and removal of biodegradable DON (bDON) in wastewater treatment and the composition and test protocol methods for inert DON (iDON) in receiving waters. The WERF Nutrient Challenge Program has identified key research needs on DON and is fostering collaborative efforts to make research more efficient and effective. An overview of key areas and researchers currently working on projects on DON is summarized in Table 3-1.

Table 3-1. Research Topics on Dissolved Organic Nitrogen Measurement, Fate, and Environmental Impacts^a

Inert DON test methods	Biodegradable DON and fate in wastewater treatment	Inert DON Characteristics	Environmental gradient and DON
D. Sedlak UC Berkeley (WERF)	E. Khan North Dakota State University. (DC WASA)	D. Sedlak UC Berkeley (WERF)	D. Bronk and E. Canuel College of William and Mary M. Mulholland Old Dominion University N. Love University of Michigan (NSF)
J. Mąkinia and K. Czerwionka Gdansk University (Poland Gov't)	R. Sharp Manhattan College (City of Stamford)	D. Bronk and E. Canuel College of William and Mary M. Mulholland Old Dominion University N. Love University of Michigan (NSF)	
	K. Jones Howard University (HDR)		
	K. Pagilla Illinois Institute of Technology (Hazen and Sawyer)		
	J. Mąkinia and K. Czerwionka Gdansk University (Poland Gov't)		

a. The sponsoring agency is shown in parentheses

3.2 Phosphorus

Total phosphorus (TP) in domestic wastewater typically ranges between 4 and 8 mg/L but can be higher depending on industrial sources, water conservation, or whether a detergent ban is in place. Sources of phosphorus are varied. Some phosphorus is present in all biological material, as it is an essential nutrient and part of a cell's energy cycle. Phosphorus is used in fertilizers, detergents, and cleaning agents and is present in human and animal waste.

Phosphorus in wastewater is in one of three forms:

- Phosphate (also called Orthophosphate)
- Polyphosphate, or
- Organically bound phosphorus.

The orthophosphate fraction is soluble and can be in one of several forms (e.g., phosphoric acid, phosphate ion) depending on the solution pH. Polyphosphates are high-energy, condensed phosphates

such as pyrophosphate and trimetaphosphate. They are also soluble but will not be precipitated out of wastewater by metal salts or lime. They can be converted to phosphate through hydrolysis, which is very slow, or by biological activity (see Chapter 6 for a detailed discussion of biodegradation of phosphate and polyphosphate in wastewater).

Organically bound phosphorus can either be in the form of soluble colloids or particulate. It can also be divided into biodegradable and non-biodegradable fractions. Particulate organically bound phosphorus is generally precipitated out and removed with the sludge. Soluble organically bound biodegradable phosphorus can be hydrolyzed into orthophosphate during the treatment process. Soluble organically bound non-biodegradable phosphorus will pass through a wastewater treatment plant. A typical wastewater contains 3 to 4 mg/L phosphorus as phosphate, 2 to 3 mg/L as polyphosphate, and 1 mg/L as organically bound phosphorus (WEF and ASCE, 2006).

Phosphorus content in wastewater can be measured as

- Orthophosphate
- Dissolved orthophosphate
- Total phosphorus
- Total dissolved phosphorus (i.e., all forms except particulate organic phosphorus)

EPA approved laboratory methods rely on colorimetric analysis. Colorimetric analysis measures orthophosphate only, so a digestion step is needed to convert polyphosphate and organic phosphorus to orthophosphate to measure TP. The persulfate method is reported to be the most common and easiest method (WEF and ASCE, 2006). To determine dissolved phosphorus (either total dissolved phosphorus or total dissolved orthophosphate), the sample is first filtered through a 0.45 micron filter. USEPA approved colorimetric methods are routinely used to measure phosphorus levels as low as 0.01 mg/L. On-line analyzers that use the colorimetric method are available from venders (e.g., the Hach PhosphaxTM SC phosphate analyzer).

Ion chromatography is a second common technique used to measure orthophosphate in wastewater. As with colorimetric methods, digestion is required for TP measurement, with persulfate digestion recommended (WEF and ASCE, 2006).

At a workshop in May 2006, WERF members identified a need to develop a standard method for measurement of very low phosphorus levels in wastewater and characterization of the residual phosphorus fraction (Bott, 2007). The WERF Nutrient Challenge Research Plan for 2007/2008 identified "Low Phosphorus Analytical Measurement Reliability" as research to be funded in 2007 or 2008 (WERF, 2007).

4. Phosphorus Removal by Chemical Addition

The purpose of this chapter is to describe techniques for phosphorus removal by chemical addition. It summarizes issues associated with chemical feed location, mixing, and sludge production. An overview of advanced solids separation processes is also provided.

4.1 Principles

Chemical precipitation for phosphorus removal is a reliable, time-tested, wastewater treatment method that has not drastically changed over the years. To achieve removal, various coagulant aids are added to wastewater where they react with soluble phosphates to form precipitates. The precipitates are removed using a solids separation process, most commonly settling (clarification). Chemical precipitation is typically accomplished using either lime or a metal salt such as aluminum sulfate (alum) or ferric chloride. The addition of polymers and other substances can further enhance floc formation and solids settling. Operators can use existing secondary clarifiers or retrofit primary clarifiers for their specific purposes.

Aluminum and Iron Salts

Alum and ferric or ferrous salts are commonly used as coagulant and settling aids in both the water and wastewater industry. They are less corrosive, create less sludge, and are more popular with operators compared to lime. Alum is available in liquid or dry form, can be stored on site in steel or mild concrete, and has a near unlimited shelf life. Ferric chloride is similar although care is needed during handling because of corrosivity. If an industrial source is available such as waste pickle liquor, ferrous chloride or ferrous sulfate have been used for phosphorus removal. Ferrous forms should be added directly to aerobic reactors rather than to anaerobic reactors such as primary settling basins because the ferrous iron needs to oxidize to ferric iron for best results.

The following are sample reactions of aluminum and iron salts with phosphorus:

$$Al_2(SO_4)_3 \bullet (14H_2O) + 2H_2PO_4 + 4HCO_3 \rightarrow 2AIPO_4 + 4CO_2 + 3SO_4^2 + 18H_2O$$
 (4-1)

$$FeCl_3 \bullet (6H_2O) + H_2PO_4 + 2HCO_3 \rightarrow FePO_4 + 3Cl + 2CO_2 + 8H_2O$$
 (4-2)

The molar ratio of aluminum to phosphorus required for phosphorus removal ranges from about 1.38:1 for 75 percent removal, 1.72:1 for 85 percent removal, and 2.3:1 for 95 percent removal. For iron compounds, a ratio of about 1:1 is required, with a supplemental amount of iron (10 mg/L) added to satisfy the formation of hydroxide (WEF and ASCE, 1998). For additional removal of phosphorus with aluminum and iron salts, a ratio of between 2 and 6 parts metal salt to 1 part phosphorus may be required for adequate phosphorus removal.

To supplement stoichiometry calculations, designers should consider jar tests and, in some cases, full-scale pilot tests to gauge the effects on the required dose of competing reactions; the influence of pH and alkalinity, adsorption, and co-precipitation reactions; and the interaction with polymers that are added to increase coagulation and flocculation (WEF and ASCE, 1998; Bott et al. 2007).

Aluminum or ferric iron salts can be added to the primary clarifier, secondary clarifier, tertiary clarifier, or directly into the activated sludge aeration tank. Multiple additions can increase phosphorus removal efficiency. Ferrous salts can only be added to the aeration basin since it needs to be oxidized to ferric to precipitate the phosphorus.

The solubility of aluminum and iron salts is a function of pH. The optimum solubility for alum was previously reported to occur at a pH range of 5.5 to 6.5, significantly lower than most influent wastewater. Recent studies (Szabo et al., 2008) showed that the range for both iron and alum is between 3.5 and 7.5 with the highest efficiency between pH 5.5 and 7.

Chemicals such as lime compounds, caustic soda, and soda ash can be used to raise the pH of the waste stream prior to biological treatment processes or discharge. It is important to understand that alkalinity is consumed during the precipitation reactions, and precipitation will be incomplete if insufficient alkalinity is present.

Lime

Although lime had lost favor due to issues associated with chemical handling, sludge production, and re-carbonation, it has recently been considered more often because of its ability to reduce phosphorus to very low levels when combined with effluent filtration and the microbial control properties associated with its high pH. When lime is added to wastewater, it first reacts with the bicarbonate alkalinity to form calcium carbonate ($CaCO_3$). As the pH increases to more than 10, excess calcium ions will react with phosphate to precipitate hydroxylapatite [$CA_5(OH)(PO_4)_3$]. Because it reacts first with alkalinity, the lime dose is essentially independent of the influent phosphorus concentration. Tchobanoglous et al. (2003) estimates the lime dose to typically be 1.4 to 1.6 times the total alkalinity expressed as $CaCO_3$.

The typical reaction between calcium compounds and phosphorus is represented below:

$$5Ca^{2+} + 4OH^{-} + 3HPO_{4-} \rightarrow Ca_5OH(PO_4)_3 + 3H_2O$$
 (4-3)

The molar ratio required for phosphorus precipitation with lime is approximately 5:3, but can vary from between 1.3 to 2, depending on the composition of the wastewater. As with iron and aluminum salts, jar tests can be used to determine correct doses for a specific wastewater stream (WEF, 1998).

Lime addition can raise the pH to greater than 11. Because activated sludge processes require pH levels below 9, lime cannot be added directly to biological treatment processes or it will cause process upsets. Lime can be added to primary sedimentation tanks and removed with the primary sludge or it can be added as a tertiary treatment process after biological treatment. When added to primary tanks, it will also result in the removal of colloidal material through coagulation and settling, with a concomitant removal of TSS up to 80 percent and chemical oxygen demand (COD) up to 60 percent. In either case, pH adjustment is needed and typically accomplished by adding CO_2 or a liquid acid such as sulfuric acid, nitric acid, or hypochlorite (Tchobanoglous et al., 2003; USEPA, 1999a). Hortskotte et al. (1974) showed that when the primary effluent is discharged directly to a nitrifying activated sludge plant, the hydrogen ions produced may neutralize the high pH. However, when denitrification is practiced and the operator wishes to make use of the soluble COD in the primary effluent, the effluent must be neutralized before discharging it to the anoxic zone.

Lime requires special handling and operations practices that further set it apart from chemical precipitation by metal salts. Although the formation of carbonate scaling on equipment and pipes is a drawback of lime treatment, lime slaking, where quicklime (CaO) is reacted with water to form calcium hydroxide (Ca(OH)₂), is the biggest operational disadvantage.

Performance Data

Performance data are available for chemical phosphorus removal at many plants, including Breckenridge, CO, Dillon, CO, Parker, CO, Hillsboro, OR, Tigard, OR, (alum); Walton, NY (aluminum chloride); Milford, MA (poly-aluminum chloride); Alexandria, VA (ferric chloride and alum); Upper Occoquan Sewage Authority Plant Centreville, VA (high lime); and the Norman Cole Lower Potomac Plant, Fairfax County, VA (ferric chloride) (EPA Region 10, 2007).

4.2 Location of Chemical Feed and Mixing

Lime or metal salts can be added at several locations throughout the treatment plant to remove phosphorus. "Pre-precipitation" is when chemicals are added to raw water to precipitate phosphorus in the primary sedimentation basins. "Co-precipitation" involves adding chemicals to form precipitates that can be removed with biological sludge. "Post-precipitation" is when chemicals are added after secondary sedimentation and precipitants are removed in a tertiary process such as sedimentation or filtration (Tchobanoglous et al., 2003). Because it requires a high pH to achieve a low phosphorus concentration, lime cannot be added directly to biological reactors or to the secondary clarifiers. Multipoint additions of iron or aluminum salts have been very effective and can typically remove more phosphorus than single-point applications.

There are several advantages to post-precipitating phosphorous using a tertiary treatment technique (after biological processes in a separate reactor):

- Microorganisms rely on phosphorus as a food source. If too much phosphorus is removed prior to biological treatment, biological processes may suffer. For activated sludge, the minimum ratio of phosphorus to BOD₅ for a rapidly growing (low solids retention time (SRT)) system is typically about 1:100 (WEF and ASCE, 1998).
- Competing chemicals in the primary sedimentation basins can increase the required dose.
- Phosphorus enters the treatment plant as soluble orthophosphate, soluble polyphosphates, and organically bound phosphorus. Most of the polyphosphates and much of the organically bound phosphorus are converted to more simple orthophosphates during biological treatment. If the influent contains significant polyphosphates and/or organically bound phosphorus, locating chemical treatment after biological processes would be more efficient and achieve lower effluent levels.
- The removal of carbonate alkalinity and phosphorus by lime prior to biological treatment can have a negative impact on nitrification processes (WEF and ASCE, 1998). Also, removing phosphorus to very low concentrations upstream of denitrification filters can negatively affect the denitrification process. Previous studies showed that the hydroxide alkalinity can be balanced by the hydrogen ions produced during nitrification.

• Sludge recalcification can be used to achieve high removal efficiencies using lime in tertiary treatment.

One potential advantage to adding chemicals during primary treatment instead of tertiary treatment is reduced capital costs and space requirements as a result of removing additional BOD and TSS and reducing the load to downstream processes, thereby reducing the size of the subsequent activated sludge basins and the amount of oxygen transfer needed.

Chemicals should be well mixed with the wastewater to ensure reaction with soluble phosphates and formation of precipitates. Chemicals may either be mixed in separate tanks or can be added at a point in the process where mixing already occurs. Bench-scale and pilot scale tests are often used to determine the correct mixing rate for a given composition of wastewater and chemicals used, including polymer (USEPA, 1999a).

4.3 Advanced Solids Separation Processes

The effectiveness of phosphorus removal by chemical addition is highly dependent on the solids separation process following chemical precipitation. Direct addition of metal salts to activated sludge processes followed by conventional clarification can typically remove TP to effluent levels between 0.5 and 1.0 mg/L (Bott et al., 2007). Tertiary processes (post-secondary treatment) can be used to remove phosphorus to very low (< 0.1 mg/L) concentrations. For example, Reardon (2005) reports that four WWTP with tertiary clarifiers achieved TP levels of between 0.032 and 0.62 mg/L.

Two common tertiary processes are clarification and effluent filtration. These approaches can be used separately or in combination. Chapter 7 presents a detailed discussion of effluent filtration. Advances in tertiary clarification processes are discussed below.

The types of clarifiers used for tertiary processes include conventional, one or two-stage lime, solids-contact, high-rate, and ballasted high-rate (BHRC). Several patented BHRC using different types of ballast such as recycled sludge, microsand, and magnetic ballast (USEPA, 2008a) have been developed in recent years. The advantages of high-rate clarification are that the clarifiers have a smaller footprint and are able to treat larger quantities of wastewater in a shorter period of time. In addition, as an add-on during wet weather, they can help prevent sanitary sewer overflows (SSOs) and combined sewer overflows (CSOs). The following patented processes are examples of high rate clarification including performance estimates:

- DensaDeg® uses a coagulant in a rapid mix basin to destabilize suspended solids. The water
 flows into a second tank where polymer (for aiding flocculation) and sludge are added. The
 sludge acts as the "seed" for formation of high density floc. This floc is removed in settling
 tubes (USEPA, 2008). The main advantages of this process are a smaller footprint and
 denser sludge which is easier to dewater. Pilot testing for City of Fort Worth, Texas found a
 phosphorus removal rate of 88-95% for DensaDeg® (USEPA, 2003).
- Actiflo® uses a coagulant in a rapid mix basin to destabilize suspended solids. The water
 flows to a second tank where polymer (for aiding flocculation) and microsand are added.
 Microsand provides a large surface onto which suspended solids attach, creating a dense
 floc that settles out quickly. Clarification is assisted by lamella settling. Product pilot testing
 in Fort Worth, Texas showed a phosphorus removal efficiency of 92-96% for Actiflo®
 (USEPA, 2003).

 The CoMag process uses the addition of magnetic ballast with metal salts to promote floc formation. Settling is followed by high gradient magnetic separation for effluent polishing and recovery of the magnetic ballast (USEPA, 2008a). CoMag is currently in operation at a 4.0 million gallons per day (MGD) wastewater treatment plant in Concord, Massachusetts. The vendor has guaranteed an effluent phosphorus concentration not to exceed 0.05 mg/L (EPA Region 10, 2007).

4.4 Other Design and Operational Issues

Phosphorus removal by chemical addition is limited to the soluble phosphates in the waste stream. Organically bound phosphorus and polyphosphates will not be removed by chemical treatment unless they are coagulated with the chemicals and removed in the sludge. As noted in Section 4.2, chemicals can be added after biological treatment to capitalize on the conversion of polyphosphates and organically bound phosphorus to phosphates by microorganisms in activated sludge.

The success of phosphorus removal by chemical addition depends on proper instrumentation and control. Dosage control typically takes the form of manual operation (for small systems), adjustments based on automatic flow measurements, or the more advanced on-line analyzers with computer-assisted dosage control.

Chemical properties of any water used for making solutions should be considered – tap water high in suspended solids could cause sludge to form when mixed with coagulants (WEF and ASCE, 1998) and could lead to clogging of chemical feed lines. Smith et al. (2008) found that factors such as pH, complexation, mixing, and the coagulant used can limit the removal of phosphorus, especially in the range of <0.1 mg/L.

4.5 Impacts on Sludge Handling and Production

Sludge handling and production is generally considered to be one of the main downsides of chemical addition. Chemical precipitation methods always produce additional solids due to generation of metal- or calcium- phosphate precipitates and additional suspended solids (WEF and ASCE, 1998). Chemically treated sludge has a higher inorganic content compared to primary and activated sludge and will increase the required size of aerobic and anaerobic digesters. Additional sludge production can be estimated using reaction equations.

The use of metal salts can result in increased inorganic salts (salinity) in the sludge and in the effluent. Salinity can create problems when biosolids are land applied or when the effluent is returned to existing water supply reservoirs. Biological phosphorus removal was developed in South Africa due to the high rate of indirect recycling of wastewater effluent which led to excessive total dissolved solids (TDS) during dry periods. High total salts can reduce germination rates for crops and negatively affect the soil structure.

Lime traditionally produces a higher sludge volume compared to metal salts because of its reaction with natural alkalinity. An advantage of lime sludge is that some stabilization can occur due to the high pH levels required. One disadvantage is that lime can cause scaling in mechanical thickening and dewatering systems. There are also differences in the amount and characteristics of sludge generated by alum versus ferric salts. Although alum tends to produce less sludge than do ferric salts, alum sludge can be more difficult to concentrate and dewater compared to ferric sludge.

5. Biological Nitrogen Removal

This chapter provides an overview of the principles behind biological nitrogen removal and describes the common design configurations in use today. It identifies key operational and design issues (including impacts on sludge handling and production), provides general guidelines on process selection, and summarizes ongoing research efforts in this area. Process configurations that are designed to remove both nitrogen and phosphorus are described in Chapter 6.

5.1 Principles

In wastewater treatment, nitrogen removal occurs in two sequential processes: nitrification and denitrification. An overview of each process is provided below.

5.1.1 Nitrification

Nitrification is an aerobic process in which autotrophic bacteria oxidize ammonia or nitrite for energy production. Nitrification is normally a two-step aerobic biological process for the oxidation of ammonia to nitrate. Ammonia-nitrogen (NH_3-N) is first converted to nitrite (NO_2) by ammonia oxidizing bacteria (AOB). The nitrite produced is then converted to nitrate (NO_3) by nitrite oxidizing bacteria (NO_3). Both reactions usually occur in the same process unit at a wastewater treatment plant (e.g., activated sludge mixed liquor or fixed film biofilm).

