ABSTRACT

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Thesis Title: Measurement Of The Removal Of Selected VOCs From A Municipal Treatment Plant

Industrial wastewater contains a variety of volatile chemical constituents. The large majority of the volatiles are organics. Many of these volatile organic compounds (VOCs) end up in the effluent to wastewater treatment plants. It is necessary to estimate the emission of the VOCs from sewerage plants in order to study the fate of these volatile organic compounds.

This study focuses on the estimation and comparison of the emission of 28 volatile organic compounds from the water and air in four operation units of Linden Roselle Sewerage Authority (LRSA) wastewater treatment plant. The removal rates of these target compounds have been calculated via mass balance by determining the difference between their concentration in water at each stage and the previous stage. Although the effect of

specific removal mechanisms was not studied, thermodynamic calculations were made to check the results of air and water sampling.

The total calculated removal rate of all 28 target compounds was 3251 kg/day. Of this total, it was assumed that 70% of the nonpolar compounds and 10% of the polar compounds were emitted to the air.

Measurement Of The Removal Of Selected VOCs From A Municipal Treatment Plant

by

Hong Yu

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Dedicated To My Parents

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Chapter 1

Introduction

1.1 Background

Large quantities of volatile organic solvents are used routinely in manufacturing and service industries. Many of these solvents end up in the effluent to wastewater treatment facilities. Although adsorption, bioaccumulation and chemical or biological transformation could affect the fate and behavior of volatile organic compounds (VOCs) in wastewater treatment processes, volatilization and air stripping have been considered to be the main mechanisms for removal of VOCs from wastewater [1]. The VOCs entering wastewater treatment plants can be released into the atmosphere from wastewater during treatment and this kind of emission could be a significant source of air pollution.

Emissions of VOCs, particularly those designated as toxic air pollutants (listed in Table 1.1) [2], have become an increasing concern to state and

Table 1.1: List of VOCs which are Priority Pollutants

1	Acrolein	17	1,2-Dichloropropane
2	Acrylonitrile	18	1,3-Dichloropropane
3	Benzene	19	Ethylbenzene
4	Bis(Chloromethyl)Ether	20	Methyl Bromide
5	Bromoform	21	Methyl Chloride
6	Carbon Tetrachloride	22	Methylene Chloride
7	Chlorobenzene	23	1,1,2,2-Tetrachloroethane
8	Chlorodibromomethane	24	Tetrachloroethylene
9	Chloroethane	25	Toluene
10	2-Chloroethyl vinyl Ether	26	1,2-Trans-Dichloroethylene
11	Chloroform	27	1,1,1-Trichloroethane
12	Dichlorobromomethane	28	1,1,2-Trichloroethane
13	Dichlorodifluoromethane	29	Trichloroethylene
14	1,1-Dichloroethane	30	Trichlorofluoromethane
15	1,2-Dichloroethane	31	Vinyl Chloride
16	1,1-Dichloroethylene		

federal agencies. The recently passed amendments to the Clean Air Act greatly expand the list of compounds that would be regulated by statute [3].

Because emitted VOCs could create potential health problems for treatment plant workers and the general public in surrounding areas, most of them have been previously evaluated for animal and human carcinogenicity [4], and some are classified as hazardous substances, or hazardous waste materials. These toxicity data are presented in Table 1.2. Assessment of

VOC emissions to the atmosphere is necessary for decision makers who must determine the appropriateness of the inputs to and the design and operation of a wastewater treatment plant.

The Linden Roselle Sewerage Authority (LRSA) has a substantial inflow of industrial solvents, which may contribute to treatment plant upsets and odor episodes, related to the concentration of various solvents as they enter the treatment plant. They are of interest to Linden Roselle Sewerage Authority, and the New Jersey Department of Environmental Protection. Data on the relative losses of VOCs to the air in each of the treatment processes would be useful in the general evaluation of the impact of treatment plants on air pollution.

1.2 Sources of Organic Containing Wastewater

Based on information developed by the Office of Water Regulations and Standards (OWRS), there are approximately 4,200 facilities in the Organic Chemicals, Plastics, and Synthetic Fibers Manufacturing Industry (OCPSE); the Pesticides Manufacturing Industry; the Pharmaceutical Manufacturing Industry; the Pulp, Paper and Paperboard and Builders Paper and Board Mill Industry (Pulp and Paper Industry); and the Hazardous

Table 1.2: Toxicity Data of Selected VOCs Examined in LRSA Plant

No	Compound Name	Carcinogen (EPA)	Hazardous Substance (EPA)	Hazardous Waste (EPA)	Priority Toxic (EPA)
1	Methanol	-	-	-	-
2	Ethanol	-	-	-	-
3	Acetonitrile	-	-	+	-
4	Acetone	-	-	+	-
5	Isopropanol	-	-	-	-
6	Diethyl Ether	-	-	-	-
7	Methylene Chloride	+	-	+	+
8	Carbon Disulfide	-	+	+	-
9	Methyl Ethyl Ketone	-	-	-	-
10	Chloroform	+/animal	+	+	+
11	Ethyl Acetate	-	-	+	-
12	1,2-Dichloroethane	+	+	+	+
13	1,1,1-Trichloroethane	-	-	+	+
14	n-Butanol	-	-	+	-
15	Benzene	+	+	+	+
16	Carbon Tetrachloride	+/animal	+	+	+
17	Trichloroethylene	+/animal	+	+	+
18	Ethylene Glycol	-	-	-	-
19	Pyridine	-	-	+	-
20	Methyl Isobutyl Ketone	-	-	+	-
21	Toluene	-	+	+	+
22	Dimethyl Formamide	-	-	+	-
23	Chlorobenzene	-	+	+	+
24	Ethylbenzene	-	+	-	+
25	m-Xylene	-	+	+	-
26	p-Xylene	-	+	+	-
27	o-Xylene	-	+	+	-
28	1,2-Dichlorobenzene	-	+	+	+

Waste Treatment, Storage, and Disposal Facilities Industry (TSDF) [5]. These industries differ in structure and manufacture a wide variety of products. However, many of the chemical processes employed within these industries use similar organic compounds as raw materials, solvents, catalysts, and extractants. In addition, many of these processes also generate similar organic by-products during reaction steps. Consequently, the five industries combined generate about 2,800 million gallons of wastewater annually, many of the wastewater streams generated by the targeted industries are similar in organic content. These organic-containing wastewater streams result from both the direct and indirect contact of water with organic compounds.

Direct Contact Wastewater: Water comes in direct contact with organic compounds due to many different chemical processing steps. As a result of this contact, wastewater streams are generated which must be discharged for treatment or disposal. A few sources of process wastewater are: water used to wash impurities from organic products or reactants, water used to cool or quench organic vapor streams, condensed steam from jet eductor systems pulling vacuum on vessels containing organics, water used as a carrier for catalysts and neutralizing agents, and water formed as a by-product during reaction steps.

Two additional types of direct contact wastewater are landfill leachate and water used in equipment washes and spill cleanups. These two types of wastewater are normally more variable in flow and concentration than the streams previously discussed. In addition, they may be collected for treatment differently than the wastewater streams discharged from process equipment such as scrubber, decanters, evaporators, and distillation columns.

Indirect Contact Wastewater: Wastewater streams which do not come in contact with organic compounds in the process equipment are defined as "indirect-contact" wastewater. However, a potential exists for organic contamination of these wastewater types. Water streams which are contaminated as a result of leaks from heat exchangers, condensers and pumps are examples of non-contact wastewater. These indirect contact wastewaters may or may not be collected and treated in the same manner as direct contact wastewaters. Pump seal water is normally collected in area drains which tie into the process wastewater collection system. This wastewater is then combined with direct contact wastewater and transported to the wastewater treatment plant. Wastewater contaminated from condenser and heat exchanger leaks are often collected in different systems and bypass some of the treatment steps used in the treatment plant. The organic content in these streams can be minimized by implementing an aggressive leak detection program.

1.3 Sources of VOCs Emission

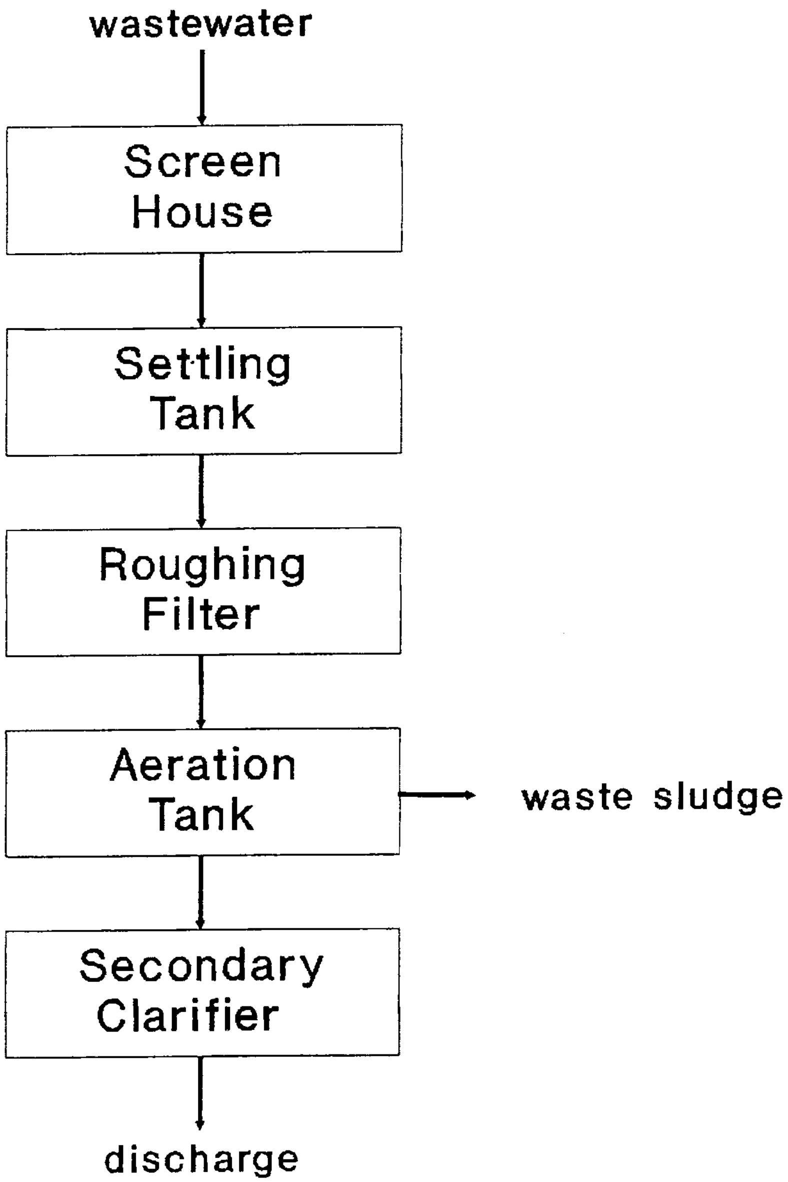
Wastewater streams are treated in a variety of ways. Generally, wastewater passes through a series of treatment units before being discharged from a wastewater treatment plant. Many of these treatment system units are open to the atmosphere and allow organic-containing wastewaters to contact ambient air. Whenever this happens, there is a potential for air emissions. The organic pollutants volatilize in an attempt to attain equilibrium partial pressure above the wastewater. In doing so, the organics are emitted to the ambient air. The magnitude of emissions depends greatly on many factors such as the physical properties of the pollutants, the temperature of the wastewater, and the design of the individual treatment units. All of these factors as well as the general scheme used to treat facility wastewater have a major effect on air emissions [6].

