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VOLATILE ORGANIC COMPOUND EMISSIONS  
FROM USAF WASTEWATER TREATMENT PLANTS  
IN OZONE NONATTAINMENT AREAS

THESIS

Brian A. Ouellette, Captain, USAF

AFIT/GEE/ENV/94S

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**THESIS**

**Presented to the Faculty of the School of Engineering  
of the Air Force Institute of Technology  
Air University  
In Partial Fulfillment of the  
Requirements for the Degree of  
Master of Science in Engineering and Environmental Management**

**Brian A. Ouellette, B.S.  
Captain, USAF**

**September 1994**

**Approved for public release; distribution unlimited**

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Brian A. Ouellette  
Captain, USAF

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## **List of Acronyms**

<b>AQC</b>	<b>Air Quality Criteria</b>
<b>AQCR</b>	<b>Air Quality Control Region</b>
<b>AQS</b>	<b>Air Quality Standard</b>
<b>ARM</b>	<b>Air Resources Management</b>
<b>BOD</b>	<b>Biological Oxygen Demand</b>
<b>BTEX</b>	<b>Benzene, Toluene, Ethyl Benzene, and Xylene</b>
<b>CAA</b>	<b>Clean Air Act</b>
<b>CAAA</b>	<b>Clean Air Act Amendments</b>
<b>CONUS</b>	<b>Continental United States</b>
<b>CWA</b>	<b>Clean Water Act</b>
<b>DoD</b>	<b>Department of Defense</b>
<b>EPA</b>	<b>Environmental Protection Agency</b>
<b>GFM</b>	<b>General fate model</b>
<b>HAP</b>	<b>Hazardous Air Pollutant</b>
<b>HWM</b>	<b>Hazardous Waste Management</b>
<b>IAW</b>	<b>in accordance with</b>
<b>IWTP</b>	<b>Industrial Wastewater Treatment Plant</b>
<b>NAAQS</b>	<b>National Ambient Air Quality Standards</b>
<b>NOV</b>	<b>Notice of Violation</b>
<b>NPDES</b>	<b>National Pollutant Discharge Elimination System</b>
<b>NSPS</b>	<b>New Source Performance Standards</b>

<b>NSR</b>	<b>New Source Review</b>
<b>PCB</b>	<b>Polychlorinated biphenyls</b>
<b>PCE</b>	<b>Perchloroethylene</b>
<b>PEEP</b>	<b>POTW Emission Estimation Program</b>
<b>POTW</b>	<b>Publicly Owned Treatment Works</b>
<b>PPA</b>	<b>Pollution Prevention Act of 1990</b>
<b>PSD</b>	<b>Prevention of Significant Deterioration</b>
<b>RACT</b>	<b>Reasonably Available Control Technology</b>
<b>ROG</b>	<b>Reactive Organic Gas</b>
<b>SIP</b>	<b>State Implementation Plan</b>
<b>STP</b>	<b>Sewage Treatment Plant</b>
<b>TCE</b>	<b>Trichloroethylene</b>
<b>TPY</b>	<b>Tons per year</b>
<b>TSS</b>	<b>Total suspended solids</b>
<b>USAF</b>	<b>United States Air Force</b>
<b>VOC</b>	<b>Volatile Organic Compound</b>
<b>VSS</b>	<b>Volatile suspended solids</b>
<b>WWTP</b>	<b>Wastewater Treatment Plant</b>

### List of Units

atm	=	atmospheres (pressure)
cm	=	centimeter (distance)
cm <sup>2</sup> /s	=	square centimeter per second (flow rate)
d	=	day (time)
h	=	hour (time)
K	=	degrees Kelvin (temperature)
kg	=	kilogram (mass)
kg/KWH	=	kilogram per kilowatt hour (power)
kg/m <sup>3</sup>	=	kilogram per cubic meter (density)
KW	=	kilowatt (energy)
lbs	=	pounds (mass)
lbs/yr	=	pounds per year (flow rate)
m	=	meter (distance)
m/s	=	meter per sec (velocity)
m <sup>2</sup>	=	square meter (area)
m <sup>3</sup>	=	cubic meter (volume)
m <sup>3</sup> /d	=	cubic meter per day (flow rate)
m <sup>3</sup> /mg-VSS·d	=	cubic meter per milligram of VSS per day
m <sup>3</sup> /s-m	=	cubic meter per second per meter (flow rate)
mg	=	milligram (mass)
mg/d	=	milligram per day (flow rate)

<b>mg/m<sup>3</sup></b>	= milligram per cubic meter (density)
<b>mg-VSS</b>	= milligram (volatile suspended solids) (mass)
<b>mg-VSS/m<sup>3</sup></b>	= milligram of VSS per cubic meter (flow rate)
<b>mole</b>	= $6.022 \times 10^{23}$ molecules per gram of substance
<b>s</b>	= second (time)
<b>TPY</b>	= tons per year (flow rate)

## **Abstract**

Federal environmental legislation has become significantly more stringent over the last five years with respect to tropospheric ozone pollution. Following the passage of the 1990 Clean Air Act Amendments (CAAA) and the Pollution Prevention Act, new emission control and reduction strategies now target a number of smaller stationary sources of ozone precursors (nitrogen oxides and hydrocarbons) for tighter air emissions regulation. Subsequently, wastewater treatment plants are now coming under increasing scrutiny relevant to their potential air emissions, particularly those of volatile organic compounds (VOCs). Despite the recent progress made by the private sector in advancing the state of understanding surrounding the fate of VOCs during wastewater treatment, this issue has not yet received the same level of attention within the Air Force environmental management community. Consequently, this research conducts an evaluation of the potential emission of volatile organic compounds from selected Air Force wastewater treatment plants which are currently located in ozone nonattainment areas.

Using a conservative mass balance equation and general fate simulation models, volatile organic emission estimates are calculated for four individual facilities--Edwards AFB, Luke AFB, McGuire AFB, and McClellan AFB--which represent a cross section of the inventory of USAF wastewater plants in ozone nonattainment areas nationwide. From these calculations, maximum facility emissions are determined which represent the upper limit for the potential VOC emissions from these wastewater plants.

Based on the calculated emission estimates, each selected wastewater facility is evaluated as a potential major stationary sources of volatile organic emissions under both

Title I of the 1990 CAAA and the plant's governing Clean Air Act state implementation plan. Next, the potential impact of the specific volatile organics being emitted is discussed relevant to their relative reactivity and individual contributions to tropospheric ozone formation. Finally, a relative comparison is made between the estimated VOC emissions for the selected wastewater facilities and the total VOC emissions for their respective host installations.

Although this research suggests that Air Force wastewater treatment plants are not likely candidates for regulation with respect to ozone nonattainment under current federal and state CAAs, it is important to note that these facilities warrant additional consideration under the Air Force Pollution Prevention Program. This thesis identifies Air Force wastewater facilities as potential sources of low level volatile organic emissions. Therefore, any VOC emission control and reduction initiatives under the Pollution Prevention Program must address the control and abatement of these potential facility emissions.

This research is intended to aid Air Force Environmental Managers in evaluating wastewater treatment plant volatile organic emissions with respect to the growing number of air quality, ozone nonattainment, and pollution prevention initiatives. This thesis should help establish the appropriate air resources management strategies and assign priority in addressing this particular problem.

# **VOLATILE ORGANIC COMPOUND EMISSIONS FROM USAF WASTEWATER TREATMENT FACILITIES IN OZONE NONATTAINMENT AREAS**

## **I. Introduction**

### **General Problem Statement**

As an affirmed leader in environmental compliance and pollution prevention, the Air Force (USAF) is committed to environmental leadership. Its goal is to prevent future pollution by reducing hazardous material usage and the release of pollutants into the environment to as near zero as possible (1:1). To achieve this goal, *air resources management* (ARM) is one of the keys to its future success. To date, such a realization has not been so apparent. Currently, only 5 percent of all USAF Notices of Violation (NOVs) are air related (2). However, as regulations enforcing the 1990 Clean Air Act Amendments (1990 CAAA) begin to be promulgated, ARM is expected to quickly become a major Air Force compliance issue in the near future (2; 3). To minimize the impact on its current management practices and to ensure continued environmental leadership, the Air Force must take actions now to successfully keep pace with pending air quality regulatory requirements.

In the past, pollution from more highly visible stationary sources (boilers, incinerators) and mobile sources (vehicles, aircraft) have been the primary focus of the Air Force ARM program. In turn, control, source reduction, and prevention initiatives have centered on resolving these more easily identifiable air emission problems. Since

wastewater treatment plants (WWTPs) did not intuitively fall into this category, they received little consideration in the past as potential sources of air pollutants. However, since the early 1990's, air emissions from WWTPs have received increasingly more attention from the environmental regulatory community. The emissions of *volatile organic compounds* (VOCs) from these facilities are of particular concern. Specifically, VOC emissions may pose a significant threat to human health and the environment for the following reasons (4:41; 5):

1. Many VOCs are classified as *reactive organic gases* (ROGs) which photochemically react within the troposphere to produce ozone (O<sub>3</sub>). Exposure to abnormally high levels of tropospheric ozone will result in a variety of detrimental effects to both human health and the environment.
2. In addition, some volatile organics have been identified as *hazardous air pollutants* (HAPs). These types of VOCs can pose serious health risks to both plant workers and the general public under acute and chronic exposure conditions.
3. Finally, certain VOCs are also known as *greenhouse gases*. Because these gases effectively absorb radiated energy from the earth, the rise in their concentrations within the earth's atmosphere has been associated with global warming phenomena.

Federal and state environmental agencies have now recognized WWTPs as potentially significant sources of volatile organic emissions. This is because, once at a treatment facility, VOCs in the wastewater may volatilize during the follow-on liquid treatment (6:46). According to the U.S. Environmental Protection Agency (EPA), over 24,100 municipal wastewater treatment plants nationwide treat an average of 27 billion gallons of wastewater per day (7:4). Using its Publicly Owned Treatment Works Emission Estimation Program (PEEP), EPA estimated in 1989 that these plants emit between

29,300 and 35,300 metric tons of VOCs per year from their wastewater treatment processes (7:4). In such staggering proportions, these figures have warranted that environmental managers formally recognize VOC emissions from these facilities as a potentially serious ARM problem.

### **Specific Problem Statement**

The Department of Defense (DoD) has long acknowledged that its wastewater treatment facilities do not have the necessary design and operational capabilities to meet the ever increasing statutory requirements. William H. Parker III, then Deputy Assistant Secretary (Environment) for the DoD, testified to the House of Representatives' Armed Services Committee:

Increasing regulations, more stringent permit requirements, and increasing interest in estuaries will continue to strain DoD's aging wastewater treatment facilities and will necessitate construction of new and/or improvements to existing facilities. (8:192)

To bring its facilities into compliance, the Air Force has invested millions of dollars (over \$105 M in FY93 alone) in a multiyear program to upgrade and renovate its wastewater treatment plants (2). Unfortunately, only those requirements identified from the National Pollutant Discharge Elimination System (NPDES) of the Federal Water Pollution Control Act have been used as the primary design criteria for these projects (2). As a result, the Air Force's most recently upgraded WWTPs, although in compliance with their NPDES limitations, are now at risk of noncompliance with the recently enhanced requirements of the Clean Air Act (CAA).

Following the passage of a far-reaching set of amendments in 1990, the Clean Air Act has now become one of the most extensive pieces of environmental legislation in our nation's history. First and foremost, the CAA has identified six *criteria pollutants*--carbon monoxide (CO), ozone (O<sub>3</sub>), particulate matter (PM-10), sulfur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>), and lead (Pb)--as the nation's top priorities with regards to air pollution. For each criteria pollutant, the law has established a *National Ambient Air Quality Standard* (NAAQS) which sets a maximum allowable limit or concentration for an individual criteria pollutant in ambient air. These standards are based on estimates of maximum pollutant concentrations measured over an established averaging time which, with an acceptable factor of safety, pose no threat to human health or the environment

(5). Under Title I of the 1990 CAAA, a new strategy was created for the attainment and maintenance of the NAAQS throughout the nation. In particular, specific timelines have been set and strict new enforcement measures are required to meet the NAAQS for ozone in regional areas where the set standard has been already exceeded. Known as *nonattainment areas*, these regions have been further categorized into one of several different nonattainment classifications for ozone--*marginal, moderate, serious, severe, and extreme*--based on the severity of the region's ozone pollution problem (9:2). Within each O<sub>3</sub> nonattainment classification, specific emission control and reduction standards are to be enforced against all *major stationary sources* of VOC emissions. The definition of a major stationary source ranged from sources emitting 100 tons per year (TPY) in a marginal nonattainment area to sources with emissions exceeding 10 TPY within an extreme nonattainment area. Necessary emission control measures also varied between

each nonattainment area where regions with a worsening ozone problem are required to implement more stringent controls.

With respect to the 1990 CAAA, the identification and control of volatile organic compound emissions from Air Force wastewater treatment plants must be an integral part of the service's future ARM program. To date, there has been no determination of which Air Force wastewater facilities possibly qualify as major stationary sources of VOC emissions and to what extent are they ultimately subject to under the revised Clean Air Act (10; 11; 12). Similarly, there has been no evaluation of the potential impact of these new regulatory measures on the future operations of Air Force wastewater facilities. Such a determination is especially critical for those USAF installations which are located in ozone nonattainment areas and which are projected to continue operating their own base wastewater treatment facility.

### **Research Objective**

The purpose of this research effort is to determine the relative extent to which USAF wastewater treatment plants contribute to ozone pollution in ozone nonattainment areas nationwide. This thesis will first identify those Air Force bases which currently operate a wastewater treatment facility within an ozone nonattainment area in the continental U.S. (CONUS). Next, the research will attempt to quantify and characterize the potential VOC emissions from these wastewater facilities using accepted emission modeling techniques. Based on their estimated total annual emissions, the thesis will then establish whether the individual wastewater facilities qualify as major stationary sources under Title I of the

1990 CAAA. If so, specific compliance requirements will be identified and their potential impact on the future operations of these Air Force facilities will be evaluated. If not, the research will examine the organic reactivity of the individual volatile organics being emitted relative to ozone formation and discuss the impact of these projected emissions on the local air quality. The thesis will then demonstrate the relative importance of these plant emissions with respect to the total baseline volatile organic emissions for the specific installation. Finally, an overall determination will be made if the emission of VOCs from its wastewater treatment facilities is a significant future ARM problem for the Air Force.

### **Scope**

This research effort will focus only on volatile organic compound emissions from USAF wastewater treatment facilities and the determination of their potential impact with respect to ozone nonattainment under Title I of the 1990 CAAA. The thesis recognizes that some volatile organic compounds are also classified as HAPs and are subject to additional regulatory requirements under the CAA's Title III. However, the issue of toxic organics and any related statutory requirements will not be addressed as part of this thesis.

Specifically, this thesis will characterize and quantify potential VOC emissions from Air Force WWTPs which are currently located in CONUS ozone nonattainment areas. The wastewater facilities to be evaluated will include both plants that receive mixed domestic and industrial wastewater (sewage treatment plants) and plants which treat only industrial wastewater (industrial wastewater treatment plants). Using empirical or semi-empirical mathematical simulation models, estimates will be calculated for the

**emissions from the facility's major liquid treatment processes only. Emissions from wastewater collection and distribution systems, solids handling and treatment operations, and other facility point sources, such as diesel generators, will not be included in the estimation calculations.**

**In determining existing statutory mandates and future compliance strategies, only those requirements identified in the 1990 CAAA, the 1990 Pollution Prevention Act (PPA) and their supportive federal regulations will be considered. In addition, USAF regulations and directives associated with these two federal statutes will be also evaluated. Other federal, state, and local environmental laws pertaining to the control, treatment, and reduction of VOC emissions from these facilities will be considered, as required.**

### **Research Goals**

**The following goals have been established for this research effort:**

- 1. Within both the civilian and military environmental management fields, conduct a thorough research of existing literature to establish the current level of understanding of VOC emissions from wastewater treatment plants and of their role as precursors to the formation of ozone in the troposphere.**
- 2. Report on the general statutory requirements for the inventory, control, and reduction of volatile organic emissions under the CAA, the 1990 CAAA, the 1990 PPA, subsequent EPA and state regulations, and associated USAF Policy Directives.**
- 3. Establish an inventory of the Air Force WWTPs currently located in ozone nonattainment areas to include the plant's servicing installation, a description of its wastewater treatment processes, its average daily flow, and any current emission control practices from an air quality perspective.**
- 4. Quantify and characterize the volatile organic emissions for a representative sample of the Air Force wastewater facility inventory. Calculate representative**

emission estimations using recognized empirical and semi-empirical mathematical evaluation methods.

5. Examine the organic reactivity of the individual volatile organics which may be emitted from the Air Force wastewater facilities under evaluation. With respect to tropospheric ozone production, discuss the potential impact of these emissions on the local air quality. Make a relative determination between the estimated wastewater treatment plant organic emissions and the total volatile organic emissions for the plant's host installation.
6. Determine if any USAF wastewater treatment plant potentially qualifies as a major stationary source under the 1990 CAAA. Discuss the possible impact of this determination on the future operations of this facility. If no Air Force wastewater facility qualifies as a major stationary source, determine any additional specific compliance nonattainment requirements from the CAA which may apply to the continued operation of these facilities.
7. Evaluate the capabilities of current Air Force WWTPs in meeting any regulatory requirements. Develop general organic emission control and reduction strategies to satisfy current statutory mandates.

The specific methods used to achieve these goals and the results of the overall research effort are detailed in Chapters III and IV of this thesis.

## **II. Literature Review**

### **Overview**

This part of the research effort will conduct a comprehensive review of the state-of-the-art concerning volatile organic air emissions from wastewater treatment plants. By examining both the private industry's and the military's perspective, the current level of understanding and any prevalent ARM trends, particularly within the Air Force, will be determined. More specifically, the literature review will focus on the following major points:

1. Briefly review the federal legislative history governing VOC emissions and discuss the associated Air Force policies and compliance programs.
2. In general terms, summarize the major adverse effects on human health and the environment associated with increased emissions of volatile organic compounds into the ambient atmosphere. Focus on the role of VOCs as precursors to the formation of ozone in the troposphere. Discuss the relative organic reactivity of individual volatile organics with respect to increased ozone production.
3. Overview the design and operation of the various types of wastewater treatment processes which are currently used at Air Force wastewater treatment facilities.
4. Identify the possible sources of VOC discharges into wastewater treatment systems. Examine the major fate mechanisms and potential emission points for volatile organics within specific wastewater treatment processes. Review available VOC emissions data from private industry, federal and state regulatory agencies, and Air Force environmental management sources.
5. Examine the general fate models currently used to simulate the individual removal rates associated with the competing fate mechanisms for volatile organics in wastewater treatment processes.
6. Review the current USAF WWTP inventory. List those facilities which are located in ozone nonattainment areas. Information should include the plant's location, its type and size, description of its primary wastewater treatment processes, average daily flows, its ozone nonattainment classification IAW 1990 CAAA, and any current VOC emission control practices.

7. Provide a brief summary and analysis of the literature review. Identify any potential shortcomings in the current Air Force level of understanding of the issue which will be addressed in the value added section of the thesis (Chapters III and IV).

### **Federal Legislation**

Federal law has followed a very long and deliberate path in regulating the release of pollutants into the ambient atmosphere. However, until the recent passage of the 1990 CAAA, the United States has enjoyed limited success in preventing the continued erosion of air quality nationwide. During the 1970's, significant progress was made in reducing the emissions of some air pollutants, most notably lead. Other pollutants, particularly ozone, continued to build within the ambient environment unchecked. A general overview of past legislative efforts will show how the cultural changes set forth in the 1990 CAAA were necessary to completely reverse the worsening condition of our nation's air resources.

**Clean Air Act of 1963.** Although the original version of the CAA was not a landmark piece of legislation, it recognized the need for federal, state and local involvement in the development and implementation of effective pollution control laws (5). The act encouraged state, regional, and local programs for air pollution control, while the federal government maintained program oversight and jurisdiction over interstate air pollution issues and policies. In addition, the CAA led to the development of preliminary air quality criteria (AQC) for the nation. As *descriptive* air quality factors, AQC identified the potential effects from exposure to specific ambient levels of pollutants over a given period of time (13:11). Later amendments to the CAA (in 1967 and 1970) used the AQC

as guidelines to determining the nation's first air quality standards (AQS) and specific source emission standards. As the first federal air pollution control and prevention statute, the original CAA served as the starting point towards establishing and maintaining acceptable air quality for the nation. However, in terms of air quality, its impact on wastewater treatment plants was not realized until much later.

**Air Quality Act of 1967.** Under this new law, several major provisions were enacted which had the potential to influence WWTP operations (5). First and foremost, the law called for the designation of Air Quality Control Regions (AQCRs) nationwide and required a detailed study of air quality issues within each region. Next, the promulgation of AQC was again mandated specifically for pollutants which had identifiable effects on human health and welfare. The development of federal recommendations for pollution control technologies was also directed. Using these recommendations, the federal government would assist state and local authorities in implementing technologies intended to achieve existing AQC. Finally, states were required to establish air quality standards consistent with the federal AQC within a strict timeline. Unfortunately, despite its potential, the law was able to achieve very little beyond the designation of a limited number of AQCRs. The subsequent effect on wastewater facility operations was not notably significant.

**Clean Air Act Amendments of 1970.** Considered a hallmark in environmental law, the 1970 CAAA broke the regulatory stalemate which had preceded it through earlier legislation. Heralded as the start of a new environmental decade, the 1970 CAAA were aimed at the prevention, control, and abatement of pollutant emissions from a variety of

stationary and mobile sources. Major initiatives under the new law included (5;

14:125-127):

1. The requirement to complete the final designation of AQCRs. The new amendments recognized that air pollution is not contained within any fixed geographical boundaries and is indeed a regional problem.
2. The identification of seven criteria pollutants--carbon monoxide, ozone, suspended particulate matter, sulfur dioxide, nitrogen dioxide, hydrocarbons, and lead--as the nation's worst air pollutants. The law also established a National Ambient Air Quality Standard (NAAQS) for each criteria pollutant. Each NAAQS set specific threshold concentration levels which would result in no adverse effect on human health, welfare, and the environment.
3. Provisions which delegated overall responsibility for compliance and enforcement of the act to the state and local levels. Federal oversight responsibility was given to the newly formed EPA. The law also required the submittal of State Implementation Plans (SIPs) as the primary means for compliance with NAAQS and other CAA initiatives.
4. The requirement for EPA to identify categories of stationary emission sources which contribute significantly to regional air pollution. For each source category, New Source Performance Standards (NSPS) were to be established by EPA which set minimum emission control requirements for each source type.
5. Mandates which required industry to monitor their source emissions and maintain accurate emission records. Also, the law authorized EPA with exclusive "right of entry" privileges to examine individual source records, as necessary.

With regards to wastewater treatment plants, the most immediate effect of the 1970 CAAA was the initiation of limited research into whether these facilities qualified as potential stationary sources. However, this research focused on possible emission levels of only a few select pollutant types. For example, research conducted by Schmidt, et al. and Lawrence, et al. examined the fate of polynuclear aromatic hydrocarbons and polychlorinated biphenyls (PCBs) in wastewater treatment systems (15:886).

Unfortunately, more extensive emission studies were not conducted. In particular, no research was accomplished which quantified emissions of the newly established criteria pollutants from WWTPs. As a result, the overall impact of these amendments on wastewater treatment operations was very limited.

**Clean Air Act Amendments of 1977.** Despite the sweeping changes of the 1970 CAAA, most metropolitan areas of the U.S. had failed to attain at least one of the criteria pollutant NAAQS by 1977 (5). Therefore, a second set of amendments was passed by Congress which included several new provisions (5; 14:125-127):

1. The law established separate attainment and nonattainment classifications for individual air quality regions based upon whether criteria NAAQS were attained or not.
2. For attainment areas where NAAQS were met, the Prevention of Significant Deterioration (PSD) permit program was created to regulate future growth of potential sources within the region. Under PSD, only certain attainment areas were authorized to increase pollutant emission levels. In all cases, NAAQS were not to be exceeded.
3. For nonattainment areas, the New Source Review (NSR) program was established for air emissions permitting. NSR placed stringent emission control limitations on the construction of new major sources and the modification of existing major sources of air emissions within a nonattainment area.
4. The amendments also set forth an emissions allowance and offset policy. Under this initiative, new industrial sources could locate in nonattainment area if the level of emissions from the new source was offset by reduction in emissions from other existing sources.
5. An aggressive time table was established for the attainment of NAAQS within existing nonattainment areas. SIPs were revised to include provisions necessary to meet the new compliance deadlines.

In response to the new CAAA, research into pollutant emissions from WWTPs was intensified. In particular, a number of studies during the late 1970's and throughout the 1980's examined organic and toxic compound emissions from wastewater treatment plants (15; 16; 17). As a result, the understanding of the fate and release of these compounds in wastewater increased tremendously. However, despite this progress, regulators continued to give low emphasis to CAA enforcement actions against these particular facilities. Faced with higher priority air pollution problems, EPA continued to struggle within the limited capabilities of the law for the next 10 years. Meanwhile, the operations at wastewater facilities nationwide remained virtually unchanged with regards to air emissions control.