The group of AOB most associated with nitrification is the *Nitrosomonas* genus, although other AOB such as *Nitrosococcus* and *Nitrosospira* can contribute to the process. *Nitrobacter* are the NOB most associated with the second step, although other bacteria including *Nitrospina*, *Nitrococcus*, and *Nitrospira* have been found to also oxidize nitrite (Tchobanoglous et al., 2003; USEPA, 2007c). AOB and NOB are classified as autotrophic bacteria because they derive energy from the oxidation of reduced inorganic compounds (in this case, nitrogenous compounds) and use inorganic carbon (CO₂) as a food source. Nitrifying bacteria require a significant amount of oxygen to complete the reactions, produce a small amount of biomass, and cause destruction of alkalinity through the consumption of carbon dioxide and production of hydrogen ions. For each gram (g) of NH₃-N converted to nitrate, 4.57 g of oxygen are used, 0.16 g of new cells are formed, 7.14 g of alkalinity are removed, and 0.08 g of inorganic carbon are utilized in formation of new cells (Tchobanoglous et al., 2003).

Nitrifying bacteria grow slower and have much lower yields as a function of substrate consumed, compared to the heterotrophic bacteria in biological treatment processes. The maximum specific growth rate of the nitrifying bacteria is 10 to 20 times less than the maximum specific growth rate of heterotrophic bacteria responsible for oxidation of carbonaceous organic compounds in wastewater treatment. Thus, the nitrification process needs a significantly higher SRT to work compared to conventional activated sludge processes. The SRT needed for nitrification in an activated sludge process is a function of the maximum specific growth rate (which is related to temperature), the reactor dissolved oxygen concentration, and pH. Nitrification rates decline as the DO concentration decreases below 3.0 mg/L and the pH decreases below 7.0 mg/L. With sufficient DO and adequate pH, typical nitrification design SRTs range from 10 to 20 days at 10°C and 4 to 7 days at 20°C (Randall et al., 1992).

5.1.2 Denitrification

In municipal and industrial wastewater treatment processes, denitrification is the biological reduction of nitrate or nitrite to nitrogen gas (N_2) as indicated by equation 5-1 below.

$$NO_3 \rightarrow NO_2 \rightarrow NO \rightarrow N_2O \rightarrow N_2$$
 (5-1)

It is accomplished by a variety of common heterotrophic microorganisms that are normally present in aerobic biological processes. Most are facultative aerobic bacteria with the ability to use elemental oxygen, nitrate, or nitrite as their terminal electron acceptors for the oxidation of organic material. Heterotrophic bacteria capable of denitrification include the following genera: *Achromobacter, Acinetobacter, Agrobacterium, Alcaligenes, Arthrobacter, Bacillus, Chromobacterium, Corynebacterium, Flavobacterium, Hypomicrobium, Moraxella, Nesseria, Paracoccus, Propionibacteria, Pseudomonas, Rhizobium, Rhodopseudmonas, Spirillum and Vibrio* (Tchobanoglous et al., 2003). Recent research has shown that nitrite reduction is accomplished by a much more specialized group of heterotrophic bacteria than those performing the conversion of nitrate to nitrite (Katehis, 2007).

Denitrification by heterotrophic nitrifying bacteria and by autotrophic bacteria has also been observed. An example of a heterotrophic nitrifying bacteria that can denitrify is *Parococcus pantotropha*, which obtains energy by nitrate or nitrite reduction while oxidizing ammonia under aerobic conditions. A readily available carbon source, such as acetate, is needed (Robertson and Kuenen, 1990). The conditions required for this form of denitrification are not practical in biological wastewater treatment. An autotrophic denitrifying bacteria of practical significance in wastewater treatment is that in the Anammox process used to remove nitrogen in return streams from anaerobic digestion sludge dewatering filtrate or centrate. These bacteria have been identified as a member of bacteria in the order *Planctomycetales* (Strous et al, 1999). Under anaerobic conditions, ammonia is oxidized with the reduction of nitrite with the final product as nitrogen gas. The reaction is best accomplished at temperatures above 25°C and they are slow growing organisms.

Facultative denitrifying bacteria will preferentially use oxygen instead of nitrate. In the absence of oxygen, however, they will carry out nitrite and/or nitrate reduction. Microbiologists generally use the term anaerobic to describe biological reactions in the absence of oxygen. To distinguish anaerobic conditions for which the biological activity occurs mainly with nitrate or nitrite as the electron acceptor, the term "anoxic" has been applied.

Although oxygen is known to inhibit denitrification, denitrification has been observed in activated sludge and fixed film systems in which the bulk liquid DO concentration is positive. This is due to the establishment of an anoxic zone within the floc or biofilm depth. Hence, a single system can carry out simultaneous nitrification and denitrification. The DO concentration that is possible for simultaneous nitrification and denitrification depends on a number of factors including the mixed liquor concentration, temperature, and substrate loading. The DO concentration above which denitrification is inhibited may vary from 0.10 to 0.50 mg/L (WEF and ASCE, 2006; Tchobanoglous et al., 2003; Barker and Dold, 1997).

The organic carbon source for denitrifying bacteria can be in the form of:

- Soluble degradable organics in the influent wastewater
- Soluble organic material produced by hydrolysis of influent particulate material

Organic matter released during biomass endogenous decay

A general rule of thumb is that 4 g of wastewater influent BOD is needed per g of NO_3 -N to be removed through biological treatment (Tchobanoglous et al., 2003). When denitrification occurs after secondary treatment, there is little BOD remaining so a supplemental carbon source is often needed. The most common exogenous carbon source in use is methanol; however, due to issues regarding its safety, cost, and availability, some wastewater systems are using alternative carbon sources such as acetic acid, ethanol, sugar, glycerol, and proprietary solutions depending on the needs of their particular facility (deBarbadillo et al., 2008). See Section 5.3 for additional discussion on supplemental carbon sources.

Biological denitrification reactions produce alkalinity and heterotrophic biomass. Based on the stoichiometry of the reactions, denitrification will produce a 3.57 mg/L of alkalinity as CaCO₃ for each mg/L of NO₃ –N consumed. Heterotrophic biomass produced can be estimated as 0.4 g volatile suspended solids (VSS) produced for every gram of COD consumed. Growth kinetics for denitrifiers are dependent on a number of factors including carbon substrate type and concentration, DO concentration, alkalinity, pH, and temperature, with carbon source being the most important.

5.2 Current Configurations

Biological nitrogen removal can be accomplished by a variety of treatment configurations using suspended growth, attached growth, or combined systems. In the past, some WWTPs were required to only remove ammonia-nitrogen in wastewater to reduce toxicity to aquatic organisms with no limits on nitrate or total nitrogen. However, most treatment plants are now required to remove nitrogen because both ammonia-nitrogen and nitrate-nitrogen can stimulate algae and phytoplankton growth and lead to eutrophication of U.S. waterways (See Chapter 2 for additional discussion). For biological nitrogen removal, it is essential that nitrification occur first followed by denitrification.

Section 5.2.1 presents process configurations that are designed to achieve nitrification and denitrification in a single process unit. Section 5.2.2 discusses separate-stage nitrification and denitrification designs.

5.2.1 Biological Nitrogen Removal Process Configurations

Biological nitrogen removal systems achieve nitrification and denitrification along with BOD reduction in bioreactors followed by secondary clarification. Processes can be either suspended growth or hybrid systems that use a combination of attached growth (biofilms) and suspended growth technologies. Configurations within each of these classifications are discussed below. Note that biological processes that removal both nitrogen and phosphorus are discussed in Chapter 6.

5.2.1.1 Suspended Growth Systems

Modified Ludzck Ettinger (MLE) process

The most common nitrogen removal process used at WWTPs is the Modified Ludzck Ettinger (MLE) process, which is considered a pre-denitrification, single sludge system. The process includes an initial anoxic zone, followed by an aerobic zone. In the anoxic zone, nitrate produced in the aerobic zone is reduced to nitrogen gas. This process uses some of the BOD in the incoming waste. Nitrification occurs in the aerobic zone along with the removal of most of the remaining BOD. At the end of the

aerobic zone, pumps recycle the nitrate-rich mixed liquor to the anoxic zone for denitrification. Total nitrogen removal for the MLE process is typically 80 percent, and the process achieves total effluent nitrogen concentrations ranging from approximately 5 to 8 mg/L with internal nitrate recycle ratios of 2 to 4 based on the influent flowrate (2-4Q).

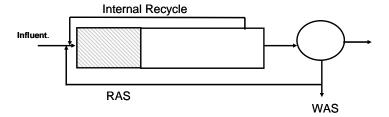


Figure 5-1 Modified Ludzck Ettinger Process

Four-Stage Bardenpho Process

The four-stage Bardenpho process builds on the MLE process, with the first two stages being identical to the MLE system (anoxic zone followed by an aeration zone with a nitrate-rich recycle from the aeration to the anoxic zone). The third stage is a secondary anoxic zone to provide denitrification to the portion of the flow that is not recycled to the primary anoxic zone. Methanol or another carbon source can be added to this zone to enhance denitrification. The fourth and final zone is a re-aeration zone that serves to strip any nitrogen gas and increase the DO concentration before clarification. Some configurations have used an oxidation ditch instead of the first two stages. This process can achieve effluent TN levels of 3 to 5 mg/L.

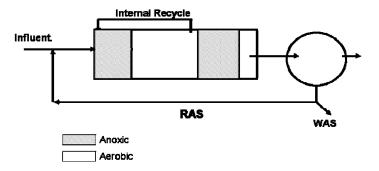


Figure 5-2 Four stage Bardenpho Process

Sequencing Batch Reactors

Sequencing batch reactors (SBRs) are fill and draw batch systems in which all treatment steps are performed in sequence for a discreet volume of water in a single or set of reactor basins. SBRs use four basic phases for most systems:

Fill: water is added to the basin and is aerated and mixed

React: Biological processes are performed

Settle: All aeration and mixing is turned off and the biomass is allowed to settle

Decant: Clarified effluent is removed and biomass is wasted as necessary

The SBR control system allows it to mimic most other suspended growth processes such as the MLE or Four-Stage Bardenpho system. It typically completes 4 to 6 cycles per day per tank for domestic wastewater. If properly designed and operated, SBRs can achieve about 90 percent removal of nitrogen (WEF and ASCE, 2006). SBR applications for small systems are discussed in Section 9.3 of this report.

Oxidation Ditches

Oxidation ditches are looped channels that provide continuous circulation of wastewater and biomass. A number of operating methods and designs have been developed to achieve nitrogen removal, all of which work by cycling the flow within the ditch between aerobic and anoxic conditions. DO can be added to the aerated zone using horizontal brush aerators, diffused aerators with submersible mixers, or vertical shaft aerators (WEF and ASCE, 2006). Patented designs include the NITROX process, Carrousel, and BioDenitro (WERF, 2000a). Many oxidation ditch configurations can achieve simultaneous nitrogen and phosphorus removal. See Section 6.2.6 of this report for additional information.

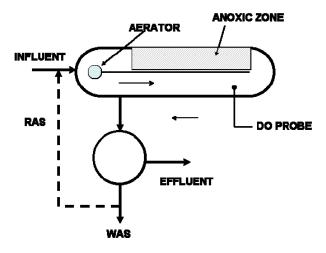


Figure 5-3 Oxidation Ditch with Aerobic and Anoxic Zones

The step feed biological nitrogen removal process splits the influent flow and directs a portion of it to each of several anoxic zones, with the highest proportion of influent flow going to the first zone and steadily decreasing until the last anoxic zone prior to clarification. The biomass in the later stages are not just treating influent flow but are also used to reduce nitrate from the upstream zones.

The step feed system provides flexibility for systems to handle wet-weather events. It can also be compatible with existing conventional "plug flow" activated sludge processes and it does not require the installation of recycle pumps and piping. Disadvantages include the need to control the DO concentration of aeration zones preceding the downstream anoxic zones and the need to control the flow splitting to the step feed points.

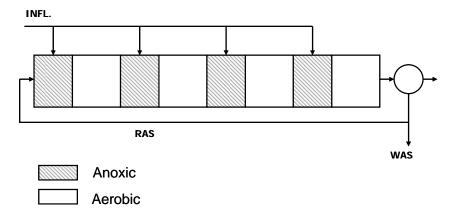


Figure 5-4 Step Feed Biological Nitrogen Removal

5.2.1.2 Attached Growth and Hybrid Systems

Integrated Fixed-Film Activated Sludge (IFAS)

Integrated fixed-film activated sludge (IFAS) is any suspended growth system (e.g., MLE, Four-Stage Bardenpho) that incorporates an attached growth media within the suspended growth reactor in order to increase the amount of biomass in the basin. IFAS systems have higher treatment rates than suspended growth systems and generate sludge with better settling characteristics. Many types of fixed and floating media are available, including:

- Rope: also called looped-cord or strand media. Consists of a polyvinyl chloride-based material woven into rope with loops along the length to provide surface area for the biomass (WERF, 2000b). Proprietary designs include Ringlace, Bioweb, and Biomatrix (USEPA, 2008a).
- Moving Bed with Sponge: proprietary products include Captor and Linpor (USEPA, 2008a).
- Plastic Media: several types of free-floating plastic media are available from Kaldness.

Other media types include fabric mesh (e.g., AccuWeb) and textile material (Cleartec).

Moving-Bed Biofilm Reactor (MBBR)

The moving-bed biofilm reactor (MBBR) is similar to the IFAS system in that it uses plastic media with a large surface area to increase biomass within the biological reactor. The MBBR media is submerged in a completely mixed anoxic or aerobic zone. The plastic media are typically shaped like small cylinders to maximize surface area for biomass growth. The difference between MBBR and IFAS is that MBBR does not incorporate return sludge (WERF, 2000b).

Membrane Bioreactor (MBR)

MBRs are commonly designed for nitrogen removal, using membranes for liquid-solids separation following the anoxic and aerobic zones instead of conventional clarification. Membranes can be submersed in the biological reactor or located in a separate stage or compartment. Low-pressure membranes (ultrafiltration or microfiltration) are commonly used. Systems can be pressure driven or vacuum. All systems use an air scour technique to reduce buildup on the membranes (USEPA, 2007d; USEPA, 2008a).

Membrane materials are either organic polymers or inorganic materials such as ceramics. They are designed in modular units and are typically configured as either hollow fiber bundles or plate membranes (USEPA, 2007d)

For biological nutrient removal applications, the design SRTs and design principals for MBR systems are similar to those used for systems with secondary clarifiers. One of the main differences is that the MBR systems operate at a higher MLSS concentration which results in smaller tanks and smaller space requirements. In addition, membrane separation provides for greatly reduced TSS in the effluent, typically below 1.0 mg/L, and hence slightly greater removal of nitrogen and phosphorus. Operational issues include potential for membrane biofouling and increase pumping costs (USEPA, 2007d; WEF, 2005).

5.2.2 Separate Stage Nitrification and Denitrification Systems

5.2.2.1 Suspended Growth Nitrification

Single-sludge systems for BOD removal and nitrification require that the biomass inventory be retained long enough to establish a stable population of nitrifiers and that the HRT be such that the biomass can react with the ammonia-nitrogen entering the system. The overall approach for designing such systems is to determine the target SRT for the system based on influent characteristics (i.e., BOD, ammonia-nitrogen, organic nitrogen), environmental conditions such as temperature and flow characteristics (i.e., average daily, maximum monthly, diurnal peak).

Most activated sludge treatment plants will readily nitrify if they have sufficient aerobic SRT and can deliver sufficient oxygen maintaining 2 mg/L DO or greater. For plants having difficulty in nitrifying due to insufficient tank volume, there are some emerging technologies which can improve the process. One of these is bioaugmentation. Bioaugmentation is accomplished by seeding the activated sludge process with an external source of nitrifying bacteria (also known as external bioaugmentation) or making process improvements to increase the activity of or enrich the nitrifier population (also known as *in situ* bioaugmentation).

External bioaugmentation uses either commercial sources of nitrifiers or sidestream processes to grow nitrifiers onsite. Early experiences with commercial sources were not consistent, so most work to date has been with sidestream production onsite (USEPA, 2008a). Two patented sidestream configurations for external bioaugmentation are the Single reactor High-activity Ammonia Removal Over Nitrite (SHARON) process and the In-Nitri® process. Both provide high temperature sidestream nitrification using ammonia from the anaerobically digested sludge dewatering liquid or digested supernatant. The nitrifiers grown in the sidestream reactor are fed to the main liquid treatment stream. Both use flow through reactors with hydraulic retention times (HRT) in the 2 to 3 day range. In the SHARON process, nitrification is stopped mainly at nitrite by such process control methods as low DO concentration, low pH and/or low SRT. Full-scale operating systems for the SHARON process include installations at Utrecht, Rotterdam, Zwolle, Beverwijk, Groningen, The Hague in the Netherlands, and a system is expected to start up in New York City in 2009. Seeding from a diffused air biological nutrient removal process to stimulate nitrification in a parallel oxygen process has proved successful at a number of locations (Bott et al., 2007).

Emerging *in situ* bioaugmentation technologies used to enhance nitrifier growth and shown to be successful in bench, pilot, and/or full-scale trials are described briefly below (USEPA, 2008a):

- The Bio-Augmentation Regeneration/Reaeration (BAR) process was developed in the U.S. and is identical to the Regeneration-DeNitrification (R-DN) process developed independently in the Czech Republic. It works by recycling ammonia-laden filtrate or centrate from dewatering of aerobically digested sludge to the head of the aeration tank. The sidestream is fully nitrified, seeding the aeration tank with additional nitrifying bacteria which allows for reduced SRT. There are numerous full scale applications in the Czech Republic, U.S., and Canada. The Aeration Tank 3 (AT3) is similar to the BAR process except that it sends a smaller fraction of the return activated sludge (RAS) to the aeration tank in order to stop the nitrification process at the nitrite stage.
- Bio-Augmentation Batch Enhanced (BABE) process uses a SBR to grow nitrifiers by feeding it RAS
 and reject water from the sludge dewatering process. After treatment, concentrated nitrifiers
 are recycled to the head of the aeration tank.
- The Mainstream Autotrophic Recycle Enhanced N-removal (MAUREEN) Process was developed
 for the two-sludge treatment configuration at the Blue Plains Advanced Wastewater Treatment
 Plant in Washington, DC. The process involves sidestream treatment of WAS from the second
 stage to preferentially select AOB for bioaugmentation to the first sludge stage.

5.2.2.2 Attached Growth Nitrification

Attached growth processes will also nitrify. Trickling filters and rotating biological contactors (RBCs) have historically been used for biological treatment of wastewater and can achieve nitrification with a low organic loading and a relatively high media volume. Typically, nitrification is achieved on the media after most of the BOD is removed since the heterotrophic population competes with the nitrifying organisms for oxygen and space on the media. A major disadvantage of these technologies compared to suspended growth systems is that denitrification is fully dependent on addition of a supplemental carbon source. Suspended growth processes, on the other hand, can be designed to denitrify 80 percent or more of nitrate using the incoming BOD as the carbon source, which is a lower cost solution. Consequently, trickling filters and RBCs have fallen out of favor for nutrient removal applications.

In recent years, manufacturers have developed new technologies called biological aerated filters (BAF) to achieve BOD removal and nitrification. USEPA (2008a) identifies two existing BAF designs as established technologies: the Biofor® system and the Biostyr® system. The Biofor® filtration system is a fixed bed, upflow system with a dense granular media that is designed to expand during filtration. Air is sprayed into the filter to maintain an aerobic environment. The Biostyr® system is similar but uses a media that is less dense than water and held in place during operation by a screen at the top of the cell.

BAF can be configured in series to remove BOD in one unit and ammonia-nitrogen in the next or it can be designed for BOD removal and nitrification in a single unit depending on process goals. Advantages of BAF include its smaller footprint, higher hydraulic loading rates, and less susceptibility to washout than suspended sludge systems (Verma et al., 2006).

Another fixed film process that has gained popularity lately is moving bed biofilm reactors (MBBR). These reactors involve biofilm attached to a plastic media in a series of fluidized bed reactors. The plastic media help promote specialization of the biofilm within each reactor for either nitrification or denitrification (WEF and ASCE, 2006). Mixers or medium bubble diffuse aeration are used to keep the media suspended, depending on whether the system is anaerobic or aerobic. MBBR has a shorter SRT and smaller footprint than activated sludge processes. It has also proven to be effective in cold temperatures (Bott et al., 2007).