Wastewater treatment schemes are facility specific. The flow rate and organic composition of wastewater streams at a particular facility are functions of the processes used. Figure 1.1 illustrates a scheme of the Linden Roselle Sewerage Authority wastewater treatment plant for treating municipal and industrial wastewater. Figure 1.1 illustrates the wastewater flows through screens to remove large solids, which are collected in rolling carts for later disposal. The screen house is ventilated through two stacks located in opposite corners of the room, with the room air exhausted through two vent grills.

The wastewater is carried through the settling tanks and on to the roughing filters. The settling tanks or primary sedimentation tanks are a pair of pools where the incoming water is allowed to stand without agitation, so that the large particulates settle to the bottom where they are drawn off. The hydraulic residence time is about 2 hours. The water surface is constantly skimmed to remove the film of oil and scum which rises to the top. The water is allowed to flow out from the top of this tank, and proceeds to the roughing filter.

The roughing filters are broad towers, containing porous grids, coated with a film of bacterial matter. Air flows through the grids in an upward direction. The water is distributed over the upper surface of the towers by rotating arms. The water, pumped through these arms, is sprayed to a height of about 1 meter above the surface, and falls on to the surface. After trickling through the filter, the water passes through collection wells and is pumped into the aeration tanks.

Figure 1.1: Flow Schematic for LRSA Sewerage Plant



The aeration tanks are a series of large tanks. Water is pumped into these tanks along their length, and air is forced through the water to keep the dissolved oxygen levels high enough for efficient aerobic digestion. The water is exposed to the biologically active sludge in this system.

Wastewater leaving the aeration tanks normally flows through a secondary clarifier for solids removal before it is discharged from the treatment plant.

As mentioned above, these wastewater treatment system units are open to the atmosphere, and all of them are sources of VOC emission.

1.4 VOCs Emission Mechanisms

In a wastewater treatment plant, VOCs emission could be considered as volatilization of VOCs from wastewater to air or air stripping of VOCs in wastewater. The mechanisms of volatilization and air stripping involve diffusion and convection between liquid phase and vapor phase due to concentration gradient and temperature gradient of various VOCs [7]. In different treatment units, their effects are different and depend on different factors.

Screen House: As wastewater flows through the screen house the hydraulic residence times are low, so there is turbulence at the surface of the wastewater. This increases the potential for stripping to the atmosphere. The liquid and vapor phase resistances to mass transfer are reduced, and convective mass transfer in both phases is increased. On the other hand, there is volatilization. Organics volatilize in an attempt to reach equilibrium between the aqueous and vapor phases. The organic vapor concentration in the headspace at the inflow pit is much higher than ambient concentration. Due to this concentration gradient, organics diffuse from the inflow pit into the ambient air through the opening at the top of the pit. In addition, if the temperature of the wastewater flowing through the pit is greater than the ambient air temperature, this temperature gradient will induce air flow from the vapor headspace in the pit. This air flow rises into the surrounding air. The convective forces created by this air flow establishes convective mass transfer of the organics.

Emission rates from the screen house are influenced by a number of factors. These factors include the composition and physical properties of the pollutants in the wastewater flowing through the inflow pit, the temperature of the wastewater, ventilation rate, inflow pit design characteristics, and climatic factors.

Primary Settling Tank: Residence times in here are generally much longer than those in the screen house, and since the settling surfaces are large and open, this can lead to volatilization of the VOCs [8]. The wastewater pollutants in the primary settling tank diffuse through the water to the liquid surface. These pollutants volatilize into the ambient air above the liquid surface in an attempt to reach equilibrium between liquid and vapor phases. Since the organic vapors above the liquid are in contact with ambient air, these organic vapors can be swept into the air by wind blowing across the surface of the clarifier.

The factors effecting emissions from a primary settling tank are the wastewater characteristics such as temperature, pollutant's concentration, volatility, diffusivity, wind speed, as well as settling tank design characteristics such as liquid surface area, the fetch to depth ratio, and the hydraulic retention time.

Roughing Filter: The roughing filters contain porous grids, which are coated with a film of bacterial matter. The wastewater is distributed over the upper surface of the towers by rotating arms. It is pumped through these arms, then is sprayed upward to a height of about 1 meter above the surface, and falls onto the surface. This action increases the air-water interface, and accelerates stripping of volatile organics contained in the wastewater. This reduces the resistance to mass transfer and increases convection mass transfer rate. This treatment unit also presents additional opportunities for volatilization. The organics volatilize from the surface of the spray in an attempt to reach equilibrium between the liquid and vapor phases.

The major factors effecting emissions from the roughing filter are the characteristics of the wastewater itself such as pollutant diffusivity and temperature. Ambient wind speed has a significant effect on convective mass transfer. The characteristics of the spray pattern such as drop size, height of spray stream and the roughing filter design characteristics such as the length of the rotating arms or the rate of rotating, also effects emissions.

Aeration Tank: In order to supply the aerobic organisms with oxygen, air is introduced into the wastewater by the aerator. The aerator induces turbulence and thus reduces resistance between liquid and vapor phases as well as increasing the convective mass transfer in both phases [9]. This system is similar to those designed for air stripping. Aeration also promotes volatilization because the wastewater in this stage has a relatively long residence time. The pollutants volatilize into the ambient air above the liquid surface in an attempt to reach equilibrium between liquid and vapor phases.

The factors effecting emission from the aeration tank include wastewater characteristics, degree of ambient air motion, and design characteristics such as the quiescent and turbulent surface areas, the depth of the tank, air flow through the aerator, and the hydraulic retention time.

Secondary Clarifier: As water flows slowly through the clarifier, pollutants diffuse through the water to the surface, then volatilize into the ambient air above the liquid surface in an attempt to reach equilibrium between liquid and vapor phases. Since the organic vapors above the liquid are in contact with the ambient air, these organic vapors can be swept into the air by air moving across the surface of the clarifier.

The factors effecting emissions from clarifier are the wastewater characteristics, degree of ambient air motion, and clarifier design characteristics.

Chapter 2

Research Objective

The main objective of this research is the determination of concentration levels of target compounds both in water and air samples and the estimation of the emission of 28 selected volatile organic compounds from various locations in the Linden Roselle Sewerage Authority wastewater treatment plant.

Emission rate can be estimated by comparing the difference in the air levels of target compounds above the treatment units and in the surrounding areas and by measuring the decrease in water concentration of the target compounds in successive plant operations, and also by the calculating the levels of concentration of target compounds with measurable concentration levels based on vapor-liquid equilibrium and mass transfer.

In order to get significant data on the concentration of VOCs in wastewater and air, it is necessary to select the appropriate sampling sites, sampling methods, and analysis methods.

Chapter 3

Literature Review

Many of studies have been done on assessment the loss of organic compounds from wastewater treatment plants by partition to the air. The literature search in this study concentrated on papers involving the use of theoretical models, laboratory studies employing closed systems, and real measurement data applied to estimates of the emission of the VOCs from wastewater treatment plants.

The search was conducted by using the subject index and the author index for the institutions, referring to authors known to be active in this field, and consulting Chemical Abstracts for the years 1982-1991 inclusive.

3.1 Theoretical Models

Donald Macky et al. [10], developed a Comprehensive Model to describe the rates of process of organic chemical volatilization, absorption at the water surface, dissolution in rainfall, and wet and dry particle deposition, which, when viewed in total, comprise the dominant air-water exchange process. Correlations were suggested for partitioning between air and airborne particles and for washout ratios as a function of the chemical's physical-chemical properties. It was suggested that chemicals with high Henry's law constants, which were subjected to volatilization, but had low vapor pressures, are subjected to appreciable sorption to atmospheric particles, and may cycle between water and air with intermittent periods of intense deposition followed by slower but prolonged volatilization. A steady-state but non-equilibrium condition is achieved in which the water was supersaturated with respect to the air; i.e., the chemical potential or fugacity of the chemical in the water exceeded that in the air. These effects are pronounced at low temperatures.

This mathematical model included all five processes in similar algebraic format which conveniently enabled process rates and transfer coefficients to be compared in identical units. It was shown that this facilitates interpretation of environmental behavior and identification of predominant pollutant pathways. In addition, a theoretically based correlation equation for washout ratios for organic chemicals was used to assess the extent to which a given chemical had been expected to become concentrated in precipitation. The model was formulated by using fugacities, which simplifies the derivation and provides new insights into chemical partitioning and transport in the environment [11][12][13]. The final model equation was expressed in traditional concentration units.

Eun Namkung et al. [14], developed a General Fate Model (GFM) for the activated sludge treatment process of wastewater treatment plant from the fundamentals of VOC convection, volatilization to the air, adsorption to biological solids, and biodegradation. The main source for volatilization emissions was assumed to be an activated sludge tank that had diffused aeration. This model includes three processes, expressed by a mass balance equation, which was useful for interpretation and prediction of the fate of organic chemicals in wastewater treatment plant.

The VOCs were divided into "biodegradable" and "nonbiodegradable" categories and a GFM was used to study the relative importance of volatilization, biodegradation, and adsorption [15]. The GFM results showed that, in activated sludge systems, biodegradation was the most important removal mechanism for total volatile organic compounds. This was true only when the VOCs, such as benzene, chlorobenzene, ethylbenzene, and toluene which were the majority of total VOCs in influent wastewater, were biodegradable. The GFM prediction agreed well with the laboratory activated sludge experimental results reported by other researchers [16][17]. Thus, was considered that the VOCs emission rate was significantly affected by biodegradability, because the emission rate of a VOC decreased if biodegradation occurs. The key point for successful estimation of VOC emission rate from a wastewater treatment plant to the air during the activated sludge treatment process using this model was to choose which compounds could be biodegraded aerobically.

Douglas A. Barton et al. [18][19], studied the intermedia transfer of potentially toxic compounds from the aqueous phase to the atmosphere and sludges during wastewater treatment and developed a NCASI computer model [20] to predict the fate of organic compounds during treatment.

The model was based on equilibrium relationships between the aqueous phase and the air and soil phases and a second order biodegradation rate expression, coupled with the necessary terms defining hydraulic transport. The model simulated compound removal by four different pathways: forced stripping, natural volatilization, biosorption and biodegradation. The model estimated the distribution of the fate of organic compounds influent to biological treatment. For volatilization, they assumed 75% stripping of nonpolar compounds and 10% stripping of polar compounds. The model was written for execution on personal computers and included a data base containing the various chemical and physical properties for each pathway required to simulate organic compound removal.

Richard L. Corsi et al. [21], developed a Toxic Emissions during Sewage Treatment (TEST) model to estimate Volatile toxic organic compounds (VTOCs) emission from entire wastewater treatment systems. This semi-empirical mass transport model was an attractive and valuable method to study the emissions associated with wastewater treatment. The resulting emissions estimates can then be used to analyze the effects of treatment modifications on the fate of organic contaminants.

The model was based upon the assumption of steady-state conditions. It included several individual process models such as different trickling filter models. The TEST model was user-oriented, and flexible in its ability to model user-specified treatment configurations.

The model was used in an application which exemplified the significance of aerated secondary treatment processes as emissions sources. For VTOCs, the primary removal mechanism appears to be volatilization.

3.2 Laboratory Simulations

Weber and Jones [22] used a laboratory-scale, completely-mixed flow activated sludge reactor to evaluate the relative importance of volatilization, adsorption, and biodegradation as removal mechanisms under conditions considered representative of municipal activated-sludge treatment. Their steady-state results showed that approximately 80% of the influent VOCs tested (that is benzene, chlorobenzene, ethylbenzene, and toluene) were removed by biodegradation, while about 20% of influent VOCs were removed by volatilization. Removal by adsorption was below 1% for all VOCs.

Kincannon et al. [23] found that, in a laboratory-scale activated sludge reactor, tetrachloroethane, 1,2-dichloroethane, and 1,1,1-trichloroethane were completely removed by volatilization, whereas benzene and methylene chloride were removed mainly by biodegradation. Adsorption played no significant role in removal of any VOCs tested.

Blackburn et al. [24] also reported similar experimental results.