By the late 1980's, Congress and public interest groups joined in demanding the immediate revision of the CAA. They cited as evidence of the law's failure that 60 metropolitan areas did not achieve ozone NAAQS by the 1977 CAAA deadline of December 31, 1987 (18:8). Discouraged with EPA's inability to establish an effective air quality program under the existing law, Congress resigned itself to adopting a new approach in 1990.

**Clean Air Act Amendments of 1990.** When President Bush signed the new amendments in November 1990, he called them "simply the most significant air pollution legislation in our nation's history" (19:16). This comprehensive set of statutory mandates comprised a virtual rewrite of the original law. Where the original CAA was less than 50 pages long, the 1990 CAAA were nearly 800 pages long (19:16). Congress' intent was to give the EPA, through the revised law, both the time and means to implement effective air

quality control and maintenance programs. Of particular concern to this research effort, the 1990 CAAA covered four specific areas of potentially significant impact on the future operation of WWTPs (20:24; 21:26-29).

**Title I - Nonattainment.** This title focused on widespread failure for communities across the country to meet the NAAQS established for the six criteria pollutants. In 1990, 74 million people in the U.S. resided in counties where air quality standards were exceeded (22:Sec 1, 1). The overwhelming number and diversity of air emissions source types were the primary contributors to this threatening situation. In response, the CAAA established a new strategy to first attain and then maintain compliance with the criteria pollutant NAAQS. This strategy combined timeline extension for compliance (based on a schedule previously established under 1977 CAAA) with specific emission control and reduction requirements.

Several major programs were created to implement this new strategy with respect to ozone nonattainment (19:17-19; 21:26-28). These new initiatives would have a direct impact on wastewater treatment facilities throughout the U.S.. First, ranked categories were established for ozone nonattainment regions--*marginal, moderate, serious, severe,* and *extreme*--based on the severity of the region's current ozone pollution level. For each respective ozone nonattainment category, specific emission control and reduction measures were mandated for every major stationary source of volatile organic emissions. Table 1 identifies the requirements for major stationary source classifications within each regional O<sub>3</sub> nonattainment category.

Similarly, mandatory emission control measures also varied between each nonattainment area where regions with a worsening ozone problem were required to implement more stringent controls. Finally, specific deadlines were set for each category in meeting emission reduction goals and attaining the ozone NAAQS.

Next, new long range planning requirements under the 1990 CAAA mandated a revalidation of many state implementation plans (21:26). First, the states were required to maintain a complete emissions inventory from all possible stationary sources, including wastewater treatment plants. In addition, SIPs had to implement a policy to complete the application of *reasonably available control technology* (RACT) to all major stationary sources within an ozone nonattainment area. Finally, new emission offset ratios were developed for each nonattainment category. In marginal nonattainment areas, offsets in VOC emissions were allowed at 1:1 ratio while in an extreme nonattainment region, emission offsets were allowed under a 1.5:1 ratio. SIPs were require to develop revised procedures to enforce these new offset measures.

TABLE 1.  
MAJOR EXISTING STATIONARY SOURCE CLASSIFICATIONS  
UNDER THE 1990 CAAA

<u>Nonattainment Category</u>	<u>Major Emission Source Size</u>
Extreme	10 TPY
Severe	25 TPY
Serious	50 TPY
Moderate, Marginal	100 TPY

(23:19)

**Title V - Permits.** This title strengthened the CAA's compliance capabilities to a level on par with other major environmental laws. Under Title V, the 1990 CAAA borrowed heavily from the Clean Water Act's NPDES in modeling its revised source permitting program (5:5-6; 24:56). Under the new program, operational permits were required for all major stationary sources as defined under the amendments. These sources were required to submit comprehensive permit applications which included a detailed compliance plan for achieving the specific requirements established under the revised SIPs. The issued permit will set specific emission limitations, monitoring and testing measures, and mandatory RACT requirements. Once permitted, the source facility is then required to perform emissions monitoring and submit emissions reports to states every six months. Finally, annual recertification of the permit is required to ensure continued compliance with the measures set forth in the original permit order.

**Title VII - Enforcement.** This title served as the compliment to Title V by providing regulators with more stringent enforcement provisions. Federal and state environmental agencies were now authorized to levy on-the-spot fines up to \$5,000 per day per violation. Likewise, criminal violations were upgraded to felony status and new criminal sanctions were added for knowing endangerment and negligence (19:19). Finally, the burden of proof was transferred to the accused violator to show that "continuous compliance" had been achieved (25:10).

As one of its underlying cultural changes, the 1990 CAAA recognized the need to shift regulatory focus away from the control and reduction of volatile organic emissions

from highly visible, major stationary sources. The revised law now targeted less conspicuous smaller sources, generally those that emit less than 100 tons of VOCs per year. These sources, such as auto body shops and dry cleaners, may individually emit less than 10 tons per year, but collectively, they have the potential to emit hundreds of tons of pollutants per year (26:2).

From a regulatory perspective, wastewater treatment facilities have historically fallen within the small sources category. However, this perspective changed when these facilities were formally identified by the EPA as potential major air emissions sources under Section 112 of the 1990 CAAA (27:31591). Subsequently, specific air emissions standards for wastewater treatment plants will be developed by the EPA. However, they are not expected to be promulgated until 1995 (28). Even in the absence of these regulations, the 1990 CAAA will have a potentially unprecedented impact on the continued operation of our nation's WWTPs.

**Pollution Prevention Act of 1990.** In addition to the CAA, the Pollution Prevention Act (PPA) will also effect wastewater treatment plant operations through two new pollution prevention policies (29:2-5). The PPA first advocated *source reduction* as the preferred hazardous waste management practice nationwide. Under this law, Congress clearly mandated "that pollution should be prevented or reduced at the source whenever feasible" (29:3). Next, a *pollution prevention hierarchy* of hazardous waste management (HWM) measures was created. Figure 1 shows the hierarchy of HWM options from the most desirable (source reduction) to the least desirable method (waste treatment and disposal). The PPA was enacted to force acceptable HWM practices away from the

traditional end-of-pipe control, treatment, and disposal of pollutants. Instead, source reduction practices such as material substitution and individual process changes were identified as more environmentally sound hazardous waste management measures.

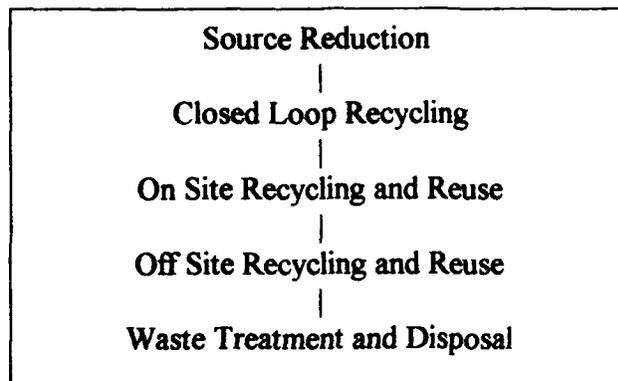


Figure 1. Pollution Prevention Hierarchy (29:3; 30)

Relevant to the emissions of volatile organics from wastewater treatment plants, the resulting effects associated with the Pollution Prevention Act are two-fold. First, as upstream industries reduce their total organic discharges through pollution prevention initiatives, the receiving wastewater facility will experience a similar reduction in the release of these compounds during follow-on wastewater treatment. Second, the PPA reinforced the need for specific volatile organic air emission control and reduction strategies at the wastewater treatment plants themselves.

## **Air Force Policy**

The number of Air Force regulations which govern wastewater treatment and the potential air emissions from these facilities is limited. Under the original Clean Air Act, federal sovereign immunity has been categorically waived in Paragraph 118 (31).

Therefore, with respect to air resources management, the USAF has traditionally deferred to the specific compliance requirements of this law. Relevant to pollutant emissions from Air Force WWTPs, there are two additional service directives which regulate the operations of these treatment facilities.

**Air Force Manual 86-1.** This manual governs the overall operation and maintenance of Air Force wastewater treatment plants. Specifically, the Air Force wastewater management program advocates a *regional connection* policy where installations utilize municipal or regional waste collection and disposal systems to the greatest degree possible (32:22). If more strictly enforced in response to the revised CAA, this policy will have a significant impact on future USAF wastewater facility operations. Despite a recent facility upgrade program, some Air Force wastewater treatment plants are still operating out of compliance with major environmental statutes, including the Clean Air Act. As a result, the Air Force may be forced to fully implement a regional connection policy in the face of increasing regulatory requirements and legal liabilities under this statute.

**Air Force Policy Directive 19-4.** This directive established the service's pollution prevention program to implement the requirements of the 1990 Pollution Prevention Act. A number of new initiatives under this directive will have a potential impact on the future operation of USAF WWTPs (1:4-5; 33:1-3). First and foremost, the policy mandates the

elimination or reduction, to as near zero as possible, of both the use of hazardous materials within the USAF and the subsequent release of hazardous wastes by the Air Force into the nation's air, land, surface waters, or groundwaters. Next, all Air Force operations, to include wastewater treatment plants, must comply with current statutory requirements for air and water quality by reducing emissions of volatile organics into the air, eliminating pollutants from sewage and stormwater, and controlling industrial discharges. Finally, each Air Force installation must conduct a basewide survey of all VOC air emissions and characterize all base waste streams which lead into the local ambient air. In turn, they must reduce their total base volatile organic emissions by 50 percent by 1999 (1:5).

### **Volatile Organic Compounds (VOCs)**

To better understand the current regulatory initiatives governing volatile organic pollutant emissions, a review of the nature of these volatile compounds, their subsequent role in the formation of tropospheric ozone, and the major environmental effects associated with rising VOC concentrations in the atmosphere is warranted. Volatile organic compounds are defined as any organic compound with a vapor pressure greater than 0.1 mm Hg which will volatilize (evaporate) at standard climatic temperature and pressure (20°C and 760 mm Hg) (16:2; 17:4). In turn, volatilization under ambient atmospheric conditions can be the dominant environmental fate mechanism for VOCs especially for those organics which are released into wastewater collection and treatment systems (34:1332).

Increasing VOC emissions are a potentially significant ARM problem for two distinct reasons. First, many volatile organics are classified as hazardous air pollutants (HAPs) and subsequently pose a serious threat to human health and the environment under acute, high dose exposures. EPA reports that over 200 million pounds of the 2.7 billion pounds of HAPs released annually in U.S. are emissions of sixty suspected carcinogenic pollutants (24:49). More specifically, EPA estimates that sewage treatment plants nationwide emit 24.2 million pounds of toxic organic compounds annually which result in an additional 1.49 cancer cases for the nation per year (35:43). As a result, the potential exposure of wastewater treatment plant workers to unsafe levels of toxic volatile organics warrants serious consideration by the managers of these facilities.

Most important to this research effort is the role of volatile organics in promoting increased atmospheric ozone pollution. Along with oxides of nitrogen ( $\text{NO}_x$ ), VOCs are the primary precursors for the photochemical formation of ozone in the troposphere. In 1990, VOC emissions from reported sources totaled 18.7 million metric tons and ranked #4 on the list of criteria pollutant emissions (22: Sec 1, 13). In that same year, 63 million people (85%) of the 74 million people who resided in U.S. counties where a NAAQS was exceeded lived in areas where the ozone standard was not being met (22:Sec 1, 1). Based on these recent air quality trends, ozone has been cited as the most widespread and persistent urban pollution problem in the U.S. (26:22). In turn, current legislative measures, such as the 1990 CAAA, have advocated that the most effective way of reducing ozone pollution is to control volatile organic emissions (36:69).

**VOCs and Tropospheric Ozone.** As reactive organic gases, VOCs play a significant role in promoting increased tropospheric ozone concentrations. Volatile organic compounds generally persist for long times in the atmosphere (17:2). As a result, they are free to sustain a series of photochemical reactions which eventually upset the natural ozone balance. Under normal ambient conditions, the formation and decay of ozone within the troposphere is governed by the following equations (37:154-156; 38:49-51):



where:

$h\nu$  = sunlight which provides the required energy of reaction

M = an additional molecule which absorbs excess energy and stabilizes the newly formed  $\text{O}_3$  molecule

$\text{O}^*$  = atomic oxygen free radical

In the absence of other chemicals, Equations (1), (2), and (3) can be simplified into two balance equations which represents the natural  $\text{NO}_2$ - $\text{NO}$ - $\text{O}_3$  *photostationary state relation* in the troposphere (37:120; 39:286):



and

$$[O_3] = k_1[NO_2] / k_3[NO] \quad (5)$$

where:

$[O_3]$  = steady state concentration of ozone

$[NO_2]$  = steady state concentration of nitrogen dioxide

$[NO]$  = steady state concentration of nitrous oxide

$k_1$  = photodisassociation rate for  $NO_2$

$k_3$  = reactionary decay rate for NO

Under these conditions, ozone is formed through Equation (2) but it immediately reacts with NO in Equation (3) to regenerate  $NO_2$  in a continuous cycle. As a result, a steady state is achieved where relatively low concentrations of ozone exist naturally in the troposphere. However, when excessive VOC emissions are introduced, this natural balance is upset through a second series of chemical reactions.

The key to this reaction series lies in the presence of both the VOCs and, most importantly, the hydroxyl radical ( $OH^*$ ) (37:155). The hydroxyl radical is naturally produced in the troposphere when atomic oxygen reacts with water vapor:



The  $OH^*$  radical is highly reactive and subsequently, it quickly consumes the increased tropospheric levels of volatile organics (represented as RH) to form increased concentrations of the alkyl peroxy radical ( $RO_2^*$ ). Ultimately, the alkyl peroxy radical reacts with NO to form more  $NO_2$  (37:155-156):



The effect on the natural balance of ozone within the troposphere is devastating.

First, increasing amounts of NO are consumed through its secondary reaction with the alkyl peroxy radical. In turn, less NO is available for its decomposing reaction with O<sub>3</sub>.

Second, as more NO<sub>2</sub> is created through Equation (9), more NO<sub>2</sub> is available for increased O<sub>3</sub> production. As a result, the steady state equilibrium between the O<sub>3</sub> production and depletion cycles is lost. In summary:

The key to elevated tropospheric ozone levels is chemical reactions that convert NO to NO<sub>2</sub> without consuming O<sub>3</sub>. In polluted and even weakly polluted atmospheres, such shifts in ozone chemistry occur in the presence of peroxy radicals (RO<sub>2</sub><sup>\*</sup>) produced by oxidation of [hydrocarbons]." (38:50)

**Effects of Increased Tropospheric Ozone.** Rising tropospheric ozone

concentrations as a result of uncontrolled VOC emissions present a serious threat to human health and the environment. Ninety percent of all air available for consumption by living organisms is located in the troposphere (5). As ozone concentrations build within this critical resource pool, human, animal, and plant life, which depend on air for life, are increasingly vulnerable to a variety of health effects.

**Human Health Effects.** Ozone is a highly reactive compound which damages human biological tissue very easily and in several different ways (5; 17:1-13; 38:159-161).

The primary route of human ozone exposure is through the lungs via the natural breathing process. Overexposure to O<sub>3</sub> can result in injuries to the respiratory system at "concentrations that are within the range of those measured in polluted ambient environments" (38:159). Specifically, acute ozone exposure will cause reduction in lung function (ability to absorb oxygen from inhaled air) in both normal, healthy people and those more highly susceptible such as the young, old, and sick. Chronic exposure can produce permanent structural damage to the lungs by accelerating the rates of lung function loss and of natural lung aging. It may also inhibit the human immune system's ability to defend against infection. Finally, ozone is classified as a possible mutagenic substance with the potential to damage human genetic structure.

**Effects on Plants.** Overexposure to ozone can have a variety of effects on plants and trees (38:174-183; 40:58-59; 41:83-85). As with humans, exposure to plants occurs primarily through their respiratory system. As a result, their leaves are highly susceptible to damage. Acute exposure injuries include spotting on the leaf surface and the actual destruction of small areas of tissue. Chronic overexposure can cause the leaves to turn color and possibly result in the early loss of the leaves or the plant's fruit. Secondary effects of elevated O<sub>3</sub> concentrations include inhibited root development and above ground growth, reduced productivity and yield, and increased plant susceptibility to insects and disease. As a result, ozone is reportedly responsible for 90 percent of all plant injury in North America due to air pollution (38:183).

**Effects on Materials.** A number of common materials are susceptible to damage from exposure to high ozone levels (38:203-206). The durability and overall appearance

of paint is significantly worsened by chronic ozone exposure. Similarly, overexposure to O<sub>3</sub> may result in accelerated deterioration and weakening of textile fibers such as cotton, linen, and hemp. Ozone may also react with fabric dyes and cause materials to fade. Rubber is especially sensitive to high O<sub>3</sub> concentrations. Chronic exposure of rubber can cause cracking and loss of tensile strength in rubber compounds such as tires, hoses and electrical wire insulation.

**Global Environmental Effects.** Ozone is also classified as a *greenhouse gas* (5; 39:385). In the ambient environment, greenhouse gases, such as O<sub>3</sub>, CO<sub>2</sub>, N<sub>2</sub>O, and H<sub>2</sub>O, turn the troposphere into a type of global thermal blanket (5). By trapping some of the thermal energy radiated by the earth's surface, these gases help preserve those climatic conditions and temperature balance necessary to sustain life throughout the planet. This phenomena is referred to as the *greenhouse effect* (39:386). However, when O<sub>3</sub> concentrations increase as the result of uncontrolled VOC emissions, the influence of the greenhouse effect is intensified. Significant global change, as measured by increasing ambient temperature of the earth and shift in global weather patterns, could potentially result.

### **Relative Organic Reactivity**

With respect to atmospheric chemistry, *organic reactivity* refers to the potential of an organic compound to promote the formation of secondary pollutants (including ozone) in the ambient atmosphere (37:157). Secondary pollutant production is sensitive to a number of different environmental factors including the individual species and

concentrations within the initial organic mixture being emitted into the ambient air, as well as their respective rates of reaction within the atmosphere (42:692; 43:625, 44:881-882). To accurately reflect these relationships, the concept of *relative reactivity scales* was established to rank order organics in terms of their potential for secondary pollutant formation (43:625; 44:881). There are several different scales for determining the organic reactivity of individual organics relative to one another, each based on a measurement of a particular environmental effect of secondary pollutants (ozone formation, eye irritation, crop damage, visibility reduction). Regardless of the scale, Figure 2 depicts the general ordering of organic compounds with respect to the organic reactivities.

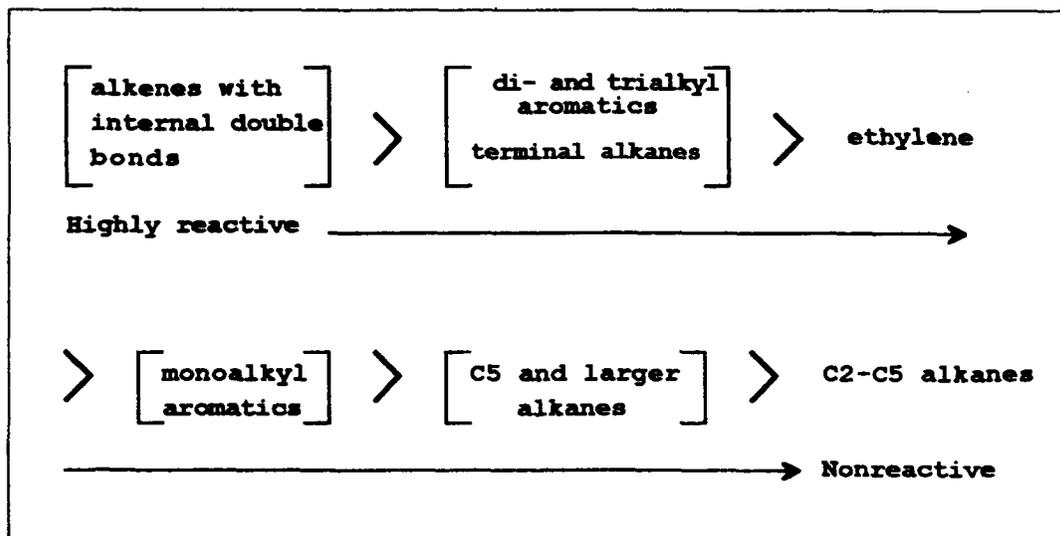


Figure 2. General ranking of organic compounds by reactivity (43:627)

A relative reactivity scale can be used to distinguish between individual organic compounds and identify those compounds which are more highly reactive (and, in turn, pose a more immediate threat to human health and the environment) as priority pollutants

under an overall regional air quality control strategy. Because of the recent promulgation of more stringent air quality standards relating to tropospheric ozone, the organic reactivity measure of greatest interest to this research effort is the scale which relates the reaction of VOCs (represented by RH) with the hydroxyl radical (OH\*) as a precursor to tropospheric ozone formation. This scale is based on the assumption that, for most volatile organics, their reaction with the OH radical dominates their degradation within the troposphere (44:882; 45:908).

As depicted in Equation (7), (8), and (9), the RH-OH reaction is the primary precursor reaction to the formation of increased levels of tropospheric ozone. In turn, it is generally accepted that the rate constant for a particular RH-OH reaction accurately represents the overall reactivity of the organic compound with respect to ozone formation (43:625-627). The faster and more completely the organic reacts with OH, the faster more tropospheric ozone can be expected to be formed, and, subsequently, the higher the overall organic reactivity of the compound. Based on the OH reactivity scale, Table 2 contains the grouping of specific volatile organic compounds into five general reactivity classes.

### **VOCs at Wastewater Treatment Plants**

With a better understanding of the role of volatile organics in tropospheric ozone formation and the subsequent effects of elevated urban O<sub>3</sub> concentrations, Congress enacted the 1990 CAAA to focus on the identification and control of all potential volatile organic air emission sources as the primary means to curb the urban ozone pollution

problem throughout the U.S.. In turn, wastewater treatment plants, once given little consideration in terms of air emissions, have become the subject of several recent studies aimed towards quantifying the possible VOC emissions from these facilities. The purpose of these studies was to more closely examine the dynamics of wastewater treatment from an air emissions perspective. As a result, these efforts have more clearly identified the possible sources of VOC discharges into wastewater collection and treatment systems, the major environmental release mechanisms for volatile organics in wastewater, and the potential fugitive emission and stack emission points within a typical wastewater treatment facility.

TABLE 2.

OH REACTIVITY CLASSIFICATION OF SELECTED VOLATILE ORGANICS

<u>Class I Nonreactive</u>	<u>Class II Reactive</u>	<u>Class III Reactive</u>	<u>Class IV Reactive</u>	<u>Class V Highly Reactive</u>
C1-C3 Alkanes Acetylene	Mono-alkyl benzenes	C4+ Alkanes Cycloparaffins	Primary, secondary alkyl benzenes	Aliphatic olefins
Benzene Benzaldehyde	Cyclic ketones 2-Nitropropane	Styrene n-Alkyl ketones	Branched alkyl ketones Primary, secondary alkyl alcohols	Aliphatic aldehydes Unsaturated ketones
Acetone	tert-Alkyl acetates	Primary, secondary alkyl acetates	Cellosolve acetate	Diacetone alcohol
Methanol		N-methyl pyrrolidone	Partially halogenated olefins	Ethers
tert-Alkyl alcohols Phenyl acetate		N,N-dimethyl acetamide Partially halogenated paraffins		Cellosolves
Methyl benzoate Ethyl amines Dimethyl formamide Perhalogenated hydrocarbons				

(42:695; 45:912)

**Municipal Wastewater Treatment.** Wastewater treatment plants employ a variety of treatment technologies. The required level of treatment and the specific treatment processes used by a particular wastewater facility depends on the chemical makeup of the influent the plant receives and the required limitations on the quality of the plant's final discharge. Figure 3 contains a schematic of a typical municipal sewage treatment plant.

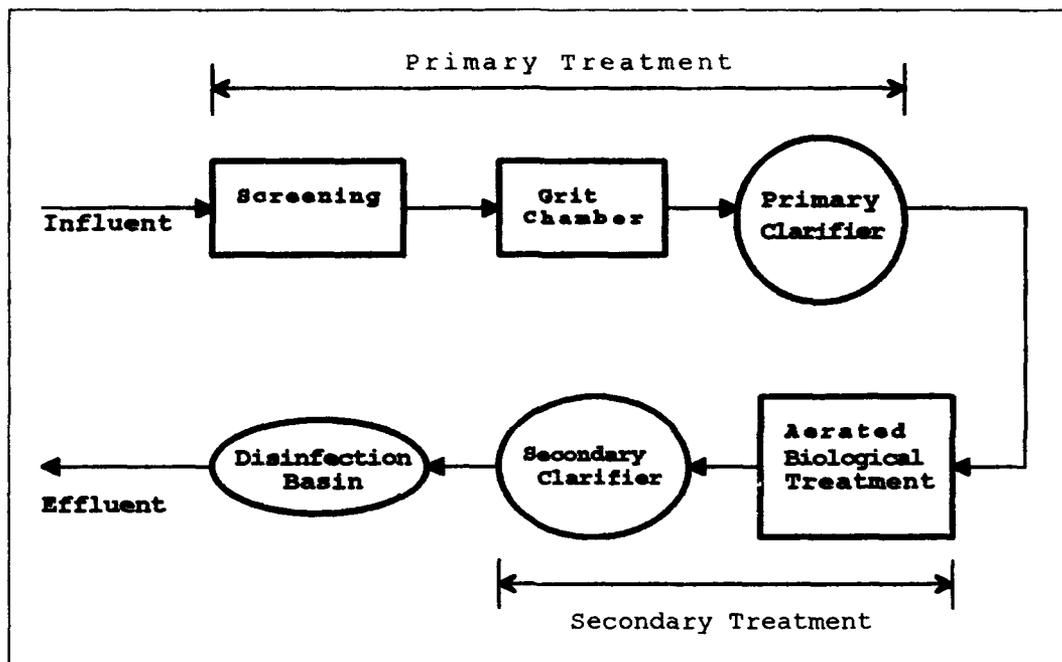


Figure 3. Typical sewage treatment plant with primary and secondary treatment (39:242).