5.2.2.3 Separate-Stage Denitrification

A separate-stage denitrification system may be appropriate for plants that are regularly achieving nitrification and need to add denitrification capabilities. Attached growth systems (denitrifying filters) are more common than suspended growth systems, although suspended growth systems have been used for some treatment plants. Suspended growth reactors typically have short SRTs (2 to 3 hrs) and a small aerated zone following the denitrification zone to oxidize excess methanol and release contained nitrogen gas bubbles (WEF and ASCE, 2006).

Denitrification filters typically have a small footprint compared to suspended growth systems and have the added advantage of achieving denitrification and solids removal simultaneously. They were first installed in the 1970s and have evolved into two main process configurations (USEPA, 2007c):

- Downflow denitrification filters are deep bed filters consisting of media, support gravel, and a block underdrain system. Wastewater flow is directed over weirs onto the top of the filter where a supplemental carbon source, typically methanol, is added. Backwashing (typically air scouring and backwashing with air and water) is conducted at regular intervals to remove entrapped solids from the filter. During operation, nitrate is converted to nitrogen gas and becomes entrained in the filter media, increasing head loss through the filter. To release entrained nitrogen, most denitrification systems have a nitrogen-release cycle operation that essentially "bumps" the filter by turning on the backwash pump(s) for a short period of time.
- Upflow continuous backflow filters do not have to be taken off-line for backwashing, as it is an integral part of the filtering process. Wastewater enters the bottom of the filter where a carbon source, typically methanol, is added. Water flows up through an influent pipe and is dispersed into the filter media through distributors. Filtered water discharges at the top of the filter. Filter media continuously travels downward, is drawn into an airlift pipe at the center of the filter, and is scoured before being returned to the filter bed.

Performance of denitrifying filters depends on many factors including:

- Influent weir configuration
- Filter media
- Underdrain system
- Backwash system
- Flow and methanol feed control

One wastewater system in Connecticut reported that key design issues for them were influent piping design to minimize aeration, maintaining a consistent flow to the filters, and control of methanol feed based on influent COD (Pearson et al., 2008).

5.3 Key Design and Operational Issues

Temperature

In general, as temperature of the wastewater increases, the rate of nitrification and denitrification increases. For the typical range of liquid temperatures between 10 and 25 °C, the nitrification rate will approximately double for every 8 to 10 °C increase in temperature (WEF and ASCE, 2006). Rapid decreases in temperature without acclimation time will, however, cause even slower nitrification rates than predicted, strictly by the temperature change. Denitrification rates will also increase with increasing temperature, although not at the same magnitude as nitrification rates.

Dissolved Oxygen

Nitrifying bacteria are also more sensitive to DO levels as compared to aerobic heterotrophic bacteria, with growth rates starting to decline below 3 to 4 mg/L with significant reduction below 2 mg/L. The nitrification rate at a DO concentration of 0.50 mg/L is only about 60 percent of that at a 2.0 mg/L DO concentration. Studies have shown that the amount of oxygen available to nitrifying bacteria can be limited by floc size, requiring higher bulk DO concentrations under higher organic loading conditions (Stenstrom and Song, 1991). At DO concentrations less than 0.5 mg/L, the effect is greater for *Nitrobacter* than for *Nitrosomonas*. This can result in higher NO₂-N in the effluent and have a negative impact on chlorine disinfection as 1 g of NO₂-N consumes 5 g chlorine for oxidation. As noted in Section 5.1, DO must normally be less than 0.2 to 0.5 mg/L, otherwise there will be inhibition of the denitrification process.

pH and Alkalinity

Nitrification generally operates well within a pH range of 6.8 to 8.0 (WEF and ASCE, 2006). At lower pH values the nitrification rate is much slower and at pH values near 6.0 the nitrification rate may only be about 20 percent of that with a pH of 7.0 (Tchobanoglous et al., 2003). Alkalinity is consumed during the nitrification process but partially replenished (up to 62.5 percent) during the denitrification process. Depending on the influent wastewater alkalinity, there may be a sufficient alkalinity reduction due to nitrification to decrease to unacceptable levels. Addition of chemicals such as lime, sodium

hydroxide, or soda ash can be used to replace the alkalinity consumed by nitrification to maintain acceptable pH levels.

Carbon Sources for Denitrification

Denitrifying bacteria need a readily available carbon food source, such as soluble BOD, to ultimately convert nitrate to nitrogen gas. WWTPs that meet very low total nitrogen limits typically use a secondary anoxic zone in which supplemental carbon is added. Supplemental sources can be "internal" such as fermented wastewater or sludge, or "external" sources such as purchased chemicals.

Methanol is currently the most common external carbon source used in denitrification because of it low cost. It has several drawbacks, however, namely:

- It is highly flammable and implicated in some storage tank explosions and fires (Dolan, 2007); however with proper design and operation problems can be minimized.
- It is not the most efficient source for most treatment configurations.
- Costs have begun to fluctuate widely (deBarbadillo et al., 2008).
- Availability is a problem in some areas (Neethling et al. 2008).
- Reported low growth rates under cold temperatures (Dold et al. 2008).

Other sources of carbon include ethanol, acetic acid, corn syrup, molasses, glucose, glycerol, and industrial waste products. The WEF Nutrient Challenge Research Plan (2007) identified research on alternative carbon sources as priority for operators, owners, and engineers of wastewater systems. In December of 2007, the 2nd External Carbon Workshop was held in Washington, DC to discuss the state of the technology and research needs. WERF is also currently formulating a standard protocol for evaluation of external carbon alternatives.

Nitrification Inhibition from Toxic Chemicals

Nitrifying bacteria are very sensitive to heavy metals and other inorganic compounds in wastewater. The Local Limits Development Guidance Manual (USEPA 2004) has been the main source of information on inhibitory effects for a variety of wastewater treatment processes including nitrification. Appendix G of the 2004 version provides a summary table with the reported range of nitrification inhibition threshold levels for a number of metals, non-metal inorganics, and organic compounds. Actual inhibitory effects are site-specific and depend on many factors including the nature of biodegradable organic material, microorganism speciation, acclimation effects, temperature, and water quality conditions.

Wet Weather Events

Wet weather events can increase inflow and infiltration into the collection system and subsequently increase the hydraulic load to the wastewater treatment plant. This can in turn reduce the SRT leading to reduced performance of nitrification process units. In addition, wet weather flows have different characteristics than typical wastewater influent flow and can be less favorable for nitrification and denitrification. Conditions that are less favorable for nitrification include decreased alkalinity and

sudden temperature drops. Lower biodegradable COD concentrations and increased DO make wet weather flows less amenable to denitrification.

Flow equalization basins can be used to handle wet weather events; however, this requires available space and capital investment. USEPA (2008a) identifies a number of innovative storage and treatment technologies used to manage influent flows during wet weather events.

5.4 Guidance for Selecting Process Modifications

Nitrogen removal requires first that a biological nitrification process be present or that the facility be modified to accomplish nitrification. Considerably more volume is needed for activated sludge nitrification compared to designs for BOD removal only. If there is insufficient space to accommodate the increased volume, suspended growth or hybrid process options that require less space such as the MBR process or IFAS systems with suspended media in the activated sludge process should be considered. Another option is to use a fixed film nitrification process after the suspended growth process clarification step. This could be a BAF or a plastic media trickling filter. However, if nitrogen removal is required, an exogenous carbon source is needed, which has higher operating costs than using the influent BOD for denitrification.

Nitrification systems need sufficient oxygen transfer for ammonia oxidation in addition to BOD removal. Such systems should consider the impact to diurnal loadings and ammonia addition in recycle streams. The influent TN concentration may have daily peak values that are 1.5 to 2.0 times the daily average loading. Higher peak loadings require longer SRTs to assure that sufficient nitrifying bacteria are present to remove ammonia at a greater rate, while maintaining a low effluent ammonia concentration. Often anaerobic digester sludge dewatering operations occur during the day and produce return recycle streams high in ammonia concentration (500-1000 mg/L) at times that coincide with the high influent diurnal ammonia loads. Recycle equalization or treatment helps to provide a more stable nitrification system and lower effluent NH₃-N concentrations.

In many cases, it is advantageous to incorporate a denitrification pre-anoxic step with nitrification (MLE process) due to the many benefits and improved operational stability. The advantages include 1) less aeration energy as the nitrate produced can be used for BOD removal, 2) the production of alkalinity to offset the alkalinity used by nitrification, which in some cases eliminates the need to purchase alkalinity, and 3) a more stable, better settling activated sludge process as the anoxic-aerobic processes favor good settling floc-forming bacteria over filamentous growth.

The effluent nitrogen goals greatly affect the process design choices and system operation. For an effluent goal of 10 mg/L TN, an MLE process is often sufficient for activated sludge treatment with secondary clarifiers or membrane separation. However, with water conservation leading to more concentrated wastewater, these processes alone may not be sufficient due to the fact that they are limited to 80-85% removal of the influent TN.

For TN effluent goals of 3 to 5 mg/L or lower, some form of post anoxic treatment is generally needed. One option is to convert an MLE process to a Bardenpho process by adding another anoxicaerobic set of tanks. Although the endogenous respiration rate of the bacteria can be used to consume nitrate in the post anoxic tanks, it is often necessary to add an exogenous carbon source. Other alternatives to using exogenous carbon sources include denitrification filters instead of adding more activated sludge tank volume, step feed with carbon addition in the last pass, and IFAS processes.

Denitrification processes require sufficient carbon to drive the nitrate/nitrite reduction reactions. Characterization of the influent wastewater with regard to its organic strength and soluble fraction and the TN and ammonia concentrations is needed to fully understand a system's carbon needs. In addition, design and operating methods that eliminate or minimize DO feeding to anoxic zones can reduce the amount of exogenous carbon needed and provide a more stable operation. Low DO zones prior to downstream anoxic tanks or for withdrawal of recycle to preanoxic zones should be considered.

5.5 Impacts on Sludge Production and Handling

It has been documented by both research and full scale experiments that BOD removal by activated sludge using nitrate as the electron acceptor instead of DO will result in a 20% or more reduction in waste activated sludge (WAS) production for the same operating conditions. Full-scale investigations near Melbourne, Australia achieved as high as a 40% reduction in WAS, and implementation of nitrogen removal at the York River, VA, plant resulted in a reduction of more than 50% in WAS production. The impact this will have on total sludge production by a treatment plant will depend upon how much waste sludge is produced by other treatment units such as primary clarifiers and chemical treatment with precipitating chemicals. Additionally, implementation of nitrogen removal at conventional activated sludge plants can improve the thickening characteristics due to decreasing the amounts of filamentous bacteria in the activated sludge. If an external carbon source is added to improve the rate of denitrification, there will be an increase in WAS production compared to when no external carbon source is added. If an external carbon source is used to supplement denitrification, it is likely that the small increase in solids production will be offset by endogenous respiration due to longer SRTs. Solids produced from nitrogen removal processes generally thicken and dewater well and show no negative impact on any solids processing system.

6. Biological Phosphorus Removal and Combination Processes

This chapter provides an overview of the principles behind biological phosphorus removal (BPR). It describes existing configurations that can achieve phosphorus removal and in many cases, simultaneous nitrogen removal. Key operational issues, impacts on sludge handling, and a summary of ongoing research related to BPR removal are also provided.

6.1 Principles

Biological phosphorus removal is achieved by contacting phosphorus accumulating organisms (PAOs) in the RAS with feed, containing volatile fatty acids (VFA), in a zone free of nitrates and DO (anaerobic zone). Phosphorus is released in this zone providing energy for uptake of VFAs that are polymerized and stored inside the PAO cells. The anaerobic zone is followed by an aeration zone where the polymerized VFAs are metabolized and phosphorus is taken up again to store excess energy from the metabolism. The phosphorus content of the mixed liquor suspended solids (MLSS) would be similar to that of the waste activated sludge (WAS). When nitrification occurs in the aeration basin, nitrates will be present in the RAS, resulting in some metabolism of the VFA before storage, thereby reducing subsequent phosphorus uptake. Some form of denitrification (anoxic zones) must be used to reduce/remove the nitrates from the RAS. The process flow sheets now known as Pho-redox (A/O) and 3 Stage Pho-redox (A2/O) as well as the modified Bardenpho process were first published by Barnard (1975) as the Pho-redox flow sheets for the removal of phosphorus. The theory for the functioning of the PAO was first suggested by Fuhs & Chen (1975) and can briefly be described in conjunction with Figure 6.1 below.

Fuhs & Chen Theory

PAOs have the ability to store a large mass of phosphorus in their cells in the form of polyphosphates. Polyphosphates are formed by a series of high-energy bonds. The organisms can subsequently get energy from breaking these bonds. The polyphosphate globules within the cells function just like energy storage batteries. The storage of polyphosphates (energy), takes place in the aeration zone. In the anaerobic zone, these obligate aerobic bacteria can take up short chain VFA such as acetate and propionate and store them in the form of intermediate products such as poly-β-hydroxy-butyrate (PHB). The energy for transferring the food across the cell membranes in the anaerobic zone is derived from breaking phosphorus bonds. Excess phosphates are released to the liquid in the anaerobic zone. Some magnesium and potassium ions are co-transported across the cell walls with phosphates. PAOs can only get energy from the food they have taken up in the anaerobic zone when they pass to the aerobic zone where oxygen is available. They use oxygen to metabolize the stored products, deriving enough energy to take up all the released phosphates as well as those in the influent, and store them in the cells. The WAS will contain sufficient phosphate-enriched PAOs to remove most of the phosphorus from the waste steam once enhanced BPR is established.

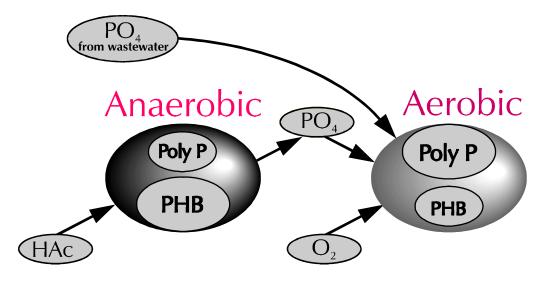


Figure 6-1 Theory of biological phosphorus removal in activated sludge

The right carbon source, in this case a combination of acetates and propionates, is essential for BPR. The wastewater characteristics are thus important. In general, it can be said that you need at least 40:1 COD:TP or about $18:1 \text{ BOD}_5:TP$ in the process influent wastewater to reduce effluent phosphorus to less than 1.0 mg/L. In addition, some of the COD should consist of short chain VFAs. More COD may be required if nitrates must also be denitrified.

Biological phosphorus removal can work in with or without nitrification. When nitrification occurs, denitrification within the process is important to reduce the nitrates that may be returned with the RAS. While the anaerobic zone serves mostly as a contact zone for VFAs and PAOs, some fermentation of easily biodegradable carbon compounds (rbCOD) to acetate and propionate may take place. In most plants the readily biodegradable material is in short supply and must be reserved for the PAOs.

When nitrate or oxygen is discharged to the anaerobic zone, two things may happen, both undesirable:

- They will prevent fermentation of rbCOD to acetic and propionic acid
- Nitrates or DO could serve as electron acceptors for PAOs and other organisms that will
 metabolize the VFA and so deprive the PAOs of the substance that they need to store for
 growth and phosphorus removal.

In the absence of electron acceptors such as DO and nitrates in the anaerobic zone, PAOs are favored to grow since they can take up and store the VFA under anaerobic conditions, thereby making it unavailable for other aerobic and facultative heterotrophs in the aerobic zone.

Biological removal of both nitrogen and phosphorus at the same WWTP is common. Both functions require a carbon source. While denitrification organisms can feed on quite a number of easily degradable materials such as methanol, sugar, glucose, acetate and propionate, PAOs are restricted to the latter two for polymerization and storage (e.g. adding methanol to the anaerobic zone will reduce nitrates but not assist in the removal of phosphorus). See section 6.4.1 for detailed discussion on carbon sources for biological phosphorus removal.

6.2 Current Configurations

The basic design of anaerobic, anoxic, and aerobic zones, in that order, has been achieved in many different configurations. The configurations vary in the number of stages, the nature and location of recycles, and the operation of the process. Each process was modified from the standard biological activated sludge design in order to accomplish various design goals (e.g., protection of the anaerobic zone from excess nitrate recycle). The primary processes are listed below. Of these, all will also biologically remove nitrogen except for the Pho-redox process.

- Pho-redox (A/O)
- 3 Stage Pho-redox (A2/O)
- Modified Bardenpho
- University of Capetown (UCT) and Modified UCT (MUCT)
- Johannesburg (JHB), Modified Johannesburg, and Westbank
- Orange Water and Sewer Authority (OWASA)
- Oxidation ditches with anaerobic zones or phases added
- SBR operated with an anaerobic phase
- Hybrid chemical/biological processes

The performance of these technologies depends on many site specific factors, including but not limited to temperature, hydraulic and organic loading, recycle rates, and return streams. The technologies described in this section are generally capable of phosphorus removal to effluent levels between 0.5 and 1.0 mg/L. Operating strategies that can be used to enhance biological treatment and achieve these and, in some cases, even lower effluent levels are described in Section 6.4.

Biological phosphorus removal can be combined with other technologies to achieve very low effluent concentrations (< 0.2 mg/L). Chemical addition combined with biological removal of phosphorus has been used to consistently achieve low levels. WEF and ASCE (1998) recommend that WWTPs have chemical addition capabilities even for well operating BPR plants to provide backup phosphorus removal in the event of power outages, pipe breaks, or other unforeseen events.

Solids removal can also be a limiting factor in achieving phosphorus removal below 0.2 mg/L. Very low phosphorus levels generally require a TSS level of less than 5 mg/L. Tertiary filtration (see Chapter 7), membrane bioreactors (see Chapter 5), and advanced clarification processes (see Chapter 4) can achieve TSS levels less than 5 mg/L.

6.2.1 Pho-redox (A/O) and 3 Stage Pho-redox (A2/O)

The Pho-redox (A/O) process is a conventional activated sludge system with an anaerobic zone at the head of the aeration basin. The RAS is pumped from the clarifier to the anaerobic zone. It is a low SRT process, operated to avoid nitrification. With no nitrates in the RAS the process is reliable and easy to operate except at temperatures in excess of 25°C when nitrification is difficult to avoid. The 3 Stage Pho-redox (A2/O) process adds an anoxic zone after the anaerobic zone to achieve de-nitrification. In addition, a nitrate rich liquor is recycled from the end of the aerobic zone to the head of the anoxic zone to enhance de-nitrification. A shortcoming of the 3 Stage Pho-redox process is that there will be nitrates present in the RAS, potentially making the process unreliable.

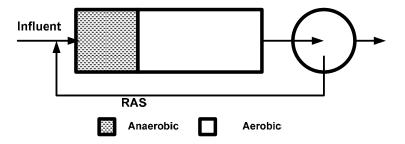


Figure 6-2 Pho-redox Process (A/O)

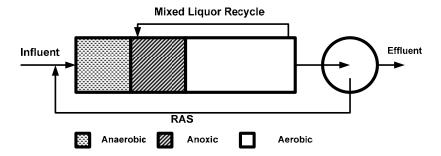


Figure 6-3 3 Stage Pho-redox Process (A2/O)

There are existing Pho-redox plants in Pontiac, MI and Titusville, FL. Performance data for these plants exists in WEF (1998). Performance data on 3 Stage Pho-redox plants in Largo, FL; Fayetteville, AR; Montgomery County, PA; Warminster, PA; Newark, OH; Goldsboro, NC; Frederick, MD; and Sod Run, MD are available in WEF (1998) and WEF and ASCE (2006). Neethling et al. (2005) reported data for 3 Stage Pho-redox plants in Durham, NC and Nine Springs, WI and for Pho-redox plants in Missoula, MT and Grand Prairie, Alberta.

6.2.2 Modified Bardenpho

The Bardenpho process removes nitrogen to low concentrations. The addition of an anaerobic zone at the head of the process enables phosphorus removal as well. The process consists of 5 stages: an anaerobic stage followed by alternating anoxic and aerobic stages. A nitrate-rich liquor is recycled from the first aerobic stage, designed for complete nitrification, to the first anoxic stage. The RAS is recycled from the clarifier to the beginning of the anaerobic zone. Since the nitrates in the RAS ranges from 1 to 3 mg/L, it does not seriously interfere with the mechanism for phosphorus removal as can happen in the 3 Stage Pho-redox process.