Alex R. Gholson et al. [25] recently published a paper to evaluate an enclosure method for direct measurement of volatile organic emissions from quiescent liquid surfaces under simulated conditions in the laboratory. The methods have been used to measure a variety of emissions from many different sources [26][27]. Among them, the flux chamber method has been used to make direct air measurements of emissions from surface impoundments, land farms, landfills, and contaminated soil [28][29]. Emission measurements made with the flux chamber provided a database for regulatory decision making and validated predictive air emission models.

The flux chamber was installed [30], then a series of laboratory studies were performed using a simulated surface impoundment to investigate the effect of the operational parameters and environmental conditions on the method's accuracy and precision.

The results of the laboratory studies indicated that liquid surface emission measurements can be made with precision and that operational and environmental parameters had only a minor effect on the precision and accuracy of the method. The flux chamber method proved to be a reliable method for measuring emission rates from liquid surfaces to evaluate control technology and to assess the relative potential of emission from different sources.

3.3 Studies of Working Treatment Facilities

V.S. Dunovant et al. [31] investigated the emission of three wastewater treatment plants. They compared air concentration variability of volatile organic chemicals at or between the three sewerage plants under specified plant and weather conditions and determined the relationship between the total combustible organic vapor concentration and individual compounds in the air, and between air and wastewater concentrations. These three plants served a diversified group of chemical processing, soap, electrical, metal finishing, pharmaceutical and organic pigment industries.

The samples were collected by charcoal tube and analyzed by flame ionization detector-organic vapor analyzer (FID-OVA).

The results of this study indicated that total vapor concentrations responsive to FID-OVA were highest at the treatment plant with the highest portion of industrial wastewater in its influent. Also, the total concentrations tended to be higher later in the day and later in the week. At the largest plant studied, air concentrations of methyl isobutyl ketone, chlorobenzene, toluene, and benzene correlated significantly with total organics in the air. There were few correlations between specific organics in the wastewater grab samples and in the headspace, or between specific or total organics in the wastewater and total organics in the headspace. Most of the specific volatiles in the periods of peak total organic concentrations in the air were non-aliphatic halocarbons although only perchloroethylene, 1,1,1-trichloroethane concentrations in both air and wastewater were significantly correlated at these plants.

Eun Namkung et al. [14] also investigated the two wastewater treatment plants. They selected eleven VOCs which were detected in the influent wastewater at the sewerage plant and ten VOCs which were found in the influent wastewater at another sewerage plant as the target compounds. They found that 58% and 51% of removed VOCs from these two sewerage plants respectively were emitted to the air. Estimates of VOC emissions from wastewater treatment plants were calculated by simple mass balances that are parameterized to account for VOC losses observed between the influent and effluent streams. Worst-case emissions result from an assumption that removal results entirely from volatile losses. They also used these results to prove their GFM model and indicated biodegradation was the most important mechanism in removal of VOCs, since volatilization and adsorption were not significant compared to biodegradation when biodegradation occurs.

The results from the Rhode Island Toxic Integration Project [32] provided a large volume of data on VOC emissions from the POTW. This project was a multimedia evaluation of toxic pollutants in the vicinity of the Upper Narragansett Bay. It involved a comparative analysis of VOC emissions from six Publicly Owned Treatment Works (POTWs) in the upper bay area with VOC emissions from selected industrial sources. It characterized the fate of VOCs in POTWs by monitoring and analyzing influent, effluent, sludge, and ambient air surrounding the plant; developed data on VOC air emissions that could be used to establish annual average emission estimates and ambient concentrations of those pollutants.

The data showed that measurable increases of target VOCs were present at on-site monitoring points immediately downwind of the POTW aeration tanks. This suggested that these units were major sources of VOC emissions due to volatilization. Average wastewater influent and effluent concentrations of target VOCs were observed. Many of the pollutants were removed by POTW treatment processes. Generally, as influent levels of VOCs increased, so did effluent concentrations, suggesting constant removal rates.

Given the absence of significant levels of target VOCs in POTW sludge, the relatively high removals of VOCs observed throughout the plant, and the evidence of VOCs in ambient air adjacent to the headworks and aeration tank, it was likely that air stripping, and to a much lesser extent biodegradation, were the more likely removal mechanisms than adsorption to solid particles. If it was assumed that all the target VOCs were removed from the POTW by stripping, then many pollutants were being emitted to the atmosphere. It was important to note that atmospheric and receiving water dilution substantially reduced any potential impacts associated with these discharges.

Chapter 4

Experiments

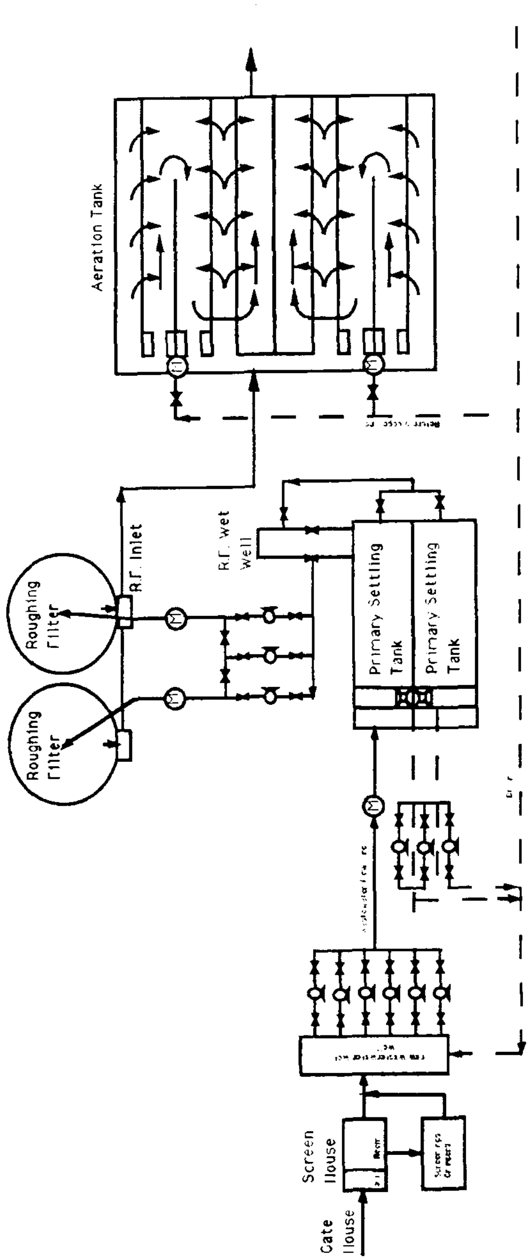
4.1 Sampling

In this project, air and water sampling sites were selected in consultation with representatives of Merck and LRSA. The plant is diagrammed in Figure 4.1, and it was divided into four main locations where loss of volatiles would be measured: screen house, settling tank, roughing filter and aeration tank. Air and water sampling points were indicated in Figure 4.2. Samples were collected on ten randomly selected days between August 22 and December 22, 1990.

4.1.1 Air Sampling

The samples were collected by opening the valve on the evacuated internally polished six liter stainless steel canister. An inlet tube with a needle restrictor moderated the flow, so that the canister was filled over a span