Generally, a sewage treatment plant receives either domestic or a mixture of domestic and industrial wastewaters. Follow-on treatment of the waste liquid is intended to remove a variety of organic and inorganic wastes, suspended solids, hazardous pollutants, and pathogenic microorganisms. The *treatment train* at a conventional STP consists of three

major treatment components--*primary, secondary, and disinfection*. At more advanced treatment facilities, a *tertiary* stage of treatment is added to remove specific pollutant types from the wastewater. A review of the specific processes within each of the major treatment components is detailed below.

**Primary Treatment.** The objective of primary treatment is to remove solid materials through various physical processes which include *screens, grit chambers, and primary clarifiers* (46:159-160). Screens remove large, floating objects which may damage or block downstream pipes and equipment. After screening, the wastewater is passed through a grit chamber where large sand and heavy grit particles settle out. As the final primary treatment step, the wastewater is detained in large sedimentation tanks where remaining solid organic matter settles out under gravity. To facilitate this, clarifiers provide long retention times, reduced flow rates, and minimum turbulence (39:243; 46:160). Having passed through the primary settling tank, the clarified liquid flows out of the tank over a V-notch weir. The weir promotes an equal and steady flow discharge of wastewater all the way around the tank (46:161). The wastewater leaving primary treatment has now lost much of its solid organic matter and all of its solid inorganic matter.

**Secondary Treatment.** Secondary treatment removes the remaining organic materials still suspended or dissolved in the wastewater stream. Commonly referred to as *biological oxygen demand (BOD)*, this material can be decomposed through microbial digestion and oxidation (46:170). The three most common treatment techniques--*trickling filters, oxidation ponds, and activated sludge reactors*--use

microorganisms to remove the remaining organic wastes by allowing the microbes to feed on the wastes and convert them into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and other stable compounds (39:243).

**Trickling Filters.** A trickling filter consists of a bed of large rocks or other coarse material over which the wastewater is sprayed from a rotating distribution arm (39:243). The coarse material is covered with highly active, biological growth which absorbs the organic matter from the wastewater dripping down through the bed (46:171). This growth typically consists of bacteria but it may also include fungi, algae, worms, insect larvae, and snails (39:244). These organisms consume the organic wastes under the aerobic conditions maintained by the circulation of air throughout the filter bed. After running through the trickling filter, the wastewater enters a secondary clarifier to remove any biological growth that may have sloughed off the filter bed.

**Oxidation Ponds.** This is a relatively simplistic treatment technology which uses large, shallow ponds to support the microbial decomposition of the partially treated wastewater. Oxidation ponds are essentially large pools used to retain and treat the plant's effluent before it is discharged (46:189). These ponds are generally designed for aerobic biodegradation conditions using algae and other aerobic bacteria. However, *facultative* conditions often exist where aerobic decomposition takes place near the surface of the pond and anaerobic decomposition prevails at its bottom (39:249). Oxidation ponds require large surface areas to maximize surface aeration and light penetration in support of the necessary algal growth. Often times, oxidation ponds are mechanically agitated to introduce more dissolved oxygen into the wastewater and to better maintain the aerobic conditions of the pond.

**Activated Sludge Reactors.** This type of treatment system uses recycled microorganisms to remove BOD while they are freely suspended in the waste liquid (46:171). Following primary treatment, the wastewater enters another retention basin called an *aeration tank*. The waste liquid is then mixed with an organic or *activated* sludge. The microorganisms within the sludge consume the remaining organic matter while free floating. Air is bubbled into the aeration tank to provide oxygen to the aerobic microbes. The wastewater and sludge are slowly mixed to allow for greater contact between the microorganisms and the organic wastes. After the aeration tank, the wastewater-sludge mix is sent to a secondary clarifier where the suspended microbes are settled out under gravity. The final clarified liquid is then sent for follow-on treatment. Meanwhile, some of the settled microorganisms are returned back to the head of the aeration tank. Here, they are mixed with a new batch of wastewater and the process repeats itself (39:245-246).

**Tertiary Treatment.** This level of treatment is required when the effluent from secondary treatment still contains significant concentrations of organic or inorganic pollutants (46:189). Typically, tertiary treatment is employed to remove excess nitrogen and phosphorus, inorganic metals, or excess BOD (39:250). Tertiary treatment generally involves the use of precipitating or coagulating chemicals and an additional filtration system (a sand filter or a reverse osmosis pressure filter).

**Disinfection.** As the final wastewater treatment step, disinfection destroys any pathogenic microorganisms in the waste stream through chemical oxidation. This is traditionally accomplished through the *chlorination* of the wastewater. Chlorine is a

strong oxidizing agent which is mixed with the wastewater in a final contact basin. Alternative disinfection methods include *ozonation* and *ultraviolet (UV) radiation*. Ozonation involves the bubbling of ozone, another powerful oxidizer, through the wastewater within the final contact tank. UV radiation is accomplished by passing ultraviolet light through the wastewater from inside a special contact light chamber. Following disinfection, the treated wastewater is ready for final discharge from the plant.

**Industrial Wastewater Treatment.** Industrial wastewater treatment typically involves a combination of conventional wastewater treatment methods with more specialized chemical treatment processes. Generally, an industrial wastewater treatment plant receives highly variable flows of industrial discharges whose hazardous characteristics can fluctuate over time (46:10). Therefore, the follow-on treatment of the industrial wastewater is specifically designed to remove a variety of target organic and hazardous wastes. A typical IWTP treatment train consists of four major components--*primary treatment and flow equalization, chemical treatment, secondary treatment, and tertiary treatment*. A schematic of a conventional industrial wastewater facility is contained in Figure 4.

Operational differences between municipal and industrial wastewater treatment trains exist primarily within the first two major components. For both systems, secondary and tertiary treatment processes are relatively the same. A discussion of additional primary and chemical treatment processes used at an industrial wastewater facility follows.

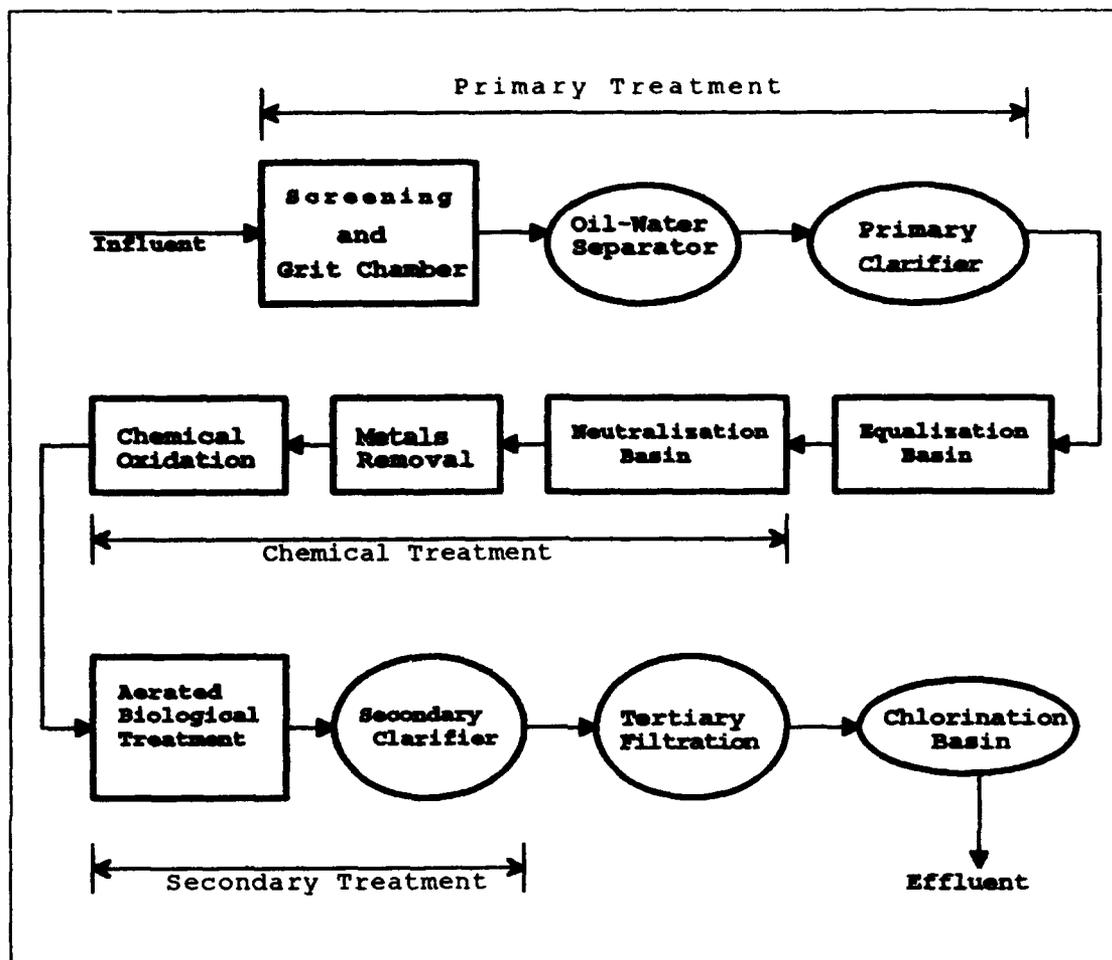


Figure 4. Typical industrial wastewater treatment plant (47:Sec 3, 37-38)

**Primary Treatment and Flow Equalization.** Primary treatment at an industrial wastewater facility employs the same treatment processes as those used at a sewage treatment facility. In addition, *oil-water separators* are used to separate out any free phase petroleum products from the wastewater. Within these baffled retention tanks, the wastewater is retained long enough to allow oil and fuel to float to the surface of the waste liquid and be skimmed off.

The wastewater entering an IWTP is often highly variable in its chemical characteristics and sanitary conditions. To level out peak loadings and slug discharges of contaminants, the wastewater enters an *equalization basin* as the final step to primary treatment (48:121). Here, the waste liquid is retained long enough to allow for a thorough mixing of the wastewater. Once the wastewater has reached fairly uniform composition, it is discharged to the next level of treatment.

**Chemical Treatment.** To allow for effective secondary biological treatment, chemical pretreatment of the industrial wastewater is often necessary. This level of treatment creates more favorable wastewater conditions by balancing pH and removing any toxic constituents. Chemical treatment processes include *neutralization*, *air stripping*, *metals removal*, and *chemical oxidation* (47:247-248; 48:115, 497-498; 49:98-116, 50:173-174).

**Neutralization.** Follow-on secondary treatment of industrial wastewater is more efficient at pH conditions closer to neutral (pH = 7.0). Therefore, wastewater with excessive acidity or alkalinity must be neutralized typically by adding chemicals to raise or lower the pH, as necessary.

**Air Stripping.** This treatment method specifically targets the removal of VOCs from the wastewater. Typical treatment methods include *spray towers* and *packed towers*. These contact systems create conditions which facilitate high rates of mass transfer of the VOCs out of the waste liquid and into the air within the tower. Once the volatile organics have been evaporated, the air from the tower is either blown off or collected and passed through an activated carbon filter to trap the VOCs.

**Metals Removal.** Heavy metals are often found in industrial discharges.

These compounds are highly toxic and require removal prior to secondary biological treatment. *Chemical precipitation* is the standard treatment method for heavy metals. First, chemicals are added to neutralize the wastewater and minimize the solubility of the target metal. As the wastewater's pH lowers, the dissolved metals will precipitate out. Similarly, some metals are removed through *gravity clarifiers* where the industrial wastewater is sufficiently retained to allow for the natural settling of any suspended metal compounds. *Ion exchange* is a direct removal technique where the waste liquid is passed through a special activated filter. Along the filter surface, the heavy metal ions are then chemically exchanged with nontoxic ions and adsorbed onto the filter media.

**Chemical Oxidation.** This type of treatment removes both organic and inorganic toxic compounds from the industrial wastewater. Under chemical oxidation, chemicals such as ozone, chlorine, hydrogen peroxide, and potassium permanganate are added to degrade compounds which are more resistive to natural decay. The extent of oxidation can range from structural compound changes to improve biodegradability and reduce toxicity to complete destruction of the compound into more stable CO<sub>2</sub> and H<sub>2</sub>O.

**Sources of VOCs in Wastewater.** Sewage treatment plants generally receive highly variable wastewater flows containing low, but variable, concentrations of volatile organics (46:50). Conversely, industrial wastewater treatment plants typically handle more predictable flows in terms of quantity and pollutant composition of the wastewater. A number of specific VOCs usually comprise the majority of air emissions from a typical wastewater facility. This group includes chloroform, methylene chloride, carbon

tetrachloride, trichloroethylene (TCE), perchloroethylene (PCE), and ethylene dichloride (16:1). The primary upstream point sources for these volatile organic discharges are highly diverse. However, in general, they fall into three categories-- water and wastewater treatment, industrial sources, and household products (16:33-35; 51:51-53; 52:56; 53:6-7).

**Water and Wastewater Treatment.** Chlorine is typically added to drinking water and wastewater for disinfection treatment. In addition, chlorine is also used for odor control at many WWTPs. Relevant to potential volatile organic emissions, compounds such as chloroform, methylene chloride, and carbon tetrachloride may be formed as volatile organic byproducts of the chlorination treatment process. In turn, these compounds may be volatilized during subsequent treatment or discharge of the chlorinated wastewater.

**Industrial Sources.** The release of spent industrial solvents and strippers will introduce volatile organics such as carbon tetrachloride, trichloroethylene (TCE), perchloroethylene (PCE), methylene chloride, and acetone into wastewater treatment systems. Petroleum based wastes from motor vehicle servicing operations and liquid fuel spills carry in benzene, toluene, ethyl benzene, and xylene (BTEX) while waste dry-cleaning solvents are primary sources of tetrachloroethene.

**Household Products.** Cleaners, personal care items (deodorants, cosmetics, deodorizers), lawn and garden products, paints and solvents, soaps and detergents, polishes, medicine, photographic materials, and automotive specialty products all contain a

number of volatile organics. The uncontrolled discharge of these household items introduces BTEX, TCE, and other VOCs into the receiving sewer system.

**Fate Mechanisms for VOCs in Wastewater.** Once in a wastewater collection and treatment system, VOCs pose a significant environmental problem primarily because of their ability to volatilize from the wastewater under ambient atmospheric conditions. However, volatilization is only one of several distinct *fate* or *release mechanisms* which govern the removal of volatile organic compounds from wastewater flows (4:43; 53:3; 54:288).

**Volatilization.** Also referred to as evaporation, this process involves the transfer of volatile organics from wastewater to ambient air across open, agitated surfaces or airborne water droplets. Releases of VOCs by volatilization depends on the duration of contact between the wastewater and the ambient air, the temperature and turbulence of the wastewater, the compound concentration gradient between the water and gas phases, and the total exposed surface area (52:57; 54:288). The species of the VOC also plays a role in determining an individual compound's overall removal effectiveness through volatilization.

**Gas Stripping.** This organic compound fate mechanism takes place when a gas (typically air) is introduced into the wastewater. This can occur through mechanical agitation of the wastewater, as the wastewater passes over weirs and drops, or if a gas is injected into the wastewater as part of a treatment process. As the gas bubbles through the waste liquid, volatile organics are transferred out of the liquid phase and into the gaseous phase. When the gas bubble breaks the surface of the wastewater, the VOCs are

released into the open atmosphere. Overall, volatilization and gas stripping are the primary release mechanisms for those volatile organic compounds which are more resistive to natural decay (54:287). Conversely, a combination of volatilization, stripping, and biodegradation dominates the removal of degradable volatile organic compounds (55:7).

**Biodegradation.** Many types of volatile organics, including toluene, benzene, and methylene chloride, are naturally biodegradable under aerobic conditions (4:43; 55:8). As a result, they will be readily degraded during the follow-on biological treatment of the transporting wastewater. Typically, biodegradation is one of the primary fate mechanisms for VOCs during wastewater treatment, particularly for degradable volatile organics (4:43; 55:8).

**Adsorption to and from the Solid Phase.** Also referred to as bioaccumulation, some VOCs, most notably BTEX, can be removed from a wastewater stream by adsorbing onto the surfaces of organic material suspended in the waste liquid (4:43). VOC adsorption is often completely reversible if the liquid phase concentrations of the volatile organics or the temperature of the wastewater changes. Subsequently, this removal mechanism is not considered a major factor in the fate of most volatile organics in wastewater (55:8).

**Absorption to and from the Liquid Phase.** It is common for immiscible liquid materials, especially petroleum based wastes and food, to exist freely within a wastewater collection and treatment system. These materials often have a high affinity for absorbing volatile organics and subsequently reducing the potential emission of these compounds (4:43). This method of removal is dependent upon contact time, temperature, and the

individual VOC concentration gradients across the different liquid phases (56:75).

Overall, absorption has a limited effect on the fate of volatile organics during wastewater treatment.

**Chemical Oxidation.** In the absence of any aerobic microorganisms in the wastewater stream, certain VOCs may be oxidized through a chemical reaction with dissolved oxygen in the waste liquid (4:43). In addition, chemicals such as chlorine, hydrogen peroxide, ozone, and potassium permanganate are often added to the wastewater to initiate the oxidation of specific target organics. Generally, chemical oxidation does not play a major role in the removal of volatile organics from a wastewater stream.

For the majority of VOCs, volatilization remains the predominant fate mechanism once these organic compounds are introduced into a wastewater collection and treatment system. However, it is recognized that biodegradation plays an equally important role in the removal of more degradable volatile organics from a wastewater stream. The overall degree of removal through volatilization is dependent on several factors--contact time between the wastewater and the ambient air, turbulence of the wastewater, temperature of the wastewater and the ambient air, total surface contact area, and the effective removal rates of any other competing fate mechanism.

**Potential VOC Emission Sources at WWTPs.** Wastewater treatment plants are host to a number of treatment processes which will sustain the rapid evaporation of volatile organic compounds from the treated wastewater (4:41; 16:2). Wastewater treatment processes can be categorized with respect to their potential air emissions into

two general source types—*stack* and *fugitive sources* (51:50-51; 57:6). Stack emission sources include covered and ducted wastewater sludge treatment equipment, combustion exhaust vents from equipment, sludge digester gases, and stacks from off-gas incineration. Fugitive emissions primarily come off large, uncovered wastewater treatment areas such as clarifiers, settling basins, trickling filters, and aeration lagoons. In addition, weirs, channels, and sludge handling and treatment units are also possible fugitive emission sources. Figure 5 depicts the potential release points throughout a typical wastewater treatment facility and their associated fate mechanisms for volatile organic compounds.

Table 3 provides emission estimates for the major unit processes within a typical wastewater treatment facility. Overall, VOC removal through a wastewater plant via all potential removal mechanisms is estimated at 75-95 percent (53:6).

TABLE 3.  
PERCENTAGE REMOVAL OF VOCs FOR TYPICAL WWTP UNIT PROCESSES

<u>Unit Process</u>	<u>% Removed</u>
Collector sewer	10-15
Preliminary treatment	5-50
Primary treatment	10-20
Equalization basin	25-35
Secondary treatment	10-34
Solids handling	up to 10
Primary sludge	< 1-8
Secondary sludge	< 0.1
Filtration	1-5
Chlorination	up to 10
<b>TOTAL</b>	<b>75-95</b>

(53:6)

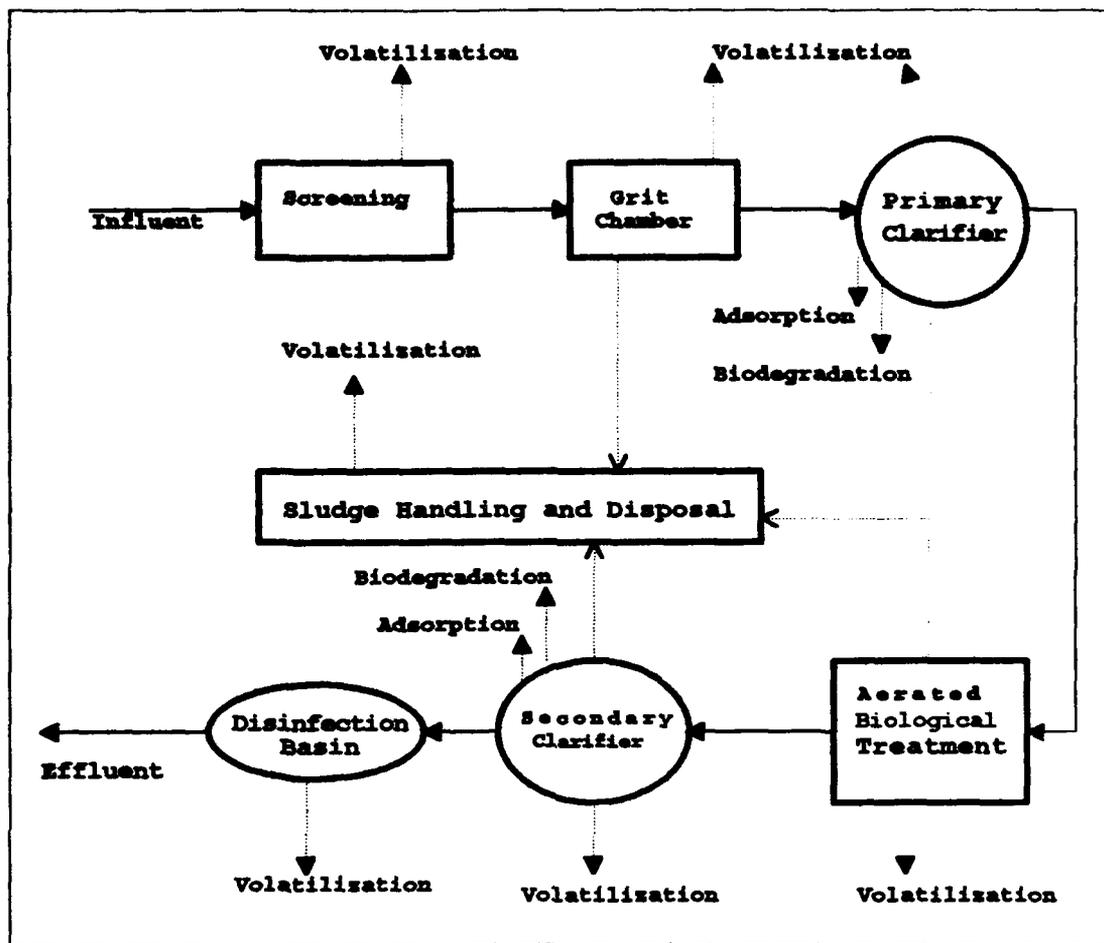


Figure 5. VOC mass flow in a typical wastewater treatment facility (58:98)

Focusing on air emissions from individual wastewater treatment processes, primary treatment units often sustain conditions highly favorable for the rapid volatilization of volatile organic compounds from the passing wastewater. Screens and grit chambers typically cause turbulent mixing of the wastewater thereby increasing the wastewater to air contact and allowing for more VOCs to volatilize. The long liquid retention times and large, open surface areas associated with primary clarifying tanks also permit VOCs to readily evaporate. At the primary clarifier weir, increased wastewater to air contact

during the outfall and increased bubbling action in the weir's tailwaters sustain higher volatile organic volatilization rates. At industrial wastewater plants, oil-water separators and equalization basins may also allow for the volatilization of significant amounts of organics. The accumulation of free floating oil and fuel within an oil-water separator could result in the buildup and eventual release of increased levels of VOCs from the headspace of the separation unit. Under operating conditions similar to those of a primary clarifier, an equalization basin will also allow volatile organics to readily escape into the ambient atmosphere. Overall, up to 30 percent of a typical wastewater plant's incoming volatile organic loading may be volatilized during primary treatment (58:101).

Likewise, secondary wastewater treatment processes are potentially significant sources of volatile organic emissions (54:289). The spraying, dripping, and forced air circulation actions of a trickling filter greatly increase the wastewater to air contact and the subsequent release of any volatile compounds out of the treated wastewater. At oxidation ponds and activated sludge reactors, large, open surface areas and long retention times combine with mechanical agitation to sustain higher evaporation rates for the VOCs from the waste liquid. Similarly, when air is bubbled through the wastewater as part of an activated sludge system, the stripping of the volatile organics by the forced air is significantly enhanced.