Performance data on existing plants in Palmetto, FL; Kelowna, BC; Orange County, FL; Fort Myers, FL; City of Cocoa, FL; Tarpon Springs, FL; Johannesburg, South Africa (Goudkoppies); and Medford Lakes, NJ are published in WEF (1998) and WEF and ASCE (2006). Neethling et al. (2005) reported performance data on modified Bardenpho plants at Reedy Creek (Disney World) and Iron Bridge, FL.

6.2.3 University of Cape Town (UCT) and Modified UCT (MUCT)

The UCT process was designed to reduce nitrates to the anaerobic zone when high removal of nitrates in the effluent is not required. It consists of three stages: an anaerobic stage, an anoxic stage, and an aerobic stage. The RAS is returned from the clarifier to the anoxic zone instead of the anaerobic

zone to allow for denitrification and to avoid interference from nitrate with the activation of the PAOs in the anaerobic stage. A nitrate rich stream is recycled from the aerobic zone to the anoxic zone. Denitrified mixed liquor is recycled from the anoxic zone to the anaerobic zone.

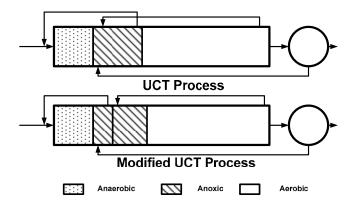


Figure 6-4 UCT and Modified UCT Process

Several modifications of the process exist. Sometimes it can be difficult to achieve the level of denitrification in the anoxic zone required to protect the anaerobic zone from nitrates when the zone is receiving both RAS and high internal nitrate recycle flows. This problem led to the development of the modified UCT process, which splits the anoxic zone into two stages. The nitrate rich recycle from the aerobic zone is recycled to the head of the second anoxic stage. The nitrate containing RAS is recycled to the first anoxic stage where it is denitrified. Next, the denitrified RAS is recycled from the end of the first anoxic stage back to the head of the anaerobic stage and mixed with the incoming wastewater. The Virginia Initiative Plant (VIP) is similar to the UCT process, but the anaerobic and anoxic zones are baffled into two or more sections each to increase rates of reaction in the first section of each zone, thereby firmly establishing the desired anaerobic and anoxic condition in the second section.

Performance data for existing VIP plants operated by the Hampton Roads Sanitation District (HRSD) at Norfolk and Nansemond, VA, for UCT plants in Traverse City, MI, and Lethbridge, Alberta and for modified UCT plants in King County South, WA and Kalispell, MT are available in WEF and ASCE (2006). Performance data are also available for the HRSD VIP plants along with the modified UCT plants at Kalispell, MT and McDowell Creek, NC in Neethling et al. (2005).

6.2.4 Johannesburg (JHB), Modified Johannesburg and Westbank

The JHB process is similar to the 3 Stage Pho-redox process, but has a pre-anoxic tank ahead of the anaerobic zone to protect the zone from nitrates when low effluent nitrates are not required. The low COD of the wastewater limited the de-nitrification capacity in the original plant (Nothern Works), resulting in nitrates in the RAS. This reduced BPR so much that a pre-anoxic tank was included on the RAS line to remove the nitrates from the RAS flow using endogenous respiration, before the flow entered the anaerobic zone. The modified JHB process adds a recycle from the end of the anaerobic zone to the head of the pre-anoxic zone to provide residual, readily biodegradable compounds for denitrification.

The Westbank process is similar to the JHB process but adds some primary effluent to the anaerobic zone to assist in denitrification with the remainder of the primary effluent being discharged to the anaerobic zone. During storm flows, excess flow is passed directly to the main anoxic zone. VFA obtained from acid fermentation of the primary sludge is passed to the anaerobic zone.

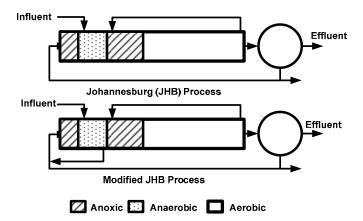
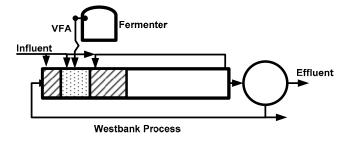


Figure 6-5 JHB and Modified JHB Process



Figures 6-6 Westbank Process

6.2.5 Orange Water and Sewer Authority (OWASA)

The OWASA process was developed by adding activated sludge from a biological nitrogen removal process to a trickling filter plant. Then, nitrified effluent from the trickling filter is fed to the aerobic zone of the activated sludge system. Because the VFAs have been destroyed by the trickling filter, it is necessary to ferment the settled organic solids from the primary clarifier to produce sufficient VFAs for BPR. Next, the fermented supernatant is passed to an anaerobic (nutrition) zone and mixed with the RAS to initiate BPR.

Mixed liquor then flows from the nutrition zone to an anoxic zone and then to an aerobic zone. Alternatively, simultaneous nitrification and denitrification takes place in the aeration zone, as shown in Figure 6-7. Performance data for the original plant in Orange County, NC, are available in WEF and ASCE (2006).

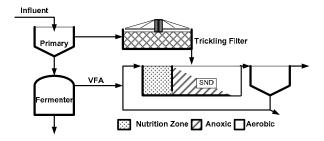


Figure 6-7 OWASA Process

6.2.6 Oxidation Ditches

There are several oxidation ditch designs that can remove phosphorus. They normally consist of an anaerobic zone ahead of the oxidation ditch whereas simultaneous nitrification and denitrification takes place within the ditches. Oxidation ditches typically operate as racetrack configurations around a central barrier, with forward mixed liquor flows of approximately 1 foot per second or more. It is possible, by manipulating the DO transferred to the mixed liquor, to establish both anoxic, aerobic and near anaerobic zones within the racetrack configuration, even though the high flow velocities accomplish complete mixing of the wastewater with the RAS.

There are many forms of oxidation ditches, such as the Carousel, the Pasveer Ditch and the Orbal process. The Orbal process creates anaerobic and anoxic zones in the outer of three concentric oval shaped ditches with the RAS recycled from the clarifier to the anoxic zone. It is also possible to introduce an anaerobic tank before the ditch to accomplish BPR in the combined system. The Pasveer Ditch and the Carousel system also can be used in conjunction with an anaerobic zone to accomplish BPR, in addition to simultaneous nitrification and denitrification within the ditches. Because of the very high internal recycle within the ditches, very low nitrate concentrations can be achieved in the mixed liquor before settling, and anaerobic conditions are easy to maintain in the anaerobic zone, thereby resulting in efficient BPR. The layout would resemble a Pho-redox process with simultaneous nitrification-denitrification (SND) in the aeration basin. Alternatively the Carousel or Pasveer Ditch could be used as the aeration stage in either the 3 Stage Pho-redox or the Modified Bardenpho process.

The VT2 process at Bowie, MD, operates two Pasveer ditches in series with dedicated anoxic, near anaerobic and aerobic zones. It also has a side stream anaerobic zone that receives only 30 percent of the influent flow to enhance BPR. Denitrified MLSS for the anaerobic zone are obtained from the end of the near anaerobic zone of the adjacent ditch. Operated without primary sedimentation, the system consistently obtains very low (<0.25 mg/L) effluent TP without chemicals or effluent filtration. The ditches are operated in series because the plant has limited clarification capacity, and series operation results in lower MLSS concentrations to the clarifiers. The biodenipho process also uses pairs of ditches. The ditches in the biodenipho process operate in alternating anoxic-aerobic modes. An anaerobic tank is placed before the ditches for BPR and the ditches are alternated between nitrification and denitrification.

Performance data for existing plants at Bowie, MD and North Cary, NC are available in WEF and ASCE (2006).

6.2.7 Sequencing Batch Reactors (SBR)

SBRs are fill-and-draw reactors that operate sequentially through the various phases by means of adjusting the mixing and aeration. The reactor phases can be set and automated to allow the mixed liquor to go through an anaerobic/anoxic/aerobic progression as is necessary for removal of phosphorus and nitrates. Because of the fill-and-draw nature of SBRs, it actually is necessary to remove the nitrates remaining from the previous cycle before anaerobic conditions can be established, thus the typical treatment progression becomes anoxic/anaerobic/aerobic. However, SBRs are almost always operated without primary sedimentation, so they still usually have a favorable BOD₅:TP ratio for effluent TP of somewhat less than 1.0 mg/L during the settling phase.

Performance data for plants in Oak Point, MI; Grundy Center IA; Culver City, IN; Armada, MI; and Manchester, MI are in WEF and ASCE (2006).

6.2.8 Hybrid Chemical / Biological Processes

The PhoStrip configuration, used mainly in non-nitrifying plants, pulls a side stream off the RAS in a conventional activated sludge plant. The side stream is concentrated and retained for a day or more in a thickening tank where the solids blanket is deep enough to produce anaerobic conditions and fermentation, resulting in the release of phosphates by the microorganisms. Lime is then added to the supernatant stream to precipitate and remove phosphate. The thickened, fermented sludge is passed back to the main aeration basin. Existing plants include Seneca Falls, NY; Lansdale, PA; Adrian, MI; Savage, MD; Southtowns, NY; Amherst, NY; and Reno-Sparks, NV.

The Biological Chemical Phosphorus and Nitrogen Removal (BCFS) configuration is similar to the modified UCT process. In this process, a sludge stream is removed from the anaerobic zone. Ferric chloride is added to the sludge thickener to remove phosphate. This provides an advantage over chemical addition to the secondary clarifier because it does not require the chemical sludge to be recycled. There is an existing plant at Holten in the Netherlands (WEF and ASCE, 2006), but no performance data are available.

6.3 Emerging Technologies

Many plants that are not specifically configured for BPR nevertheless achieve phosphorus removal to less than 1 mg/L. The first such observation in a nitrifying plant was in a four-stage Bardenpho plant where mixed liquor was recycled from the second anoxic zone to an unstirred fermenter, then returned to the anoxic zone. The CATABOL™ and Cannibal Processes claim to reduce excess secondary sludge production by passing mixed liquor or RAS through an anaerobic (fermenting) stage and then back to the main stream aeration system. In addition, both processes pass the mixed liquor through a process for removal of some of the inert solids. Both processes claim to get similar phosphorus removal to that for the Bardenpho plant described above. All of these processes rely on the fermentation of some of the mixed liquor for producing VFA that assists in the biological removal of phosphorus. The Town of Cary, NC, has been using a system by which some of the sludge in the return streams of a biological nitrogen removal plant is subjected to anaerobic conditions similar to that of the other processes described above resulting in an effluent phosphorus concentration of less than 0.5 mg/L.

There is a similarity between these processes and *ad hoc* processes for switching off aeration in plug-flow plants for promoting phosphorus removal. These *ad hoc* processes take various forms. The

Piney Water, CO, plant is a 5-stage Bardenpho plant with no primary sedimentation and little VFA in the influent, which resulted in little phosphorus removal. By switching off a mixer in one of the anaerobic zones, sludge settled to the bottom and fermented, which supplied the VFAs for reducing the orthophosphorus to less than 0.2 mg/L. A similar operation at the Henderson, NV, plant in a JHB type process had the same effect. Some plug-flow aeration plants succeeded in reducing phosphorus to below 1 mg/L by turning off aeration at the feed end of the plant, such as the Blue Lakes and Seneca plants operated by the Metropolitan Council Environmental Service in Minnesota and the St. Cloud, MN, plant. The Joppatowne plant operated by Harford County, MD, consists of an MLE plant with some sludge accumulation in the anoxic zone while reducing the phosphorus from 7 mg/L in the influent to around 1 mg/L in the effluent.

All of these plants use the same principle of fermenting some of the mixed liquor sludge or underflow from the final clarifiers, either inside the main stream tanks or in a side stream basin. There are many instances where enterprising operators can achieve 80 percent or more phosphorus removal by turning off air or mixers in conventional treatment plants.

There is a Catabol plant in Cartersville, GA (USEPA, 2008a); however, there are no published data for this plant.

6.4 Operational and Design Considerations

Important factors that affect BPR include:

- Bioavailable COD:P ratio in the anaerobic zone influent, including adjustments by VFA addition and sludge fermentation
- SRT and HRT
- Presence of oxygen or nitrate in the anaerobic zone
- Backmixing of oxygen
- Temperature
- pH
- Secondary release under anaerobic conditions
- Sufficient oxygen in the aerobic zone
- Inhibition
- Flow and load balancing

6.4.1 COD:P Ratio

The PAOs need VFAs in the form of acetic and propionic acid. These acids may be in the feed or can be produced through fermentation of soluble rbCOD such as sugar, ethanol, etc., in the anaerobic zone. As a rough estimate of the propensity for phosphorus removal to an effluent concentration less than 1.0 mg/L, the COD:P ratio typically should be about 40 or more.

VFA is produced through fermentation of municipal wastewater or it can be added as a commercial or waste product. Some wastewater collection systems that are relatively flat and have long collection times may have sufficient fermentation in the collection system to provide the necessary VFAs, but it will vary monthly depending upon the temperature and flow conditions in the collection system. Force mains are excellent fermenters for the production of VFA. Systems that do not have a COD/P ratio of at least 40 will most likely need to supplement VFAs to achieve effluent phosphorus

concentrations below 1.0 mg/L. However, they will still achieve substantial BPR with lower ratios if appropriately operated. See below for a more detailed discussion of VFAs.

Recent studies suggest that the instantaneous COD:P ratio is more important than the overall average (Neethling et al., 2005). Short term drops in the BOD:P ratio in the primary effluent to below that required for sustainable phosphorus removal correlated well with rises in effluent phosphorus. Intermittent recycles of phosphorus rich return streams may cause short term variability in the BOD:P ratio. Controlling or eliminating these recycles can improve plant performance. Weekend changes in the BOD:P ratio also can affect performance.

Another group of organisms, glycogen accumulating organisms (GAOs), also has the ability to take up acetate in the anaerobic zone, not by using energy in phosphate bonds but by using stored glycogen as the energy source. Under certain conditions, such as high temperatures or low phosphorus concentrations relative to the influent bioavailable COD, they may out-compete PAOs for the VFAs, which would result in less or no release of phosphorus in the anaerobic zone. This in turn will result in less or no overall phosphorus removal. GAOs use the stored energy in the form of glycogen to take up VFAs and store them as a complex carbohydrate containing poly-hydroxy valerate (PHV), instead of PHB formed with poly-phosphorus as the energy source. When this begins to happen, there is a slow decline of phosphorus removal by the biological system.

There is still a debate amongst researchers about the conditions likely to favor GAOs over PAOs. Summarizing a number of publications, it would appear that the following conditions favor the growth of GAOs over that of PAOs:

- High SRT
- High temperature over 28 °C
- Longer non-aerated zones
- Stronger wastes with low TKN content
- Periods of intermittent low BOD loads
- If the VFA consists mostly of either acetate or propionate
- Polysaccharides such as glucose are fed to the anaerobic zone.
- Low pH in the aerobic zone

Further confirmation is needed for some of these factors.

Volatile Fatty Acid Addition

Only VFAs such as acetic and propionic are taken up by PAOs. Reported doses of VFA for successful phosphorus removal range from 3 to 20 mg/L VFA per gram of phosphorus removed. These numbers, however, do not take into account the rbCOD that is fermented in the anaerobic zone. It is more accurate to look at the rbCOD/P ratio for good phosphorus removal, which ranges from 10 to 16. (Barnard, 2006). Surveys show that it is rare for a WWTP treating municipal sewage to achieve more than 95 percent removal of phosphorus by biological processes without adding VFAs (Neethling et al., 2005).

An Australian study shows that while both PAOs and GAOs could use acetate, PAOs will have a competitive advantage when the VFAs consist of roughly equal parts of acetic and propionic acid as a growth medium. PAOs that are fed on acetate are able to switch to propionate much more quickly and effectively than GAOs (Oehmen et al., 2005). This finding led to a strategy to feed equal amounts of acetic acid and propionic acid as the optimal for stimulating PAO growth (Oehmen et al., 2006, Bott et

al., 2007). One study shows that isovaleric acid drives BPR even better than acetic acid (Bott et al., 2007). Isovaleric acid, however, is much more expensive than acetic acid and is more odorous. It also is not significantly generated in the primary sludge fermentation process. Addition of rbCOD such as sugars and alcohols containing two carbons or more can increase phosphorus uptake by PAOs when added to the anaerobic zone but may cause sludge bulking if dosed in excess (Jenkins and Harper, 2003).

Sludge Fermentation

Anaerobic fermentation produces VFA consisting mainly of acetic and propionic acid. Some configurations, such as the Westbank and OWASA configurations, make use of anaerobic fermentation of the primary sludge to provide VFAs to the nutrient removal process. A fermentation process, however, can be added to any configuration to provide VFAs, especially in areas where little fermentation takes place in the collection system. Fermentation of the primary sludge or the RAS will produce VFA. Primary sludge fermentation is used more frequently.

There are several primary sludge fermenter designs that can accomplish this. The simplest configuration involves allowing the formation of a thicker sludge blanket in the primary clarifier itself and returning some of the thickened sludge to either the primary clarifier or to a mixing tank ahead of the primary clarifier to allow elutriation of the VFA to the primary effluent. This is referred to as an activated primary sedimentation tank (Barnard, 1984). Another variation is to pump some sludge to a complete-mix tank ahead of the primary clarifier, to accomplish fermentation. The sludge is then passed to the primary clarifier for elutriation of the VFA. Both of these processes lead to an increased load on the primary clarifier and some VFA may be lost due to aeration between the primary clarifier and the anaerobic zone. Sludge age should also be controlled to prevent methanogenic bacteria from growing and converting the VFA to methane. Usually, a SRT less than 4 days is sufficient for this.

Alternative methods accomplish fermentation in a gravity sludge thickener by holding the sludge under anaerobic conditions for 4 to 8 days. The supernatant can then be fed directly to the anaerobic zone and a high load on the primary clarifier can be avoided. Thickening can either be accomplished with a single thickener or in two stages. The two-stage process can either be a complete mix tank, followed by a thickener or two thickeners in series. It has been shown that adding molasses or other sources of readily biodegrable COD can improve the performance of fermenters (Bott et al., 2007).

RAS can also be fermented in a side stream process. The fermentation zone is similar to the anaerobic or anoxic zone of many biological processes. RAS fermentation could be used in any BPR process, but is most common in processes without primary clarifiers.

Research and experience have revealed some key design considerations for primary fermenters (WEF and ASCE, 2006). These processes can have high solids content and may need a positive displacement pump to operate properly. Because fermentation can lower the pH and produce carbon dioxide and hydrogen sulfide, corrosion resistant materials should be used. Odor control may also be necessary if hydrogen sulfide is produced. Monitoring of pH and oxidation reduction potential (ORP) may be desirable to control the process.

6.4.2 Retention Time

The concentration of phosphorus in the sludge typically increases as the SRT increases, although the impact is very small over the SRT range of 4 to 30 days. Efficient phosphorus uptake typically requires a minimum SRT of 3 to 4 days depending on temperature. Higher SRTs will not increase phosphorus uptake, given there is sufficient VFAs available. If SRT becomes too great, however, effluent

quality can degrade. This can be due to release of phosphorus as biomass degrades (WEF and ASCE, 2006).

Both anaerobic and aerobic HRT can affect the amount of phosphorus stored by PAOs. Sufficient time should be allowed for the formation of VFAs and storage of the polyhydroxyalkanoates (PHAs) in the anaerobic zone, although the reactions are relatively fast. If the time is too short, phosphorus uptake in the aerobic zone will be lower than achievable because insufficient PHAs were stored in the anaerobic zone. It has been reported that the ratio of HRT in the anaerobic zone to the HRT in the aerobic zone is important. One study found that a ratio of between 3 and 4 for aerobic HRT to anaerobic HRT led to optimal plant operation (Neethling et al., 2005).

6.4.3 Temperature

High temperatures can have an adverse effect on phosphorus removal. At temperatures greater than 28°C, phosphorus removal will generally be impaired, apparently by the predominance of the GAOs (Bott et al., 2007). At the low end of the temperature scale, Erdal et al. (2002) found that PAOs outcompeted GAOs at 5 °C even though the PAO metabolism was slower at 5 °C than at 20 °C. The GAOs virtually disappeared in the 5 °C reactor.