Figure 4.1: Diagram of LRSA Sewerage Plant



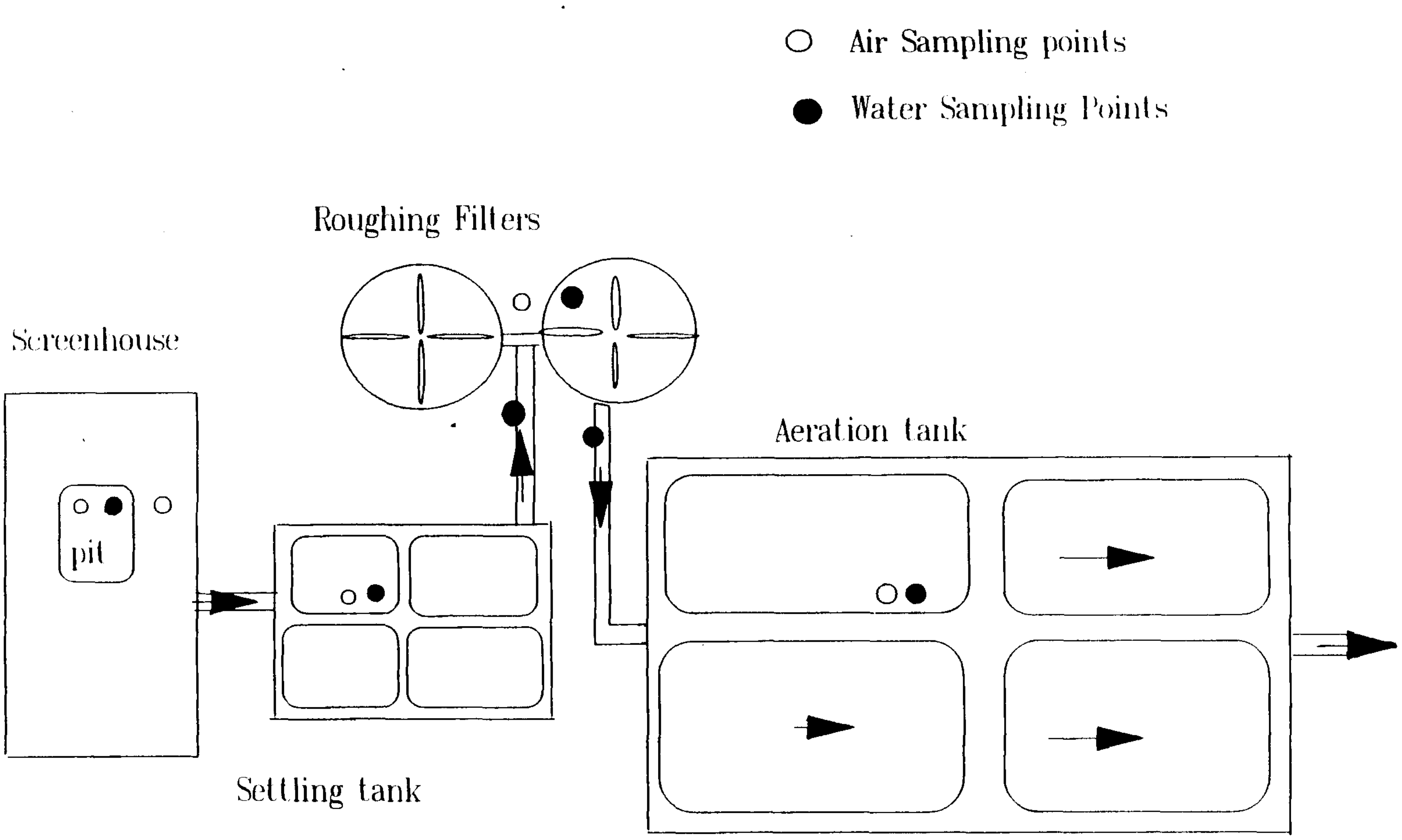


Figure 4.2: Diagram of Sampling Sites in LRSA Sewerage Plant

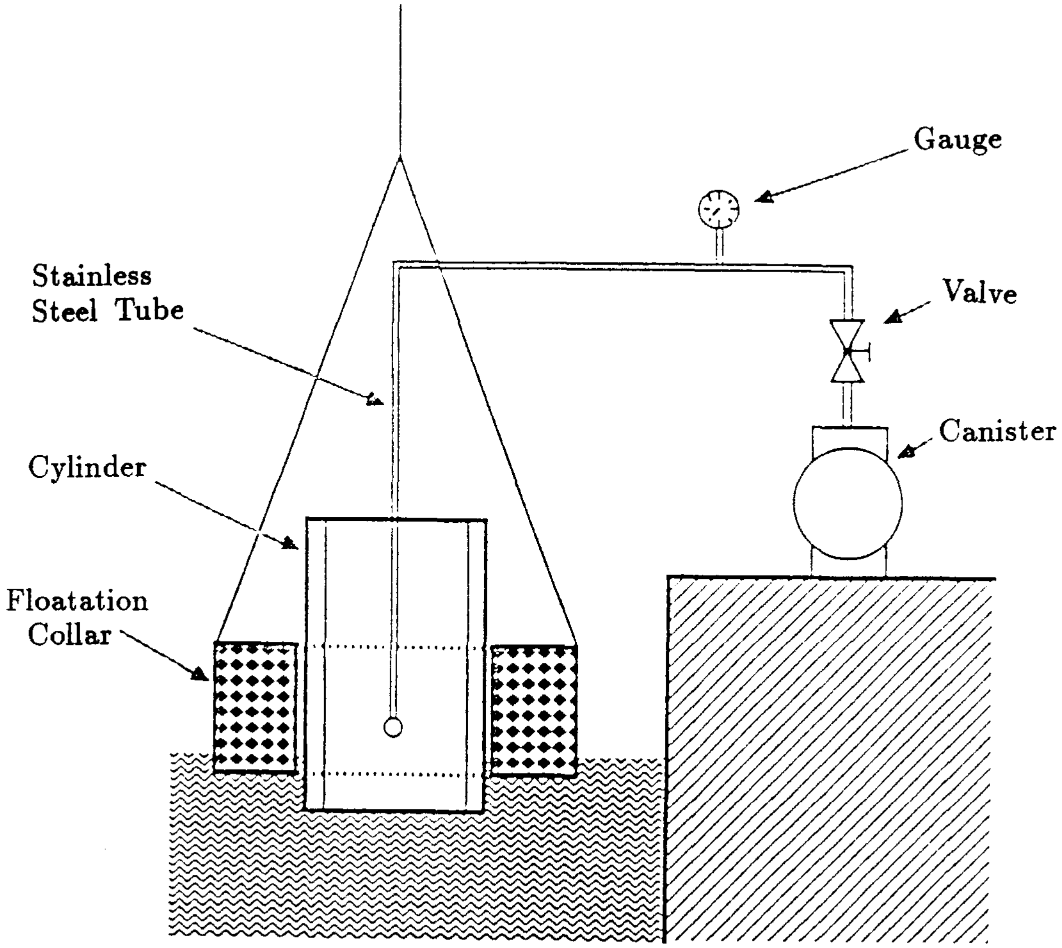
of 10-15 minutes under the atmospheric pressure. The final pressure of the canister was about 0.9 atm.

Screen House Pit: The sample was collected about 1 meter above the surface of the incoming water, with the inlet tube lowered into the pit, and the intake located about 0.5 m above the water, and about 1 meter below the floor of the screen house.

Screen House Room: Sample was collected in the center of the room, about 30 cm above the floor, without the inlet tube. This sample was intended to be representative of the air in the room, and the amount of target substance exhausted from the room was calculated from this concentration and the outgoing air flow.

Settling Tank: This sample was taken using a floating draft shield sampler, depicted in Figure 4.3. The sampler is an open ended metal cylinder, 60 cm in height and 25 cm in diameter. It was fitted with a styrofoam collar, so that it could be floated onto the water. The draft shield was allowed to float for a few minutes before the sample was taken. The inlet tube of the sampling canister was then placed into the center of the cylinder and the valve opened to draw the sample in.

Figure 4.3: Diagram of A Floating Draft Shield Sampler



Roughing Filter: The sampling canister without the inlet tube was placed between the centers of the two tricking filters at a level with the top of the filters. The general wind speed and direction, which was determined with a rotary anemometer was also recorded during the sample collection time.

Aeration Tank: The same draft shield used in the settling tank was employed also, and the sample was collected toward the center of the aeration tank system. Since the pool was subjected to air bubbling through it, a longer collection time was used to avoid biasing the sample.

4.1.2 Water Sampling

In each case four replicate 40ml samples were collected by filling teflon capped septum glass bottles to overflowing and capping them tightly. The samples were preserved by the addition of 4 drops of 6M HCl to the bottles before filling them. Samples were returned to the lab within two hours and were refrigerated until analyzed. A field blank was prepared before each trip. Subsequently it was stored with the samples and analyzed at the same time.

Screen House: Sample was taken from the inflow pit. This sample represents the inflow concentration of the target compounds.

Settling Tank: Sample was taken from the center portion of the tank system, in the vicinity of the floating air sampler.

Roughing Filter Wet Well: This sample was collected from the wet well feeding water into the roughing filter. It represents the inflow concentration to the roughing filter.

Roughing Filter Top: This sample was taken in a shallow container under the cascade from the distributor arm. The difference between the concentration in the inlet wet well and that of the water on the top of the roughing filter should be indicative of the amount of volatile material lost in the spraying action.

Roughing Filter Outlet: The outlet well from the roughing filter was sampled. The stripping which occurs as the water trickles down the filter can be determined by the difference between this sample and the previous one.

Aeration Tank: Sample was collected in the vicinity of the floating sampler used for air samples. The difference between the concentration of this stage and roughing filter outlet indicated the VOCs lost in this section.

4.2 Analysis

Volatile organic compounds in the air samples were determined by cryogenically concentrating the volatiles from the air samples and injecting them into a high resolution gas chromatographic column [33]. Water samples were analyzed by high resolution gas chromatography, using a Tekmar purge and trap inlet apparatus [34]. The analytical reproducibility, calculated from replicate analysis of air and water samples was on the order of 10-20% relative standard deviation.

4.2.1 Air Analysis

1. Apparatus

The apparatus used in this project incorporates an adapted cryogenic inlet on a Varian 3700 Gas Chromatograph with a Flame Ionization Detector, and Electron Capture Detector. Data were collected and processed with a microcomputer using an analog to digital converter and integration software supplied by IMI Co., State College, PA.

The GC column utilized in this project was:

(1) 50m×0.2mm Crosslinked Methyl Silicone Gum with a 0.5μ film thickness (PONA, Hewlett Packard).

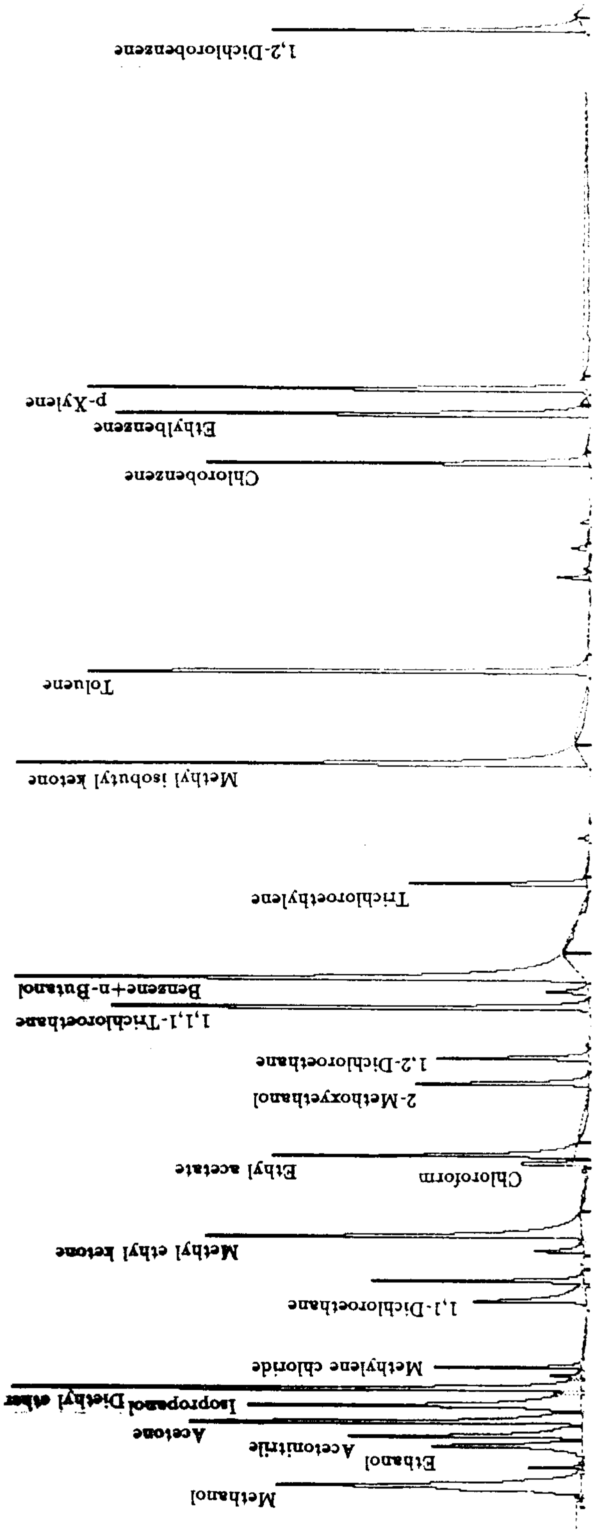
2. Calibration Standards

The GC was calibrated against a gaseous standard (Alphagaz, Morrisville, PA), containing the 28 target compounds at low ppm concentration, before each batch of samples. The chromatogram of standard is shown in Figure 4.4. The FID detector was used for quantitation for most compounds, while the ECD was used to assist in peak identification and to quantitate halogenated compounds at low concentrations.

3. Instrumental Parameters

The temperature of injection system: 60°C
The initial column temperature and held time: 30°C, 8min.
Column temperature rises at a rate: 6°C/min.
The final column temperature and held time: 210°C, 8min.
The carrier gas flow rate: He, 2ml/min.
The temperature of detectors: 220°C
The FID detector operating conditions:
Air: 300ml/min.

Figure 4.4: The Chromatogram of Gas Standard



H_2: 30ml/min.

N_2 (make-up gas): 28ml/min.

The ECD detector operating conditions:

N_2 (make-up gas): 27ml/min.

4. Analytical Procedure

(1) Preheat: The canister with air sample was heated to about 40°, and the sample injection tubing was heated to 60°C. The tubing was flushed by air sample and then evacuated.

(2) First trap: The cryogenic trap was adjusted to a temperature between -110°C to -120°C by adding liquid nitrogen to n-propanol contained in a small Dewar flask and measuring the temperature with thermocouple. The Dewar flask was placed over the glass bead filled tubing and held for a few minutes to cool it to about -120°C. At this temperature, the target compounds were condensed. The canister valve was opened and the sample passed through the first cryogenic trap and into the ballast volume. The pressure in the known ballast volume was read from an accurate pressure gauge.

(3) Second trap: After injecting the desired volume, the focusing cold trap was placed into liquid nitrogen, forming cryogenic trap 2, and the first

cryogenic trap was replaced with a hot water bath, at around 90°C, which allowed the condensed volatile compounds to vaporize. The gas sampling value was switched to allow the carrier gas to transfer the sample to the focusing trap 2, which is cooled to -150°C by liquid nitrogen. Eight to ten minutes were required for the complete transfer.