Finally, tertiary treatment and disinfection provide only limited opportunities for the volatilization of VOCs during the treatment of wastewater. Typically, these processes do not include the open, agitated conditions and long waste liquid retention times necessary for the efficient evaporation of any remaining volatile organics from the wastewater.

However, it is important to again note that chlorination may result in the formation of additional volatile organic compounds as by products of the disinfecting process. These compounds may subsequently be volatilized during or after the final discharge of the plant's effluent and serve to increase the overall emissions for the wastewater facility.

### **VOC Emission Estimation Methods for Wastewater Treatment Plants**

There are several distinct methods for measuring or estimating wastewater treatment plant air emissions to include *mass balance analysis*, *general fate models* (GFMs), and *direct or indirect source measurements* (6:46-47; 51:51; 59:60-61). Of most interest to this research effort, mass balancing and general fate modeling provide relatively straightforward, mathematical approaches for generating representative VOC emission estimates for these facilities. Both mass balancing and general fate modeling are based on the fundamental engineering principle of *conservation of mass* (39:5). This law states that during chemical reactions, mass is neither created nor destroyed. In turn, the materials involved in any chemical reaction can be completely accounted for such that the mass balance of the original reaction is maintained. Therefore, the mass balance of any chemical reaction can be expressed by the following equation (39:5):

$$\text{Input rate} = \text{Output rate} + \text{Decay rate} + \text{Accumulation rate} \quad (10)$$

With respect to wastewater treatment, Equation (10) can be further refined for the volatile organic reactions which typically occur within a wastewater treatment facility.

First, general *steady state* or *equilibrium* conditions are assumed to exist (39:5; 60:294). Since VOC concentrations in the waste liquid are assumed constant over time, the accumulation rate for any volatile organic in the wastewater is equal to zero. Second, as discussed previously, VOCs are subject to a number of physical, chemical, and biological fate mechanisms which subsequently remove these compounds from the treated wastewater. As a result, volatile organic compounds are generally considered to be *nonconservative* materials in wastewater treatment systems. Accounting for these additional conditions, the overall mass balance equation for volatile organic compounds in wastewater across a treatment facility or an individual treatment process can be expressed as (60:294):

$$\text{Output rate} = \text{Input rate} + \text{Volatilization rate} + \text{Biodegradation rate} + \text{Sorption rate} \quad (11)$$

and

$$Q_w C_e = Q_w C_i + R_v + R_b + R_s \quad (12)$$

where:

$Q_w$  = wastewater flow rate through a plant or process ( $\text{m}^3/\text{d}$ )

$C_e$  = VOC concentration in plant or process effluent ( $\text{mg}/\text{m}^3$ )

$C_i$  = VOC concentration in plant or process influent ( $\text{mg}/\text{m}^3$ )

$R_v$  = VOC mass transfer rate by volatilization ( $\text{mg}/\text{d}$ )

$R_b$  = VOC mass transfer rate by biodegradation ( $\text{mg}/\text{d}$ )

$R_s$  = VOC mass transfer rate by sorption ( $\text{mg}/\text{d}$ )

**Mass Balance Analysis.** This method is based on the assumption that 100 percent of volatile organic removal during wastewater treatment is attributed entirely to volatilization. As a result, the mass balance expressed in Equation (12) is simplified to the form:

$$Q_w C_i = Q_w C_e + R_v \quad (13)$$

Rearranging this equation, the total VOC emissions are calculated as the difference between the volatile organic mass loadings into and out of a wastewater treatment plant or individual treatment process. This approach typically results in highly conservative emission estimations because it does not account for the other major fate mechanisms for the VOCs in the wastewater. Therefore, mass balance emission estimates can range upto 4 to 8 times greater than the estimates from more refined methods (51:51; 59:60). However, mass balancing is considered a useful screening tool in making a initial determination if VOC emissions are a potential facility problem and if additional, more refined emissions studies are warranted (60:290-291).

**General Fate Models.** Using this approach, emission estimates are calculated from theoretical and field developed mathematical models. These general fate models simulate the major competing fate mechanisms for volatile organics (volatilization, biodegradation, and sorption) within specific wastewater treatment processes. Relative to mass balancing, these models are less conservative and they provide more accurate emission estimates. However, GFMs are typically more difficult to use since they require extensive empirical

input data (51:51; 59:61). In particular, the following information is generally required for most general fate models:

1. VOC concentrations in the wastewater entering a plant or a specific treatment process.
2. Individual compound properties (solubility, Henry's law constant).
3. Wastewater flow characteristics (rate, depth, turbulence).
4. Fluid characteristics (temperature, total suspended solids).
5. Specific process operational parameters (basin depth, surface area, aeration rate).

In addition to their extensive data requirements, most general fate models are limited to simulating VOC removal within a single- or two-unit wastewater treatment process, typically an activated sludge system (4:40). Past modeling efforts have focused on the secondary treatment processes primarily because the combined action of the major volatile organic fate mechanisms within these systems are expected to result in maximum emissions (57:4). However, with the recent development of several computer based simulation models such as the Bay Area Sewage Toxics Emissions (BASTE) model by Corsi and Card (1991), general fate modeling of VOC emissions during wastewater treatment has improved dramatically. The BASTE model has since been recognized as the premier flexible fate model for simulating volatile organic mass loss associated with the wide range of wastewater treatment plant configurations currently being used. Therefore, its theoretical development is used as the basis for the following discussion of general fate modeling principles.

**Volatilization.** The mass transfer of VOCs out of wastewater through volatilization,  $R_v$ , can be modeled from the following general equation (51:288; 60:292):

$$R_v = -K_L A [C_l - (C_g/H_c)] \quad (14)$$

where:

$R_v$  = VOC mass transfer rate by volatilization (mg/d)

$K_L$  = overall mass transfer coefficient for the specific VOC (m/s)

$A$  = total interfacial surface area available for VOC transfer (m<sup>2</sup>)

$C_l$  = initial liquid concentration of the specific VOC in the process influent (mg/m<sup>3</sup>)

$C_g$  = gaseous concentration of the specific VOC in the air over the wastewater (mg/m<sup>3</sup>)

$H_c$  = dimensionless Henry's law coefficient for the specific VOC

The overall VOC mass transfer coefficient,  $K_L$ , represents the total resistance to the movement of volatile organics across the two individual thin films (liquid and gas) which comprise the wastewater-air interface (61:330A).  $K_L$  is expressed as a combination of the liquid phase mass transfer coefficient,  $k_l$ , and the gas phase mass transfer coefficient,  $k_g$ , of a particular volatile organic (55:83):

$$K_L = k_l + k_g H_c \quad (15)$$

For highly volatile VOCs,  $k_g$  is considered to be negligible. Therefore,  $k_l$  becomes the sole limiting factor to their volatilization such that  $K_L \approx k_l$ . It has been shown that,

within a particular treatment process, the liquid phase mass transfer coefficient for a volatile organic ( $k_{l, VOC}$ ) can be estimated from the following equation (62:83):

$$k_{l, VOC} = [2.605 \times 10^{-9} (F/D) + 1.277 \times 10^{-7}] \times (U^2) \times (D_w/D_{other})^{0.666} \quad (16)$$

where:

$k_{l, VOC}$  = liquid phase mass transfer coefficient for a specific VOC (m/s)

F = distance across the surface of the treatment process unit (m)

D = depth of the treatment process unit (m)

U = the average wind speed 10 m above the wastewater surface (m<sup>2</sup>/s)

$D_w$  = the diffusivity of the specific VOC in water (cm<sup>2</sup>/s)

$D_{other}$  = the diffusivity of ether in water (cm<sup>2</sup>/s)

Similarly, research has determined that  $k_{l, VOC}$  is proportional to the liquid phase mass transfer coefficient for oxygen ( $k_{l, O_2}$ ) (54:288; 60:292). For a particular wastewater treatment process,  $k_{l, O_2}$  can also be estimated. In turn,  $k_{l, VOC}$  for a specific volatile organic passing through the process can be calculated from the relationship (54:288; 60:292):

$$k_{l, VOC} = \Psi k_{l, O_2} \quad (17)$$

where  $\Psi$  is the coefficient of proportionality for the specific VOC. Values for  $\Psi$  range from 0.52 to 0.63 (63:735)

Overall, the total volatilization of a volatile organic through a wastewater treatment facility is generally expressed as the sum of three separate components

(60:294):

$$R_v = R_{v,n} + R_{v,s} + R_{v,b} \quad (18)$$

where:

$R_v$  = total VOC mass transfer by volatilization (mg/d)

$R_{v,n}$  = volatilization across open surfaces (mg/d)

$R_{v,s}$  = volatilization across mechanically agitated surfaces (mg/d)

$R_{v,b}$  = volatilization via subsurface aeration (air stripping) (mg/d)

For each separate volatilization component, Equation (14) is modified to represent the different volatile organic mass transfer rates across its specific wastewater to air interface.

**Volatilization across Open Surfaces.** For wastewater treatment processes which are open to the atmosphere, any accumulation of volatile organics in the gaseous state will be negligible such that  $C_g$  is assumed to be zero (53:328A). Therefore, Equation (14) is reduced to the form (47:83; 61:292):

$$R_{v,n} = -k_{l,vo}AC_l \quad (19)$$

where:

$R_{v, n}$  = volatilization across open surfaces (mg/d)

$k_{l, voc}$  = liquid phase mass transfer coefficient for the specific VOC (m/s)

$A$  = total interfacial surface area available for VOC transfer ( $m^2$ )

$C_l$  = the liquid concentration of the specific VOC in the process wastewater stream ( $mg/m^3$ )

Equation (19) is referred to as an *infinite ventilation condition* (61:330A). It is used to estimate volatile organic emissions for open surfaces including clarifiers, ponds, channels, and the quiescent portions of activated sludge reactors or surface aerated basins.

**Volatilization across Mechanically Agitated Surfaces.** For wastewater treatment processes involving surface mechanical aeration,  $R_{v, s}$  is estimated directly from Equation (14). However, a revised value for  $k_{l, O_2}$  is calculated using the following equation (60:294; 64:1048):

$$k_{l, O_2} = N_c P / 3600 A C^* \quad (20)$$

where:

$k_{l, O_2}$  = the liquid phase mass transfer coefficient for oxygen (m/s)

$N_c$  = the oxygen transfer rate for the mechanical aerator ( $kg_{O_2} / KWH$ )

$P$  = the brake power of the mechanical aerator (KW)

$A$  = total surface area available for VOC transfer ( $m^2$ )

$C^*$  = the oxygen saturation concentration for a specific atmospheric temperature and barometric pressure ( $kg_{O_2} / m^3$ )

**Volatilization via Rising Air Bubbles.** For aerated grit chambers and activated sludge reactors which operate under subsurface aeration conditions, the stripping of volatile organics by the rising air bubbles,  $R_{v,b}$ , can be calculated from the expression (60:292; 61:331A):

$$R_{v,b} = -Q_g C_i H_c \quad (21)$$

where:

$R_{v,b}$  = volatilization via subsurface aeration (air stripping) (mg/d)

$Q_g$  = the forced aeration rate for the wastewater basin ( $m^3/s$ )

$C_i$  = the initial liquid VOC concentration in the wastewater influent ( $mg/m^3$ )

$H_c$  = Henry's law coefficient for the specific VOC (dimensionless)

For Equation (21), it is assumed that the rising air bubbles become fully saturated with gaseous volatile organics before they reach the wastewater surface. This assumption may not be appropriate under all conditions (60:292; 61:331A). Diffused aeration leads to turbulent mixing conditions where the overall volatilization of VOCs is dominated by evaporation across the wastewater surface. In turn, the rising air bubbles may only reach partial saturation, particularly with more highly volatile organics. Therefore, Equation (20) can be modified to include a partial saturation term (60:292; 61:331A):

$$R_{v,b} = -Q_g C_i H_c \{1 - \exp[(-K_1 a_o V)/H_c Q_g]\} \quad (22)$$

where:

$R_{v,b}$  = volatilization via subsurface aeration (air stripping) (mg/d)

and

$Q_s$  = the forced aeration rate for the wastewater basin ( $\text{m}^3/\text{s}$ )

$C_i$  = the initial liquid VOC concentration in the wastewater influent ( $\text{mg}/\text{m}^3$ )

$H_c$  = dimensionless Henry's law coefficient for the specific VOC

$K_1 a_o$  = oxygen mass transfer rate constant ( $1/\text{h}$ )

$V$  = the aeration basin volume ( $\text{m}^3$ )

**Biodegradation.** Biodegradation of volatile organics in wastewater is estimated using the Monod Kinetics Model (60:292; 61:332A). This model relates the rate of organic compound removal with compound concentration and active microbial cell mass:

$$R_b = (-kX_a C_i V) / (K_s + C_i) \quad (23)$$

where:

$R_b$  = rate of VOC biological degradation ( $\text{mg}/\text{d}$ )

$k$  = maximum first-order biodegradation rate constant for the specific VOC ( $\text{m}^3/\text{mg-volatile suspended solids (VSS)} \cdot \text{s}$ )

$X_a$  = active microbial biomass concentration ( $\text{mg-VSS}/\text{m}^3$ )

$C_i$  = initial liquid concentration of the specific VOC in the wastewater influent ( $\text{mg}/\text{m}^3$ )

$V$  = activated sludge reactor volume ( $\text{m}^3$ )

$K_s$  = Monod half-saturation constant ( $\text{mg}/\text{m}^3$ )

Since municipal wastewaters typically have low volatile organic concentrations, it is expected that  $C_i$  will be significantly less than  $K_s$ . Typically, the concentrations of VOCs

in wastewater are below levels required for these compounds to adequately support microbial growth by themselves (61:332A). Similarly, volatile organic concentrations are significantly smaller relative to the concentrations of other biodegradable organic materials in the wastewater. For these reasons, *secondary utilization* or *cometabolism* is the likely biodegradation mechanism for the VOCs (61:332A). Therefore, the Monod equation can be reduced to (60:292; 61:332A):

$$R_b = k_1 X_a C_1 V \quad (24)$$

where:

$R_b$  = rate of VOC biological degradation (mg/d)

$k_1$  = maximum first-order biodegradation rate constant for the specific VOC (m<sup>3</sup>/mg-volatile suspended solids (VSS) · d)

$X_a$  = active microbial biomass concentration (mg-VSS/m<sup>3</sup>)

$C_1$  = initial liquid concentration of the specific VOC in the wastewater influent (mg/m<sup>3</sup>)

$V$  = activated sludge reactor volume (m<sup>3</sup>)

Equations (23) and (24) are primarily used to calculate biodegradation removal rates for activated sludge reactors. However, there are two major limitations to using these equations to estimate rates of secondary biological degradation. First, measured values for  $k_1$  are not readily available for most biodegradable VOCs. Suggested estimates for  $k_1$  range from 0.1 to 100 m<sup>3</sup>/g-VSS·d with highly degradable compounds having values > 10 m<sup>3</sup>/g-VSS·d (60:292). Next, there have been problems in defining and determining

the active cell concentration,  $X_a$ , for an activated sludge system. For all biodegradation fate models, the activated sludge biomass is assumed to be completely acclimated to the volatile organics in the received wastewater. However, some models use the total or a fraction of the suspended solids and biomass to define  $X_a$  while others interpret  $X_a$  as the total biomass that would consume the volatile organics through secondary utilization (61:332A).

**Adsorption to Solid Particles and Biomass.** Some volatile organic compounds readily adsorb to solid particles during transport in wastewater or onto the suspended activated sludge during biological treatment. Although considered a major removal mechanism for VOCs in wastewater, adsorption losses are relatively small compared to the losses associated with volatilization and biodegradation. Furthermore, unlike other fate mechanisms, the sorption process is partially, and in many instances, completely reversible (60:291). At the low concentrations typically found in wastewater flows, the adsorption of VOCs can be modeled by the following equation (60:291):

$$R_s = -Q^w X K_p C_i \quad (25)$$

where:

$R_s$  = rate of VOC adsorption to solids or activated sludge biomass (mg/d)

$Q^w$  = wasted sludge flow rate ( $m^3/d$ )

$X$  = solid particles or biomass concentration ( $mg/m^3$ )

$K_p$  = liquid-solid partition coefficient ( $m^3/mg$ -solids)

$C_i$  = initial VOC concentration in wastewater ( $mg/m^3$ )

The liquid-solid partition coefficient,  $K_p$ , for a specific volatile organic is linearly proportional to its octanol-water partition coefficient ( $K_{ow}$ ).  $K_{ow}$  is the ratio of the volatile organic in (*n*)-octanol to its concentration in water at equilibrium. A high values for  $K_{ow}$  suggests that a VOC has a high affinity to adsorb to organic particles and biomass. In turn,  $K_{ow}$  can be used to calculate  $K_p$  (60:291-292):

$$K_p = 3.345 \times 10^{-7} K_{ow} \quad (26)$$

Because maximum adsorption losses are expected to occur within secondary biological treatment, Equations (25) and (26) are used primarily to calculate the losses for activated sludge systems.

**Process Specific Fate Models.** In addition to the general fate models already presented, there are several additional models which describe the removal of volatile organics from specific wastewater treatment processes.

**Volatilization across Drop Structures.** Typically used to calculate volatile organic emissions across weirs, this model has a form distinctly different from the other volatilization fate models discussed earlier. For weir drops, it is not possible to accurately measure the interfacial surface area (*A*) for the multitude of droplets formed as the wastewater falls over the weir. Similarly, the interfacial area for the entrained air bubbles in the drop structure's tailwaters cannot be readily determined (61: 331A). Therefore, Equation (14) cannot be used in estimating the emissions for these structures.

As a result, volatilization models for weirs are based on empirical equations which correlate the release of VOCs from the wastewater with a predicted oxygen reaeration coefficient,  $r_{o_2}$ , for clean water flowing over the same drop structure (65:114). Also referred to as the *deficit ratio*,  $r_{o_2}$  measures the ratio of the oxygen deficit in the water upstream of the weir to the oxygen deficit downstream of the weir. Because travel time from the wastewater surface immediately upstream to the surface immediately downstream is so short, oxygen uptake due to biological activity in the wastewater is negligible (65:114). Therefore, the oxygen deficit ratio, which represents the driving force for oxygen transfer for the wastewater, can be used to predict the potential emission of volatile organics out of the waste stream as it flows over the weir.

From several studies, it has been determined that  $r_{o_2}$  is dependent on the drop height and the discharge flow over the weir (58:101-102; 61:331A). Therefore,  $r_{o_2}$  can be calculated for a primary clarifier and a secondary clarifier, respectively, using the following equations (58:101-102):

$$\ln r_{o_2} = 0.042 Z^{0.872} q^{0.509} \quad (27)$$

and

$$\ln r_{o_2} = 0.077 Z^{0.623} q^{0.66} \quad (28)$$

where  $Z$  is the distance (m) between the upper and lower wastewater levels and  $q$  is the discharge flow rate per unit length of the weir ( $m^3/s\cdot m$ ).

For volatile organics in a weir waste stream, their driving force out of solution and into the ambient air is their individual gaseous concentrations in the wastewater itself. This force is called the *concentration ratio* ( $r_{voc}$ ) and is equal to the ratio of the VOC concentration in the wastewater immediately upstream from the weir ( $C_{1-voc}$ ) to the VOC concentration immediately downstream of the weir ( $C_{2-voc}$ ) (65:114). Using the estimated value for  $r_{O_2}$ ,  $r_{voc}$  can be calculated from the following equation (59:102; 60:293):

$$\ln r_{voc} = [(K_1 a)_{voc} / (K_1 a)_{O_2}] \ln r_{O_2} \quad (29)$$

where the product  $(K_1 a)_{voc}$  is the specific VOC mass transfer rate constant (1/d) and the product  $(K_1 a)_{O_2}$  is the oxygen mass transfer rate constant (1/d), or,

$$\ln r_{voc} = \alpha \Psi \ln r_{O_2} \quad (30)$$

where  $\alpha$  is the wastewater's matrix coefficient and  $\Psi$  is the coefficient of proportionality for the specific volatile organic compound.

The fraction of the specific volatile organic which is volatilized across the drop structure is given by the equation (58:102):

$$fraction\ emitted = 1 - (r_{voc})^{-1} \quad (31)$$

In turn, the emission estimate for a specific VOC is calculated from:

$$R_{v,d} = Q_w C_{1-voc} (fraction\ emitted) \quad (32)$$

where:

$R_{v,d}$  = the total compound volatilization across the drop structure (mg/d)

$Q_w$  = the wastewater flow rate over the weir (m<sup>3</sup>/d)

$C_{1-voc}$  = the concentration of the specific VOC in the wastewater immediately upstream of the weir (mg/m<sup>3</sup>)

$C_{2-voc}$  = the concentration of the specific VOC in the wastewater immediately downstream of the weir (mg/m<sup>3</sup>)

**Volatilization within Trickling Filters.** As wastewater drips down through a trickling filter, volatile organics can be potentially removed by volatilization, biodegradation, and to a much lesser extent, sorption (60:295). Typically, losses due to sorption can be assumed to be negligible. Similarly, there is little information available on the effectiveness of the biodegradation of volatile organics within these packed media systems. Therefore, for practical purposes, volatilization is considered to be the dominant VOC release mechanism (60:295). However, this is a particularly conservative assumption with respect to biodegradable volatile organics.

Trickling filters are typically classified as *counter-current* systems where the waste liquid and forced air are flowing through the filter in opposite directions. A simplified mass balance equating wastewater volatile organics loss to gaseous VOC gain leads to (60:295):

$$Q_w(C_{11} - C_{12}) = Q_g(C_{g1} - C_{g2}) \quad (33)$$

where:

$Q_w$  = the wastewater flow down through the trickling filter ( $m^3/s$ )

$Q_g$  = the forced air flow up through the trickling filter ( $m^3/s$ )

$C_1$  = the specific VOC concentration in the wastewater ( $mg/m^3$ )

$C_g$  = the specific VOC concentration in the forced air ( $mg/m^3$ )

and the subscripts 1 and 2 refer to the physical top and bottom of the trickling filter, respectively.