Modeling studies have shown that GAOs can predominate at higher temperatures because of their increased ability to uptake acetate at those temperatures compared to PAOs (Whang et al., 2007). Low temperatures can also lower phosphorus uptake but have been shown to not be an issue in well operated and properly acclimatized plants (WEF and ASCE, 2006).

6.4.4 Presence of Oxygen or Nitrate in the Aerobic Zone

If oxygen or nitrate is present in the anaerobic zone, organisms that use oxygen or nitrates as electron acceptors will preferentially grow by fully oxidizing the organics to CO₂ and H₂O, thereby reducing the VFAs available for polymerization and storage by the PAOs. Nitrate can also inhibit fermentation of rbCOD because most of the fermenters are facultative and can use the nitrate as an electron acceptor to fully oxidize the rbCOD instead of producing VFAs as an end product of fermentation, thus depriving the PAOs of organics they can polymerize and store. Therefore, recycle of streams containing high DO and nitrate concentrations to the anaerobic zone should be avoided. Introduction of oxygen through pumps and other devices should also be avoided.

6.4.5 Avoiding Backmixing of Oxygen

Another potential source of oxygen and nitrates to the anaerobic zone is backmixing from downstream zones. In configurations where the anaerobic zone is followed immediately by an anoxic or aerobic zone, backmixing can cause elevated concentrations of nitrates and/or DO in the anaerobic zone leading to favoring of organisms other than PAOs. The problem can be avoided by increased baffling or changing the mixing rates. This problem is more likely to occur when the downstream zone is aerated, because aeration of mixed liquor increases the liquid depth, making the liquid level in the aerobic zone higher than in the non-aerated zone.

6.4.6 pH

Low pH can reduce and even prevent BPR. Below pH 6.9 the process has been shown to decline in efficiency (WEF and ASCE, 2006). This is possibly due to competition with GAOs. Filipe, et al.

(2001), found that GAOs grow faster than PAOs at a pH of less than 7.25. Because many wastewater processes such as chemical addition and nitrification can lower pH, this should be monitored and adjusted if necessary. It also has been shown that it is not possible to establish enhanced biological phosphorus removal (EBPR) when the pH is less than 5.5, even though an abundant amount of acetic acid is present in the anaerobic zone (Tracy and Flammino, 1987; Randall and Chapin, 1997).

6.4.7 Anaerobic Release

Secondary release of phosphorus occurs when the PAOs are under anaerobic conditions in the absence of a source of VFA. The energy stored as polyphosphate is used for cell maintenance and phosphorus is released to the liquid phase (Barnard, 1984). There will then be no stored food to supply energy for the uptake of phosphorus upon subsequent aeration. This may occur in the following process stages:

- In the anaerobic zone if the retention time is too high and the VFA is depleted well within the required retention time.
- In the main anoxic zone when that runs out of nitrates.
- In the second anoxic zone as shown in Figure 6.8 when there are no nitrates to be removed.
- In the sludge blankets of final clarifiers when the RAS rate is too low and sludge is not removed fast enough.

Additionally, release may happen in aerobic zones that are too large, resulting in stored substrate depletion and destruction of PAO cells by endogenous metabolism.

Since there was no food storage associated with the phosphorus release, additional carbon is then required to take up the phosphorus released, but the amount in the influent may be insufficient. Therefore, chemicals must be added to remove the excess phosphorus. Over-design of biological nutrient removal systems could thus lead to a higher demand for an external source of VFA.

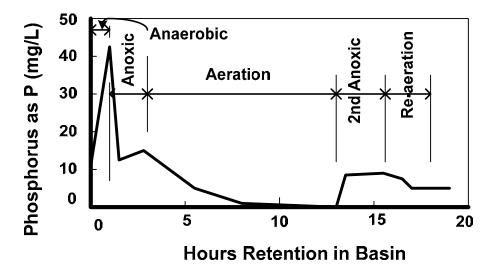


Figure 6-8 Example of Secondary release in Second Anoxic Zone

Phosphorus will be released in sludge treatment processes that are anaerobic. Gravity thickening of BPR sludge can lead to phosphorus release if long retention times are used. Using

mechanical dewatering instead of gravity dewatering allows less retention time and less phosphorus release (Bott et al., 2007). It is usually recommended that dissolved air flotation (DAF) be used to thicken BPR sludge to reduce the amount of phosphorus release. DAF thickening can be quite successful for the reduction of release, but if the thickened sludge is left on the DAF beach too long before removal, excessive release will occur, just as it will when the sludge is left too long in a gravity thickener.

Anaerobic digestion will also lead to phosphorus release although some phosphorus will be precipitated as either a metal salt (e.g. calcium phosphate) or as struvite (magnesium ammonium phosphate, MgNH₄PO₄). BPR sludge takes up and releases magnesium along with phosphates, and these two ions combine with ammonium, also present in abundance in anaerobic digesters, to form struvite. Struvite formation is very fast, and will continue until one of the three ions is reduced to that ion's solubility level. Magnesium is usually present in the lowest concentration, and its depletion typically limits struvite formation within the anaerobic digester. Calcium phosphate precipitates also tend to form in anaerobic digesters, but they form much more slowly than struvite and the formation tends to be non-stoichiometric. If substantial amounts of phosphates are precipitated by calcium along with the struvite formation, there will be little if any propensity for struvite to form when the sludge exits the anaerobic digesters. Also, if the digested sludge is composted after dewatering, the resulting Class A sludge will be enriched in magnesium, phosphorus, nitrogen, and, to a lesser extent, potassium, which also is taken up and released with phosphorus by PAOs. Thirty percent of the phosphorus entering the anaerobic digesters at the York River plant during BPR experimentation was recycled back to the headworks from belt filter press dewatering (Randall et al., 1992).

Alternatives to anaerobic digestion such as composting, drying, or alkaline treatment can be used to reduce phosphorus release. There have been several studies which have examined using struvite precipitation as a way of recovering phosphorus from supernatant from digesters. These processes have been tested on full scale facilities in Treviso, Italy and Vancouver, Canada (SCOPE, 2004).

When anaerobic release of phosphorus occurs, recycling these streams can overload phosphorus removal processes. The effect can be worsened when the waste handling process is only operated intermittently. In some instances there is a high degree of phosphorus precipitation in the anaerobic digesters and with sufficient VFA in the influent the returned phosphorus may be removed. However, in most circumstances, some chemicals need to be added to the return streams or to the anaerobic digester itself so that the metal precipitate will be removed with the dewatered sludge.

6.4.8 Sufficient Oxygen in the Aerobic Zone

It is necessary for oxygen to be present in the aerobic zone for phosphorus to be taken up and retained in the activated sludge. Maintaining a sufficiently high DO transfer in the aerobic zone enhances process stability and has been found to be a key factor in phosphorus removal. (Bott et al., 2007)

6.4.9 Inhibition

EBPR, like any biological process, can be inhibited by chemicals toxic to the organisms. Although not as sensitive to inhibition as nitrification and rare in practice, the BPR process can be inhibited by toxic chemicals, including high concentrations of acetate (Randall and Chapin, 1997).

6.4.10 Flow and Load Balancing

Flows and loads to wastewater treatment plants can vary widely because of regular diurnal use patterns and because of larger, more irregular disturbances such as storm events. Peaks in either flow, or nutrient load can stress the system and cause poor performance. Peaks can be evened out using equalization tanks to balance the flow. Equalization tanks in combination with nutrient sensors can also be used to balance nutrient loads. In this case, recycle streams high in nutrient concentrations such as digester supernatant can be stored during peak nutrient loads and recycled during times when concentrations are lower.

6.5 Impacts on Sludge Handling and Removal

Stored phosphorus adds dry weight to the sludge; however, the actual PAO VSS production will be less because the reaction is less efficient than heterotrophic metabolism using DO as the electron acceptor.

Sludge from BPR will be similar to sludge from conventional activated sludge plants, although it will have a higher phosphorus content. Varying results have been found with some plants reporting little or no change in settling and dewatering (Knocke et al., 1992) and others reporting enhanced settling and dewatering properties (Bott et al., 2007). The sludge produced from the process will also have higher magnesium and potassium concentrations due to co-uptake of these elements with phosphorus.

Struvite can precipitate in anaerobic processes. With abundant phosphorus and ammonia it is usually only the magnesium that is in short supply. Some magnesium is released from the digested cells with the phosphorus and may increase struvite precipitation. Some processes have proposed precipitating out struvite or other phosphate solids to avoid phosphorus return in recycle streams (Bott et al., 2007). The struvite crystals, however, depending upon where they form, can plug centrifuge ports, and pumps and pipes used to convey the sludge, if not controlled. Plugged lines are very difficult to clean.

6.6 Guidance for Selecting Process Modifications

If an existing activated sludge WWTP needs to lower phosphorus levels in its effluent, a number of options are available. Some key considerations are summarized below.

For systems that do not have BPR, an anaerobic zone can be added at the head of the plant. This may be achieved by switching off aerators at the head of the reactor or by adding a separate reactor. Mixing in the anaerobic zone should be sufficient to retain biological solids in suspension without introducing oxygen. If baffling is not already present, it could be added to achieve separation of the anaerobic and aerobic zones. Note that baffling is essential to prevent backmixing because the liquid level in the aerated zone will always be higher than that in the non-aerated zone. Therefore, an overflow baffle should be used between zones. Considerations should also be made for additional pumping needed for any recycle streams. Proper sizing of the anaerobic zone is important to ensure sufficient VFA is formed and taken up in the aeration basin. If an aerobic zone is converted to an anaerobic zone, care should be taken to ensure that the remaining aerobic zone is sufficiently sized to achieve treatment objectives. This usually is not a problem because the anaerobic zone seldom needs to be more than 15 percent of the total volume, and can be considerably less if fermentation is practiced

or VFA are added. Note that much of the BOD in typical municipal sewage will be removed from solution in the anaerobic zone, and this reduces the required size of the aerobic zone, even though most of the stored BOD will be stabilized in either the anoxic or aerobic zone, or both.

For plants that already have BPR but need additional phosphorus removal, the designers should start by identifying areas that may be limiting the current process. For example, if recycle streams are intermittent, overloading of the process may occur during recycle and the process performance may suffer. Flow equalization to enable constant recycle flows may be an option in these cases. RAS when returned to the anaerobic zone may introduce nitrates or oxygen that will interfere with PAO performance. The phosphorus content of the return streams could be reduced by adding some chemicals to precipitate some of the phosphorus. Reducing oxygen introduction to the anaerobic zone from upstream processes may be needed to optimize phosphorus removal.

Plants looking to improve phosphorus removal performance should also closely examine the plant for secondary release of phosphorus. If sludge blankets in clarifiers are too deep, anaerobic conditions can develop and cause secondary phosphorus release. This can be minimized by using deeper clarifiers, maintaining low sludge blankets, and increasing the RAS rate, so that the released phosphorus is pumped from the bottom of the clarifier rather than flowing over the effluent weir. Sludge handling can also cause excessive phosphorus release such as in gravity thickeners, DAFs and anaerobic digesters. If supernatant from these processes when poorly managed is recycled, it can overload the process. Options in this case would be to eliminate the recycle, improve operation of the process, change the process, or treat the recycle stream to remove phosphorus before it is returned to the plant.

Another area to examine in seeking improved phosphorus removal is the COD:P ratio. If the ratio is low, supplementing the current process with VFAs may provide additional removal. VFAs can either be added as a chemical addition process or produced through fermentation of primary or secondary sludge.

Other ways of improving TP removal include filtration and chemical addition. Phosphorus is often attached to colloidal particles and very low phosphorus levels usually require removal of TSS. Membrane bioreactors (MBR) in combination with biological and/or chemical phosphorus removal can result in very low effluent levels due to enhanced solids removal. Chemical addition with or without filtration can also achieve low phosphorus levels.

6.7 Ongoing Research

Research into BPR is ongoing. The Water Environment Research Foundation has committed to several research goals considered high priority in this area. These include research on selecting the best external carbon sources and analytical methods for low phosphorus detection. Other research is being conducted into the competition between PAOs and GAOs and the conditions favoring PAO growth. Research into carbon augmentation is also ongoing.

7. Effluent Filtration

Effluent filtration in combination with chemical precipitation can be used to remove phosphorous down to very low levels (< 0.1 mg/L). USEPA Region 10 (2007) found that 2-stage filtration through use of a first and second stage filter or by providing tertiary clarification prior to filtration, resulted in the lowest effluent phosphorus concentrations of 23 WWTPs evaluated. Effluent filtration can also be used to remove soluble organic nitrogen that is not removed through biological treatment or settling.

A wide variety of filter types have been used for wastewater treatment, including:

- Conventional down-flow filters
- Deep-bed down-flow filters
- Continuous backwashing upflow sand filters
- Pulsed bed filters
- Traveling bridge filters
- Fuzzy filters
- Discfilter
- Cloth media disk filters
- Membranes
- Blue PROTM process
- Pressure filters

This chapter describes the various filters listed above, presents key design and operating principles, and summarizes ongoing research and emerging technologies in this area.

7.1 Types of Filters

7.1.1 Conventional Down-flow Filters

These filters consist of fixed-media beds typically up to 3 feet in depth and are similar to filters used to treat drinking water. Media can be single media, dual media, or multi media. Single media is typically sand or anthracite. Dual media combines anthracite and sand. Multi-media filters include a layer of garnet or ilmenite. Flow in these filters is by gravity from the top down. Most of the removal occurs in the top few inches of the media. The filter must be taken off-line periodically to backwash the filter to prevent clogging and too high of a pressure loss.

Performance data on plants in Breckenridge (Farmers Korner), CO; Dillon, CO; Hillsboro, OR; Tigard, OR; Alexandria, VA; Occoquan, VA; and Fairfax, VA can be found in USEPA Region 10 (2007).

7.1.2 Deep-bed Down-flow Filters

These filters are similar to conventional down-flow filters but have deeper beds and larger media size. This gives the advantage of longer run times between backwashes. The size of the media is limited by the ability to backwash the filter. Because these filters are more difficult to backwash, air scour is necessary to fully clean the filter bed.

7.1.3 Continuous Backwashing Upflow Sand Filters

During operation of the continuous backwashing upflow filter, water is introduced through risers at the bottom of a deep sand bed. Water flows upward through the sand bed and over an overflow weir. Sand and trapped solids flow downward through the filter and are drawn into the suction of an airlift pipe in the center of the filter. As the sand travels up the airlift pipe, energy from the air scours the particles and separates the sand from filtered solids. At the top of the airlift pipe, the clean sand settles back onto the top of the filter and the solids are carried away into a reject line.

These filters have the advantage of having no moving parts other than the air compressor and requiring less energy and maintenance than traditionally backwashed filters. They are sometimes referred to by the trade name Dynasand.

EPA Region 10's (2007) report on plants with LOT phosphorus removal includes performance data for these filters in plants in Aurora, CO; Breckenridge (Iowa Hill), CO; Stamford, NY; and Walton, NY.

7.1.4 Pulsed Bed Filters

Pulsed bed filters are shallow filters with an unstratified fine sand media. An air pulse disturbs the media and allows penetration of solids into media bed, allowing the entire filter bed to be used for removal of solids. The pulse is designed to expand the filter operation and reduce the number of backwash cycles, although the filter must still be periodically backwashed to remove the solids.

7.1.5 Traveling-Bridge Filters

Traveling-bridge filters consist of long shallow beds of granular media. Wastewater is applied to the top of the media and flows downward. Each cell is individually backwashed by a traveling-bridge while the other cells continue to operate. The bridge uses filtered water to backwash the filters and includes surface wash to breakup matted solids or clumps of solids.

EPA Region 10's (2007) report on plants with LOT phosphorus removal includes performance data for the filters in plants in McMinneville, OR and Milford, MA.

7.1.6 Fuzzy Filters

The fuzzy filter uses a proprietary synthetic filter media that is highly porous. Water flows not only around the media but also through it, allowing much higher filtration rates. The media is held in place by a metal plate and flow is from the bottom of the bed upwards. The filter is backwashed by

raising the plate and introducing a horizontal air stream from alternating sides causing the media to roll back and forth. The effluent is returned to the plant.

Plants in the following locations have fuzzy filters: Columbus, GA (CSO); Clayton County NE, GA; Yountville, CA; Rogersville, MO; Golden Poultry/Golden Kist, NC; Orange County, CA; and King County, Seattle, WA. Performance data for these plants were not available.

7.1.7 Discfilters

Discfilters are a series of parallel mounted disks used to support a cloth filter media. Water enters a central tube and flows out between the two layers of cloth in each disk. The disks rotate and are normally 60 to 70 percent submerged. The portion above the water is backwashed using spray nozzles.

7.1.8 Cloth Media Disk Filters

The cloth media disk filter is similar to the discfilter listed above. In this case the water flows from the outside of the partially submerged cloth disks and into a center pipe. Disks continue to rotate during backwash and water is sucked into the disc using suction heads.

7.1.9 Membranes

Membrane systems use a pressure head to drive water through a permeable membrane. Membrane filters are typically classified by their pore size which in turn determines the size of the particles they exclude. Microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (RO) remove increasingly smaller particles. Microfiltration and ultrafiltration remove 3 to 6 logs of bacteria, 95 percent or more BOD, along with most particles (WEF, 2006). Nanofiltration removes nearly all particles including some viruses. RO removes all particles as well as most large dissolved constituents. The energy cost for applying the pressure head and the need to replace membranes make membrane filtration a more expensive technology. It can achieve very low concentrations of nutrients and other contaminants, however, and is common in water re-use projects.

Membranes can be configured a number of ways including hollow fiber, spiral wound, plate and frame, cartridge, or in pressure vessels. Membranes can foul from organics, biological activity, or metals in the wastewater. Typically the water must be pre-treated before using these membranes. Pre-treatment could be conventional filters, cartridge filters, or larger membrane filters. Disinfection may also be required to prevent biological fouling.

EPA Region 10's (2007) report on plants with phosphorus removal includes performance data for the filters in plants in Clifton, CO; Grand Gorge, NY; Ashland, OR; and Parker, CO.

7.1.10 Blue PROTM Process

The Blue PROTM process uses a continuous backwashing filter that is designed remove phosphorus. Filters can be run in series for even greater removal. The filter media (sand) is coated with a hydrous ferric oxide coating, which enhances phosphorus removal through adsorption. A ferric salt is added prior to the filter to aid in coagulation and to replace the ferric coating which is abraded from the sand. Water flows up through the filter while the sand travels down. An airlift tube at the bottom of the filter carries the sand upward. Turbulence from the compressed air knocks accumulated iron and

phosphorus along with any solids off the particle as it travels upward. The iron, phosphorus, and particles are wasted, while the clean sand is deposited on the top of the bed. The filters can be run biologically active to achieve denitrification.

The Blu-CAT process combines the Blu-Pro process with addition of advanced oxidants. Early pilot tests show that this process is capable of removing other emerging contaminants along with phosphorus and microorganisms (USEPA, 2008a).

Performance data are available from a plant in Hayden, OH (USEPA Region 10, 2007) and from a demonstration plant in Florida (Blue Water Technologies, 2008).

7.1.11 Pressure Filters

Pressure filters are similar to conventional media filters except they are contained in closed containers and are filtered under pressure. The increased pressure creates a greater head loss and allows longer times between backwashes.

7.2 Design and Operating Principles

Filtration is mainly affected by the concentration and size distribution of particles entering the filter. Turbidity is often used as a surrogate for particle concentration. The concentration of particles will affect run-time in filters and will also affect the required surface area to achieve the desired filtration. The size distribution of the particles and its relevance to pore size of the granular or membrane filters will affect the removal mechanisms.

Filtration rate is also an important design parameter. Too fast of a filtration rate can cause floc to break up and pass through the filter. The optimal filtration rate depends on floc strength, which in turn depends on the biological treatment processes prior to filtration (e.g., Higher SRTs lead to weaker flocs). The filtration rate, along with the loading rate will determine the area of the filter required. The higher the loading rate, the more frequent backwashes will be required and the greater the head loss across the filters. Typical filtration rates are 5 to 15 meters per hour for gravity filters and up to 20 meters per hour for pressure filters (WEF and ASCE, 1998).