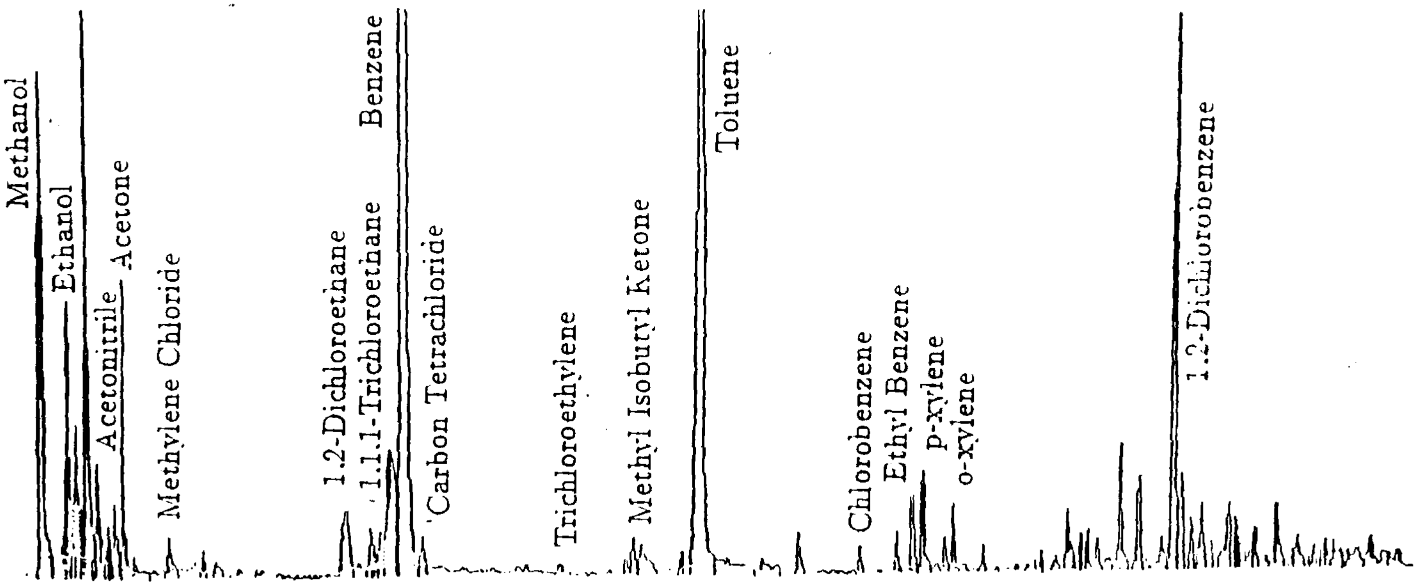
(4) GC run: After the sample was transferred into focusing trap, the cryogenic trap 2 was placed into a 95°C hot water bath for 8 minutes. Then the hot water was removed and GC oven temperature program was started. The program began at 30°C, held for 8 minutes, rose at a rate of 6°C/min., to a final temperature of 210°C.

(5) Repeat: To reduce variability, three replicate sequential analyses were made on each sample and averaged. The typical sample chromatogram is represented in Figure 4.5.

5. Quality Assurance

Each canister was blanked before being used for sampling. The chromatograph was calibrated daily, and the flows to the detectors were adjusted if the sensitivity and response began to change.

Figure 4.5: The Chromatogram of Typical Air Sample in LRSA Sewerage Plant



The reproducibility for replicate sample analyses was in the range of about 40% RSD. Using this method, detection levels determined from the standard deviations at various concentrations and extrapolated to the SD at zero concentration, showed that the detection limits were about 4 ppb for the tested compounds [33].

4.2.2 Water Analysis

1. Apparatus

The apparatus used in this project incorporated a Tekmar LSC-2000 Purge-and-Trap concentrator interfaced to a Varian 3400 Gas Chromatograph with a Flame Ionization Detector, Photoionization Detector, and Electrolytic Conductivity Detector. The cryogenic trap was equipped with the Tekmar Capillary Interface for sample focusing before injection. Cryofocusing was done with liquid nitrogen. Data were collected and processed with a Minichrom (R), Chromatograph Data System.

Columns utilized in this project were:

(1) 25m×0.2mm Crosslinked 5% Ph Me Silicone with a 0.3μm film thickness (Ultra 2);

(2) 50m×0.2mm Crosslinked Methyl Silicone Gem with a 0.5μm film thickness (PONA).

2. Calibration Standards

Stock standards were prepared by adding 10μl portions of pure target compounds to a weighed 10ml portion of methanol, and weighing each addition to the nearest 0.1mg. The standard was stored at 4°C and was diluted to ppm levels with methanol, as needed. This working standard was rapidly injected into distilled water using a microsyringe, and purged for calibration of the GC before each analysis session. The chromatogram of this standard was shown in Figure 4.6.

3. Instrumental Parameters

Tekmar LSC 2000 operation parameters:

Purging preheat: 40°C, 2min.
Purge time: 15min.
Purge gas flow rate: 80ml/min.
Dry purge: 2min
Cryotrap cooldown: -150°C

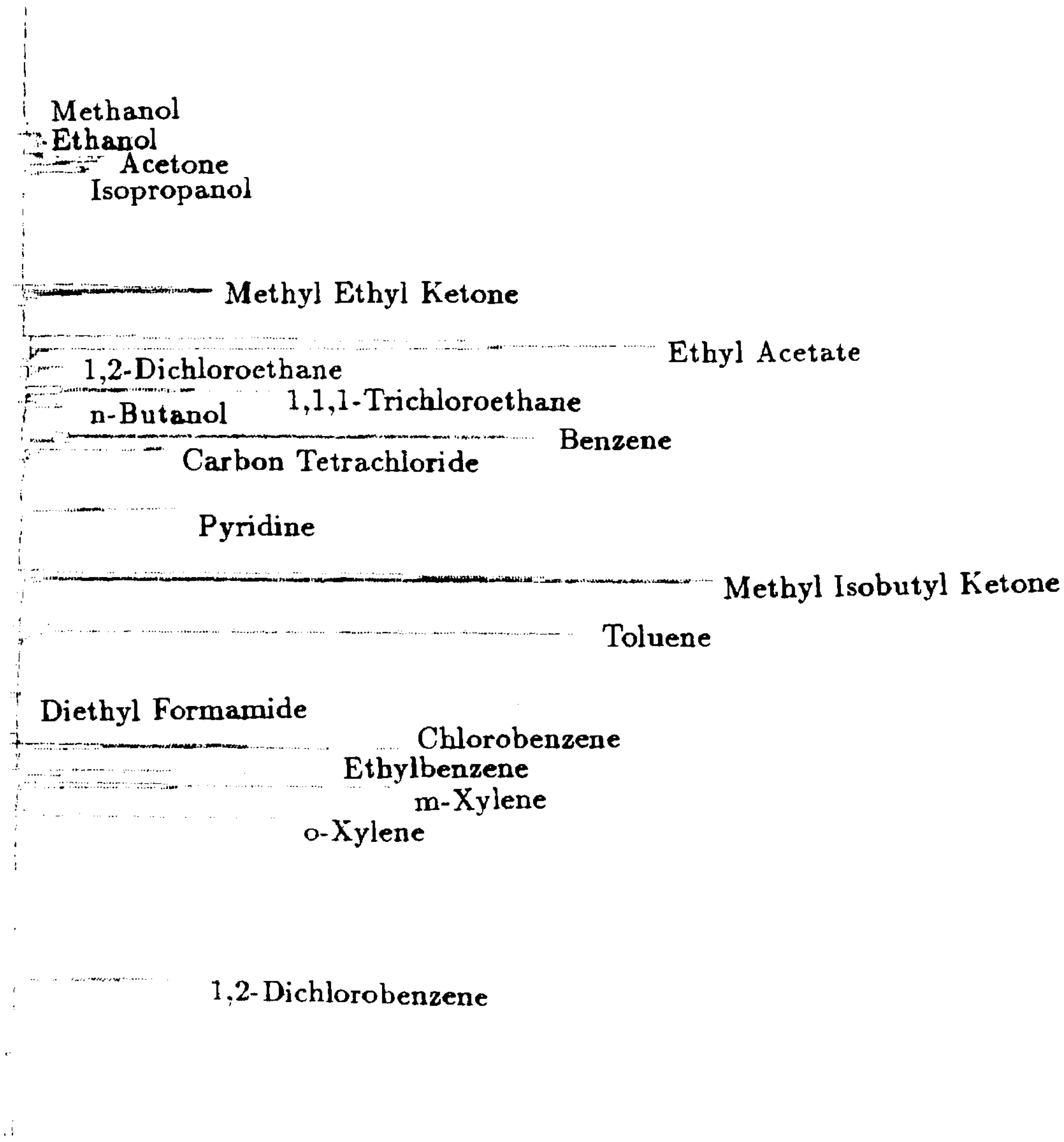


Figure 4.6: The Chromatogram of Water Standard

Desorb time: 12min., 180°C

Inject time: 1min., 180°C

Bake time: 10min., 250°C

Varian 3400 GC operation parameters:

The initial temperature and held time: 20°C, 10min.

A rate of temperature program: 6°C/min.

The final temperature and held time: 180°C, 8min.

The carrier gas and flow rate: He, 2ml/min.

The FID detector operating conditions:

Air: 300ml/min.

H_2: 30ml/min.

H_e (make-up gas): 20ml/min.

The PID/ECLD detector operating conditions:

H_2: 100ml/min.

Electrolyte flow rate: 20-50μl/min.

ELCD reactor temperature: 850°C

4. Analytical Procedure

The analysis was done on a Tekmar LSC 2000 Purge-and-Trap concentrator interfaced to a Varian 3400 Gas Chromatograph. 5ml of aqueous sample was loaded into a purge vessel. When Tekmar LSC 2000 was in

"Purge Ready Status", "Start" key on the keyboard was pressed, and operations began automatically according to following steps:

(1) Preheat: A sample heater heated the sample in a static condition (without purge gas flow). This process allowed the sample temperature to equilibrate before purging, which enhanced quantitative reproducibility.

(2) Purge: Volatile organics were removed from the sample by passing purge gas through it.

(3) Dry purge: The purge gas remained on, but flowed only through the trap to remove the water vapor from the trap.

(4) Cooldown: The cryogenic trap was cooled with liquid nitrogen in order to freeze the analyses to improve peak shape during the injection.

(5) Desorb preheat: In this mode, the trap was heated before the 6-port valve was switched on, so that the trap was hot before the analyses were backflushed.

(6) Desorb: The sample was backflushed into the cryogenic trap in this mode.

(7) Inject: The cryogenic trap was heated rapidly to release the analyses into the GC column in this step.

(8) Bake: The trap was cleaned for the next run by flowing purge gas at high temperature.

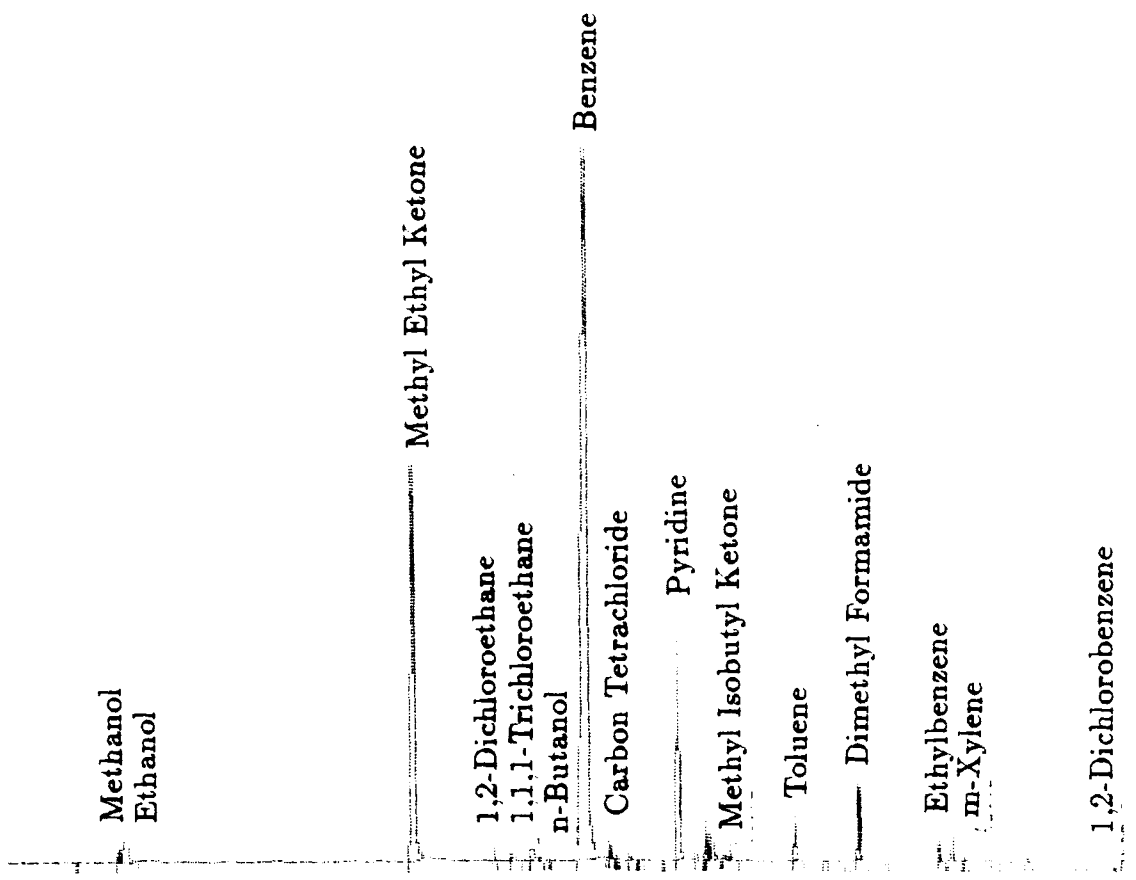
(9) GC run: As soon as the purge-and-trap system was on the inject mode, the GC started to run. The program began at 30°C holding for 10 minutes, then programmed to 180°C at 6°C/min. If with the PONA capillary column, the column was held at 20°C for 10 minutes, then programed to 180°C at 6°C/min.