To further simplify Equation (33), it can be assumed that the inlet air being blown into the trickling filter has negligible VOC concentrations such that  $C_{g2}$  is approximately equal to zero. An additional assumption is that the volatile organics in the effluent gas are in equilibrium with the VOCs in the adjacent wastewater influent where  $C_{g1} = H_c C_{11}$ . Taking these two assumptions into consideration, Equation (33) will reduce to the following form (60:295):

$$Q_w (C_{11} - C_{12}) = Q_g H_c C_{11} \quad (34)$$

where:

$Q_w$  = the wastewater flow down through the trickling filter ( $m^3/s$ )

$Q_g$  = the forced air flow up through the trickling filter ( $m^3/s$ )

$C_1$  = the specific VOC concentration in the wastewater ( $mg/m^3$ )

$H_c$  = dimensionless Henry's law coefficient

Rearranging Equation (34) allows for the specific VOC concentration in the wastewater at the bottom of the trickling filter ( $C_{i2}$ ) to be calculated. Since volatilization is assumed to be the dominant volatile organic release mechanism, the resulting mass transfer via volatilization,  $R_{v,i}$ , is given from the equation (60:295):

$$R_{v,i} = Q_w(C_{i1} - C_{i2}) \quad (35)$$

where:

$R_{v,i}$  = total VOC volatilization through the trickling filter (mg/d)

$Q_w$  = the wastewater flow down through the trickling filter ( $m^3/s$ )

$C_{i1}$  = the specific VOC concentration in the wastewater at the top of the trickling filter ( $mg/m^3$ )

$C_{i2}$  = the specific VOC concentration in the wastewater at the bottom of the trickling filter ( $mg/m^3$ )

**Liquid VOC Concentration within a Wastewater Treatment Unit.** To calculate the potential emissions from a specific wastewater treatment process, Equation (12) can be modified to describe the mass balance of the volatile organics across the process unit (60:294):

$$Q_w C_i = Q_w C_{i,i} + R_v + R_b + R_s \quad (36)$$

where:

$Q_w$  = the wastewater flow through the process unit ( $m^3/d$ )

$C_i$  = the liquid VOC concentration within the wastewater ( $mg/m^3$ )

and

$C_{i,i}$  = the liquid VOC concentration in the process unit's influent (mg/m<sup>3</sup>)

$R_v$  = VOC mass transfer rate by volatilization (mg/d)

$R_b$  = VOC mass transfer rate by biodegradation (mg/d)

$R_s$  = VOC mass transfer rate by sorption (mg/d)

Using Equations (14) through (25), Equation (36) can be arranged to calculate for  $C_i$ , the liquid VOC concentration within the specific wastewater treatment process, which accounts for the combined effect of competing fate mechanisms (60:294):

$$C_i = C_{i,i} / \left[ 1 + (Q^w/Q_w) + [(6.3 \times 10^7 K_{ow} Q^w X)/Q_w] + [(k_f X_a V)/Q_w] + (k_{i,n} + k_{i,g})A/Q_w + \{1 - \exp[(-K \rho_o V/H_c Q_w)]\}/Q_w \right] \quad (37)$$

where:

$C_i$  = the liquid VOC concentration within the wastewater (mg/m<sup>3</sup>)

$C_{i,i}$  = the liquid VOC concentration in the process unit's influent (mg/m<sup>3</sup>)

$Q^w$  = the wasted sludge flow rate (m<sup>3</sup>/d)

$Q_w$  = the wastewater flow through the process unit (m<sup>3</sup>/d)

$K_{ow}$  = the ratio of the volatile organic in (*n*)-octanol to its concentration in water at equilibrium (m<sup>3</sup>/m<sup>3</sup>)

$X$  = the concentration of biomass within the process unit (mg/m<sup>3</sup>)

$k_i$  = maximum first-order biodegradation rate constant for the specific VOC (m<sup>3</sup>/mg-VSS·s)

$X_a$  = active microbial biomass concentration (mg-VSS/m<sup>3</sup>)

$V$  = process unit volume (m<sup>3</sup>)

and

$k_{l,n}$  = the liquid mass transfer coefficient via volatilization across open surface of the process unit (m/s)

$k_{l,s}$  = the liquid mass transfer coefficient via sorption (m/s)

$A$  = the total interfacial wastewater surface area within the process unit ( $m^2$ )

$K_a$  = oxygen mass transfer rate constant (1/h)

$H_c$  = dimensionless Henry's law coefficient for the specific VOC

$Q_g$  = the forced aeration rate for the process unit ( $m^3/s$ )

**Three Mechanism Model for Activated Sludge Reactor.** One of the most widely used general fate model is the three mechanism model developed by Namkung and Rittmann (57). This model depicts the simultaneous effect of three major release mechanisms (volatilization, biodegradation, and sorption) in removing volatile organics from within an activated sludge reactor. When all three mechanisms are considered, the concentration of a specific VOC ( $C_i$ ) within the reactor is given by (57:672-673; 58:6):

$$C_i = Q_w C_i / [Q_w + Q_g / RTK_H + (3.345 \times 10^7) Q_w X K_{ow} + k X_o V] \quad (38)$$

where:

$Q_w$  = the wastewater flow down through the trickling filter ( $m^3/d$ )

$C_i$  = VOC concentration in plant or process influent ( $mg/m^3$ )

$Q_g$  = the forced air flow up through the trickling filter ( $mg/m^3$ )

$R$  = gas law constant ( $8.206 \times 10^{-5} m^3 \cdot atm / K \cdot mole$ )

and

$T$  = absolute temperature (degrees K)

$K_H$  = Henry's law constant (mole/m<sup>3</sup>-atm)

$Q^w$  = wasted sludge flow rate (m<sup>3</sup>/d)

$X$  = solid particles or biomass concentration (g-VSS/m<sup>3</sup>)

$K_{ow}$  = the ratio of the volatile organic in (*n*)-octanol to its concentration in water at equilibrium (m<sup>3</sup>/m<sup>3</sup>)

$k$  = maximum first-order biodegradation rate constant for the specific VOC (m<sup>3</sup>/mg-VSS · s)

$X_a$  = active microbial biomass concentration (mg-VSS/m<sup>3</sup>)

$V$  = activated sludge reactor volume (m<sup>3</sup>)

The total loss of a specific volatile organic is then calculated from the equation:

$$Total\ loss = R_v + R_b + R_s \quad (39)$$

where:

$R_v$  = VOC mass transfer rate by volatilization (mg/d)

$R_b$  = VOC mass transfer rate by biodegradation (mg/d)

$R_s$  = VOC mass transfer rate by sorption (mg/d)

In turn,  $R_v$ ,  $R_b$ , and  $R_s$  are calculated from Equation (18), (24), and (25) respectively.

**Computer Based Fate Models.** Beginning in the late 1980's, several computer based fate models have been developed and fielded (4:41; 51; 61:332A-333A; 66:51).

Most of these models are based on the process specific general fate models previously discussed. Subsequently, the majority of these models simulate the VOC fate mechanisms associated with only one or possible two wastewater treatment processes. The specific differences between the individual models include (4:44; 61:3332A-333A):

1. The use of different measures to calculate variables such as biological degradation rate constants ( $k_b$ ) and mass transfer rate constants ( $K_L$ ).
2. The numbers and types of wastewater treatment processes which are simulated.
3. The number and types of volatile organic compounds for which the model is applicable.
4. The model's associated mass transfer assumptions, such as saturated versus unsaturated subsurface aeration.
5. The individual model's flexibility in terms of its ability to simulate a wide range of treatment process configurations.
6. The model's ability to be modified to reflect current, process specific operating conditions.

A summary of the major computer based models that are currently in use is contained in Appendix E.

### **VOC Emissions from Civilian WWTPs**

In 1990, over 24,100 civilian WWTPs nationwide treated an estimated 27 billion gallons per day of wastewater including 4.3 billion gallons per day of industrial discharges (16:4). Of these facilities, 127 plants handled 50 million gallons per day or more of wastewater with an additional 81 plants of equal capacity projected to go into operation over the next fifteen years (67:2). The presence of even trace concentrations of VOCs

entering these facilities poses a potential air quality issue. As a result, these wastewater treatment plants have the capability to be major sources of VOC emissions because of the large volumes of wastewater processed each day.

Since the early 1980's, several research projects have focused on quantifying VOC emissions from specific wastewater treatment plants and individual treatment processes (15; 16; 57; 62; 67; 68; 69; 70). Table 4 highlights the results from several major wastewater facilities in the U.S..

**TABLE 4.**  
**VOC EMISSIONS FROM SELECTED STUDIES OF MAJOR CIVILIAN WWTPs**

<u>Plant Type</u>	<u>Daily Flow (ltr/d)</u>	<u>Daily VOC Loading (ug/l)</u>	<u>Annual Emissions (TPY)</u>	<u>Estimation Method</u>
Calumet STP (Chicago)	8.5 x 10 <sup>8</sup>	87	1.0	3 Mechanism Model <sup>1</sup>
MSDGC <sup>2</sup>	4.7 x 10 <sup>9</sup>	256	7.2	3 Mechanism Model
Deer Island (Boston)	1.8 x 10 <sup>9</sup>	3500	98.0	2 Mechanism Model <sup>3</sup>
CMSD <sup>4</sup>	6.3 x 10 <sup>8</sup>	1500	See Note #5	Source Emissions
JWPCP <sup>6</sup> IWTP (L.A.)	1.4 x 10 <sup>9</sup>	393	101.5	Mass Balance
EBMUD <sup>7</sup> STP (L.A.)	3.1 x 10 <sup>8</sup>	NA	25.0	Mass Balance

**Notes:**

1. This model by Namkung and Rittman (1985) simulates the volatilization, adsorption, and biodegradation fate mechanisms.
2. Metropolitan Sanitary District of Greater Chicago.
3. This Model simulates the volatilization and biodegradation fate mechanisms.
4. Cincinnati Metropolitan Sewer District.
5. Total emissions were not available. Actual ambient concentrations of organics throughout the plant were measured.
6. Joint Water Pollution Control Plant of Los Angeles.
7. East Bay Municipal Utility Plant of Oakland, CA.

(15; 16; 57; 61; 62; 68; 69)

Collectively, these studies have shown that, although considerable variability in plant influent volatile organic concentrations were detected, most compounds were measured at concentrations close to the detection levels of the waste liquid sampling equipment. Subsequently, the estimated emissions for the receiving wastewater facilities were relatively small when compared to the emissions for other major sources in the same geographical location. Similarly, VOC emissions from wastewater treatment facilities typically comprised only a small fraction (< 1 percent) of the total organic emissions for the air quality region in which the facility was located.

**VOC Emissions at Air Force Wastewater Treatment Plants.** As of 1987, thirty-three Air Force sewage treatment plants nationwide were discharging a total of 37 million gallons of treated wastewater a day (71:59-61, 69-70). Similarly, another twenty-two industrial wastewater treatment plants were in operation on CONUS Air Force bases (71:62-63). Table 5 lists those USAF wastewater facilities which are located in ozone nonattainment areas.

It is important to note that both Edwards AFB and Hanscom AFB are located in ozone nonattainment areas; however, they did not respond to the 1987 Air Force wide facility inventory conducted by Renault in 1987 (71). Therefore, it is not known if these installations currently operate a wastewater treatment facility.

With respect to volatile organic air emissions, research efforts at Air Force wastewater treatment facilities have been limited to wastewater characterization studies to determine the VOC constituents in an individual plant's influent (74; 75; 76; 77; 78).

**TABLE 5.**  
**USAF WWTPs IN OZONE NONATTAINMENT AREAS**

<u>Base</u>	<u>Ozone Classification</u>	<u>Plant Type</u>	<u>Treatment Train</u>	<u>Avg Daily Flow (MGD)</u>
Beale	(see note)	STP	Primary clarifier, trickling filter with secondary clarifier, chlorination	1.0-1.9
Bolling	Serious	IWTP	Batch processing	NA*
Hill	Moderate	IWTP	Pretreatment facility	NA
Luke	Moderate	STP	Primary clarifier, trickling filter with secondary clarifier, chlorination	1.0-1.9
Macdill	Marginal	STP	Activated sludge	NA
March	(See note)	STP	Trickling filter	1.0-1.9
McClellan	Serious	STP	Trickling filter	NA
		IWTP	Batch processing plant	NA
McGuire	Severe	STP	Primary clarifier, trickling filter, sand filter, chlorination, dechlorination	NA
Scott	Moderate	STP	Primary clarifier, trickling filter with secondary clarifier, sand filter, chlorination, dechlorination	1.0-1.9
		IWTP	Sludge reduction	NA

**Note:** This base is located in an ozone nonattainment area designated under the State of California Ambient Air Quality Standards. To date, California has not classified its ozone nonattainment areas by pollution severity.

\* - Not available

(71:59-70; 72:63-91; 73)

These studies have shown that, unlike civilian wastewater facilities, Air Force sewage treatment plants receive a relatively smaller variety of volatile organic species in typically

trace concentrations. From the cited studies, only 5 percent of all sample tests showed an individual volatile organic at a concentration above 1 ug/l while only three VOCs were found at concentrations greater than 1 ug/l at least 50 percent of the time. Similar wastewater characterization studies for Air Force industrial wastewater treatment plants have not been published for public review. In turn, a comprehensive study has yet to have been conducted to estimate the potential volatile organic emissions from the facilities listed in Table 5 (2; 10; 11; 12; 79)

### **Analysis and Summary**

Overall, the level of understanding concerning VOC emissions from WWTPs has progressed dramatically over the last ten years. Several distinct factors have contributed to these advancements in the *state of the art centered on this issue*. First, additional research in atmospheric chemistry has clearly established the critical role of VOCs in the formation of ozone within the troposphere. Next, the United States continued to experience a worsening of air quality with respect to ozone pollution during the 1980's. Similarly, the EPA suffered repeated failures under the CAA to reverse this trend. Finally, with the passage of the 1990 CAAA, a revised national air quality strategy was established which recognized the need for improved emission controls, particularly for small source facilities (< 100 TPY). As a result, the identification, reduction, and prevention of VOC emissions from these facilities has become a major ARM issue within the civilian environmental management arena. In turn, expanded research within the private sector

has generated extensive information and data related to the fate and emission of VOCs during municipal and industrial wastewater treatment.

From the literature review, it is apparent that this issue has not yet enjoyed the same level of attention within the Air Force. Traditional compliance efforts at Air Force wastewater treatment facilities have focused solely on water quality initiatives. Although recognized as a potential ARM problem, no published research has been generated by the Air Force which determines the potential problems associated with VOC emissions from these facilities. Such an effort is still required especially at the eleven installations which currently operate a wastewater plant within an ozone nonattainment area. At these bases, the increasingly stringent air quality standards of the 1990 CAAA could have a significant impact on the future operation of their wastewater treatment facilities. Therefore, this research effort will attempt to quantify and characterize the potential volatile organic emissions from these Air Force wastewater plants. It will then determine the possible operational impact on the future operation of these facilities with respect to ozone nonattainment under Title I of the 1990 CAAA.

### **III. Methodology**

The focus of this thesis was to estimate the potential volatile organic emissions from selected Air Force wastewater facilities and to determine the possible impact of these emissions with regards to ozone nonattainment. This research has recognized that there are highly refined methods, such as computer based simulation models and direct or indirect source sampling, which exist to estimate and measure volatile organic emissions from a wastewater treatment facility. However, from the civilian studies examined during the literature review, it has been suggested that these facilities may not be significant sources of ozone precursors as originally anticipated. Therefore, this thesis employed a conservative, worst case approach using mass balancing and empirical general fate models to formulate representative emission estimates for those Air Force wastewater treatment plants which currently operate within an ozone nonattainment areas.

#### **Data Requirements**

Specific data required in support of the selected evaluation methodology included:

1. An updated inventory of Air Force wastewater treatment plants located in ozone nonattainment areas. Information should include the plant's location, a description of its major wastewater treatment processes, specific operational and design characteristics of the plant, and its average daily flow.
2. Wastewater characterization data for these facilities which identified the species and concentration levels of individual volatile organics in the plant's influent and effluent.
3. Calculated estimates of the potential VOC emissions from these facilities.

4. Additional state level statutory requirements which may govern ozone nonattainment and the control of wastewater facility volatile organic emissions with respect to Title I of the CAAA.

### **Data Collection Plan**

A number of different methodologies were used in collecting the necessary data for the selected evaluation. Because of the fundamental approach of this research effort, sufficient information was required only to make a positive or negative determination concerning the issue under evaluation. In turn, the necessary data collection methodologies were relatively straightforward. Specific methods used in this study included:

1. Conducting formal facility surveys to collect detailed information relative to the design and current operation of the Air Force wastewater treatment facilities located in ozone nonattainment areas.
2. Collecting existing wastewater quality data from the individual Air Force plants. Extrapolating suitable data from other published Air Force wastewater characterization studies, if plant specific data is not available.
3. Calculating representative volatile organic emission estimations using both general fate models and mass balancing. Selected general fate mathematical models simulated the release of VOCs from the specific treatment processes employed at individual Air Force wastewater plants.
4. Conducting an additional legislative review and survey to determine any additional state level requirements with respect to ozone nonattainment and volatile organic emission from wastewater treatment facilities.

The data collection plan began with a telephone survey of the candidate installations previously identified in Table 5 of the literature review. Information was collected on the

operational characteristics of the individual base wastewater plants and on the availability of source specific wastewater quality data. The specific base survey questions are listed in Appendix D.

From this initial survey, a comprehensive inventory was compiled of all Air Force wastewater facilities which currently operate within an ozone nonattainment area. Similarly, available source specific wastewater quality data was collected. To determine the suitability of existing Air Force wastewater characterization data, two specific decision criteria were used. First, the data was to be dated no later than 1990. This date was selected to ensure the data most closely represented the current operating conditions at the respective Air Force plant. Next, it was necessary that the data identified specific concentrations of individual volatile organic species in the plant's influent and effluent. Data speciation was required to make a follow on *determination of the relative reactivity* and overall contribution of the individual volatile organic emissions to regional ozone formation.

#### **Data Evaluation Plan**

The overall data evaluation plan involved a two phase effort which began with the selection of a number of representative facilities from the updated inventory of Air Force wastewater treatment plants in ozone nonattainment areas. Two specific criteria were used in choosing the representative facilities. First, it was desired that each major type of sewage or industrial wastewater treatment plant (trickling filter, activated sludge,

evaporation ponds) be included in the study. This was necessary to ensure a cross sectional evaluation of this particular Air Force facility inventory.

Next, the individual ozone nonattainment classifications associated with each wastewater facility were used to distinguish between facilities within a specific plant type. With respects to the worst case analysis, a facility located in a region with a worse nonattainment classification was selected over a similar type facility operating in an area with a lesser degree of ozone nonattainment. By focusing on those Air Force facilities located within our nation's worst ozone nonattainment areas, the impact of their potential VOC emissions were subsequently evaluated with respect to the most stringent ozone nonattainment requirements under the CAA.

Likewise, the primary mission of the plant's host installation (fighter wing, administrative, logistics center) and the total base worker population serviced by the plant (military and civilian) were also used as alternate comparison criteria. Bases with operational (flying) missions and larger populations were favored under the worst case approach over smaller installations with support or administrative functions. It was assumed that the wastewater flows at larger, operational installations typically contain higher volatile organic concentrations since the majority of VOC discharges into a base wastewater treatment system originate from aircraft maintenance and flightline operations.

Once the representative wastewater facilities were selected, two separate emissions estimates were calculated for each plant using both mass balancing and the appropriate general fate models. Emissions were estimated for the major treatment processes at each representative facility to include primary clarifiers, trickling filters, oxidation ponds,

activated sludge reactors, and secondary clarifiers. Using the individual process fate models as building blocks, a combined simulation model was developed and applied for each of the treatment trains being evaluated.

It was expected that the emission estimates would be calculated for each representative facility using source specific wastewater characterization data. However, if plant specific data was not available, suitable data was extrapolated from another Air Force wastewater plant which serviced an installation with similar military mission and total worker population.

Subsequently, the two conservative emission estimates (combined fate models and mass balancing) were used as the basis for a qualitative analysis of the possible impact of these potential facility emissions. First, it was determined, based on maximum emission estimates, if each facility qualified as major stationary source IAW both Title I of the CAAA and their respective state implementation plan (SIP). If so, then specific operational and administrative requirements were identified and their potential impact on future plant operations were evaluated.

Next, a discussion was developed concerning the relative organic reactivity of the individual volatile compounds being emitted and their overall contribution to ozone production within the plant's respective nonattainment area.

A relative comparison was then made between the maximum volatile organic emission estimate for each representative WWTP and the total VOC emissions for its respective host installation. The purpose of this evaluation was to establish the relative importance of these particular source emissions within the context of an installation air emissions

control strategy. Finally, general conclusions were drawn concerning the future significance of these particular facility emissions relevant to the overall Air Force ARM program.

### **Assumptions and Limitations**

The selected data evaluation plan was based on facility emission estimates calculated from conservative mathematical simulation models and simplified mass balancing. To support this worst case approach, four key assumptions were made:

1. In using general fate modeling, volatilization and biodegradation were assumed to be the only removal mechanisms for all VOCs entering each representative wastewater treatment plant.
2. Steady state conditions within the individual plant wastewater flows were also assumed such that influent concentrations into each representative facility were considered constant over time. Similarly, uniform concentrations of the volatile organics within a plant or specific treatment process wastewater stream were assumed to exist. Consequently, spike or slug loadings and varying liquid VOC concentration gradients within a waste stream were not accounted for in the GFMs.
3. For the mass balance calculations, an overall evaporation rate of 100 percent was assumed such that all volatile compounds lost during the wastewater treatment process were due to direct volatilization into the ambient atmosphere.
4. Wastewater characterization data extrapolated from alternative Air Force wastewater treatment plants was an accurate representation of the quality of wastewater entering the respective representative facility. In turn, the calculated facility emission estimates were representative of the emissions most likely to be released from the plant.

Similarly a number of distinct limitations to the selected evaluation methodology served to increase the conservative nature of the research results. Specific limitations to the research plan included:

1. Volatile organic mass losses due to volatilization and biodegradation were calculated using GFMs for major wastewater treatment processes (primary clarifiers, trickling filters, oxidation ponds, activated sludge reactors, and secondary clarifiers). Losses occurring across preliminary and tertiary treatment processes as well as conveyances were not accounted for.
2. Additional removal mechanisms such as adsorption, absorption, and chemical oxidation were taken into account by the general fate models. Since these mechanisms play a recognized role in the fate of specific types of volatile organics during wastewater treatment, actual facility emissions of these compounds will be reduced by their action.
3. The steady state assumption of the general fate models may not accurately reflect the actual volatile organic loading conditions at the individual plants. Possible slug discharges which may actually occur are not accounted for by these models. The same reasoning holds true for the assumption of uniform concentrations throughout the passing wastewater streams. Spikes in volatile organic loadings and the existence of volatile organic concentration gradients within the wastewater may effect the overall VOC emissions for the respective treatment facility.
4. The calculated mass balance emission estimates may have been influenced by influent concentrations and flow rates. Spikes in incoming organic concentrations and variations in influent flow may have occurred during the collection of the wastewater data which was used in the emission estimation calculations. As a result, both the wastewater data and the calculated emissions may not reflect normal operating conditions of the respective wastewater plant.

## IV. Findings and Analysis

### Results from the Data Collection

Data collection began with a survey of the candidate wastewater plants identified in Table 5. The purpose to validate the initial facility inventory taken from Renaud and Ford (71; 72). The updated wastewater treatment plant inventory is presented in Table 6.

TABLE 6.  
CURRENT INVENTORY OF  
USAF WWTPs IN OZONE NONATTAINMENT AREAS

<u>Base</u>	<u>Nonattainment Classification</u>	<u>Plant Type</u>	<u>Treatment Train</u>	<u>Avg Daily Flow (MGD)</u>
Beale	NA	STP	Primary clarifier, trickling filter with secondary clarifier, chlorination	0.5
Edwards	NA	STP	Primary clarifier, evaporation ponds	1.75
Luke	Moderate	STP	Aerated grit chamber, primary clarifier, activated sludge reactor, tertiary sand filter, UV disinfection	0.4
Macdill	Marginal	STP	Primary clarifier, activated sludge with secondary clarifier, tertiary sand filter, chlorination	0.5
McGuire	Severe	STP	Primary clarifier, trickling filter with secondary clarifier, sand filter, chlorination, dechlorination	1.25
March	NA	STP	Primary clarifier, trickling filter, chlorination, aeration ponds	0.75
McClellan	Severe	IWTP	Primary screening, equalization basin, chromium reduction, aeration tank, secondary clarifier, chlorination	0.5
Scott	Moderate	STP	Primary clarifier, trickling filter with secondary clarifier, sand filter, chlorination and dechlorination	1.5

Existing wastewater characterization data was also compiled from the initial telephone survey. Routine testing for volatile organics in a plant's wastewater flow is not a standard operating procedure for most Air Force wastewater facilities. Instead, detailed wastewater characterization studies are accomplished as requested through the Armstrong Laboratory at Brooks AFB. As a result, only two plants, Edwards AFB and McClellan AFB, had suitable wastewater quality data which satisfied the selection criteria identified in Chapter III. This data is tabulated in Tables 7 and 8.

TABLE 7.

EDWARDS AFB SEWAGE TREATMENT PLANT  
WASTEWATER CHARACTERIZATION DATA

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Plant Type	Facultative Lagoons	
Avg Daily Flow	6,493,000 ltr/day	
	Mean VOC Conc. (ug/l)	
<u>Compound</u>	<u>Influent</u>	<u>Effluent*</u>
1,4-Dichlorobenzene	9.0	< 0.5
1,1,1-Trichloroethane	3.5	< 0.5
Toluene	1.9	< 0.3
p-Xylene	1.3	< 0.5
o-Xylene	0.7	< 0.3
Total	16.4	-----

\* - Effluent VOC concentrations were below minimum detection limits.

(74)

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TABLE 8.

McCLELLAN AFB INDUSTRIAL WASTEWATER PLANT  
WASTEWATER CHARACTERIZATION DATA

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Plant Type	Activated Sludge	
Avg Daily Flow	1,855,000 ltr/day	
	Mean Influent Conc. (ug/l)	
<u>Compound</u>	<u>Influent</u>	<u>Effluent*</u>
Methylene Chloride	82.0	< 10
Total Xylenes	8.0	< 5
Acetone	168.0	< 10
Total	258.0	-----

\* - Effluent VOC concentrations were below minimum detection limits.

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(80)

To calculate a worst case emission estimate, the effluent volatile organic concentrations for both the Edwards AFB sewage treatment plant and the McClellan industrial wastewater treatment plant were assumed to be zero for the follow-on mass balance analysis.

In lieu of having source specific data for each plant listed in Table 6, a second survey was conducted to identify additional wastewater quality data from other Air Force wastewater plants. It was intended that representative samples would be extrapolated from this data for use in evaluating those facilities which did not have available their own wastewater data. A number of other Air Force plants had current, speciated data on-hand for this purpose (75; 76; 77; 78).

Next, a set of *representative facilities* were selected from the wastewater plants listed in Table 6 based on the selection criteria presented earlier in Chapter III. The intent was to focus the research evaluation on each major plant type (evaporation ponds, trickling filters, activated sludge) under the most stringent ozone nonattainment conditions. In turn, a total of four facilities were chosen--Edwards AFB, Luke AFB, McGuire AFB, and McClellan AFB--for the follow-on analysis.

Edwards AFB was identified as the representative evaporation ponds plant. Luke AFB was chosen over Macdill AFB as the representative activated sludge plant since Luke AFB was located in a worse ozone nonattainment region (moderate versus marginal) and had an operational base mission (two fighter wings versus administrative). Similarly, McGuire AFB was selected as the representative trickling filter sewage treatment plant over Scott AFB. The two plants handled similar flows and supported bases of same relative size and mission (strategic airlift). However, McGuire was located in a severe ozone nonattainment area while Scott AFB was located in a moderate zone. Finally, since McClellan AFB operated the only industrial wastewater treatment plant within an ozone nonattainment area, it was the logical choice as the sole IWTP amongst the representative facilities.