Addition of polymers or other coagulant aids can greatly aid filtration. Typical doses for filter influent are 0.05 to 0.15 mg/L of organic polyelectrolyte (WEF and ASCE, 1998), although jar tests are conducted to determine the proper dose. Too low a dose can allow uncoagulated particles through the filter and too high a dose can lead to mudballs and filter clogging.

There are several ways the flow rate can be controlled in filters. Constant-rate fixed head filtration maintains a constant flow through the filter. This will lead to an increased head above the filter as the filter run progresses. In constant-rate variable head filtration the rate is kept the same and the filter is backwashed when the head reaches a certain value. In variable-rate filtration, the rate of filtration decreases throughout the filter run until it reaches a minimum value and is backwashed. Variable-rate filtration is less common than constant-rate filtration.

Proper backwashing is also important to filter operation. Without proper backwashing there can be breakthrough of particles and turbidity. Lack of a proper backwash can also lead to accumulation of materials on the surface of the filter that can form mudballs and cracks, which can allow solids to pass through the filter. A surface wash or air scour may also be helpful to prevent accumulation of mudballs or grease. Surface wash or air scour is also helpful for traveling bridge filters. Without surface wash

traveling bridge filters are limited to an influent TSS concentration of 40 to 50 mg/L (WEF and ASCE, 1998).

If membrane filters are used, fouling can be an important consideration. Cellulose acetate membranes can be damaged by biological activity. Disinfection is often used to prevent biological fouling of the membranes. Some membrane materials such as polyacramides, however, can be damaged by chlorine. This can be avoided by using an alternative disinfectant, a different membrane material, or by de-chlorination. Lowering the pH can help to prevent mineral fouling of nanofiltration or reverse osmosis membranes. Besides pre-treatment, chemical cleaning of the membranes may also be required periodically. Monitoring of effluent quality and pressure differential can be important to help identify membrane fouling or failure.

7.3 Ongoing Research and Emerging Technologies

The use of membranes as tertiary filtration is an area that has recently expanded. Research continues on various membrane configurations along with topics such as pre-treatment, membrane cleaning, and removal of emerging contaminants. Fuzzy filters are also an innovative technology that is beginning to be established in the wastewater community with several full scale projects. Other research has focused on enhancements to existing technology. For example, the Blue-Pro system combines continuous backwashing filters, a well known technology, with a hydrous ferric oxide coating and ferric salt addition to remove phosphorus by adsorption as well as filtration.

8. Mathematical Modeling

8.1 The Need for Models

WWTPs are complex systems that depend on numerous biological, chemical, and physical processes to achieve effluent goals. Because of the complex behavior of the processes and the variability in wastewater characteristics, biological populations, and plant design, it is not always possible to predict how changing any one variable will affect the effluent quality. Plant designs that work for one influent wastewater and climate may not perform well in different conditions. Pilot scale or full scale trials can help to determine the effect of various parameters, but costs and time to cover all possibilities may be prohibitive. Therefore, models fill an important need by enabling simulation of a process and estimating the impact that changing parameters will have on the treatment effectiveness.

Models can be used for a number of purposes including the design of new WWTPs, the design of retrofits or upgrades to existing plants, determining how changes in operations may affect effluent concentrations of permitted contaminants, determining how plants will respond to changes in influent quality or flow, and for training operators. Not all models can achieve all of these purposes, so models should be selected with the desired use in mind.

There is some disagreement in the literature in the use of the term model. Some references use the term to refer to sets of mathematical equations that characterize a process, other references use model to refer to the computer program used to solve these equations. This chapter will use the former and will use the term "simulator" to describe the computer program.

8.2 Overview of Available Models

Models are sets of equations, generally based on theory and grounded in empirical data, that represent a wastewater treatment process. Each unit process is represented by its own model. Model equations for processes such as clarification and settling are well known and fairly simple. Modeling biological wastewater processes such as activated sludge, however, is much more complicated. The primary set of models for activated sludge processes has been compiled by the International Water Association (IWA). The first model was developed in 1986 and was called the activated sludge model (ASM). Later known as ASM1, this model was able to model the biological oxidation of carbon, nitrification, and de-nitrification.

Although the ASM model gained widespread use among both academia and industry, it had limitations. For example the model assumed constant temperature and pH, did not include EBPR, and the biological reactions did not depend on the carbon source. In order to improve the model, IWA developed four other ASM models; ASM2, ASM2d, ASM3, and ASM3 with BioP. ASM2 and ASM2d were intended to add EBPR. The ASM3 models were intended to deal with limitations such as the independence of the ASM1 model of temperature and carbon source. In addition, other models were developed to seek to improve upon the ASM model. The metabolic biological phosphorus model of the Delft University of Technology (TUDP) was developed to fully account for the metabolism occurring in PAOs during EBPR. Barker and Dold (1997) developed a model (B&D) to include different rates of growth depending on the carbon source.

Table 8-1 lists each mathematical model for wastewater treatment, the processes it can simulate, and the reference where the model equations along with its limitations and valid range of

operating parameters can be found. When selecting models, the processes required and the range of normal operating parameters for the plant should be considered and compared to the available models. For example, if chemical phosphorus removal is to be used in a plant, the plant is limited to using either the ASM2 or ASM2d models. Each model also has a range of temperatures and pH over which it is valid.

Table 8-1 Available Activated Sludge Models

Model Name	Wastewater Treatment Unit Processes	Reference
ASM1	Carbon oxidation, nitrification, de-nitrification	Henze et al. 1987
ASM2	Carbon oxidation, nitrification, de-nitrification, enhanced	Henze et al. 1995
	biological phosphorus removal, fermentation, chemical	
	phosphorus removal	
ASM2d	Carbon oxidation, nitrification, de-nitrification, enhanced	Henze et al. 1999
	biological phosphorus removal, fermentation, chemical	
	phosphorus removal	
ASM3	Carbon oxidation, nitrification, de-nitrification	Henze et al. 1999
ASM3 w/ BioP	Carbon oxidation, nitrification, de-nitrification, enhanced	Reiger et al. 2001
	biological phosphorus removal	
TUDP	Carbon oxidation, nitrification, de-nitrification, enhanced	Brdjanovic et al. 2000
	biological phosphorus removal, fermentation	
B&D	Carbon oxidation, nitrification, de-nitrification, enhanced	Barker and Dold 1997
	biological phosphorus removal, fermentation	

Sources: WERF 2003, Gernaey et al. 2004

Fixed film processes are gaining popularity in nutrient removal. The modeling of these processes is more complicated because of the added dimension of diffusion to and from the biofilm. An equivalent to the ASM models does not exist for fixed film processes. IWA, however, did publish a reference in 2006 (Wanner et al., 2006) listing all of the model equations available for fixed film processes. These models fall into three categories: semi-empirical models, 1-dimensional models, and 2-dimensional models. 3-dimensional models exist, but do not yield significantly better results for the added computation time. Semi-empirical models can be solved analytically, run the fastest, and require more assumptions on the limiting factors in the reactor and biofilm. 1-dimensional and 2-dimensional models must be solved numerically. Semi-empirical values for kinetic constants, carbon removal, nitrification, de-nitrification, and biomass growth can increase run speeds. The reference also discusses methods for solving the sets of equations governing fixed film processes. Solution methods vary from analytical solutions for more simplified sets of equations to numerical solutions for more complex model equations. Many simulators now can accommodate these new equations as well.

There are numerous simulators available that run combinations of the various models. Simulators typically have a graphical interface which allows the user to specify the unit processes included in the plant. Most simulators allow the selection from a number of models appropriate for the unit processes to be represented. Different simulators run different sets of models so the selection of the right simulator is important. In addition to selecting the required processes, the user also sets the flow rates including recycle streams and the influent wastewater characteristics. Parameters such as kinetic constants for biological growth and stoichiometric constants for reactions can be specified, or the user can select default values. Given the process layout, the input parameters, and the selected model, the simulator solves the system of equations to predict the wastewater characteristics throughout the plant.

Simulators currently available include: GPS-X, EFOR, STOAT, BioWin, ASIM, SIMBA, WEST, AQUASIM, and AQUIFAS. Simulators vary in the models they can run, the degree of skill required to run the simulator, the user interface, and the cost. Some models allow a high degree of customization, but will require greater user knowledge of the underlying models. Others are more user friendly for less skilled users but in such cases the limitations of the models may not be as obvious to the user.

8.3 Model Inputs

Model parameters are the input variables entered by the user and fall into three categories:

- Parameters defining reactions within the process
- Wastewater characteristics
- Process inputs

Parameters defining the reactions are selected when the user selects the model. In some cases the user may wish to modify a model default value. Process inputs include the flows for each stream, recycle flows, and the size of each process. These inputs are generally design parameters or are known values in the case of an existing plant. Wastewater characteristics include influent BOD or COD, nitrogen, and phosphorus along with temperature and pH. Most models ask for detailed breakdowns of these parameters. COD is usually broken down into slowly biodegradable, readily biodegradable, particulate unbiodegradable, and soluble unbiodegradable. Nitrogen is typically broken into ammonia, soluble unbiodegradable TKN, biodegradable TKN, and particulate unbiodegradable TKN. For models with EBPR, orthophosphate, soluble unbiodegradable phosphorus, organically bound biodegradable phosphorus, and particulate unbiodegradable phosphorus fractions are required. Some models require the wastewater characteristics as concentrations while others require both total concentration and fractions.

Additional sampling and laboratory analysis to characterize the influent wastewater is needed to fulfill model input requirements. At a minimum, the fractions of each of the wastewater components must be determined. It may also be beneficial to determine some reaction constants through laboratory experiments with the biomass to be used. For example, the nitrifier growth rate frequently varies from plant to plant and measuring it directly may yield better design results.

8.4 Model Calibration

Because the models are not exact descriptions of the process and because measurement of parameters is not exact, every model will need to be calibrated. A model is calibrated by running the simulator and comparing predicted values of wastewater components with measured values throughout the plant, or through a similar plant. Model parameters are then adjusted to obtain the best fit between the simulator results and the plant data. In general the parameters for which the input values are the least certain are the ones that are adjusted. Parameters that are commonly adjusted include the sludge waste rate or nitrifier growth rate. Parameters are not adjusted unless they significantly improve the model fit and the resulting parameter is still within realistic bounds. The parameters are adjusted so the model is valid over the widest range possible rather than trying to get as close a fit as possible for a single set of circumstances.

9. Nutrient Removal for Small Communities and Decentralized Wastewater Treatment Systems

Approximately 25 percent of the U.S. population is served by onsite septic or decentralized systems. Onsite septic systems treat and dispose of effluent on the same property that produces the wastewater, whereas decentralized treatment refers to onsite or cluster systems that are used to treat and dispose of relatively small volumes of wastewater, generally from dwellings and businesses that are located relatively close together. In many cases, wastewater from several homes is pretreated onsite by individual septic tanks before being transported through alternative sewers to an offsite decentralized treatment unit that is relatively simple to operate and maintain. The remaining 75 percent of the population is served by centralized wastewater treatment facilities, which collect and treat large volumes of wastewater.

There is, in fact, a growing movement toward decentralized or clustered wastewater treatment systems to reduce cost, to provide groundwater recharge near the source, and for speed and ease in siting since they are generally located underground. The use of residential cluster development is gaining in popularity across the U.S. as a means to permanently protect open space, preserve agricultural land, and protect wildlife habitat (Mega et al., 1998). As part of these developments, wastewater systems such as community drainfields, irrigation systems, and package plants are being installed to reduce infrastructure investment and minimize adverse environmental impacts. Additional alternatives that include aerobic tanks, sand filters, and constructed wetlands can be used to reduce nutrient pollution; particularly in sensitive coastal areas or over sensitive, unconfined aquifers used for drinking water (Anderson and Gustafson, 1998).

9.1 Phosphorus Removal

Few phosphorus removal processes are well developed for onsite wastewater systems application (USEPA, 2008e). The controlled addition of chemicals such as aluminum, iron, and calcium compounds with subsequent flocculation and sedimentation has had only limited success because of inadequate operation and maintenance of mechanical equipment and excessive sludge production. Most notable successes have come with special filter materials that are naturally high in their concentration of the above chemicals, but their service lives are finite. Studies of high-iron sands and high-aluminum muds indicate that 50 to 95 percent of the phosphorus can be removed. However, the life of these systems has yet to be determined, after which the filter media will have to be removed and replaced. Use of supplemental iron powder mixed with natural sands is also being researched. Aside from specialized filter media, the most likely phosphorus-reduction systems are iron-rich intermittent sand filter (ISF) media and SBRs. These are discussed in more detail below.

9.2 Nitrogen Removal

Processes that remove 25 to 50 percent of total nitrogen include aerobic biological systems and media filters, especially recirculating filters (USEPA, 2008f). The vast majority of on-site and cluster nitrogen-removal systems employ nitrification and denitrification biological reactions. Most notable of these are recirculating sand filters (RSFs) with enhanced anoxic modifications, SBRs, and an array of aerobic nitrification processes combined with an anoxic/anaerobic process to perform denitrification. Some of the combinations are proprietary. A few recently developed highly instrumented systems that

utilize membrane solids separation following biological nitrification and denitrification are capable of removing total nitrogen down to very low concentrations (i.e. 3 - 4 mg/L TN).

Nitrogen removal systems generally are located last in the treatment train prior to subsurface wastewater infiltration system (SWIS) disposal or surface water disposal, in which case a disinfection step is typically required. Usually, the minimum total nitrogen standard that can be regularly met is about 10 mg/L. These technologies can be either above ground or below ground.

9.3 Nitrogen and Phosphorus Removal Technologies

9.3.1 Introduction

This section provides information on a number of different technologies that can reduce nitrogen and phosphorus levels. The actual technology selected will be site-specific and dependent on many factors including soil conditions, influent water quality, required effluent levels, disposal options, availability of land, cost, etc. In some cases, a combination of technologies may be necessary to effectively remove all the contaminants of concern. Small system owners and operators should work closely with their state onsite and decentralized program staff as well as engineers to ensure that the technologies selected will work effectively in combination to achieve the effluent goals.

9.3.2 Nutrient Removal Technologies

Fixed-film systems - Aerobic/anaerobic trickling filter package plant

Fixed-film systems (FFSs) are biological treatment processes that employ a medium such as rock, plastic, wood, or other natural or synthetic solid material that will support biomass on its surface and within its porous structure (USEPA, 2008c). Trickling filter FFSs are typically constructed as beds of media through which wastewater flows. Oxygen is normally provided by natural or forced ventilation. Commercial on-site systems use synthetic media and receive wastewater from overlying sprayheads for aerobic treatment and nitrification. Nitrified effluent returns to the anoxic zone to mix with either septic tank contents or incoming septic tank effluent for denitrification. A portion of the denitrified effluent is discharged for disposal or further treatment. Aerobic tanks are available in residential or smallcommunity sizes. Typical trickling filters systems currently available are capable of producing effluent BOD and TSS concentrations of 5 to 40 mg/L. Nitrogen removal typically varies from 0 to 35 percent although removal percentages as high as 65% have been demonstrated through USEPA's Environmental Technology Verification (ETV) program. Phosphorus removal is typically 10 to 15 percent. Higher removal occurs at low loading rates in warm climates. Systems can be configured for single-pass use where the treated water is applied to the trickling filter once before being disposed of, or for multi-pass use where a portion of the treated water is cycled back to the septic tank and re-treated via a closedloop. Multi-pass systems result in higher treatment quality and assist in removing Total Nitrogen (TN) levels by promoting nitrification in the aerobic media bed and denitrification in the anaerobic septic tank.

Factors affecting performance include influent wastewater characteristics, hydraulic and organic loading, medium type, maintenance of optimal DO levels, and recirculation rates.

Sequencing batch reactor (SBR)

The SBR process is a sequential suspended growth (activated sludge) process in which all major steps occur in the same tank in sequential order (USEPA, 2008d). The SBR system is typically found in packaged configurations for onsite and small community or cluster applications. The major components of the package include the batch tank, aerator, mixer, decanter device, process control system (including timers), pumps, piping, and appurtenances. Aeration may be provided by diffused air or mechanical devices. SBRs are often sized to provide mixing as well and are operated by the process control timers. Mechanical aerators have the added value of potential operation as mixers or aerators. The decanter is a critical element in the process. Several decanter configurations are available, including fixed and floating units. At least one commercial package employs a thermal processing step for the excess sludge produced and wasted during the "idle" step. The key to the SBR process is the control system, which consists of a combination of level sensors, timers, and microprocessors which can be configured to meet the needs of the system.

SBRs can be designed and operated to enhance removal of nitrogen, phosphorus, and ammonia, in addition to removing TSS and BOD. Package plant SBRs are suitable for areas with little land, stringent treatment requirements, and small wastewater flows such as RV parks or mobile homes, campgrounds, construction sites, rural schools, hotels, and other small applications. These systems are also useful for treating pharmaceutical, brewery, dairy, pulp and paper, and chemical wastes (USEPA, 2000d).

Intermittent sand filters (ISF)

ISF is used to describe a variety of packed-bed filters of sand or other granular materials available on the market (USEPA, 2008g). Sand filters provide advanced secondary treatment of settled wastewater or septic tank effluent. They consist of a lined (e.g., impervious PVC liner on sand bedding) excavation or structure filled with uniform washed sand that is placed over an underdrain system. The wastewater is directed onto the surface of the sand through a distribution network and allowed to percolate through the sand to the underdrain system. The underdrain system collects the filter effluent for further processing or discharge.

Sand filters are aerobic, fixed-film bioreactors. Bioslimes from the growth of microorganisms develop as films on the sand particle surfaces. The microorganisms in the slimes capture soluble and colloidal waste materials in the wastewater as it percolates over the sand surfaces. The captured materials are metabolized into new cell mass or degraded under aerobic conditions to carbon dioxide and water. Most biochemical treatment occurs within approximately 6 inches of the filter surface.

Other treatment mechanisms that occur in sand filters include physical processes, such as straining and sedimentation, to remove suspended solids within the pores of the media. Most suspended solids are strained out at the filter surface. Chemical adsorption can occur throughout the media bed. Adsorption sites in the media are usually limited, however. The capacity of the media to retain ions depends on the target constituent, the pH, and the mineralogy of the media. Phosphorous is one element of concern in wastewater that can be removed in this manner, but the number of available adsorption sites is limited by the characteristics of the media.

Sand filters can be used for a broad range of applications, including single-family residences, large commercial establishments, and small communities. Sand filters are frequently used to pretreat septic tank effluent prior to subsurface infiltration onsite where the soil has insufficient unsaturated depth above ground water or bedrock to achieve adequate treatment. They are also used to meet water quality requirements (with the possible exception of fecal coliform removal) before direct

discharge to surface water. Sand filters are used primarily to treat domestic wastewater, but they have been used successfully in treatment trains to treat wastewaters high in organic materials such as those from restaurants and supermarkets. Single-pass ISF filters are most frequently used for smaller applications and sites where nitrogen removal is not required. However, they can be combined with anoxic processes to significantly increase nitrogen removal.

Recirculating sand filters (RSF)

Recirculating filters using sand, gravel, or other media provide advanced secondary treatment of settled wastewater or septic tank effluent (USEPA, 2008h). They consist of a lined (e.g., impervious PVC liner on sand bedding) excavation or structure filled with uniform washed sand that is placed over an underdrain system. The wastewater is directed onto the surface of the sand through a distribution network and allowed to percolate through the sand to the underdrain system. The underdrain system collects and recycles the filter effluent to the recirculation tank for further processing or discharge.

The basic components of recirculating filters include a recirculation/dosing tank, pump and controls, distribution network, filter bed with an underdrain system, and a return line. The return line or the underdrain must split the flow to recycle a portion of the filtrate to the recirculation/dosing tank. A small volume of wastewater and filtrate is dosed to the filter surface on a timed cycle 1 to 3 times per hour. Recirculation ratios are typically between 3:1 and 5:1. In the recirculation tank, the returned aerobic filtrate mixes with the anaerobic septic tank effluent before being reapplied to the filter.