(10) Repeat: To reduce variability, three replicate analyses were made on each sample and averaged. The typical sample chromatogram present in Figure 4.7.

5. Quality Assurance

Before each batch of samples was analyzed, the field blank was analyzed to insure that the analytical system, the reagents, the sampling process, and the trap had not caused contamination of the samples. No cases of contami-

Figure 4.7: The Chromatogram of Typical Water Sample in LRSA Sewerage Plant



nated blanks were found in the ten sets of samples analyzed in this project. Since the same group of workers was involved in both the sampling and analysis, problems of contamination, and sample custody were minimized.

The recovery of the target compounds from water ranged from 75 to 114%, determined by spiking with the standard mixture. The reproducibility for replicate sample analyses was in the range of 10 to 20% RSD. The method detection levels determined from the standard deviations at various concentrations and extrapolated to the SD at zero concentration, showed that the detection limits were about 5 ppb for tested compounds [35].

Chapter 5

Results and Discussion

The results of the sampling and analysis program provided a large volume of data on VOC emissions from the LRSA wastewater treatment plant. All 28 target VOCs but one were detected at least once in LRSA plant air and wastewater samples. These target VOCs are shown in Table 5.1.

5.1 Target Compounds in Air

Only 20 targeted VOCs were detected in the air above screen house, settling tank, roughing filter, and aeration tank at least once. The most frequently occurring VOCs in the air in the screen house unit were: methanol, acetonitrile, acetone, benzene, toluene, chlorobenzene, ethylbenzene, m&p-xylene, 1,2-dichlorobenzene. The highest concentration of VOC in air was 19 ppm for benzene. The most frequently occurring VOCs in the air above settling tank unit were: methanol, acetone, benzene, toluene, chlorobenzene, 1,2-

Table 5.1: List of 28 Targe VOCs Detected from LRSA Plant

No	Compound Name	Abbre. Name	Times Found in Water or Air	MW	BP (°C)
1	Methanol	MeOH	10	32.04	64.96
2	Ethanol	EtOH	10	46.07	78.50
3	Acetonitrile	ACN	9	41.05	81.60
4	Acetone	Ace	10	58.03	56.20
5	Isopropanol	IPA	8	60.11	82.40
6	Diethyl Ether	Ether	8	74.12	34.51
7	Methylene Chloride	$MeCl_2$	8	84.00	40.10
8	Carbon Disulfide	CS_2	4	76.14	46.30
9	Methyl Ethyl Ketone	MEK	4	87.12	152.00
10	Chloroform	Clform	4	119.50	61.20
11	Ethyl Acetate	EtAcet	1	88.11	77.10
12	1,2-Dichloroethane	$EtCl_2$	2	99.00	83.50
13	1,1,1-Trichloroethane	111-TCE	3	133.40	74.10
14	n-Butanol	ButOH	5	74.12	117.25
15	Benzene	Bz	10	78.10	80.10
16	Carbon Tetrachloride	CCl_4	4	153.80	76.70
17	Trichloroethylene	Tric	4	131.40	86.70
18	Ethylene Glycol	EG	0	62.07	198.00
19	Pyridine	Pyr	10	79.10	115.20
20	Methyl Isobutyl Ketone	MIK	10	100.16	116.85
21	Toluene	Tol	10	92.00	110.70
22	Diethyl Formamide	DMF	8	73.10	153.00
23	Chlorobenzene	ClBz	7	112.56	132.00
24	Ethylbenzene	EtBz	7	106.17	136.20
25	m-Xylene	m-X	9	106.17	139.10
26	p-Xylene	p-X	9	106.17	144.40
27	o-Xylene	o-X	9	106.17	138.35
28	1,2-Dichlorobenzene	1,2-DiClBz	10	147.01	180.50

dichlorobenzene. The highest air concentration was 1.1 ppm for chlorobenzene. The most frequently occurring VOCs in the air above the roughing filter unit were: methanol, acetone, benzene, toluene, 1,2-dichlorobenzene. The highest air concentration was 0.67 ppm for toluene. The most frequently occurring VOCs in the air above the aeration tank were: acetone, benzene, methyl isobutyl ketone, toluene, 1,2-dichlorobenzene. The highest air concentration was 1.7 ppm for methyl isobutyl ketone. These data are listed in Table 5.2. In the table, the c is the average concentration of 10 samples.

The data showed that the highest observed ambient air VOC concentration were, as expected, at the screen house. This should occur because of the high level of VOC loading in the influent wastewater, and the high turbulence at the grit screens. Also, the screen house is enclosed. The other principal sources of volatilization should be the roughing filters and aeration tanks, although that will also depend on the biodegradability of individual compounds [36].

Upon reviewing the overall concentrations of VOCs in air at the settling tank, the roughing filter, and the aeration tank, no obvious difference was seen to occur in VOC concentrations at these three sites when consideration was given to the sampling and analysis variability.

Table 5.2: Average Concentrations of Target VOCs in Air of LRSA Plant

Compound Name	Screen House		Settling Tank		Roughing Filter		Aeration Tank	
	c(ppm)	S.D.	c(ppm)	S.D.	c(ppm)	S.D.	c(ppm)	S.D.
MeOH	0.971	0.017	0.280	0.188	0.129	0.098	0.353	0.078
EtOH	0.340	0.450	0.106	0.158	0.021	0.018	0.053	0.090
ACN	0.448	0.492	0.062	0.098	0.040	0.055	0.070	0.094
Ace	1.562	0.719	0.109	0.102	0.039	0.045	0.173	0.209
Ether	0.625	0.056	0.045	0.031	0.143	0.165	0.121	0.100
$MeCl_2$	8.442	6.864	0.081	0.014	0.121	0.197	0.276	0.061
CS_2	0.288	0.075	0.107	0.111			0.220	0.054
Clfrom	0.628	0.001	0.052	0.054	0.096	0.001	0.229	0.069
$EtCl_2$	0.230	0.001			0.050	0.001		
111-TCE	0.029	0.001					0.070	0.001
Bz	6.279	5.304	0.240	0.192	0.249	0.241	0.051	0.047
CCl_4	0.304	0.410	0.025	0.018	0.001	0.018		
Tric	0.098	0.088	0.009	0.002			0.100	0.127
MIBK	0.045	0.001	0.017	0.004	0.010	0.001	0.188	0.126
Tol	1.126	0.756	0.101	0.153	0.163	0.220	0.095	0.064
ClBz	1.702	0.196	0.209	0.043	0.176	0.041	0.049	0.115
EtBz	0.042	0.050	0.002	0.001	0.002	0.001	0.009	0.008
m&p-X	0.064	0.075	0.002	0.003	0.004	0.004	0.010	0.010
o-X	0.061	0.054	0.004	0.005	0.002	0.001	0.008	0.006
1,2-DiClBz	0.334	0.046	0.019	0.015	0.022	0.020	0.136	0.023

In general there were to be no significant trends in magnitudes of target VOC concentrations found in the ambient air at the sampling points in the wastewater treatment plant versus the day of the week.

One unusual case occurred in the LRSA plant: the average concentration of methyl isobutyl ketone in the air above the aeration tank was greater than that of the screen house, the settling tank, and the roughing filter. The cause of the greater concentrations was not apparent, but one possible explanation was its formation as a product during biodegradation of other ketone compounds. Another possible cause was a batch release of VOCs by industries, which made the concentrations fluctuate hour by hour. Although an explanation could not be ascertained from the data alone, industry production and discharge of different materials seemed to be a likely cause for the variability.

5.2 Target Compounds in Wastewater

Only 25 targeted VOCs were detected in the water of the screen house, the settling tank, the roughing filter, and the aeration tank at least once. The most frequently occurring VOCs in the wastewater samples from the screen house were: acetone, isopropanol, methyl chloride, chloroform, 1,1,1-

trichloroethane, benzene, pyridine, methyl isobutyl ketone, toluene, dimethyl formamide, chlorobenzene, ethylbenzene, m&p-xylene, o-xylene, 1,2-dichlorobenzene. The greatest observed target VOC concentration in wastewater was 261 ppm for benzene. The most frequently occurring VOCs in the water samples from the settling tank were: acetone, isopropanol, methyl chloride, chloroform, benzene, pyridine, methyl isobutyl ketone, toluene, dimethyl formamide, chlorobenzene, ethylbenzene, m&p-xylene, o-xylene, 1,2-dichlorobenzene. The highest water concentration recorded was 220 ppm for benzene. The most frequently occurring VOCs in the water samples from the roughing filter were: acetone, isopropanol, methyl chloride, chloroform, benzene, pyridine, methyl isobutyl ketone, toluene, dimethyl formamide, chlorobenzene, ethylbenzene, m&p-xylene, o-xylene, 1,2-dichlorobenzene. The highest water concentration found was 99 ppm for benzene. The frequently occurring VOCs in the water samples from the aeration tank were: benzene, methyl isobutyl ketone, toluene, ethylbenzene, m&p-xylene, o-xylene, 1,2-dichlorobenzene. The highest concentration in water samples was 1.6 ppm for benzene. These data are listed in Table 5.3. In the table, the c is the average concentration of 10 samples.