Having selected the representative facilities, it was further determined that suitable wastewater characterization data was needed for two of the plants--McGuire AFB and Luke AFB. Using the criteria identified in Chapter III, alternate data from other Air Force wastewater was evaluated. In turn, representative data for McGuire AFB was taken from McChord AFB. Both installations have the same mission (strategic airlift) and supported

industrial complex although McChord's base population was smaller than McGuire's (8600 versus 12000) (81:107, 125). However, it was assumed that any changes in wastewater constituency because of differences in population were negligible given that each installation performed the same primary mission. Representative wastewater data for McGuire AFB is listed in Table 9.

TABLE 9.  
McGUIRE AFB SEWAGE TREATMENT PLANT  
REPRESENTATIVE WASTEWATER CHARACTERIZATION DATA

Plant Type Avg Daily Flow	Trickling Filter 4637500 ltrs/day	
	Mean Influent Conc. (ug/l)	
<u>Compound</u>	<u>Influent</u>	<u>Effluent*</u>
Benzene	4.82	NA
Chlorobenzene	1.10	NA
Chloroform	5.06	NA
Ethyl Benzene	7.04	NA
Methylene Chloride	11.95	NA
Toluene	6.82	NA
1,1,1-Trichloroethane	1.04	NA
Trichloroethylene	1.34	NA
Total	39.17	----

\* - Effluent concentrations were not available.

(76)

It was important to highlight that the representative effluent VOC concentrations for McGuire AFB were not available from McChord AFB. Therefore, in estimating the worst

case facility emissions for the McGuire AFB sewage treatment plant, these compound concentrations were assumed to be zero.

For Luke AFB, wastewater data from Holloman AFB was chosen for the follow-on analysis. Both bases support the same mission (tactical fighter wings) and have relatively the same populations (8500 versus 9500) (81:9, 110). The representative data for Luke AB is listed in Table 10.

TABLE 10.  
LUKE AFB SEWAGE TREATMENT PLANT  
REPRESENTATIVE WASTEWATER CHARACTERIZATION DATA

Plant Type	Trickling Filter	
Avg Daily Flow	1484000 ltrs/day	
	Mean Influent Conc. (ug/l)	
<u>Compound</u>	<u>Influent</u>	<u>Effluent*</u>
Benzene	56.1	< 0.5
Bromodichloromethane	2.7	< 0.4
Chlorobenzene	1.0	< 0.6
1,4-Dichlorobenzene	1.7	< 0.3
1,2-Dichloroethene	1.0	< 0.4
Ethyl Benzene	48.0	< 0.3
Methylene Chloride	4.1	< 0.4
Toluene	99.0	< 0.3
Totals	214.8	-----

\* - Effluent concentrations were below minimum detection limits.

(77)

Again, since the representative effluent VOC concentrations for Luke AFB were below the minimum detection limits, they were assumed to be zero for the subsequent mass balancing calculations.

### **Results from the Estimated Emissions Calculations**

Based on available wastewater quality data, two separate volatile organic emissions estimates were made for each representative Air Force wastewater facility using the mass balance equations and general fate models reviewed in Chapter III. Discussion of the analysis of individual facilities is presented below.

**Mass Balancing.** The first emission estimate was calculated using the mass balance approach described in Equation (13). Using this method, it was assumed that 100 percent of VOC removal during treatment at the representative Air Force plants was attributed to volatilization. From Equation (13), the total volatile organic emissions were calculated as the difference between mass loadings in and out of the representative facilities. Detailed mass balance calculations are contained in Appendix F with the individual plant estimates listed in Table 12.

**General Fate Modeling.** Using the appropriate general fate models presented in Equations (14) through (37) as building blocks, combined fate models were developed to simulate the volatile organic emissions from the major treatment processes employed at each of the representative Air Force wastewater facilities. Using the Luke AFB sewage treatment plant as an example, the major wastewater treatment processes which were modeled included an aerated grit chamber, a primary clarifier, and an activated sludge

reactor with mechanical surface aeration. Using the representative influent volatile organic concentrations from Table 10, the estimated emissions from the aerated grit chamber,  $R_{v,b}$ , were first calculated from Equation (21):

$$R_{v,b} = -Q_g C_{l,i} H_c \quad (21)$$

where:

$R_{v,b}$  = volatilization via subsurface aeration (air stripping) (mg/d)

$Q_g$  = the forced aeration rate for the grit chamber ( $m^3/s$ )

$C_{l,i}$  = the initial liquid VOC concentration in the grit chamber influent ( $mg/m^3$ )

$H_c$  = Henry's law coefficient for the specific VOC (dimensionless)

The individual concentrations of the volatile organics leaving the aerated grit chamber were calculated using a modified version of Equation (37) which accounted only for the volatilization of the organics as they passed through the grit chamber (sorption and biodegradation losses assumed to be negligible):

$$C_l = C_{l,i} / (1 + (H_c Q_g / Q_w)) \quad (37)$$

where:

$C_l$  = the liquid VOC concentration leaving the aerated grit chamber ( $mg/m^3$ )

$C_{l,i}$  = the liquid VOC concentration in the grit chamber influent ( $mg/m^3$ )

$H_c$  = dimensionless Henry's law coefficient for the specific VOC

$Q_g$  = the forced aeration rate for the grit chamber ( $m^3/s$ )

and

$Q_w$  = the wastewater flow through the grit chamber ( $m^3/d$ )

In turn, the compound concentrations coming out of the grit chamber were used as the influent VOC concentrations feeding into the primary clarifiers. For this treatment unit, two separate emissions estimates were calculated. First, the amount of volatile organics which evaporated across the wastewater surface within the clarifier,  $R_{v,n}$ , was calculated using Equation (19):

$$R_{v,n} = -k_{l,voc}AC_l \quad (19)$$

where:

$R_{v,n}$  = volatilization across open clarifier surface ( $mg/d$ )

$k_{l,voc}$  = liquid phase mass transfer coefficient for the specific VOC ( $m/s$ )

$A$  = total clarifier surface area available for VOC transfer ( $m^2$ )

$C_l$  = the liquid concentration of the specific VOC in the clarifier wastewater stream ( $mg/m^3$ )

The liquid phase mass transfer coefficients for the individual VOCs,  $k_{l,voc}$ , were calculated from Equation (16):

$$k_{l,voc} = [2.605 \times 10^{-9} (F/D) + 1.277 \times 10^{-7}] \times (U^2) \times (D_w / D_{ether})^{0.666} \quad (16)$$

where:

$F$  = the distance across the surface of the clarifier ( $m$ )

$D$  = the depth of the clarifier ( $m$ )

and

$U$  = the average wind speed 10 m above the clarifier surface ( $m^2/s$ )

$D_w$  = the diffusivity of the specific VOC in water ( $cm^2/s$ )

$D_{other}$  = the diffusivity of ether in water ( $cm^2/s$ )

The liquid concentration of the VOCs,  $C_l$ , in the clarifier wastewater stream were calculated from a modified Equation (37) which accounted for volatilization and biodegradation fate mechanisms within the primary clarifier:

$$C_l = C_{l_i} / [1 + [(k_1 X_a V)/Q_w] + [k_{1n} A/Q_w]] \quad (32)$$

where:

$C_l$  = the liquid VOC concentration within the clarifier wastewater ( $mg/m^3$ )

$C_{l_i}$  = the liquid VOC concentration in the clarifier influent from the aerated grit chamber ( $mg/m^3$ )

$k_1$  = maximum first-order biodegradation rate constant for the specific VOC ( $m^3/mg-VSS \cdot s$ )

$X_a$  = active microbial biomass concentration within the clarifier ( $mg-VSS/m^3$ )

$V$  = the clarifier volume ( $m^3$ )

$Q_w$  = the wastewater flow through the clarifier ( $m^3/d$ )

$k_{1n}$  = the liquid mass transfer coefficient via volatilization across open surface of the clarifier ( $m/s$ )

$A$  = the total clarifier surface area available for VOC transfer ( $m^2$ )

Next, a second emission estimate for the primary clarifier was made for the volatilization of organics as the wastewater passed over the clarifier weir ( $R_{v,w}$ ). Using  $C_1$  from the proceeding emission estimate as the individual influent VOC concentrations reaching the weir ( $C_{1-voc}$ ),  $R_{v,w}$  was calculated from Equation (32):

$$R_{v,w} = Q_w (C_{1-voc} - C_{2-voc}) \quad (32)$$

where:

$R_{v,w}$  = the total compound volatilization across the clarifier weir (mg/d)

$Q_w$  = the wastewater flow rate over the weir (m<sup>3</sup>/d)

$C_{1-voc}$  = the concentration of the specific VOC in the wastewater immediately upstream of the weir (mg/m<sup>3</sup>)

$C_{2-voc}$  = the concentration of the specific VOC in the wastewater immediately downstream of the weir (mg/m<sup>3</sup>)

In turn,  $C_{2-voc}$  was calculated from the equation:

$$C_{2-voc} = C_{1-voc} / r_{voc} \quad (40)$$

where  $r_{voc}$  is the specific volatile organic compound concentration ratio from Equations (27) and (30):

$$\ln r_{o_2} = 0.042 Z^{0.872} q^{0.509} \quad (27)$$

and

$$\ln r_{voc} = 0,1, \ln r_{o_2} \quad (30)$$

where:

$Z$  = the weir drop height (m)

$q$  = the discharge flow rate per unit length of the weir ( $m^3/s\cdot m$ )

$\alpha$  = the wastewater's matrix coefficient

$\gamma$  = the coefficient of proportionality for the specific volatile organic compound.

For the activated sludge reactor, Equation (19) was used to calculate the estimated process unit emissions:

$$R_{v, n} = -k_{l, voc} A C_l \quad (19)$$

where:

$R_{v, n}$  = volatilization across open activated sludge reactor surface (mg/d)

$k_{l, voc}$  = liquid phase mass transfer coefficient for the specific VOC (m/s)

$A$  = total interfacial surface area available for VOC transfer ( $m^2$ )

$C_l$  = the liquid concentration of the specific VOC in the reactor wastewater stream ( $mg/m^3$ )

Because, the reactor used mechanical surface aeration, the individual liquid phase mass transfer coefficients for the VOCs were calculated using Equations (20) and (17):

$$k_{l, O_2} = N_e P / 3600 A C^* \quad (20)$$

and

$$k_{l, voc} = \gamma k_{l, O_2} \quad (17)$$

where:

$k_{l,O_2}$  = the liquid phase mass transfer coefficient for oxygen (m/s)

$N_c$  = the oxygen transfer rate for the mechanical aerator ( $\text{kg}_{O_2} / \text{KWH}$ )

$P$  = the brake power of the mechanical aerator (KW)

$A$  = total reactor surface area available for VOC transfer ( $\text{m}^2$ )

$C^*$  = the oxygen saturation concentration for a specific atmospheric temperature and barometric pressure ( $\text{kg}_{O_2} / \text{m}^3$ )

$\bar{y}?$  = the coefficient of proportionality for the specific VOC

The liquid concentrations of the individual VOCs in the reactor wastewater stream,  $C_l$ , were calculated using the values for  $C_{2-voc}$  from the clarifier weir in a reduced form of Equation (37) which accounted for volatilization and biodegradation of the organics within the reactor:

$$C_l = C_{2-voc} / 1 + [(k_r X_a V) / Q_w] + [k_{1n} A / Q_w] \quad (37)$$

where:

$C_l$  = the liquid VOC concentration within the reactor wastewater stream ( $\text{mg}/\text{m}^3$ )

$C_{2-voc}$  = the liquid VOC concentration in the reactor influent ( $\text{mg}/\text{m}^3$ )

$k_1$  = maximum first-order biodegradation rate constant for the specific VOC ( $\text{m}^3/\text{mg-VSS} \cdot \text{s}$ )

$X_a$  = active microbial biomass concentration in the reactor ( $\text{mg-VSS}/\text{m}^3$ )

$V$  = activated sludge reactor volume ( $\text{m}^3$ )

$Q_w$  = the wastewater flow through the process unit ( $\text{m}^3/\text{d}$ )

and

$k_{l,n}$  = the liquid mass transfer coefficient via volatilization across open surface of the reactor (m/s)

$A$  = the total reactor surface area available for VOC transfer (m<sup>2</sup>)

Finally, a total facility volatile organic emission estimate was calculated using the following equation:

$$\text{Total emissions} = [(R_{v,b})_{\text{Grit Chamber}} + (R_{v,n} + R_{v,w})_{\text{Primary Clarifier}} + (R_{v,n})_{\text{AS Reactor}}] \quad (41)$$

Table 11 contains a summary of the major wastewater treatment processes at the individual representative Air Force facilities and the associated general fate models which were used to simulate their organic emissions.

#### **Analysis with Respect to Ozone Nonattainment under the CAA**

A qualitative analysis of the potential impact of the estimated facility VOC emissions was first conducted with respect to ozone nonattainment. A determination was made whether the selected representative facilities qualified as major stationary sources of volatile organic emissions under Title I of the 1990 CAAA. Using the maximum emission estimate from Table 12, each representative facility was compared against the source classification requirements which corresponded to the plant's regional ozone nonattainment category. The results of this evaluation are contained in Table 13.

TABLE 11.

SELECTED GENERAL FATE MODELS WHICH SIMULATE THE  
 MAJOR TREATMENT PROCESSES AT THE  
 REPRESENTATIVE AIR FORCE WASTEWATER TREATMENT FACILITIES

<u>Treatment Process</u>	<u>Treatment Facility</u>			
	<u>Edwards AFB</u>	<u>Luke AFB</u>	<u>McGuire AFB</u>	<u>McClellan AFB</u>
<b>1. <u>Primary Treatment</u></b>				
Grit Chamber		Eq 21		
Primary Clarifier				
Surface	Eqs 16,19,37	Eqs 16,19,37	Eqs 16,19,37	
Weir	Eqs 27,30,32	Eqs 27,30,32	Eqs 27,30,32	
<b>2. <u>Chemical Treatment</u></b>				
Equalization Basin				Eqs 16,19,37
<b>3. <u>Secondary Treatment</u></b>				
Evaporation Ponds	Eqs 16,19,37			
Activated Sludge		Eqs 17,19,20,37		Eqs 17,19,20,37
Trickling Filter			Eqs 35,37	
Secondary Clarifier				
Surface			Eqs 16,19,37	Eqs 16,19,37
Weir			Eqs 28,30,32	Eqs 28,30,32

From this comparison, none of the four representative facilities qualified as a major stationary source of VOC emissions with respect to the existing CAA. Given the worst case approach employed in this research, it is suggested that the remaining four wastewater treatment plants (Beale AFB, Macdill AFB, March AFB, and Scott AFB) will also not qualify.

**TABLE 12.**  
**EMISSION ESTIMATES FOR**  
**REPRESENTATIVE AIR FORCE WASTEWATER TREATMENT FACILITIES**

<u>WWTP</u>	<u>Estimated Emissions (lbs/yr)</u>	
	<u>Mass Balancing</u>	<u>Combined Fate Models</u>
Edwards AFB STP	85.6	28.1
Luke AFB STP	255.8	111.5
McGuire AFB STP	146.0	10.0
McClellan AFB IWTP	384.8	87.9

From the literature review, it was determined that ozone nonattainment initiatives under the 1990 CAAA have been targeted specifically at major stationary sources of volatile organic emissions. Consequently, since no Air Force wastewater facility meets this requirement, as a group, they are not subject to any federal operational or administrative mandates promulgated under Title I of these amendments.

The ozone nonattainment analysis was extended to include the respective CAA state implementation plans which govern the representative Air Force wastewater treatment facilities. The individual SIPs for California, Arizona, and New Jersey were examined to identify additional state requirements relative to ozone nonattainment which may apply to these facilities. From this review, it was determined that Arizona has not adopted any additional ozone nonattainment requirements beyond those contained in the current federal regulations (73). However, the state ozone nonattainment programs for both California

and New Jersey have mandated the identification and review of any stationary source with measured emissions or potential emissions > 10 TPY of volatile organics (73; 82; 83). Again, none of the three representative facilities located in these states satisfied this requirement based on their maximum calculated emission estimates. Therefore, with respect to ozone nonattainment, no additional state level air quality mandates currently impact the continued operation of these Air Force facilities.

TABLE 13.  
MAJOR STATIONARY SOURCE DETERMINATION FOR  
REPRESENTATIVE USAF WASTEWATER TREATMENT PLANTS

<u>Base</u>	<u>Ozone Nonattainment Category</u>	<u>Minimum Req'd Source Size (TPY)</u>	<u>Maximum Estimated VOC Emissions (TPY)</u>	<u>Does WWTP Qualify?</u>
Edwards AFB	Extreme	> 10	0.04	No
Luke AFB	Moderate	> 100	0.13	No
McGuire AFB	Severe	> 25	0.07	No
McClellan AFB	Severe	> 25	0.19	No

**Analysis with Respect to Ozone Formation.**

A total of fourteen individual volatile organic compounds were detected in the wastewater influents of the representative Air Force wastewater treatment facilities. As presented earlier in Chapter II, the relative reactivity of these compounds with respect to tropospheric ozone formation was of specific interest to this research effort. In general

terms, the ozone production potential of a specific volatile organic is a function of its reactivity and the quantity of the compound which is emitted given that all other environmental conditions are equal (sunlight, wind, availability of OH and NO<sub>x</sub>). Table 14 presents the general reactivity classifications and the maximum total estimated emissions for each of the measured volatile organic compounds.

**TABLE 14.**  
**RELATIVE OH REACTIVITY CLASSIFICATIONS**  
**OF THE POTENTIAL VOLATILE ORGANIC COMPOUNDS**  
**EMITTED FROM THE REPRESENTATIVE AIR FORCE WWTPs**

<u>OH Reactivity Class and Compound</u>	<u>Maximum Emissions (lbs/yr)</u>				
	<u>Edwards</u>	<u>Luke</u>	<u>McGuire</u>	<u>McClellan</u>	<u>Total</u>
<u>Highly Reactive</u>					
1,4-Dichlorobenzene	47.0	2.0			49.0
1,1,1-Trichloroethane	18.3		3.9		22.2
<i>o</i> -Xylene	3.7			11.9	15.6
<i>p</i> -Xylene	6.8				6.8
<u>Moderately Reactive</u>					
Methyl Chloride		4.9	44.6	122.3	171.8
Toluene	9.9	118.2	25.4		153.5
Ethyl Benzene		58.2	26.3		84.5
Chloroform			18.9		18.9
Chlorobenzene		1.2	4.1		5.3
Trichloroethylene			5.0		5.0
Bromodichloromethane		3.2			3.2
1,2-Dichloroethane		1.2			1.2
<u>Nonreactive</u>					
Acetone				250.6	250.6
Benzene		66.9	18.0		85.9

(43:694; 44:888-890; 45:910-912)

Based on recent OH-VOC reactivity studies, moderately reactive organic compounds, such as toluene, have the potential to produce more than 5 times the amount of ozone formed by a nonreactive volatile organic compound (for example, benzene) (44:888-890). Similarly, a more highly reactive compound like *o*-Xylene can sustain the production of ozone at levels fifteen times greater than those produced by benzene (44:888-890). From Table 14, only three of the twenty-four individual VOC species emissions stand out with respect to potential tropospheric ozone formation--47 lbs/yr of 1,4-dichlorobenzene (Edwards AFB), 118 lbs/yr of toluene (Luke AFB), and 122 lbs/yr of methyl chloride (McClellan AFB). However, given the small quantities of pollutants being emitted, it is not expected that these estimated facility emissions have a significant impact on the local air quality in terms of ozone formation relative to other stationary sources.

**Analysis with Respect to the Air Force Pollution Prevention Program.**

Under this program, the Air Force has directed all installations to reduce their total base volatile organic emissions by 50 percent by 1990 (1:5). To assist in this effort, a relative comparison between the estimated VOC emissions for the representative wastewater treatment facilities and the total VOC emissions of their respective host base was made. The results of this comparison are contained in Table 15.

From this comparison, the potential volatile organic emissions from a wastewater treatment plant represented a maximum of > 0.1 percent of the total annual VOC emissions for the specific Air Force installations being evaluated--a considerably small percentage relative to other volatile organic sources. However, this information can be

useful in determining the relative priority of these particular facility emissions under an installation wide air emission control and pollution prevention strategy.

**TABLE 15.**  
**COMPARISON OF ESTIMATED VOC EMISSIONS FOR**  
**THE REPRESENTATIVE AIR FORCE WWTPs**  
**TO TOTAL HOST BASE VOC EMISSIONS**

---

<u>Base</u>	<u>Maximum Estimated WWTP Emissions</u>	<u>Total Host Base Emissions</u>	<u>Percent (%)</u>
Edwards AFB	0.04 TPY	346 TPY	> 0.1
Luke AFB	0.13 TPY	154 TPY	> 0.1
McGuire AFB	0.07 TPY	1250 TPY	> 0.1
McClellan AFB	0.19 TPY	139 TPY	> 0.1

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(84; 85; 86; 87)

## **V. Conclusions and Recommendations**

### **Conclusions**

From the literature review, it was shown that federal environmental legislation has become significantly more stringent over the last five years with respect to tropospheric ozone pollution. Following the passage of the 1990 CAAA, new emission control and reduction strategies for ozone have now targeted smaller sources of VOC emissions (> 10 TPY) nationwide. Traditionally excluded from consideration under previous air quality programs, wastewater treatment plants are now coming under increasing regulatory scrutiny relevant to air emissions, particularly volatile organics. Subsequent research efforts have generated extensive information and data within the civilian environmental management community related to the fate of these compounds during municipal and industrial wastewater treatment. From this information, it has been concluded that, in general, wastewater facilities have the potential to contribute to urban ozone pollution by emitting VOCs directly into the ambient atmosphere.

Despite the progress made by the private sector in advancing the state of understanding surrounding this issue, it had not yet received the same level of attention within the Air Force environmental program. Consequently, a comprehensive evaluation of the potential emission of volatile organics from Air Force wastewater treatment plants, especially for the nineteen prospective USAF installations currently located in ozone nonattainment areas, was warranted.

From the data collection effort, it was determined that eight bases continued to operate their own wastewater treatment facility within an ozone nonattainment area. Based on their plant type and the severity of ozone pollution associated with their respective nonattainment areas, Edwards AFB, Luke AFB, McGuire AFB, and McClellan AFB were selected as the representative facilities for a detailed, worst case analysis. As the first step to this analysis, emission estimates were calculated for each representative facility using mass balance equations and appropriate general fate simulation models. From these calculations, maximum emissions were determined for each representative facility which represented the upper limit for the potential VOC emissions from these wastewater plants. Consequently, for the purposes of this initial problem evaluation, these estimates were suitable for determining the relative impact of these facilities on local air quality with respect to current federal and state legislation.

Second, it was determined that, based on the calculated emission estimates, none of the selected representative wastewater facilities qualified as major stationary sources of volatile organic emissions under Title I of the 1990 CAAA. From these results, it can be suggested that the remaining four wastewater treatment plants which were not specifically evaluated (Beale AFB, Macdill AFB, March AFB, Scott AFB) also do not qualify as major stationary sources. Therefore, as a group, these facilities are not subject to the any of the operational and administrative requirements currently mandated by the ozone nonattainment initiatives under this title. An additional review of the individual state implementation plans from Arizona, New Jersey, and California yielded similar results.

Next, the potential impact of the specific volatile organics being emitted was discussed relevant to their relative reactivity and individual contributions to tropospheric ozone formation. Although several particular VOCs (*o*-Xylene, *p*-Xylene, 1,1,1-Trichloroethane) are highly reactive within the atmosphere, they are emitted in such low quantities that their relative impact on the quality of air in the local community is minimal. In general, the potential volatile organic emissions from Air Force wastewater treatment play a limited role in the formation of urban ozone relative to other stationary sources.

Finally, a relative comparison was made between the estimated VOC emissions for the representative wastewater facilities and the total VOC emissions for their respective host installations. From this analysis, it was shown that emissions from wastewater facilities constituted a relatively small fraction of the overall VOC emissions problem for these particular Air Force bases.

Although it has been determined that Air Force wastewater treatment plants are not strictly regulated under the current CAA with respect to ozone nonattainment, it is important to note that these facilities warrant additional consideration under the Air Force Pollution Prevention Program. This program has established requirements to identify all potential sources of VOC emissions at an installation and to initiate management strategies to achieve scheduled program emission reductions. This thesis has suggested that Air Force wastewater facilities are potential sources of some level of volatile organic emissions. Therefore, any VOC emission control and reduction initiatives under the

Pollution Prevention Program must address the control and abatement of these potential facility emissions.