RSFs can be used for a broad range of applications, including single-family residences, large commercial establishments, and small communities. They produce a high quality effluent with approximately 85 to 95 percent BOD and TSS removal. In addition, almost complete nitrification is achieved. Denitrification also has been shown to occur in RSFs. Depending on modifications in design and operation, 50 percent or more of applied nitrogen can be removed (USEPA, 1999). To enhance this capability, they can be combined with a greater supply of biodegradable organic carbon, time, and mixing than is normally available from the conventional recirculation tank.

Natural Systems

The natural systems described here include constructed wetlands and floating aquatic plant treatment systems. Wetland systems are typically described in terms of the position of the water surface and/or the type of vegetation grown. Most natural wetlands are free water surface (FWS) systems where the water surface is exposed to the atmosphere; these include bogs (primary vegetation mosses), swamps (primary vegetation trees), and marshes (primary vegetation grasses and emergent macrophytes) (USEPA, 2000e). subsurface flow (SF) wetlands are specifically designed to treat or polish wastewater and are typically constructed as a bed or channel containing appropriate media.

Constructed wetlands treat wastewater by bacterial decomposition, settling, and filtering. As in tank designs, bacteria break down organic matter in the wastewater, aerobically, anoxically and anaerobically. Oxygen for aerobic decomposition is supplied by the plants growing in the wetland. Solids are filtered and finally settle out of the wastewater within the wetland. After about two weeks in the wetland, effluent is usually discharged by gravity to an unlined wetland bed. If these systems discharge effluent to surface ditches, they require a NPDES permit.

The submerged plant roots do provide substrate for microbial processes. However, the amount of oxygen that emergent macrophytes can transmit from the leaves to their roots is negligible compared to the oxygen demand of wastewater. Therefore subsurface flow wetlands are devoid of oxygen. The

lack of oxygen in these subsurface flow systems means that ammonia oxidation via biological nitrification will not occur without the use of an additional unit process, such as a gravel trickling filter for nitrification of the wastewater ammonia. Vertical flow wetland beds are a modification of subsurface flow wetlands which contain gravel or coarse sand and are loaded intermittently at the top surface. Unlike ammonia oxidation, nitrate removal in a subsurface flow wetland can be rapid and effective because the anoxic conditions and carbon sources necessary to support the treatment reactions occur naturally in these systems.

FWS wetlands with long detention times can remove minor amounts of phosphorus through plant uptake, adsorption, complexation, and precipitation. However, removal via plant uptake is limited to phosphorus retained in plant litter that is buried by sediments before plant decomposition occurs (i.e. peat building process). Phosphorus removal is typically greater in the first year or two because of soil absorption and rapidly expanding vegetation but decreases when the system reaches equilibrium, and unburied plant litter releases phosphorus back into the water as it decomposes. Phosphorus removal is also possible with the use of an addition process, such as chemical addition and mixing prior to a final deep settling pond.

Aquatic systems using duckweed have been used for a number of years to treat wastewater for various purposes (WEF, 2001). Duckweed (*Lemna spp.*) are floating macrophytes. Duckweed fronds can double their mass in two days under ideal conditions of nutrient availability, sunlight, and temperature. Although duckweed can be found in most regions, the rate of growth is optimal at 20 to 30 °C and they grow best in a pH range of 3.5 to 8.5. Duckweed can grow about six months per year in most U.S. climates. High levels of BOD and TSS removal have been observed from duckweed systems. To achieve secondary treatment most duckweed systems are coupled with either facultative or aerated ponds. Nitrogen is removed by plant uptake and harvesting, by denitrification, or a combination of the two. Typically less than 1 mg/L of phosphorus can be removed by plant uptake and harvest. If significant phosphorus removal is required, chemical precipitation with alum, ferric chloride, or other chemicals used in a separate treatment step is necessary. The major disadvantage of duckweed systems is the large amount of biomass produced by the rapidly growing plants, which creates a solids handling requirement similar to handling sludge at an aerobic wastewater treatment facility.

Proprietary Filters/Improved and Emerging Technologies

A number of companies have developed proprietary nitrogen and phosphorus removal technologies that can be used at centralized wastewater treatment facilities as well as at onsite, decentralized systems. This section provides a general description of some of these technologies without mentioning specific trade names. Additional information on proprietary and emerging technologies is available from the Wastewater Virtual Trade Show hosted by EPA New England's Center for Environmental Industry and Technology (CEIT), available online at http://www.epa.gov/ne/assistance/ceitts/wastewater/index.html.

In one onsite technology system, the household's greywater (wash water) and blackwater (toilet and kitchen sink wastes) are plumbed separately and flow to separate septic tanks. The system consists of two septic tanks, a filter, and a conventional leaching facility, all of which are located below the ground surface. In some situations the system may be passive, requiring no pumps or other moving mechanical parts (unless finished effluent must be pumped up to an elevated leaching field to achieve adequate separation to groundwater). The blackwater flows from the septic tank to a proprietary aerobic filter where it is nitrified and then flows to the anaerobic greywater septic tank for denitrification. The filter itself is composed of several layers of in-drains which are overlain by layers of sand and filter cloth. The in-drains are composed of proprietary material and provide air to the filter so

that it remains aerobic. The in-drain media and the sand support the growth of nitrifying bacteria. As the effluent trickles through the filter, nitrification occurs. The effluent is collected by a drain at the bottom of the filter from which it flows into the greywater septic tank. The greywater septic tank is anaerobic and the greywater provides a rich source of carbon which supports the growth of denitrifying bacteria. Denitrification of the effluent is accomplished by passive mixing of the filter-treated blackwater with the greywater in this septic tank. After treatment in this tank, finished effluent flows to the leaching facility for disposal. Initial data indicate that the system is capable of producing finished effluent with total nitrogen content of 19 mg/L. Limited data show that the system may also be capable of approximately 50% removal of phosphorus. The system has also been modified for commercial use.

A centralized system for nitrogen removal has been used at full scale in the Netherlands although it is just in pilot system phase here in the U.S. This single reactor system for nitrogen removal is based on two core concepts: 1) that at temperatures between 30-40°C, the growth rate of ammonia oxidizing bacteria is greater than the growth of nitrate oxidizing bacteria; and 2) denitrifying bacteria are capable of anoxic conversions of nitrite to nitrogen gas. The reactor converts ammonia mainly to nitrite by oxidation at a minimal sludge retention time. The nitrite is then anoxically converted to nitrogen gas.

A passive wastewater nitrogen removal system has been developed at the University of Waterloo, Ontario and has been tested in several facilities in the U.S. This system, which can reduce wastewater nitrogen levels to 3 mg/L, has been demonstrated to be effective for individual properties as well as cluster and centralized wastewater systems. The proprietary patented nitrate-reactive media that converts nitrate to inert nitrogen gas (denitrification) is contained in a prefabricated tank or, for larger installations, in an engineered excavation. Nitrate contaminated wastewater is gravitationally fed through the treatment module. For septic tank applications, an oxidative pre-treatment step is required to convert ammonium (NH_4^+) to nitrate (NO_3^-) before the filter can perform the reductive denitrification step. Pre-treatment can be achieved with any of the existing oxidative technologies commonly used in wastewater treatment. The nitrate-free effluent from the filter is then discharged to a conventional tile bed or receiving water body. The filters have also been used as a permeable reactive barrier to remove groundwater nutrients close to receiving water bodies.

A passive phosphorus wastewater removal system has also been developed at the University of Waterloo that incorporates proprietary media and a filter following primary treatment/septic tanks and prior to soil dispersal. This system has been demonstrated to reduce phosphorus effluent by 94 percent, nitrogen by 54 percent and BOD by 86 percent at a test center in Massachusetts. The process incorporates reductive iron dissolution and mineralization of phosphorus.

Another manufacturer utilizes attached growth airlift reactor technology with a fully open, fully protected biomass carrier with aeration and mixing design to provide high BOD and total nitrogen removal capability. This is a fixed biofilm moving bed process, utilizing suspended biomass carriers with high specific surface area for biofilm growth, along with carefully designed reactor hydraulics. This dual action denitrification and effluent filtration solution technology has been designed for small and medium sized WWTPs as well as other industrial applications such as food and beverage, pulp and paper, oil and gas, bio fuel, chemicals, pharmaceuticals, reuse, and aquaculture.

A variety of membranes and bioreactor technologies, many using improved fixed-film processes, are also being developed for maximum exposure of waste streams to activated sludge that digests waste from plant production effluent streams. Since the membranes can retain activated sludge at high concentrations, BOD and nitrogen can be removed more efficiently. Many of these can be integrated as an upgrade/retrofit into existing treatment systems or used as package plants in smaller installations

ch as residential and commercial development projects, industrial applications, military bases, and ice parks.	

10. Sustainable Nutrient Recovery

While the U.S. is primarily addressing nutrient removal concerns through development of WQSs and treatment at centralized wastewater facilities, a number of European countries including Switzerland, Sweden, and the Netherlands are conducting research on innovative sustainable nutrient recovery systems. The concept behind these new technologies is to separate and treat toilet waste before it leaves the home or building and mixes with the larger waste stream to be carried to WWTPs. Recent studies have shown that about 80 percent of the nitrogen and 50 percent of the phosphorus in wastewater are derived from urine although urine makes up only 1 percent of the volume of wastewater (Larsen and Leinert, 2007). Separating the urine from wastewater could offer various advantages: WWTPs could be built on a smaller scale, water bodies will be better protected from nitrogen and phosphorus pollution, nutrients could be recycled for agricultural use, and various constituents of concern including hormones and pharmaceutical compounds could be removed before being mixed with wastewater and released to the environment. A major benefit would be reduced energy consumption at WWTPs as a result of reduced treatment requirements for nitrogen. Also, separating 50 to 60 percent of urine could reduce in-plant nitrogen gas discharges and result in fewer impurities in methane captured from sludge digestion.

Organizations such as the Swiss Federal Institute of Aquatic Science and Technology (Eawag) are currently experimenting with the development and application of "NoMix technology" to separate urine from solid waste at the toilet bowl. While similar in size and shape to current toilets, this new technology has two waste pipes – a small front one that collects and diverts urine into a storage tank, and a larger rear waste pipe that operates like a standard toilet. The first of these toilets were installed in two "eco-villages" in Sweden in 1994 and since then have spread to other locations throughout the country and to Denmark, the Netherlands, and Switzerland. The concept is now taking hold in Austria and Germany. While the pollutant-free urine, or "urevit," can be spray-applied directly onto agricultural fields; in the Netherlands, a company called Grontmij trucks stored urine to a special treatment plant where the phosphate is precipitated out as a mineral called struvite and used as a fertilizer. Novaguatis, a branch of Eawag is experimenting with extracting nitrogen and potassium from urine that can be sprayed directly onto crops. Eawag is also experimenting with a pilot decentralized basement sewage plant where domestic wastewater is treated in a MBR so it can be reused for flushing the toilets or watering the garden and the sewage sludge is composted. While still experimental, some of these technologies may have practical future applications if widely applicable low-cost solutions can be found for urine transport, or stable and cost-effective technologies can be developed for decentralized treatment. While studies of consumer attitudes and acceptance appear to be positive, technological improvements are still needed to prevent clogging in pipes, to identify best treatment options that can be applied in practice; and to identify how and where to convert urine to fertilizer.

Sustainability concerns are also driving the wastewater treatment industry to start looking at sludge as a renewable resource. Historically, agricultural use has been the traditional approach for disposal of municipal sludge due to its high nutrient content for fertilizing crops, and its low cost approach. As scientific advances detect smaller and smaller quantities of contaminants (i.e., heavy metals, pathogenic microorganisms, pharmaceuticals, and personal care products), the public, farming organizations, and the food industry are raising concerns about continuing this practice. As noted above, researchers are discovering that valuable products can be generated from sewage treatment byproducts such as energy extracted from anaerobic digestion, construction materials such as bricks, and nutrients such as phosphorus that can be extracted from sludge and used as fertilizer.

In February 2008, the non-profit Global Water Research Coalition, an international water research alliance formed by 12 world-leading research organizations, released a report titled, *State of Science Report: Energy and Resource Recovery from Sludge* (Kalogo and Monteith, 2008). The report focuses on:

- The international situation of energy and resource recovery from sludge
- How the use of different sludge treatment processes affects the possibility of recovering energy and/or materials from the residual sludge
- The influence of market and regulatory drivers on the fate of the sludge end-product
- The feasibility of energy and resource recovery from sludge
- The social, economic, and environmental performance (triple bottom line or TBL assessment) of current alternatives technologies
- Four market drivers are identified and discussed including:
 - Sustainability and environmental concerns, such as the threat of soil pollution, global warming and resource depletion
 - Rising energy costs and the need of more electricity and heat to operate the plants
 - Requirements for high quality of resources for industrial applications, such as calcium phosphate for the phosphate industry
 - Regulation as a factor stimulating the development of new technologies

In the report, energy recovery technologies are classified into sludge-to-biogas processes, sludge-to-syngas processes, sludge-to-oil processes, and sludge-to-liquid processes. The technologies available for resource recovery discussed in the report include those to recover phosphorus, building materials, nitrogen, and volatile acids. The report, which covers both established as well as emerging technologies, will be used as the basis for development of the coalition's future strategic research plan on energy and recovery from sludge. As a technical resource, it provides a valuable overview of sludge disposal practices in various countries such as the U.S., the Netherlands, the United Kingdom, Germany, Sweden, Japan, and China; and presents a number of treatment processes for resource recovery.

Other groups have looked at recovering phosphorus from the supernatant from anaerobic digestion. Several different processes have been proposed that rely on precipitation of the phosphorus as either struvite or calcium phosphate. Work is underway on projects in Italy, Germany, the Netherlands, and Canada (SCOPE, 2004).

11. Co-Removal of Emerging Contaminants

This chapter provides a brief background on emerging contaminants and key findings from studies on the co-removal of emerging contaminants by nutrient removal technologies.

11.1 Background on Emerging Contaminants

The term "emerging contaminants" refers broadly to those synthetic or naturally occurring chemicals, or to any microbiological organisms, that have not been commonly monitored in the environment but which are of increasing concern because of their known or suspected adverse ecological or human health effects. Emerging contaminants can fall into a wide range of groups defined by their effects, uses, or by their key chemical or microbiological characteristics. Two groups of emerging contaminants that are of particular interest and concern at present are endocrine disrupting chemicals (EDCs) and pharmaceutical and personal care products (PPCPs). These compounds are found in the environment, often as a result of human activities.

EDCs may interfere with the endocrine systems by damaging hormone-producing tissues, changing the processes by which hormones are made or metabolized, or mimicking hormones. In addition to natural and synthetic forms of human hormones that are released into the environment, there are a multitude of synthetic organic compounds that are able to disrupt the endocrine system. Public concern about EDCs in the environment has been rapidly increasing since the 1990s when researchers reported unusual sexual characteristics in wildlife. A report by the USGS, found that fish in many streams had atypical ratios of male and female sex hormones (Goodbred et al., 1997). In England, researchers found that male trout kept in cages near WWTP outfalls were developing eggs on their testes and had increased levels of the protein that is responsible for egg production (vitellogenin) (Sumpter, 1995; Kaiser, 1996). Follow-up laboratory studies showed that synthetic forms of estrogen $(17\alpha$ -ethynylestradiol (EE₂)) could increase vitellogenin production in fish at levels as low as 1-10 ng/L, with positive responses seen down to the 0.1-0.5 ng/L level (Purdom et al., 1994).

Human estrogens have the ability to alter sexual characteristics of aquatic species at trace concentrations as low as 1 ng/L (Purdom et al., 1994). WWTP effluents have been identified as a primary source for EDCs in the environment, with the bulk of their endocrine disrupting activity resulting from human estrogen compounds (Desbrow et al., 1998, Snyder et al., 2001) (Table 11-1). The synthetic estrogen, EE₂, and the natural estrogens, estrone (E₁) and 17 β -estradiol (E₂), are the greatest contributors to endocrine disrupting activity in WWTP effluent (Johnson et al., 2001) with EE₂ showing the greatest recalcitrance in WWTPs (Joss et al., 2004). Influent concentrations range from below detection to 70 ng/L for EE₂, 670 ng/L for E₁ and 150 ng/L for E₂ (Vethaak et al., 2005, Clara et al., 2005b).

Other EDCs include tributyl tin, which was previously used in paints to prevent marine organisms from sticking to ships, nonylphenol (a surfactant), and bisphenol A (platicizer and preservative).

PPCPs encompass a wide variety of products that are used by individuals for personal health or cosmetic reasons, and also include certain agricultural and veterinary medicine products. PPCPs comprise a diverse collection of thousands of chemical substances, including prescription and over-the-counter therapeutic drugs, veterinary drugs, fragrances, sun-screen products, vitamins, and cosmetics. Many of these products, notably the pharmaceuticals for human or animal use, are specifically designed to be biologically active, and some PPCPs may also fall into the category of EDCs described previously.

Table 11-1. Estrogens of Concern

Name	Chemical Structure	Name	Chemical Structure
$\mathbf{E_1}$ Estrone $\mathbf{C_{18}H_{22}O_2}$		$\mathbf{E_2}$ 17 β -estradiol $C_{18}H_{24}O_2$	HO COLOR
E ₃ Estriol C ₁₈ H ₂₄ O ₃	нд	EE_2 17 α - ethynylestradiol $C_{20}H_{24}O_2$	HO

Currently, municipal sewage treatment plants are engineered to remove conventional pollutants such as solids and biodegradable organic material but are not specifically designed for PPCP removal or for other unregulated contaminants. Wastewater treatment commonly consists of primary settling followed by biological treatment, secondary settling, and disinfection. This treatment can remove more than 90 percent of many of the most commonly known or suspected EDCs found in wastewater influent; however, low concentrations of some suspected EDCs may remain in the wastewater treatment sludge or effluent (WERF, 2005). As discussed in the next section, studies have shown enhanced nutrient removal technologies to be effective in removing low concentrations of some emerging contaminants.

11.2 Removal of Emerging Contaminants by Nutrient Removal Technologies

Several studies have examined the effectiveness of current wastewater treatment technologies in the removal of emerging contaminants. Some of these studies are discussed below and their major findings are organized under three subsections: role of activated sludge SRT in removal efficiency, role of nitrifying bacteria in biodegradation, and use of RO to improve removal efficiencies. Details regarding the study design, such as evaluated treatments and contaminants, and a summary of major study findings are provided by author in Table 11-2 at the end of this chapter. The significant findings are also presented as follows:

- Removal efficiencies were enhanced for several investigated contaminants at longer SRTs, with critical SRTs for some beyond which removal rates did not improve.
- Longer SRTs allow for the establishment of slower growing bacteria (e.g., nitrifying bacteria in activated sludge), which in turn provide a more diverse community of microorganisms with broader physiological capabilities.
- Nitrifying bacteria may play a key role in biodegradation but the role of heterotrophic bacteria may also play a significant role.
- Reverse osmosis has been found to effectively remove PPCPs below detection limits including those that that were not consistently removed at longer SRTs.

One caveat regarding studies on emerging contaminants is that their concentrations in wastewater influent are often quite low (e.g., concentrations of ng/L to μ g/L range) and may be close to method detection limits. Therefore, small variations between measured influent and effluent

concentrations may show large variations in apparent removal efficiencies, possibly even producing negative calculated removals.

Role of Solids Retention Time in Removal Efficiency

The focus of several studies has been the relationship of the SRT to the removal of emerging contaminants. In particular, many investigated whether longer SRTs would result in increased removal efficiencies for estrogens and other categories of PPCPs. Longer activated sludge SRTs allow for the establishment of slower growing bacteria (e.g., nitrifying bacteria in activated sludge), which in turn provide a more diverse community of microorganisms with broader physiological capabilities.

Clara et al. (2005a), Kreuzinger et al. (2004), and Oppenheimer et al. (2007) observed enhanced removal with increasing SRTs for most of the EDCs and pharmaceuticals tested and found no significant differences in removal performances between conventional activated sludge systems and MBR when operated at similar SRT_{10} °C. This is likely due to the molecular weight of the study compounds, which was smaller than the molecular weight cut-off of the ultrafiltration membranes in the MBR.