Most of these data showed that every compound concentration decreased from stage to stage, indicating that most of the entering VOCs were removed. However, this result did not give information concerning

Table 5.3: Average Concentrations of Target VOCs in Water of LRSA Plant

Compound	Screen House		Settling Tank		Roughing Filter		Aeration Tank	
Name	c(ppm)	S.D.	c(ppm)	S.D.	c(ppm)	S.D.	c(ppm)	S.D.
MeOH	5.937	3.593	4.504	2.949	1.887	1.391	0.449	0.023
EtOH	0.916	0.829	0.347	0.184	0.212	0.001		
ACN	0.651	0.410	0.333	0.224	0.187	0.121		
Ace	3.184	3.437	1.421	1.334	0.586	0.461	0.060	0.016
IPA	5.135	4.370	4.064	2.585	2.194	1.807	0.034	0.032
Ether	0.176	0.026	0.166	0.200	0.087	0.058		
$MeCl_2$	3.636	3.314	1.646	1.637	0.534	0.657	0.050	0.001
MEK	0.143	0.129	0.173	0.223	0.177	0.170		
Clform	0.227	0.443	0.127	0.028	0.048	0.067	0.003	0.001
EtAcet			0.024	0.001	0.006	0.001		
$EtCl_2$	0.032	0.058	0.009	0.008	0.002	0.002	0.003	0.001
111-TCE	0.763	0.038	0.751	0.312	0.438	0.095		
ButOH	1.562	0.071	0.932	0.425	0.294	0.220		
Bz	32.742	31.207	27.674	8.496	12.566	3.921	0.241	0.084
CCl_4	0.010	0.004	0.010	0.005	0.004	0.003		
Tric	0.092	0.018	0.070	0.055	0.060	0.040	0.090	0.061
Pyr	0.397	0.330	0.151	0.093	0.062	0.069	0.016	0.018
MIBK	0.191	0.123	0.151	0.113	0.078	0.079	0.096	0.011
Tol	1.709	1.033	1.499	0.210	0.780	0.264	0.007	0.043
DMF	3.813	0.122	3.015	3.429	1.037	1.105	0.159	0.001
ClBz	1.604	0.134	1.660	1.282	0.663	1.282	0.077	0.043
EtBz	0.064	0.015	0.055	0.079	0.023	0.032	0.002	0.001
m&p-X	0.109	0.086	0.093	0.070	0.039	0.036	0.003	0.003
o-X	0.043	0.034	0.033	0.030	0.016	0.014	0.001	0.001
1,2-DiClBz	0.926	0.138	0.863	0.150	0.396	0.046	0.058	0.025

how much of the removed VOCs were stripped and volatilized to the air phase. Because biodegradation and adsorption were competing mechanisms [36], the volatilization and stripping rate could be much less than the difference between input and output loads at some treatment units.

In the influent to the screen house, the concentrations of benzene and methanol were much greater than other compounds, but in the water of the aeration tank, the concentration of benzene and methanol were not significantly different from other compounds. On the other hand, the concentrations of toluene and pyridine in the influent were lower than other compounds, but in the water of the aeration tank, the concentration of toluene and pyridine were not obviously different from other compounds.

The data also showed that the decrease of the concentration of more polar compounds such as ethanol, acetonitrile, and acetone was greater than that of nonpolar compounds such as toluene, chlorobenzene, and m&p-xylene. That is, the more soluble compounds were removed more efficiently than the hydrophobic ones, most likely by biodegradation.

5.3 Comparison of Target Compounds in Air versus in Wastewater

There were 19 target VOCs which occurred both in wastewater and in air at the same site and at the same time. The most frequently found target VOCs in the air and water of the screen house were: methanol, acetone, benzene, toluene, chlorobenzene, ethylbenzene, m&p-xylene, o-xylene, 1,2-dichlorobenzene. The highest observed target VOC concentration in wastewater was 261 ppm for benzene, and in air was 19 ppm for benzene. The most frequently found target VOCs in the air and wastewater of the settling tank were: methanol, acetone, benzene, toluene, chlorobenzene, 1,2-dichlorobenzene. The highest observed target VOC concentration in wastewater was 220 ppm for benzene, and in air was 1.1 ppm for chlorobenzene. The most frequently found target VOCs in the air and wastewater of the roughing filter were: methanol, acetone, benzene, toluene, chlorobenzene, 1,2-dichlorobenzene. The highest observed target VOC concentration in wastewater was 99 ppm for benzene, and in air was 0.92 ppm for chlorobenzene. The most frequently occurring target VOCs in air and wastewater of the aeration tank were: benzene, methyl isobutyl ketone, toluene, chlorobenzene, 1,2-dichlorobenzene. The highest observed target VOC concentration in wastewater was 1.6 ppm for benzene, and in air was 1.7 ppm for methyl isobutyl ketone. These data are presented in Table 5.4.

The data showed from Table 5.2 and Table 5.3 indicated that some compounds such as butanol, pyridine, dimethyl formamide were found in water but not in air. The separation between benzene and butanol was difficult [34]. In the water samples the problem was overcome by using the photoionization detector response to benzene for quantitation, but in the air analysis butanol could not be separated. However, in air samples analysed by mass spectrometer butanol was not detected. The fact that butanol, pyridine and dimethyl formamide were not detectable in air samples may have been due to their lower volatilization, lower vapor pressure or lower concentration.

Carbon disulfide was detected in air but was not detected in water. This may have been due to its higher volatilization. Carbon disulfide is a nonpolar compound with very low solubility.

Ethylene glycol was not detectable either in air samples or vapor samples, due to its extremely low vapor pressure [37]. It was not purgeable from water, nor was it expected to be found in the air.

In general the most frequently occurring target VOCs found in wastewater were also the most frequently occurring target VOCs in the air. It

Table 5.4: List of 19 Target VOCs Found both in Water and in Air

Compound Name	Screen House Times Found	Settling Tank Times Found	Roughing Filter Times Found	Aeration Tank Times Found
MeOH	7	7	7	0
EtOH	1	0	1	0
ACN	6	5	3	0
Ace	8	8	7	2
Ether	5	2	2	0
MeOH	5	4	2	0
Clform	1	3	1	0
$EtCl_2$	1	0	0	0
111-TCE	1	0	0	0
Bz	10	10	10	7
CCl_4	4	2	1	0
Tric	1	1	0	1
MIBK	0	0	0	7
Tol	10	10	10	8
ClBz	9	9	7	4
EtBz	10	6	5	6
m&p-X	10	6	5	6
o-X	9	5	3	6
1,2-DiClBz	10	10	9	10

indicated that the volatilization and air stripping were significant mechanisms for removal of VOCs from wastewater. VOCs entering wastewater treatment plants were released to the atmosphere from wastewater during treatment.

Even though a qualitative correlation was evidenced between target VOCs found in the wastewater and target VOCs found in the air, a quantitative correlation was not apparent because the concentrations of the air and wastewater flow were not in equilibrium and also because influent and intermittent grab samples of wastewater were collected.

5.3.1 The Fraction of Saturation β

In fundamental thermodynamics, vapor-liquid equilibrium (VLE) refers to systems in which a single liquid phase is in equilibrium with its vapor [38]. When all phases in equilibrium are at the same temperature and pressure, the vapor liquid equilibrium relationship can be expressed as:

$$y_i^{sat}\Phi_i P = x_i\gamma_i P_i^{sat} \tag{5.1}$$

Where y_i^{sat} is the concentration (mole fraction) of i^{th} component in the saturated state in vapor phase; Φ_i is the ratio of corresponding fugacity coefficient in the real state and saturated state; P is the total system pressure (mmHg); x_i is the concentration (mole fraction) of i^{th} component in liquid phase; γ_i is the activity coefficient of i^{th} component (dimensionless); P_i^{sat} is the saturated vapor pressure of the i^{th} component at the system temperature (mmHg).

At low pressures (up to at least 1 bar), vapor phases usually approximate ideal gases, for which Φ_i=1, so the above equation becomes:

$$y_i^{sat}P = x_i\gamma_i P_i^{sat} \tag{5.2}$$

While the relationship between saturated state and unsaturated state is:

$$y_i = y_i^{sat}\beta_i \tag{5.3}$$

Where y_i is the concentration (mole fraction) of i^{th} component at real state in the vapor phase; y_i^{sat} is the concentration (mole fraction) of i^{th} component in the saturated state in the vapor phase; β_i is the fraction of the saturation of i^{th} component.

Substitution of equation (5.3) into equation (5.2), gives:

$$y_iP = x_i\gamma_i P_i^{sat}\beta_i \tag{5.4}$$

For x_i in mg/l, and y_i in ppm$_v$, the above equation is modified to:

$$y_iP(MW)_i = 18.02x_i\gamma_i P_i^{sat}\beta_i \tag{5.5}$$

Where $(MW)_i$ is the molecular weight of i^{th} component.

$$\beta_i = \frac{y_i P(MW)_i}{18.02 x_i \gamma_i P_i^{sat}} \tag{5.6}$$

In order to calculate β_i, the activity coefficient γ_i must be calculated. For this project, x_i is small enough, so that γ_i may be considered to be the infinite dilution activity coefficient, which is a function of temperature only. The most widely used calculational technique is the UNIFAC method [39][40][41][42], which was the method employed in this study [43][44].

The liquid and vapor concentrations have been measured, so the fraction of saturation β_i for different compounds can be calculated.

The UNIFAC calculated infinite dilution activity coefficients for compounds detected in the Linden Roselle treatment plant, and the fraction of saturation for those compounds, are given in Tables 5.5 and 5.6, respectively.

From the data of Table 5.6, we found that the magnitude of β was between 0.001 and 0.976.

Table 5.5 and Table 5.6 showed that the fraction of saturation β decreases with increasing activity coefficient γ and with decreasing polarity of the compounds. These relationships are shown in Figure 5.1 and Figure

Table 5.5: Activity Coefficient γ Calculated by UNIFAC

No	Compound	MW	P_i (mmHg)(20°C)	γ_i
1	Methanol	32.0	93.7	2.00
2	Acetonitrile	41.1	72.8	11.5
3	Acetone	58.1	178	15.5
4	Diethyl Ether	74.1	435	162
5	Methylene Chloride	84.9	338	254
6	Benzene	78.1	75.1	2580
7	Methyl Isobutyl Ketone	100	6.0	1890
8	Toluene	92.1	21.8	7270
9	Chlorobenzene	113	8.81	10100
10	Ethylbenzene	106	7.16	29600
11	m&p-Xylene	106	6.0	19100
12	o-Xylene	106	6.0	19100
13	1,2-Dichlorobenzene	147	1.00	28400

5.2.

5.3.2 Comparison of Calculated Air Concentration versus Measured Values

The air concentrations measured in the screen house, settling tank, roughing filter, aeration tank, and the calculated values based on the liquid concentrations by equation (5.5) are listed in Table 5.7.

The data indicated consistency of calculated values and measured values, because the coefficient β was used. Otherwise the calculated values

Table 5.6: Fraction of Saturation β Calculated by VLE

Compound Name	Screen House β_i	Settling Tank β_i	Roughing Filter β_i	Aeration Tank β_i
MeOH	0.976	0.564	0.423	
ACN	0.856	0.389	0.278	
Ace	0.511	0.277	0.032	
Ether	0.224			
$MeCl_2$	0.091	0.002		
Bz	0.004	0.001	0.001	0.004
MIBK				0.421
Tol	0.020	0.003	0.005	0.229
ClBz	0.060	0.011	0.017	0.035
EtBz	0.031	0.003	0.002	0.025
m&p-X	0.031	0.004	0.003	0.177
o-X	0.060	0.003	0.023	0.282
1,2-DiClBz	0.076	0.004	0.019	0.398