### **Recommendations for Additional Research**

This research effort focused only on the evaluation of volatile organic emissions from Air Force wastewater facilities with respect to ozone nonattainment under Title I of the 1990 CAAA. Many VOCs are also classified as hazardous air pollutants and are subject to additional regulatory requirements under the Air Toxics Program of Title III of these amendments. Follow-on research could conduct direct source emission monitoring to classify actual species and air emissions concentrations. Then, a detailed risk assessment could be performed to determine the potential health risks associated with possible chronic exposures experienced by Air Force wastewater treatment plant employees.

Another related research topic is to quantify the potential emissions of VOCs from a typical base wastewater collection system. Because of their volatile characteristics, many volatile organics will evaporate into the headspace of the sewage collection system piping upstream from the receiving wastewater treatment plant. Recent studies have determined that between 40 to 60 percent of total VOCs discharged into a collection system can be lost prior to reaching the servicing treatment facility (88:2-3).

A final research area would be to determine the amount of VOCs being discharged by Air Force installations which are serviced by a regional connection. As part of their Control Technology Guidelines for Wastewater Treatment Plants, the EPA is expecting to promulgate additional wastewater pretreatment standards as the primary means of

controlling volatile organic emissions from these facilities (28). These standards will subsequently limit the total amount of VOCs which can be discharged to a receiving wastewater treatment facility. This program could impact those Air Force bases which discharge their wastewater for off-base treatment. Many of these bases are located in large metropolitan or industrial ozone nonattainment areas where the servicing wastewater plant may already be experiencing problems with volatile organic emissions. Therefore, it would be necessary to quantify the amount of volatile organics leaving these installations which the Air Force may have to control under additional wastewater pretreatment standards.

### **Summary**

This research effort has successfully developed representative volatile organic emission estimations for four of the eight Air Force wastewater treatment facilities currently located within ozone nonattainment areas. From these estimates, the limited impact of these source specific emissions was determined with respect to ozone nonattainment under Title I of the Clean Air Act and selected CAA state implementation plans. It was intended that this research would assist USAF Environmental Managers in evaluating wastewater treatment plant VOC emissions with respect to the growing number of air quality and pollution prevention initiatives. With the information it provides, this thesis should assist these individuals in establishing the appropriate ARM strategies and associated priority in addressing this problem at their installations.

**Appendix A : USAF Wastewater Treatment Plant Inventory**

Table A.1 - Sewage Treatment Plants (71; 72; 89)

<u>Base</u>	<u>Treatment Level</u>			<u>Plant Type</u>	<u>Avg. Flow (MGD)</u>
	<u>1°</u>	<u>2°</u>	<u>3°</u>		
Arnold AFB, TN		x		Trickling Filter	0.50
Beale AFB, CA		x		Trickling Filter	0.50
Cannon AFB, NM		x		Aeration Ponds	0.42
Columbus AFB, MS		x		Trickling Filter	0.70
Edwards AFB, CA		x		Aeration Ponds	1.75
Eglin AFB, FL		x		Trickling Filter	----
Ellsworth AFB, SD		x		Trickling Filter	0.90
Fairchild AFB, WA		x		Trickling Filter	----
Holloman AFB, NM		x		Aeration Ponds	1.10
Laughlin AFB, TX		x		Aeration Ponds	----
Luke AFB, AZ			x	Trickling Filter	0.40
Macdill AFB, FL		x		Activated Sludge	0.50
McGuire AFB, NJ		x		Tricking Filter	1.25
March AFB, CA		x		Trickling Filter	0.75
Moody AFB, GA		x		Trickling Filter	----
Mountain Home AFB, ID		x		Aeration Ponds	0.55
Patrick AFB, FL		x		Trickling Filter	0.60
Reese AFB, TX		x		Trickling Filter	0.44
Robbins AFB, GA		x		Trickling Filter	1.80

Table A.1 - Sewage Treatment Plants (cont'd)

<u>Base</u>	<u>Treatment Level</u>			<u>Plant Type</u>	<u>Avg. Flow (MGD)</u>
	<u>1°</u>	<u>2°</u>	<u>3°</u>		
Scott AFB, IL			x	Trickling Filter	1.50
Shaw AFB, SC		x		Activated Sludge	0.91
Tinker AFB, OK		x		Trickling Filter	0.40
Tyndall AFB, FL		x		Trickling Filter	---
USAFA, CO			x	Activated Sludge	1.60
Vance AFB, OK		x		Trickling Filter	---
Whiteman AFB, MO		x		Trickling Filter	0.70
Williams AFB, AZ		x		Trickling Filter	---

**Table A.2 - Industrial Wastewater Treatment Plants**

<u>Base</u>	<u>Treatment Level</u>			<u>Plant Type</u>	<u>Avg. Flow (MGD)</u>
	<u>1°</u>	<u>2°</u>	<u>3°</u>		
Hill AFB, UT			x	Chemical Precipitation	0.30
Kelly AFB, TX			x	Activated Sludge	1.60
McClellan AFB, CA		x		Activated Sludge	0.50
Robbins AFB, GA					
Plant #1		x		Chemical Precipitation	0.30
Plant #2		x		Chemical Precipitation	0.12
Tinker AFB, OK			x	Activated Sludge	0.80

**Appendix B: USAF Points of Contact**

<u>Base</u>	<u>POCs</u>	<u>Title</u>	<u>Phone (DSN)</u>
Beale AFB	Al Fernandez	Env Engineer	368-2641
Cannon AFB	Robert Durham	Env Engineer	681-6022
Edwards AFB	Roger Bowman Virginia Russell TSgt Bonnie Aguiar	Env Engineer AQ Specialist WWTP NCOIC	527-4122 805-277-9283 525-8296
Hill AFB	Jay Gupta Pat Sullivan	AQ Specialist IWTP Manager	458-0359 458-0359
Holloman AFB	Dr. Fred Fisher Cathy Giblin	Env Engineer (AQ) AQ Specialist	867-3933 867-3933
Kelly AFB	William Ryan Greg Vallery	Wastewater Engr AQ Specialist	945-3100 945-3100
Luke AFB	Belle Matthews MSgt Melvin Huntson MSgt Dubois	Env Technician Env Technician WWTP NCOIC	896-3621 896-3621 896-6109
Macdill AFB	Dennis Korycinski	Env Engineer	968-2567
March AFB	Joe Brooks	Env Engineer	947-5456
McClellan AFB	Capt Bruce Willing Bill Taylor Hollis Mulligan George Gregory	Env Engineer Env Engineer IWTP Manager IWTP Foreman	633-0836 633-0228 633-0228 633-6818
McGuire AFB	Marty Eisenhart Lisa Taylor Ed Viveiros	Env Engineer AQ Specialist WWTP Foreman	440-2770 440-4017 440-4701
Mt. Home AFB	1Lt Rodney Momon	Env Engineer	728-6351
Robbins AFB	Shaun Politino Rodney Reid	Chief of Compliance Env Engineer	468-9777 468-9777

<u>Base</u>	<u>POCs</u>	<u>Title</u>	<u>Phone (DSN)</u>
Scott AFB	William Courtney	Env Engineer	576-4165
	Bruce Cope	WWTP Foreman	576-4226
Tinker AFB	Major Richard Ashworth	Env Engineer	884-7044
	Trudi Logan	IWTP Manager	884-2010
	Carol Barker	AQ Specialist	734-3002
Whiteman AFB	Ed Lenz	WWTP Foreman	975-6218
HQ ACC	Gene Moore	Env Engineer (AQ)	574-4430
	Larry Isaacs	Env Engineer (AQ)	574-4430
	Gary Nault	Wastewater Engineer	574-3553
HQ AFMC	James Rykeman	Env Engineer (AQ)	787-5879
	Teresa Finke	IWTP Manager	
HQ AMC	Dan Schloesser	AQ Specialist	576-5763
	Mark Pinnick	Wastewater Specialist	576-3067
HQ USAF	Jay Shah	Env Engineer	227-3360
AFCESA	Myron Anderson	WWTP Technical Mgr	523-6345
AFCEE	Capt Terry Edwards	WWTP Technical Mgr	240-3501
	Carl Lehman	PRO-ACT Technician	240-4214

### **Appendix C: Federal and State Regulatory Points of Contact**

<b><u>Agency</u></b>	<b><u>Name</u></b>	<b><u>Position</u></b>	<b><u>Phone</u></b>
U.S. EPA	Dr Lance Wallace	Chemist, Office of Research and Development	703-341-7509
	Eric Crump	AQ Specialist, POTW Air Emissions, RTP	919-541-5032
	Elaine Manning	AQ Specialist, IWTP Air Emissions, RTP	919-541-5499
	Virginia Ambrose	Technician, National Emissions Data Branch, RTP	919-541-5454
	Ron Ryan	Technician, Emissions Inventory Branch, RTP	919-541-4676
California Air Resources Board	Patrick Gaffney	AQ Specialist	916-322-7303
New Jersey EPA	Tom Robb	AQ Specialist	609-633-1104
	Ben Loh	AQ Specialist, WWTP Air Emissions	609-292-0149

### **Appendix D: Base Survey Questions**

1. Does the installation operate its own WWTP?
2. If so, what level of treatment is provided and what are the specific treatment train processes?
3. What is the WWTP's average daily flow?
4. Is the base located in an ozone NA area? If so, what NA category does it fall in?
5. Have the potential VOC emissions from the base WWTP ever been quantified? If so, is there any available air emissions data?
6. If no air data, is there any current speciated wastewater characterization data for the plant's influent and effluent?
7. Are there any current emission control technologies in place at the base WWTP?
8. Is there a major facility upgrade planned in near future? Does the proposed upgrade address potential air emissions of VOCs?
9. Have VOC emissions from the base WWTP ever been an issue or topic of discussion with local, state, and federal regulators?
10. Are there any open enforcement actions against the base which relate to this issue?
11. Are there any discharge limits for VOCs in the base WWTP's NPDES permit?
12. What are the total base VOC emissions from the 1992 Baseline Survey under the USAF Pollution Prevention Program?
13. Do you have any comments or ideas which relate to this research topic?

## **Appendix E: Computer Based Fate Models for VOCs in Wastewater (4; 61)**

**BASTE.** The Bay Area Sewage Toxics Emissions (BASTE) model was developed by Richard L. Corsi of the University of Texas, Austin for the Bay Area Air Toxics Group, San Francisco, CA. BASTE is the premier, flexible VOC fate model which uses a building block approach to simulate the fate of volatile organics throughout an entire wastewater treatment system. Specific processes simulated include conveyance channels, split flows, quiescent surfaces, drops, weirs, packed media, aerated processes, biological processes, and covered processes.

**CHEMDAT 7.** Also known as WATER 7, this model was created by the Research Triangle Institute for the EPA's Office of Air Quality Planning and Standards, Research Triangle Park, NC. CHEMDAT 7 is a fate and transport model for aerated and non-aerated wastewater treatment processes for both municipal and industrial wastewater. As one of its unique features, CHEMDAT 7 is linked with EPA's CHEM 7 database, a stand-alone computer based program used to estimate VOC specific characteristics and properties.

**CINCI.** The CINCI model was developed by the University of Cincinnati and the EPA's Risk Reduction Engineering Laboratory, Cincinnati as a process specific fate model for the Cincinnati Metropolitan Sewer District (CMSD). It consists of several conceptual model components taken from published literature to simulate biodegradation and sorption fate mechanisms peculiar to the CMSD.

**CORAL.** Created by Richard L. Corsi, the Collection System Organic Release Algorithm (CORAL) model simulates two-phase, transient volatile organic transport and gas-liquid partitioning inside wastewater collection mains. The model can predict the release of VOCs across collection main reaches and over drop structures.

**EPA FATE.** Used by the EPA's Office of Water Regulations and Standards, this model estimates VOC contaminant concentrations in effluent streams. The model is essentially an expanded version of the three mechanism model developed by Namkung and Rittman (1987).

**PAVE.** The Program to Access Volatile Emissions or PAVE model was developed by the U.S. Chemical Manufacturers' Association. It simulates the fate of volatile organic contaminants in both surface-aerated and diffused-air activated sludge systems. PAVE can also be used to determine potential emissions from accidental spills of volatile liquids.

**SIMS.** The Surface Impoundment Modeling System (SIMS) was developed by Radian Corporation for the Office of Air Quality Planning and Standards, Research Triangle Park, NC. It has been used to establish air emission regulations and standards

from wastewater surface impoundment and treatment systems. Another feature of SIMS is that it will also simulate wastewater collection systems.

**TORONTO.** This model was developed by the Institute of Environmental Studies, University of Toronto. TORONTO is based on the fugacity concept (G.N. Lewis, 1901) to simulate the fate of volatile organics in secondary biological wastewater treatment processes.

**TOXCHEM.** This model consists of various conceptual model components combined to address the fate of VOCs in all stages of wastewater treatment to include grit chambers, primary and secondary clarifiers, and aerated reactors. Created by Environment Canada's Wastewater Technology Centre, TOXCHEM features an extensive compound database developed from actual field data. It is the only model with unsteady state capability to predict the release of VOCs under spill or slug discharge conditions.

**Appendix F - Mass Balance Calculations of Air Force Wastewater Treatment  
Facility VOC Emissions**

**Table F.1 - Edwards AFB Sewage Treatment Plant Annual Mass Balance VOC Emissions**

Plant Type - Evaporation Ponds		Average Daily Flow - 6493000 liters/day		Mean VOC Concentration (ug/l)		Influent VOC Mass Loadings (lbs/day)	Effluent VOC Mass Loadings (lbs/day)	Annual Emissions (lbs/year)
Volatiles	Organic Compound	Influent	Effluent*	Influent	Effluent			
	1,4-Dichlorobenzene	9.00	< 0.5	0.13	0.00	0.00	0.00	46.98
	1,1,1-Trichloroethane	3.50	< 0.5	0.05	0.00	0.00	0.00	18.27
	Toluene	1.90	< 0.3	0.03	0.00	0.00	0.00	9.92
	p-Xylene	1.30	< 0.5	0.02	0.00	0.00	0.00	6.79
	o-Xylene	0.70	< 0.3	0.01	0.00	0.00	0.00	3.65
	Totals	16.40	0.00	0.23	0.00	0.00	0.00	85.61

\* - The effluent VOC concentrations were below minimum detection limits. Therefore, they are assumed to be zero.

**Table F.2 - Luke AFB Sewage Treatment Plant Annual Mass Balance VOC Emissions**

Plant Type -	Activated Sludge Reactor	Average Daily Flow -	1484000 liters/day	Mean VOC Concentration (ug/l)		Influent VOC Mass Loadings (lbs/day)	Effluent VOC Mass Loadings (lbs/day)	Annual Emissions (lbs/year)
				Influent	Effluent			
<u>Volatile Organic Compound</u>								
Benzene				56.1	< 0.5	0.183	0.00	66.93
Bromodichloromethane				2.70	< 0.4	0.009	0.00	3.22
Chlorobenzene				1.00	< 0.6	0.003	0.00	1.19
1,4-Dichlorobenzene				1.70	< 0.3	0.006	0.00	2.03
1,2-Dichloroethane				1.00	< 0.4	0.003	0.00	1.19
Ethyl Benzene				48.80	< 0.3	0.160	0.00	58.22
Methylene Chloride				4.10	< 0.4	0.013	0.00	4.89
Toluene				99.00	< 0.3	0.324	0.00	118.12
Totals				214.40	0.00	0.70	0.00	255.80

Notes:

1. Representative wastewater characterization data was drawn from the Holloman AFB sewage treatment plant (77).
2. The effluent VOC concentrations were below minimum detection limits. Therefore, they are assumed to be zero.

**Table F.3 - McGuire AFB Sewage Treatment Plant Annual Mass Balance VOC Emissions**

Plant Type -	Trickling Filter	Average Daily Flow - 4637500 liters/day	Mean VOC Concentration (ug/l)		Influent VOC Mass Loadings (lbs/day)	Effluent VOC Mass Loadings (lbs/day)	Annual Emissions (lbs/year)
			Influent	Effluent			
<u>Volatile Organic Compound</u>							
Benzene			4.82	NA	0.05	0.00	17.97
Chlorobenzene			1.10	NA	0.01	0.00	4.10
Chloroform			5.06	NA	0.05	0.00	18.87
Ethyl Benzene			7.04	NA	0.07	0.00	28.25
Methylene Chloride			11.95	NA	0.12	0.00	44.55
Toluene			6.82	NA	0.07	0.00	25.43
1,1,1-Trichloroethane			1.04	NA	0.01	0.00	3.88
Trichloroethylene			1.34	NA	0.01	0.00	5.00
Totals			39.17	0.00	0.40	0.00	146.04

**Notes:**

1. Representative wastewater characterization data was drawn from the McChord AFB sewage treatment plant (76).
2. The effluent VOC concentrations were below minimum detection limits. Therefore, they were assumed to be zero.

**Table F.4 - McClellan AFB Industrial Wastewater Treatment Plant Annual Mass Balance VOC Emissions**

Plant Type -		Activated Sludge Reactor		Average Daily Flow -		1855000 liters/day			
<u>Volatle Organic Compound</u>		Mean VOC Concentration (ug/l)		Influent VOC Mass Loadings (lbs/day)		Effluent VOC Mass Loadings (lbs/day)		Annual Emissions (lbs/year)	
		Influent	Effluent*						
Acetone		168.00	< 10	0.69	0.00	250.55			
Methylene Chloride		82.00	< 10	0.34	0.00	122.29			
Total Xylenes		8.00	< 5	0.03	0.00	11.93			
Totals		258.00	0.00	1.05	0.00	384.77			

\* - The effluent VOC concentrations were below minimum detection limits. Therefore, they are assumed to be zero.

**Appendix G - General Fate Modeling Calculations of Air Force Wastewater  
Treatment Facility VOC Emissions**

**Table G.1.1a - Edwards AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process -	Primary Clarifier, basin
Fate Mechanisms -	Volatilization, Biodegradation
Avg daily flow -	75.00 ltrs/sec
Width of basin -	4.88 m
Length of basin -	17.08 m
Depth of basin -	3.56 m
Surface area of basin -	83.35 m <sup>2</sup>
Volume of basin -	296.73 m <sup>3</sup>
Active biomass concentration -	100.00 mg-VSS/m <sup>3</sup>

<u>Volatile Organic Compound</u>	<u>Influent Conc. (ug/l)</u>	<u>Diffusivity (cm<sup>2</sup>/s)</u>	<u>Decay Rate (m<sup>3</sup>(g-d))</u>	<u>Mass Transfer Coeff (m/s)</u>	<u>Clarifier Conc. (ug/l)</u>	<u>Mass Loss Rate (ug/s)</u>	<u>Effluent Conc. (ug/l)</u>
1,4-Dichlorobenzene	9.00	5.00E+05	0.05	1.19E-05	7.24	7.16	7.24
1,1,1-Trichloroethane	3.50	5.65E+05	0.05	1.29E-05	2.81	3.02	2.81
Toluene	1.90	6.63E+06	0.40	6.65E-05	0.65	3.62	0.65
p-Xylene	1.30	2.00E+05	0.50	6.44E-06	0.39	0.21	0.39
o-Xylene	0.70	2.00E+05	0.50	6.44E-06	0.21	0.11	0.21

(74; 90; 91)

**Table G.1.1b - Edwards AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process -	Primary Clarifier, weir
Fate Mechanisms -	Volatilization only
Weir drop height -	6.40E-03 m
Discharge flow rate -	147.54 m <sup>3</sup> /m-h
Oxygen deficit ratio -	1.25
Matrix coefficient (alpha) -	0.2

<u>Volatile Organic Compound</u>	<u>Influent Conc. (ug/l)</u>	<u>Proportion Coefficient</u>	<u>Compound Depletion Ratio</u>	<u>Mass Loss Rate (ug/s)</u>	<u>Effluent Conc. (ug/l)</u>
1,4-Dichlorobenzene	7.24	0.53	1.00	0.38	7.24
1,1,1-Trichloroethane	2.81	0.53	1.00	0.15	2.81
Toluene	0.65	0.53	1.00	0.03	0.65
p-Xylene	0.39	0.55	1.00	0.02	0.39
o-Xylene	0.21	0.55	1.00	0.01	0.21

(90; 91)

**Table G.1.1c - Edwards AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process - Primary Clarifier

<u>Volatile Organic Compound</u>	<u>Surface Mass Loss Rate (ug/s)</u>	<u>Weir Mass Loss Rate (ug/s)</u>	<u>Total Mass Loss Rate (ug/s)</u>	<u>Total Estimated Emissions (lbs/yr)</u>
1,4-Dichlorobenzene	7.16	0.38	7.54	0.52
1,1,1-Trichloroethane	3.02	0.15	3.16	0.22
Toluene	3.62	0.03	3.65	0.25
p-Xylene	0.21	0.02	0.23	0.02
o-Xylene	0.11	0.01	0.13	0.01

**Total Estimated Process Emissions -**

**1.02 lbs per year**

**Table G.1.2 - Edwards AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process -		Evaporation Ponds	
Fate Mechanisms -		Volatilization, Biodegradation	
Avg daily flow -	75.00 ltrs/sec		
Width of pond -	456.50 m		
Length of pond -	456.50 m		
Depth of pond -	1.52 m		
Surface area of pond -	208392.25 m <sup>2</sup>		
Volume of pond -	316756.22 m <sup>3</sup>		
Active biomass concentration -	100.00 mg-VSS/m <sup>3</sup>		

Volatile Organic Compound	Influent Conc. (ug/l)	Diffusivity (cm <sup>2</sup> /s)	Decay Rate (m <sup>3</sup> /g-d)	Mass Transfer Coeff (m/s)	Clarifier Conc. (ug/l)	Mass Loss Rate (ug/s)	Effluent Conc. (ug/l)	Total Estimated Emissions (lbs/yr)
1,4-Dichlorobenzene	7.24	5.00E+05	0.05	8.22E-05	0.02	261.43	0.00	18.14
1,1,1-Trichloroethane	2.81	5.65E+05	0.05	8.92E-05	0.01	105.87	0.00	7.35
Toluene	0.65	6.63E+06	0.4	0.000461	0.00	19.34	0.00	1.34
p-Xylene	0.39	2.00E+05	0.5	4.46E-05	0.00	1.42	0.00	0.10
o-Xylene	0.21	2.00E+05	0.5	4.46E-05	0.00	0.77	0.00	0.05
<b>Total Estimated Process Emissions -</b>								<b>26.99 lbs per year</b>

(74; 90; 91)

**Table G.1.3 - Edwards AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

<u>Volatile Organic Compound</u>	Estimated Emissions (lbs/yr)				Subtotal by VOC Compound
	Primary Clarifier Basin	Primary Clarifier Weir	Evaporation Ponds		
1,4-Dichlorobenzene	0.50	0.03	18.14		18.67
1,1,1-Trichloroethane	0.21	0.01	7.35		7.57
Toluene	0.25	0.00	1.34		1.60
p-Xylene	0.01	0.00	0.10		0.11
o-Xylene	0.01	0.00	0.05		0.06
Subtotal by Process -	0.98	0.04	26.98		
<b>Total Estimated Facility Emissions -</b>					<b>28.01 lbs per year</b>

**Table G.2.1 - Luke AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process - Aerated Grit Chamber

Fate Mechanisms - Volatilization only

Avg daily flow - 17.20 ltrs/sec  
 Forced aeration rate - 0.03 m<sup>3</sup>/sec

<u>Volatile Organic Compound</u>	<u>Influent Conc. (ug/l)</u>	<u>Henry's Constant</u>	<u>Mass Loss Rate (ug/s)</u>	<u>Effluent Conc. (ug/l)</u>	<u>Total Emission Estimate (lbs/yr)</u>
Benzene	56.10	0.24	403.92	39.55	28.03
Bromodichloromethane	2.70	0.15	12.15	2.14	0.84
Chlorobenzene	1.00	0.17	5.10	0.77	0.35
1,4-Dichlorobenzene	1.70	0.20	10.20	1.26	0.71
1,2-Dichloroethene	1.00	0.15	4.50	0.79	0.31
Ethyl Benzene	48.00	0.37	532.80	29.17	36.98
Methylene Chloride	4.10	0.36	44.28	2.52	3.07
Toluene	99.00	0.28	831.60	66.52	57.71

**Total Estimated Process Emissions - 128.01 lbs per year**

(77; 92; 94)

**Table G.2.2a - Luke AFB Sewage Treatment Plant General Fate Model VOC Emissions Estimates**

Treatment Process -	Primary Clarifier, basin
Fate Mechanisms -	Volatilization, Biodegradation
Avg daily flow -	4.30 ltrs/sec
Width of basin -	4.42 m
Length of basin -	12.20 m
Depth of basin -	2.44 m
Surface area of basin -	53.92 m <sup>2</sup>
Volume of basin -	131.57 m <sup>3</sup>
Active biomass concentration -	100.00 mg-VSS/m <sup>3</sup>