Researchers have observed similar findings for natural estrogens with higher removal percentages at longer SRTs. Effluent concentrations for three natural estrogens were measured near their detection limits at SRTs_{10°C} higher than 10 days, with their critical SRTs_{10°C} estimated between 5 and 10 days (Clara et al., 2005a). High removal rates of > 90 percent were also observed by Joss et al. (2004) in a study in which they evaluated the removal of E_1 , E_2 , and EE_2 under aerobic and anaerobic conditions in WWTPs designed for nutrient removal. Joss et al. (2004) also reported that the maximum efficiency is dependent on redox conditions, with the highest removal rate occurring during the reduction of E_1 to E_2 under aerobic conditions. Clara et al. (2005a) cited examples where conflicting results were obtained for EE_2 . Ternes et al. (1999) found no significant elimination of this compound during batch experiments; however, Baronti et al. (2000) and Joss et al. (2004) report greater than 85 percent removal in full-scale WWTPs.

For the pharmaceuticals ibuprofen and bezafibrate, Clara et al. (2005a) reported more than 95 percent removal during treatment and calculated the critical value for $SRT_{10^{\circ}C}$ at 5 days for ibuprofen and about 10 days for bezafibrate. Analogous removal results were obtained in several other studies (Stumpf et al., 1998; Buser et al., 1999; Zwiener et al., 2001, as cited in Clara et al., 2005a; Oppenheimer et al., 2007). Clara et al. (2005b) noted no or slight removal of these two pharmaceuticals and two musk fragrances (tonalide and galaxolide) at a WWTP with a low SRT of 1 to 2 days (this plant is a high-loaded plant, designed to remove carbon only.) Clara et al. (2005a, 2005b) also found that the pharmaceutical carbamazepine was not removed during wastewater treatment. In addition, these studies found contradictory results for diclofenac (e.g., removal rates ranged from no removal to > 70 percent at SRTs of > 10 days (Clara et al., 2005b)). Clara et al. (2005a) also cited several examples where conflicting results were obtained for diclofenac. No significant removal was reported by Buser et al. (1999) and Heberer (2002a); whereas, Ternes et al. (1998) observed elimination rates of up to 70 percent.

Clara et al. (2005a, 2005b) concluded that the removal potential for conventional WWTPs and MBRs depends on the SRT. They further concluded that high removal rates can be achieved at $SRTs_{10\,^{\circ}C}$ of more than 10 days. These parameters correspond to the design criteria for nitrogen removal in the German Association for Water, Wastewater and Waste (ATV-DVWK, 2000) and the urban wastewater directive of the European Community (91/271/EEC) for WWTPs in sensitive areas.

In its 2005, technical brief, "Endocrine Disrupting Compounds and Implications for Wastewater Treatment," WERF summarized information from several studies that examined the effectiveness of

current wastewater treatment technologies in the removal of EDCs. The classes of EDCs included: steroids/sterols (naturally occurring, synthetic, and phytoestrogens), organohalides, metals/organometals, alkyl phenols, polycyclic aromatic hydrocarbons (PAHs)/crude oil, and plasticizers. Although the WERF 2005 technical brief states that in general, EDC treatment effectiveness is improved with increased SRT, it does not provide the specific SRTs that are associated with the cited removal rates.

Oppenheimer et al. (2007) examined the relationship of SRT to treatment removal efficiencies for 20 PPCPs that are commonly found in the influent of U.S. treatment facilities. Many of the studies already discussed here have been conducted primarily in Europe, were conducted at small-scale WWTPs and bench/pilot plants under controlled conditions, and focused on estrogens and prescription pharmaceuticals rather than PPCPs. The Oppenheimer et al. (2007) study also noted trends regarding the effect of HRT and pure oxygen systems compared to conventional aeration systems on PPCP removal.

Oppenheimer et al. (2007) defined a minimum critical SRT as the minimum time needed to consistently demonstrate greater than 80 percent removal. The results of the study showed that this critical SRT was compound dependent but that the majority of the 20 PPCPs were consistently removed in those treatment plants operating at SRTs of 5 to 15 days. Specifically, 9 of 12 frequently occurring PPCPs were effectively removed through secondary treatment (e.g., ibuprofen). Conversely, six compounds that are routinely detected in influent (i.e., detected in at least 20 percent of the influent samples) were not well removed by secondary treatment (BHA, DEET, musk ketone, triclosan, benzophenone, galaxolide). The results for galaxolide conflicted with those reported by Clara et al. (2005b) who generally found high removal rates with SRTs > 10 days and Kreuzinger et al. (2004) who reported removal at SRT between 25 to 40 days. Oppenheimer et al. (2007) found that some compounds such as octylphenol, tri-(chloroethyl) phosphate, and triphenylphosphate were not well removed by secondary treatment; however, these were seldom detected in the influent samples. Based on these results, Oppenheimer et al. (2007) concluded that secondary treatment provides an "effective first barrier" for the 20 PPCPs in the study.

Oppenheimer et al. (2007) also noted trends regarding the effect of HRT and pure oxygen systems compared to conventional aeration systems on PPCP removal but determined that insufficient data existed to make any definitive conclusions. When the PPCP removal performance of a high-purity oxygenated activated sludge plant was compared to a conventional aeration system, the pure oxygen system showed higher removal rates although its SRT was shorter than the conventional aeration plant (i.e., 1 day versus 3 days). In addition, different HRTs operating at similar SRTs had similar removal rates, and therefore suggested that HRT does not significantly affect removal effectiveness in the investigated PPCPs.

Role of Nitrifying Bacteria in Biodegradation

As discussed above, longer SRTs allow for the establishment of slow-growing nitrifying bacteria (i.e., ammonia oxidizing bacteria and nitrite-oxidizing bacteria). Several studies evaluated whether nitrifying bacteria improve the biodegradation of certain emerging contaminants. Major findings from some of these studies are discussed in this section.

The WERF (2005) technical brief indicated that secondary biological treatment that includes nitrification, nutrient removal, and disinfection may remove more than 90 percent of certain steroids, and >95 percent of alkyl phenols; whereas, secondary biological treatment without nitrification and disinfection may decrease removal of these by more than 15 percent.

Batt et al. (2006) investigated the role of nitrifying bacteria in activated sludge in the biodegradation of two pharmaceuticals, iopromide and trimethoprim. The biodegradation of these compounds was conducted in two lab-scale bioreactors using biomass from a stage-2 activated sludge WWTP (operated at an SRT of 49 days). In one of the bioreactors, nitrification was not inhibited (Batch-1 reactor); in the other, nitrification was inhibited with allylthiourea (Batch-2 reactor). Monitoring was also conducted in the WWTP and compared to results obtained from the batch reactors.

Both reactors exhibited high removal rates for iopromide; however for trimethoprim, Batch-1 showed a high removal rate of 70 percent, contrasted to the Batch-2 reactor removal rate of approximately 25 percent with nitrification inhibited. Removal rates within the treatment plant, however, were consistent for both pharmaceuticals, showing significantly higher removal rate after nitrification (approx. 60 percent for iopromide and 50 percent for trimethoprim) compared to activated sludge treatment only (<1 percent for both). Based on these results, Batt et al. (2006) concluded that nitrifying bacteria have a key role in the biodegradation of pharmaceuticals in WWTP that are operated at higher SRTs. This conclusion is supported by Marttinen et al. (2003), who investigated the fate of phthalates in a WWTP with nitrogen removal and observed that about one third of the removal occurred in the nitrification/denitrification treatment phase.

Studies by Yi and Harper (2007), Khunjar et al. (2007), and others have focused on the mechanisms of estrogen removal during nitrification. Possible mechanisms include sorption of estrogens to solids and biotransformation within the treatment facility, especially in the presence of nitrifying activated sludges (Khunjar et al., 2007). Ammonia oxidizing bacteria have monoxygenase enzymes for ammonia oxidation and these enzymes have been shown previously to be nonspecific and able to accomplish cometabolic degradation of recalcitrant organics. Cometabolic degradation is a reasonable hypothesis for estrogen degradation because this compound is present at low ng/L concentrations that are below those expected to support microbial growth on that compound alone.

One goal of the Yi and Harper (2007) study was to establish whether biotransformation of EE_2 is due to cometabolic activity. They conducted batch experiments using enriched cultures of autotrophic ammonia oxiders. Their study and others (Vader et al., 2000, Shi et al., 2004, as reported in Yi and Harper, 2007) showed a strong relationship between nitrification and EE_2 removal in enriched nitrifying cultures. Based on batch tests with and without a nitrifying bacteria inhibitor, they concluded that EE_2 biotransformation can be cometabolically mediated in bioreactors that are enriched for autotrophic nitrifiers. However, Yi and Harper (2007) noted that the heterotrophic microorganisms, if present in activated sludge processes, may also be responsible for some micropollutant biotransformations. Further work is needed in this area as these tests did not identify the EE_2 degradation product to confirm cometabolic degradation and the role of heterotrophs was not accounted for in some tests.

The focus of a Khunjar et al. (2007) study was to identify the role of ammonia oxidizing bacteria compared to heterotrophic bacteria in the biotransformation of EE_2 . They used pure cultures of ammonia oxidizing *Nitrosomonas europaea* and heterotrophic cultures that were enriched with monooxygenase and dioxygenase enzyme systems. Nitrifying activated sludge mixed liquors were taken from two WWTPs to seed the cultures. EE_2 concentrations were 10-15 μ g/L. The results of their study showed significant sorption of EE_2 to the predominantly heterotrophic culture but none to the *N. europaea* culture. In addition, biotransformation of EE_2 was significant in the *N. europaea* culture. They observed three major EE_2 metabolites at different phases of *N. europaea* culture growth that suggest differential action on each byproduct by the nitrifying bacteria; however, additional work is needed to identify these byproducts. The authors also noted that additional research is needed with continuous flow cultivated *N. europaea* to determine whether these metabolites are likely to be present in nitrifying

activated sludge. Also, N. europaea was not significantly inhibited at EE_2 concentrations at or below 10 μg EE_2/L , suggesting that ammonia oxidation may not be significantly impacted by concentrations of EE_2 that may be typical of those found in the environment.

Use of Reverse Osmosis to Improve Removal Efficiencies

Several studies describe the effectiveness of RO in the removal of PPCP and EDCs from secondary wastewater effluent. Braghetta et al. (2002) calculated the removals rates that could be achieved with a RO step following tertiary treatment for 17 PPCPs. They estimated removals to be > 90 percent for most of the selected compounds. Lower removal rates were estimated for diclofenac (55.2 to 62 percent), ketoprofen (64.3 percent), and paraxanthine (73.7 percent).

As previously discussed, the WERF (2005) technical brief evaluated RO removal rates for several compounds. Specifically, the WERF brief cites numerous studies in which RO achieved removal rates of 90 percent or better for naturally occurring and synthetic steroids, organohalides, metals/organometals, and alkyl phenols. In addition, Oppenheimer et al. (2007) found that RO was effective in removing all 20 investigated PPCPs below the detection limit including those that were not consistently removed at SRTs of 30 days (i.e., galaxolide) using conventional activated sludge treatment or media filtration. Similar findings were reported by Snyder (2003) and Everest et al. (2003) (as cited in Oppenheimer et al., 2007).

Table 11-2. Study Design Parameters

Table 11-2. Study Design Parameters				
Authors	Study Location	Study Contaminants ¹	Treatments Evaluated	Major Findings
Batt et al. (2006)	Amherst, NY	Pharmaceuticals: iopromide; trimethoprim	 Full-scale treatment plant: Nitrification, SRT = 49 d 2 Laboratory-scale tests: Nitrification was inhibited in one bioreactor but not the other. 	Both compounds more effectively removed in nitrifying activated sludge (SRT 49 d) than conventional activated sludge (SRT 6 d).
Braghetta et al. (2002)	Northern California	 17 PPCPs 1 allergy medicine: diphenhydramine 3 analgesics: acetaminophen; diclofenac; ketoprofen 2 antibiotics: sulfamethoxazole; trimethoprim 1 antiepileptic: carbamezipine 1 antihypertensive: diltiazem 1 blood glucose regulator: metformin 1 bronchodilator: albuterol 2 lipid regulators: fenofibrate; gemfibrozil 3 stimulant/stimulant metabolites: caffeine; cotinine; paraxanthine; 2 ulcer medicine/histamine receptor antagonists: cimetidine; ranitidine 	 2 WWTPs: Both use anthracite filtration as tertiary treatment. Plant A - conventional activated sludge Plant B - trickling filters/biofilters. Note: SRTs were not specified.	Calculated removals using reverse osmosis (RO) >90% for most investigated PPCPs.

Table 11-2. Study Design Parameters				
Authors	Study Location	Study Contaminants ¹	Treatments Evaluated	Major Findings
Clara et al. (2005a)	Not specified	 EDC: bisphenol-A 3 Natural Estrogens: 17β-estradiole (E₂); estrone (E₁); estriole (E₃) 5 Pharmaceuticals: bezafibrate; carbamazepine; diclofenac; 17α-ethynylestradiole (EE₂); ibuprofen 	 4 Full-scale plants: Most with N and P removal, SRT₁₀°_C from 2 - >100 d. 1 Pilot plant: Membrane bioreactor (MBR); ultrafiltration, SRT₁₀°_C from 22 - 88d. 4 Laboratory-scale tests: 1 SBR with SRT₁₀°_C of 1d. 3 Bioreactors, N removal, SRT₁₀°_C from 10-68 d. 	 Enhanced removal with increasing SRT for most investigated compounds. Critical SRT can be defined, beyond which removal rates do not improve. No significant differences in removal performances between conventional activated sludge systems and MBR when operated at similar SRTs.
Clara et al. (2005b)	MBR and WWTP (co-located) in rural community south-east of Austria; 2 WWTPs in Austria.	 9 EDCs: bisphenol-A; nonylphenol; nonylphenol diethoxylate; nonylphenol monoethoxylate; nonylphenoxyacetic acid; nonylphenoxyethoxyacetic acid; octylphenol diethoxylate; octylphenol monoethoxylate 2 Musk Fragrances: galaxolide; tonalide 8 Pharmaceuticals: bezafibrate; carbamazepine; diazepam; diclofenac; ibuprofen; iopromide; roxithromycin; sulfamethoazole 	 3 Full-scale plants: 1 N and P removal, SRT 52-237 d, 6.8-22.1 °C 1 C removal, SRT 2 d, 13.5 °C. 1 nutrient removal, SRT 46 d, 10.4 °C. 1 Pilot plant: (co-located at 1 WWTP): MBR, ultrafiltration membrane, nitrification, denitrification, SRT from 10 - 55 d, 5.5-27.2 °C. 	See findings under Clara et al. (2004a)
Joss et al. (2004)	1 WWTP in Kloten/Opfikon, Switzerland; 1 in Altenrhein, Switzerland	 2 Natural Estrogens: E1, E₂ 1 Pharmaceutical: 17α-ethynylestradiole (EE₂) 	 2 Full-scale plants: Both conventional activated-sludge treatment plants and denitrification/nitrification. 1 included P removal, SRT of 10-12 d, run in parallel w/ pilot MBR 1 run in parallel with fix-bed reactor, 	Biological degradation >90% of investigated compounds observed with nitrification and denitrification (SRT of 12-15 d).

Table 11-2. Study Design Parameters				
Authors	Study Location	Study Contaminants ¹	Treatments Evaluated	Major Findings
Kreuzinger et al.	Austria	• EDC: bisphenol-A	SRT of 22- 24 d. 1 Pilot plant: MBR, anaerobic & anoxic compartments, aerobic filtration compartments, 3 membrane filters (pore size, 0.4 μm, 0.1 μm, 0.04 μm), SRT of 30 d. Batch experiments: Aerated with air for aerobic experiments and with N for anaerobic experiments. 4 Full-scale plants: 3 are single-	Enhanced removal with increasing
(2004)		 2 Musk Fragrances: galaxolide; tonalide 3 Natural Estrogens: E1, E2, E3 9 Pharmaceuticals: bezafibrate; carbamazepine; diazepam; diclofenac; ethynylestradiol; ibuprofen; iopromide; roxithromycin; sulfathometoxazol 	stage activated sludge, 1 is 2-stage; all have P removal, 3 also include nitrification/denitrification, SRT ₂₀ ° _C of <1->100d. 1 Pilot plant: Ultrafiltration, SRT ₂₀ ° _C of 11-41d. Laboratory-scale plants: SRT ₂₀ ° _C of 1-26 d.	SRT for most investigated compounds.
Khunjar et al. (2007)	Virginia	EDC: EE ₂	Laboratory-scale plant: MBR Note: Description provided in Yi (2006), which was not reviewed.	 Significant sorption onto heterotrophic biomass versus ammonia oxidizing biomass. EE₂ is transformed in the presence of monoculture <i>N. europaea</i>. Inhibition of <i>N. europaea</i> by EE₂ is not expected at concentrations typically found in environment.

Table 11-2. Study Design Parameters				
Authors	Study Location	Study Contaminants ¹	Treatments Evaluated	Major Findings
Marttinen et al. (2003)	Finland	Plasticizer: Bis(2-ethylhexyl) phthalate	Full-scale plant: Nitrification/denitrification, P removal, SRT of 21 d at 18.5º C.	 94% removal from water phase, primarily by sorption to sludges. 29% removed during nitrification/denitrification (calculated) 32% during anaerobic digestion (calculated) 32% remained in the digested and dewatered sludge (calculated). 62% overall removal rate (calculated).
Oppenheimer (2007)	Not specified	 20 PPCPs 2 antioxidants: butylated hydroxyanisol (BHA), methylparaben 1 detergent surfactant: octylphenol 2 fire retardants: tri(chloroethyl) phosphate; tripheylphosphate 5 fragrances: ethyl 3-phenylpropionate; galaxolide; methyl 3-phenylpropionate; musk ketone; 3-phenylproprionate 2 germicides: triclosan; chloroxylenol 1 insect repellent: N,N-diethyl-3-methylbenzamide (DEET) 2 pharmacueticals: caffeine (includes non-pharmaceutical); ibuprofen 1 plasticizer: butylbenzylphthalate 4 sunscreens: benzophenone; benzyl salicylate; octyl methoxycinnamate; oxybenzone 	 6 Full-scale plants: 1 activated sludge, 1 high-purity oxygenated-activated sludge, 4 nitrification/denitrification (1 of which also includes granular microfiltration/RO, and 3 include UV), SRTs from 0.5 to 30 d. 2 Pilot-scale MBRs: 1 includes nitrification/denitrification, SRTs of 14 & 15 d. 	 Enhanced removal with increasing SRT for most investigated compounds. RO removed all 20 investigated PPCPs < detection limit. including those not consistently removed at SRTs of 30 d.

Table 11-2. Study Design Parameters				
Authors	Study Location	Study Contaminants ¹	Treatments Evaluated	Major Findings
WERF (2005)	Not specified	 EDCs (only categories were provided) Alkyl phenols (e.g., nonylphenol, bisphenol A) Metals/organometals (e.g., tributyl tin, cadmium, lead) Organohalides PAHs/crude oil Plasticizers (e.g., phthalates) Steriods: naturally occurring; synthetic; phytoestrogens 	 Indicated types of treatments only: Physical: primary settling, secondary settling, filtration (e.g., sand). Biological: activated sludge, trickling filter, anaerobic digestion. Chemical: chemical addition (e.g., phosphorus removal, polymers), disinfection (chlorination, ozonation, ultraviolet light). Advanced treatment: activated carbon, membrane separation, RO, and ion exchange. 	 Enhanced removal with increasing SRT for most investigated compounds. Water temperature may negatively impact the effectiveness of EDC removal. RO removal rates ≥ 90% for steroids, organohalides, metals/organometals, and alkyl phenols.
Yi and Harper (2007)	Auburn, AL	EDC: EE ₂	Laboratory-scale: Nitrifying completely mixed stirred tank reactor, SRT of 20 d.	 Strong relationship between nitrification and EE₂ removal. Contribution of heterotrophic microorganisms to biotransformation is unclear.

¹ Although some of the study contaminants are listed as EDCs; others are suspected to be EDCs but require additional research (e.g., health effects studies) to make that determination.

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