Volatile Organic Compound	Influent Conc. (ug/l)	Diffusivity (cm <sup>2</sup> /s)	Decay Rate (m <sup>3</sup> /g-d)	Mass Transfer Coeff (m/s)	Clarifier Conc. (ug/l)	Mass Loss Rate (ug/s)	Effluent Conc. (ug/l)
Benzene	28.03	1.02E+05	0.22	4.14E-06	3.16	0.71	3.16
Bromodichloromethane	0.84	6.00E+05	0.01	1.35E-05	0.63	0.46	0.63
Chlorobenzene	0.35	2.00E+05	0.21	6.49E-06	0.04	0.01	0.04
1,4-Dichlorobenzene	0.71	5.00E+05	0.05	1.20E-05	0.24	0.16	0.24
1,2-Dichloroethene	0.31	5.00E+05	0.05	1.20E-05	0.11	0.07	0.11
Ethyl Benzene	36.98	8.10E+04	0.23	3.55E-06	4.02	0.77	4.02
Methylene Chloride	3.07	8.64E+05	0.50	1.72E-05	0.16	0.15	0.16
Toluene	57.71	6.63E+06	0.40	6.71E-05	3.60	13.02	3.60

(60; 70; 77; 90; 92; 94)

**Table G.2.2b - Luke AFB Sewage Treatment Plant General Fate Model VOC Emissions Estimates**

Treatment Process -	Primary Clarifier, weir
Fate Mechanisms -	Volatilization only
Weir drop height -	0.15 m
Discharge flow rate -	11.18 m <sup>3</sup> /m-h
Oxygen deficit ratio -	1.25
Matrix coefficient (alpha) -	0.2

<u>Volatile Organic Compound</u>	<u>Influent</u>	<u>Proportion</u>	<u>Compound</u>	<u>Mass</u>	<u>Effluent</u>
	<u>Conc.</u>	<u>Coefficient</u>	<u>Depletion</u>	<u>Loss Rate</u>	<u>Conc.</u>
	<u>(ug/l)</u>		<u>Ratio</u>	<u>(ug/s)</u>	<u>(ug/l)</u>
Benzene	3.16	0.55	1.00	0.04	3.15
Bromodichloromethane	0.63	0.53	1.00	0.01	0.62
Chlorobenzene	0.04	0.61	1.00	0.00	0.04
1,4-Dichlorobenzene	0.24	0.53	1.00	0.00	0.24
1,2-Dichloroethene	0.11	0.62	1.00	0.00	0.11
Ethyl Benzene	4.02	0.55	1.00	0.05	4.00
Methylene Chloride	0.16	0.55	1.00	0.00	0.16
Toluene	3.60	0.53	1.00	0.04	3.59

(63; 90; 92; 94)

**Table G.2.2c - Luke AFB Sewage Treatment Plant General Fate Model VOC Emissions Estimates**

Treatment Process -	Primary Clarifier			
	Surface Mass Loss Rate (ug/s)	Weir Mass Loss Rate (ug/s)	Total Mass Loss Rate (ug/s)	Total Estimated Emissions (lbs/yr)
<u>Volatile Organic Compound</u>				
Benzene	0.71	0.04	0.75	0.05
Bromodichloromethane	0.46	0.01	0.46	0.03
Chlorobenzene	0.01	0.00	0.02	0.00
1,4-Dichlorobenzene	0.16	0.00	0.16	0.01
1,2-Dichloroethene	0.07	0.00	0.07	0.00
Ethyl Benzene	0.77	0.05	0.82	0.06
Methylene Chloride	0.15	0.00	0.15	0.01
Toluene	13.02	0.04	13.06	0.91
<b>Total Estimated Process Emissions -</b>				<b>1.06 lbs per year</b>

**Table G.2.3 - Luke AFB Sewage Treatment Plant General Fate Model VOC Emissions Estimates**

Treatment Process - Activated Sludge Reactor with Mechanical Surface Aeration

Fate Mechanisms - Volatilization, Biodegradation

Avg daily flow -	17.20 ltrs/sec	Active biomass concentration -	100.00 mg-VSS/m <sup>3</sup>
Width of reactor -	6.71 m	Oxygen transfer rate -	2.00 kg/KW-h
Length of reactor -	141.83 m	Braking power of aerator motor -	50.00 KW
Depth of reactor -	3.05 m	Oxygen saturation concentration -	0.08 kg/m <sup>3</sup>
Surface area of reactor -	951.68 m <sup>2</sup>		
Volume of reactor -	2902.62 m <sup>3</sup>		

Volatile Organic Compound	Influent Conc. (ug/l)	Proportion Coefficient	Decay Rate (m <sup>3</sup> /g-d)	Mass Transfer Coeff (m/s)	Clarifier Conc. (ug/l)	Mass Loss Rate (ug/s)	Total Estimated Emissions (lbs/yr)
Benzene	3.15	0.55	0.22	1.00E-02	0.01	50.25	3.49
Bromodichloromethane	0.62	0.53	0.01	9.65E-03	0.00	10.70	0.74
Chlorobenzene	0.04	0.61	0.21	1.11E-02	0.00	0.67	0.05
1,4-Dichlorobenzene	0.24	0.53	0.05	9.65E-03	0.00	4.07	0.28
1,2-Dichloroethene	0.11	0.62	0.05	1.13E-02	0.00	1.80	0.12
Ethyl Benzene	4.00	0.55	0.23	1.00E-02	0.01	63.58	4.41
Methylene Chloride	0.16	0.55	0.50	1.00E-02	0.00	2.36	0.16
Toluene	3.59	0.53	0.40	9.65E-03	0.01	53.73	3.73

Total Estimated Process Emissions -

12.99 lbs per year

(60; 92; 97)

**Table G.2.4 - Luke AFB Sewage Treatment Plant General Fate Model VOC Emissions Estimates**

<u>Volatile Organic Compound</u>	Estimated Emissions (lbs/yr)						Subtotal by VOC Compound
	Aerated Grit Chamber	Primary Clarifier Basins	Primary Clarifier Weirs	Activated Sludge Reactor	Subtotal		
Benzene	28.03	0.20	0.01	3.49	31.73		
Bromodichloromethane	0.84	0.13	0.00	0.74	1.71		
Chlorobenzene	0.35	0.00	0.00	0.05	0.40		
1,4-Dichlorobenzene	0.71	0.04	0.00	0.28	1.03		
1,2-Dichloroethene	0.31	0.02	0.00	0.12	0.46		
Ethyl Benzene	36.98	0.21	0.01	4.41	41.62		
Methylene Chloride	3.07	0.04	0.00	0.16	3.28		
Toluene	57.71	3.61	0.01	3.73	65.07		
Subtotal by Process -	128.01	4.26	0.04	12.99			
<b>Total Estimated Facility Emissions -</b>						<b>111.46 lbs per year</b>	

**Table G.3.1a - McGuire AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process - Primary clarifiers, basin (total of 4 each, in parallel)

Fate Mechanisms - Volatilization, Biodegradation

Avg daily flow - 13.43 ltrs/sec  
 Width of basin - 16.47 m  
 Length of basin - 19.52 m  
 Depth of basin - 3.05 m  
 Surface area of basin - 321.49 m<sup>2</sup>  
 Volume of basin - 980.56 m<sup>3</sup>  
 Active biomass concentration - 100.00 mg-VSS/m<sup>3</sup>

<u>Volatile Organic Compound</u>	<u>Influent Conc. (ug/l)</u>	<u>Diffusivity (cm<sup>2</sup>/s)</u>	<u>Decay Rate (m<sup>3</sup>/g-d)</u>	<u>Mass Transfer Coeff (m/s)</u>	<u>Clarifier Conc. (ug/l)</u>	<u>Mass Loss Rate (ug/s)</u>	<u>Effluent Conc. (ug/l)</u>
Benzene	4.82	1.02E+05	0.22	4.44E-06	0.24	0.35	0.24
Chlorobenzene	1.10	2.00E+05	0.61	6.95E-06	0.02	0.05	0.02
Chloroform	5.06	5.00E+05	0.05	1.28E-05	0.91	3.76	0.91
Ethyl Benzene	7.04	8.10E+04	0.23	3.80E-06	0.34	0.42	0.34
Methylene Chloride	11.95	8.64E+05	0.50	1.85E-05	0.27	1.62	0.27
Toluene	6.82	6.63E+05	0.40	1.55E-05	0.19	0.96	0.19
1,1,1-Trichloroethane	1.04	5.65E+05	0.05	1.39E-05	0.19	0.83	0.19
Trichloroethylene	1.34	7.87E+05	0.01	1.73E-05	0.73	4.06	0.73

**Table G.3.1b - McGuire AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process - Primary clarifiers, weir

Fate Mechanisms - Volatilization only

Weir drop height - 0.15 m  
 Discharge flow rate - 16.12 m<sup>3</sup>/m-h  
 Oxygen deficit ratio - 1.03  
 Matrix coefficient (alpha) - 0.2

Volatile Organic Compound	Influent		Compound Depletion		Effluent	
	Conc. (ug/l)	Proportion Coefficient	Ratio	Loss Rate (ug/s)	Conc. (ug/l)	
Benzene	0.24	0.55	1.00	0.01	0.24	
Chlorobenzene	0.02	0.61	1.00	0.00	0.02	
Chloroform	0.91	0.56	1.00	0.05	0.91	
Ethyl Benzene	0.34	0.55	1.00	0.02	0.34	
Methylene Chloride	0.27	0.55	1.00	0.01	0.27	
Toluene	0.19	0.53	1.00	0.01	0.19	
1,1,1-Trichloroethane	0.19	0.53	1.00	0.01	0.19	
Trichloroethylene	0.73	0.53	1.00	0.03	0.73	

(90; 93)

**Table G.3.1c - McGuire AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process - Primary clarifiers (total of 4 each, in parallel)

<u>Volatile Organic Compound</u>	<u>Surface Mass Loss Rate (ug/s)</u>	<u>Weir Mass Loss Rate (ug/s)</u>	<u>Total Mass Loss Rate (ug/s)</u>	<u>Total Estimated Emissions (lbs/yr)</u>
Benzene	1.39	0.05	1.44	0.10
Chlorobenzene	0.19	0.00	0.19	0.01
Chloroform	15.04	0.18	15.23	1.06
Ethyl Benzene	1.67	0.07	1.74	0.12
Methylene Chloride	6.48	0.05	6.53	0.45
Toluene	3.85	0.04	3.88	0.27
1,1,1-Trichloroethane	3.34	0.04	3.37	0.23
Trichloroethylene	16.25	0.14	16.39	1.14

**Total Estimated Process Emissions - 3.39 lbs per year**

**Table G.3.2 - McGuire AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process - Trickling Filter

Fate Mechanisms - Volatilization only

Avg daily flow - 53.72 ktrs/sec  
 Forced air flow rate - 100 ktrs/sec

<u>Volatile Organic Compound</u>	<u>Influent Conc. (ug/l)</u>	<u>Henry's Constant</u>	<u>Mass Loss Rate (ug/s)</u>	<u>Effluent Conc. (ug/l)</u>	<u>Total Estimated Emissions (lbs/yr)</u>
Benzene	0.24	0.24	5.84	0.13	0.41
Chlorobenzene	0.02	0.17	0.34	0.01	0.02
Chloroform	0.91	0.20	18.19	0.57	1.26
Ethyl Benzene	0.34	0.37	12.62	0.11	0.88
Methylene Chloride	0.27	0.36	9.79	0.09	0.68
Toluene	0.19	0.28	5.40	0.09	0.37
1,1,1-Trichloroethane	0.19	0.77	10.00	0.00	0.69
Trichloroethylene	0.73	0.42	30.50	0.16	2.12

**Total Estimated Process Emissions - 6.43 lbs per year**

(93; 94; 95)

**Table G.3.3a - McGuire AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process - Secondary clarifiers, basin (total of 4 each, in parallel)

Fate Mechanisms - Volatilization, Biodegradation

Avg daily flow - 13.43 ltrs/sec  
 Width of basin - 16.47 m  
 Length of basin - 19.52 m  
 Depth of basin - 3.05 m  
 Surface area of basin - 321.49 m<sup>2</sup>  
 Volume of basin - 980.56 m<sup>3</sup>  
 Active biomass concentration - 50.00 mg-VSS/m<sup>3</sup>

<u>Volatiles Organic Compound</u>	<u>Influent Conc. (ug/l)</u>	<u>Diffusivity (cm<sup>2</sup>/s)</u>	<u>Decay Rate (m<sup>3</sup>/g-d)</u>	<u>Mass Transfer Coeff (m/s)</u>	<u>Clarifier Conc. (ug/l)</u>	<u>Mass Loss Rate (ug/s)</u>	<u>Effluent Conc. (ug/l)</u>
Benzene	0.13	1.02E+05	0.22	4.44E-06	0.01	0.02	0.01
Chlorobenzene	0.01	2.00E+05	0.61	6.95E-06	0.00	0.00	0.00
Chloroform	0.57	5.00E+05	0.05	1.28E-05	0.17	0.69	0.17
Ethyl Benzene	0.11	8.10E+04	0.23	3.80E-06	0.01	0.01	0.01
Methylene Chloride	0.09	8.64E+05	0.50	1.85E-05	0.00	0.02	0.00
Toluene	0.09	6.63E+05	0.40	1.55E-05	0.01	0.03	0.01
1,1,1-Trichloroethane	0.00	5.65E+05	0.05	1.39E-05	0.00	0.00	0.00
Trichloroethylene	0.16	7.87E+05	0.01	1.73E-05	0.10	0.54	0.10

**Table G.3.3b - McGuire AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process - Secondary clarifiers, weir

Fate Mechanisms - Volatilization only

Weir drop height - 0.15 m  
 Discharge flow rate - 16.12 m<sup>3</sup>/m-h  
 Oxygen deficit ratio - 1.16  
 Matrix coefficient (alpha) - 0.2

<u>Volatile Organic Compound</u>	<u>Influent Conc. (ug/l)</u>	<u>Proportion Coefficient</u>	<u>Compound Depletion Ratio</u>	<u>Mass Loss Rate (ug/s)</u>	<u>Effluent Conc. (ug/l)</u>
Benzene	0.01	0.55	1.02	0.00	0.01
Chlorobenzene	0.00	0.61	1.02	0.00	0.00
Chloroform	0.17	0.56	1.02	0.04	0.16
Ethyl Benzene	0.01	0.55	1.02	0.00	0.01
Methylene Chloride	0.00	0.55	1.02	0.00	0.00
Toluene	0.01	0.53	1.02	0.00	0.00
1,1,1-Trichloroethane	0.00	0.53	1.02	0.00	0.00
Trichloroethylene	0.10	0.53	1.02	0.02	0.10

(90; 93)

**Table G.3.3c - McGuire AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process - Secondary clarifiers (total of 4 each, in parallel)

<u>Volatile Organic Compound</u>	<u>Surface Mass Loss Rate (ug/s)</u>	<u>Weir Mass Loss Rate (ug/s)</u>	<u>Total Mass Loss Rate (ug/s)</u>	<u>Total Estimated Emissions (lbs/yr)</u>
Benzene	0.07	0.01	0.08	0.01
Chlorobenzene	0.00	0.00	0.01	0.00
Chloroform	2.75	0.15	2.90	0.20
Ethyl Benzene	0.05	0.01	0.06	0.00
Methylene Chloride	0.09	0.00	0.10	0.01
Toluene	0.10	0.00	0.10	0.01
1,1,1-Trichloroethane	0.00	0.00	0.00	0.00
Trichloroethylene	2.17	0.08	2.25	0.16

**Total Estimated Process Emissions -**

**0.38 lbs per year**

**Table G.3.4 - McGuire AFB Sewage Treatment Plant General Fate Model VOC Emission Estimates**

<u>Volatile Organic Compound</u>	Estimated Emissions (lbs/yr)							Subtotal by Compound
	Primary		Trickling		Secondary		Subtotal	
	Clarifier Basins	Clarifier Weirs	Filter	Clarifier Basins	Clarifier Weirs	Clarifier Weirs		
Benzene	0.10	0.00	0.41	0.00	0.00	0.00	0.51	
Chlorobenzene	0.01	0.00	0.02	0.00	0.00	0.00	0.04	
Chloroform	1.04	0.01	1.26	0.05	0.00	0.00	2.37	
Ethyl Benzene	0.12	0.00	0.88	0.00	0.00	0.00	1.00	
Methylene Chloride	0.45	0.00	0.68	0.00	0.00	0.00	1.13	
Toluene	0.27	0.00	0.37	0.00	0.00	0.00	0.65	
1,1,1-Trichloroethane	0.23	0.00	0.69	0.00	0.00	0.00	0.93	
Trichloroethylene	1.13	0.01	2.12	0.04	0.00	0.00	3.29	
Subtotal by Process -	3.35	0.04	6.43	0.09	0.00	0.00	9.91	
Total Estimated Facility Emissions -							9.91	lbs per year

**Table G.4.1 - McClellan Industrial Wastewater Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process - Equalization Basins	
Fate Mechanisms - Volatilization, Biodegradation	
Avg daily flow -	21.50 ltrs/sec
Width of basin -	60.80 m
Length of basin -	81.40 m
Depth of basin -	2.40 m
Surface area of basin -	4949.12 m <sup>2</sup>
Volume of basin -	11877.89 m <sup>3</sup>
Active biomass concentration -	25.00 mg-VSS/m <sup>3</sup>

Volatile Organic Compound	Influent Conc. (ug/l)	Diffusivity (cm <sup>2</sup> /s)	Decay Rate (m <sup>3</sup> /g-d)	Mass Transfer Coeff (m/s)	Clarifier Conc. (ug/l)	Mass Loss Rate (ug/s)	Effluent Conc. (ug/l)	Total Estimated Emissions (lbs/yr)
Acetone	168.00	5.00E+05	0.05	1.75E-05	12.88	1116.10	12.88	77.46
Methylene Chloride	82.00	8.64E+05	0.50	2.52E-05	0.94	117.72	0.94	8.17
Total Xylenes	8.00	2.00E+05	0.50	9.50E-06	0.10	4.52	0.10	0.31
<b>Total Estimated Process Emissions -</b>								<b>85.94 lbs per year</b>

(80, 90, 95, 96)

**Table G.4.2 - McClellan Industrial Wastewater Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process - Activated Sludge Reactor

Fate Mechanisms - Volatilization, Biodegradation

Avg daily flow -	21.50 ltrs/sec
Width of basin -	40.70 m
Length of basin -	40.10 m
Depth of basin -	2.40 m
Surface area of basin -	1632.07 m <sup>2</sup>
Volume of basin -	3916.97 m <sup>3</sup>
Active biomass concentration -	100.00 mg-VSS/m <sup>3</sup>

<u>Volatile Organic Compound</u>	<u>Influent Conc. (ug/l)</u>	<u>Diffusivity (cm<sup>2</sup>/s)</u>	<u>Decay Rate (m<sup>3</sup>/g-d)</u>	<u>Mass Transfer Coeff (m/s)</u>	<u>Clarifier Conc. (ug/l)</u>	<u>Mass Loss Rate (ug/s)</u>	<u>Effluent Conc. (ug/l)</u>	<u>Total Estimated Emissions (lbs/yr)</u>
Acetone	12.88	5.00E+05	0.05	1.55E-05	1.01	25.62	1.01	1.78
Methylene Chloride	0.94	8.64E+05	0.50	2.24E-05	0.01	0.32	0.01	0.02
Total Xylenes	0.10	2.00E+05	0.50	8.43E-06	0.00	0.01	0.00	0.00

**Total Estimated Process Emissions -**

**1.80 lbs per year**

(80; 90; 95; 96)

**Table G.4.3a - McClellan Industrial Wastewater Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process - Secondary Clarifier, basin

Fate Mechanisms - Volatilization, Biodegradation

Avg daily flow - 21.50 ltrs/sec  
 Radius of basin - 7.60 m  
 Depth of basin - 3.04 m  
 Surface area of basin - 181.45 m<sup>2</sup>  
 Volume of basin - 551.62 m<sup>3</sup>  
 Active biomass concentration - 25.00 mg-VSS/m<sup>3</sup>

Volatile Organic Compound	Influent Conc. (ug/l)	Diffusivity (cm <sup>2</sup> /s)	Decay Rate (m <sup>3</sup> /g-d)	Mass Transfer Coeff. (m/s)	Clarifier Conc. (ug/l)	Mass Loss Rate (ug/s)	Effluent Conc. (ug/l)	Total Estimated Emissions (lbs/yr)
Acetone	1.01	5.00E+05	0.05	1.21E-05	0.69	1.51	0.69	0.10
Methylene Chloride	0.01	8.64E+05	0.50	1.75E-05	0.00	0.01	0.00	0.00
Total Xylenes	0.00	2.00E+05	0.50	6.58E-06	0.00	0.00	0.00	0.00

**Total Estimated Basin Emissions -**

**0.11 lbs per year**

(80, 90, 95, 96)

**Table G.4.3b - McClellan Industrial Wastewater Treatment Plant General Fate Model VOC Emission Estimates**

Treatment Process - Secondary Clarifier, weir

Fate Mechanisms - Volatilization only

Avg daily flow - 21.50 ktrs/sec  
 Discharge rate - 38.90 m<sup>3</sup>/m-h  
 Drop height 0.16 m  
 Oxygen deficit coeff. - 1.53  
 Matrix coefficient - 0.20

<u>Volatile Organic Compound</u>	<u>Influent Conc. (ug/l)</u>	<u>Proportion Coefficient</u>	<u>Compound Depletion Ratio</u>	<u>Mass Loss Rate (ug/s)</u>	<u>Effluent Conc. (ug/l)</u>	<u>Total Estimated Emissions (lbs/yr)</u>
Acetone	0.69	0.55	1.05	0.67	0.65	0.05
Methylene Chloride	0.00	0.50	1.04	0.00	0.00	0.00
Total Xylenes	0.00	0.50	1.04	0.00	0.00	0.00
<b>Total Estimated Weir Emissions -</b>						<b>0.05 lbs per year</b>
						<b>(80; 95; 96)</b>

**Table G.4.4 - McClellan Industrial Wastewater Treatment Plant General Fate Model VOC Emission Estimates**

<u>Volatile Organic Compound</u>	Estimated Emissions (lbs/yr)					Subtotal by VOC Compound
	Equalization		Secondary Clarifier		Secondary Clarifier	
	<u>Basin</u>	<u>Reactor</u>	<u>Basin</u>	<u>Weir</u>	<u>Compound</u>	
Acetone	77.46	1.78	0.10	0.05		79.39
Methylene Chloride	8.17	0.02	0.00	0.00		8.19
Total Xylenes	0.31	0.00	0.00	0.00		0.31
Subtotal by Process -	85.94	1.80	0.11	0.05		
<b>Total Estimated Facility Emissions -</b>						<b>87.89 lbs per year</b>

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## Vita

Captain Brian A. Ouellette was born on 7 July 1964 in Brunswick, Maine. He graduated from Cheverus High School in Portland, Maine in 1982. He then attended the University of Maine at Orono where he earned a Bachelor of Science degree in Civil Engineering in 1986. As a Distinguished Graduate of the Air Force Reserve Officer Training Corps, he was selected for a regular commission upon his graduation. His first operational assignment was with the 97th Civil Engineering Squadron at Eaker AFB, Blytheville, Arkansas from October 1987 through April 1990. While at Eaker AFB, he served as design civil engineer, Chief of Readiness, and Chief of Requirements and Logistics. Capt Ouellette then transferred to the 26th Civil Engineering Squadron at Zweibruecken AB, Zweibruecken, Germany in May 1990. As the Chief of Readiness, he directed the unit's deployment during Operations DESERT SHIELD and DESERT STORM. Afterwards, he served as the unit's Base Closure Officer until June 1991, when he was reassigned to the 435th Civil Engineering Squadron at Rhein-Main AB, Frankfurt, Germany. While at RMAB, he served first as a military programmer and then as the wing Environmental Coordinator. In May 1993, he reported as a graduate student in the Environmental and Engineering Management Program at the Air Force Institute of Technology. Upon graduation in September 1994, he will be reassigned to the Environmental Compliance Division at Headquarters, Air Combat Command, Langley AFB, Virginia.

Permanent Address: RR 5, Box 2345  
Cundy's Harbor Road  
Brunswick, ME 04011

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Brian A. Ouellette, Captain, USAF

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Air Force Institute of Technology, WPAFB OH. 45433-6583

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13. ABSTRACT

In accordance with the 1990 Clean Air Act Amendments (CAAA), this research conducts an evaluation of the potential emission of volatile organic compounds (VOCs) from selected Air Force wastewater treatment plants. Using a conservative mass balance analysis and process specific simulation models, volatile organic emission estimates are calculated for four individual facilities--Edwards AFB, Luke AFB, McGuire AFB, and McClellan AFB--which represent a cross section of the current inventory of USAF wastewater plants in ozone nonattainment areas. From these calculations, maximum facility emissions are determined which represent the upper limit for the potential VOC emissions from these wastewater plants. Based on the calculated emission estimates, each selected wastewater facility is evaluated as a potential major stationary source of volatile organic emissions under both Title I of the 1990 CAAA and the plant's governing Clean Air Act state implementation plan. Next, the potential impact of the specific volatile organics being emitted is discussed in terms of their relative reactivity and individual contribution to tropospheric ozone formation. Finally, a relative comparison is made between the estimated VOC emissions for the selected wastewater facilities and the total VOC emissions for their respective host installations.

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