Figure 5.1: The Fraction of Saturation vs. Activity Coefficient

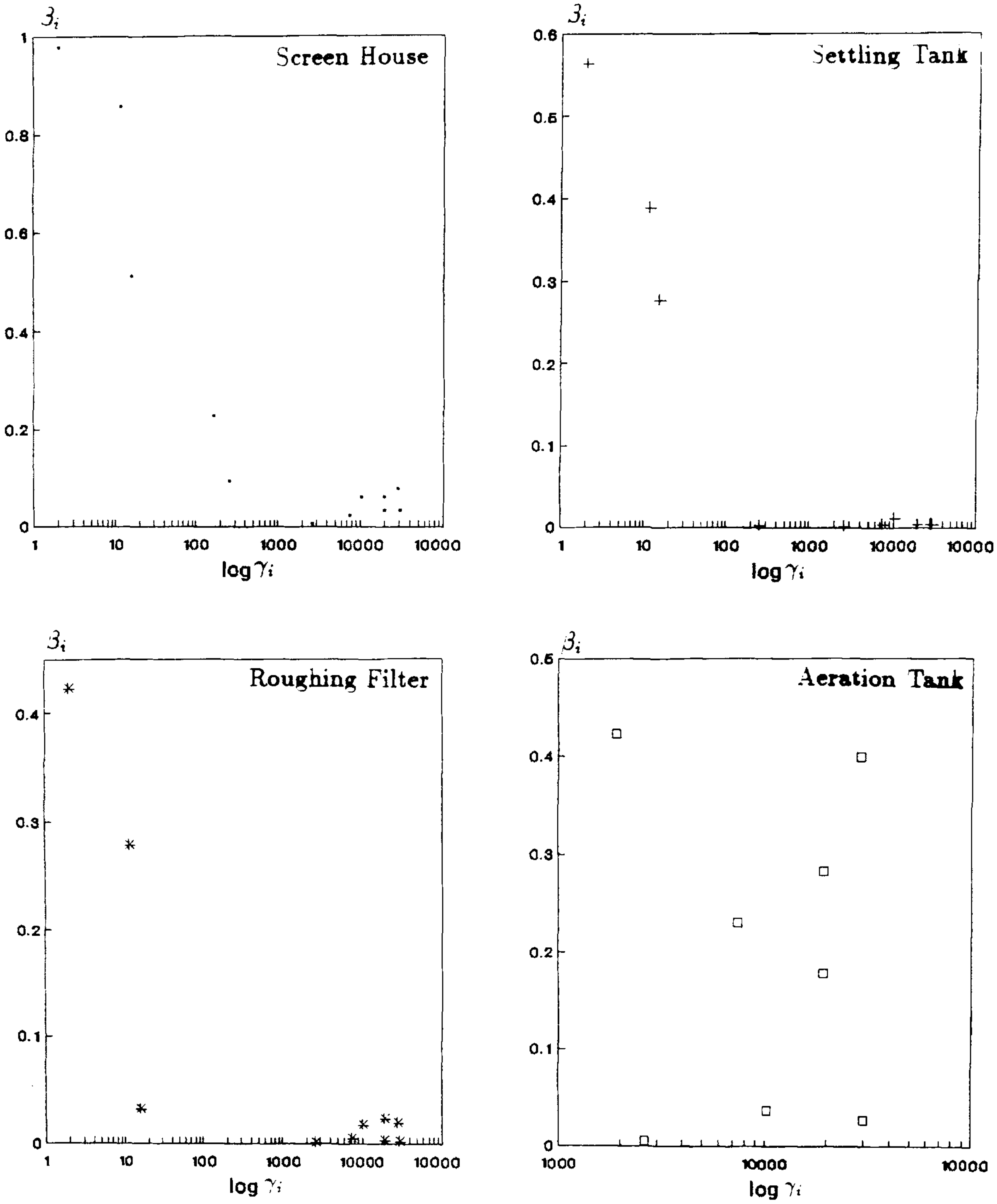


Figure 5.2: The fraction of Saturation vs. Polarity of Compounds

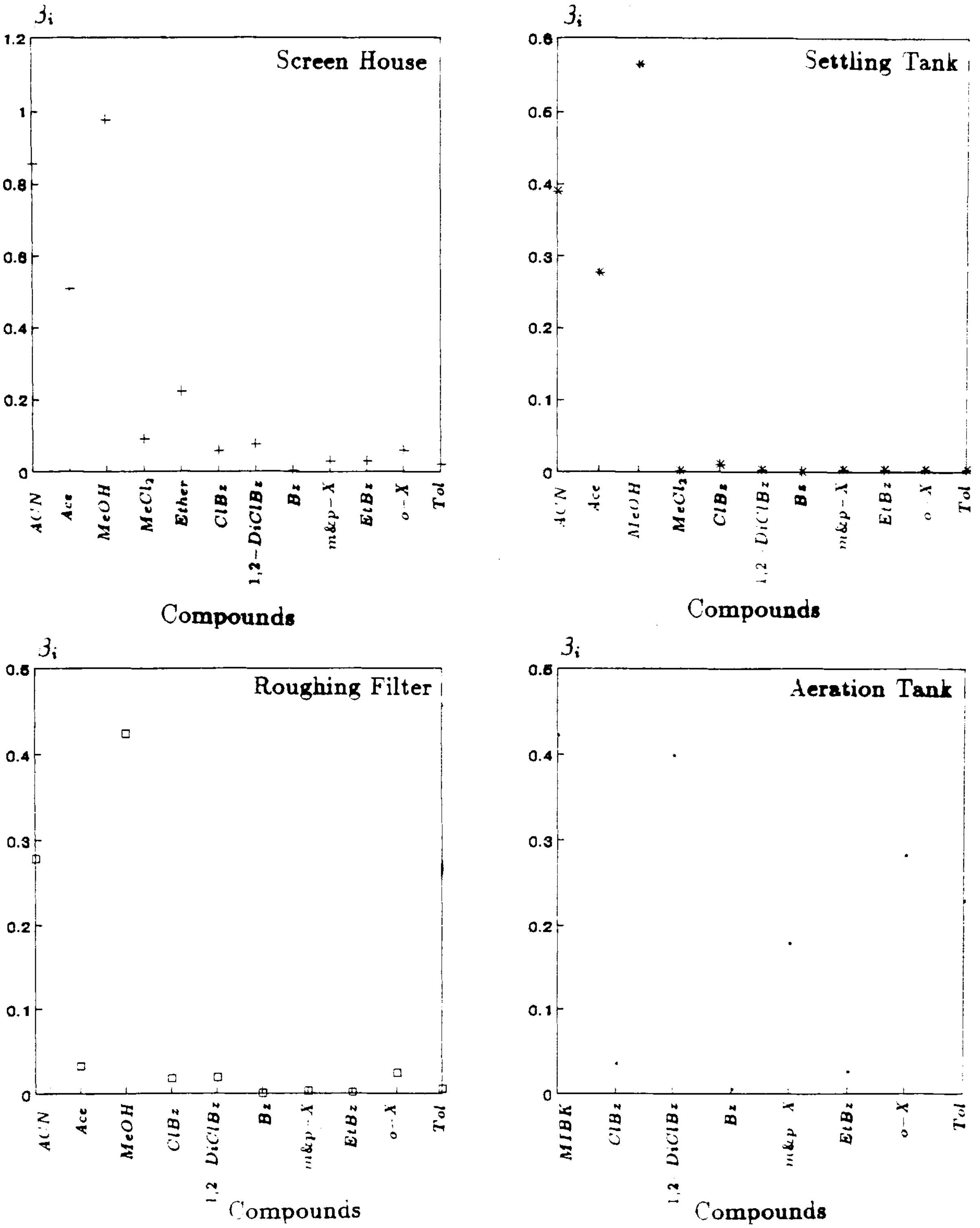


Table 5.7: Comparison of Air Concentration Calculated Values versus Measured Values

Compound	Screen House		Settling Tank		Roughing Filter		Aeration Tank	
	$y_i^{cal.}$ (ppm)	$y_i^{mea.}$ (ppm)	$y_i^{cal.}$ (ppm)	$y_i^{mea.}$ (ppm)	$y_i^{cal.}$ (ppm)	$y_i^{mea.}$ (ppm)	$y_i^{cal.}$ (ppm)	$y_i^{mea.}$ (ppm)
MeOH	0.805	0.971	0.353	0.280	0.111	0.129		
ACN	0.269	0.448	0.063	0.062	0.025	0.040		
Ace	1.832	1.562	0.443	0.109	0.021	0.039		
Ether	0.889	0.625						
$MeCl_2$	7.933	8.442	0.079	0.081				
Bz	7.704	6.279	1.628	0.376	0.739	0.249	0.057	0.051
MIBK							0.109	0.188
Tol	1.395	1.126	0.183	0.197	0.159	0.163	0.065	0.095
ClBz	1.797	1.702	0.341	0.209	0.210	0.176	0.050	0.049
EtBz	0.094	0.042	0.008	0.002	0.002	0.002	0.002	0.009
m&p-X	0.087	0.064	0.010	0.002	0.003	0.004	0.014	0.010
o-X	0.066	0.061	0.003	0.004	0.009	0.002	0.007	0.008
1,2-DiClBz	0.322	0.334	0.016	0.019	0.034	0.022	0.106	0.136

would be very different from the measured values. The variability could be influenced by the differences between the actual properties of the wastewater versus the theoretical properties of pure water used in the calculations. On the other hand, it could be from the difficulty of obtaining meaningful air concentrations, i.e., the samples may have been influenced by the variation in the air motion and some water samples may have been influenced by the flow spike, adsorption to particulate matter, partitioning to organic colloids or detergent micelles.

Therefore, equation (5.5) could be used as a semi-empirical formula to estimate the emission rate from individual treatment processes of the wastewater treatment plant.

5.4 Estimation of Target VOC Removals

Removal rates were calculated by determining the difference between the concentrations at each operation unit and the previous operation unit. While most of these data showed reasonable decreases from stage to stage, this method assumed that the inlet flow was constant over a fairly long period of time. The plant received a total wastewater flow of approximately 13.5 MGD.

The results of the calculation are listed in Table 5.8.

Because each day's samples were taken within a period of about 30 minutes, and the water sampled at each point had entered the plant over a much longer period of time, concentration variations in the inflow stream may have cause substantial errors in the calculation of the losses at each stage. The negative values found occasionally for removals were due to this factor and to the analytical variance. In order to estimate emissions reasonably, the negative values were considered to be zero.

Screen House: The primary removal mechanism was volatilization. For polar compounds such as methanol, ethanol, acetonitrile, acetone, their volatilization may have been due to their lower boiling points and lower saturation pressures. For nonpolar compounds such as benzene, toluene, their volatilization may have been due to their lower solubility. This unit accounted for about 23% of the total volatiles removal in the plant.

Settling Tank: The removal mechanisms of this section were volatilization and biodegradation. The removal here was larger for the polar compounds than for the nonpolar. The fact that the more soluble compounds were removed more efficiently than the hydrophobic ones, indicates that biodegradation may be the more important removal mechanism in this

Table 5.8: Average Quantities Removed from LRSA Plant

Compound Name	Screen House (kg/day)	Settling Tank (kg/day)	Roughing Filter (kg/day)	Aeration Tank (kg/day)	Total (kg/day)
MeOH	73.2	109.5	66.6	31.1	280.4
EtOH	29.0	6.2	11.6	0.0	46.8
ACN	16.3	7.5	0.0	0.0	23.8
Ace	90.1	22.8	29.0	17.8	159.7
IPA	54.7	57.4	46.7	101.8	260.6
Ether	0.5	3.6	2.6	0.0	6.7
$MeCl_2$	101.7	43.9	34.3	3.4	183.3
CS_2	0.0	0.0	0.0	0.0	0.0
MEK	0.0	3.7	0.0	0.0	3.7
Clform	5.1	2.2	4.1	0.0	11.4
EtAcet	0.0	0.0	0.0	0.0	0.0
$EtCl_2$	1.1	0.3	0.0	0.0	1.5
111-TCE	0.6	0.0	32.8	0.0	33.4
ButOH	32.2	14.3	32.3	0.0	78.8
Bz	259.0	0.0	1366.3	70.6	1695.9
CCl_4	0.0	0.1	0.3	0.0	0.4
Tric	1.2	0.6	0.0	0.0	1.8
EG	0.0	0.0	0.0	0.0	0.0
Pyr	12.5	0.8	5.3	0.8	19.4
MIBK	2.1	1.4	2.9	0.0	6.4
Tol	10.7	0.0	76.8	12.6	100.1
DMF	40.8	44.7	95.0	6.3	186.8
ClBz	0.0	16.4	51.3	13.2	80.9
EtBz	0.5	0.4	2.0	0.4	3.3
m&p-X	0.8	1.0	3.0	0.6	5.4
o-X	0.5	0.2	1.2	0.3	2.2
1,2-DiClBz	3.2	5.0	29.1	7.1	44.4
Total	735.9	356.3	1893.2	266.0	3251.4

area, as the polar compounds are much more easily degraded. This unit accounted for 11% of total VOC removal.

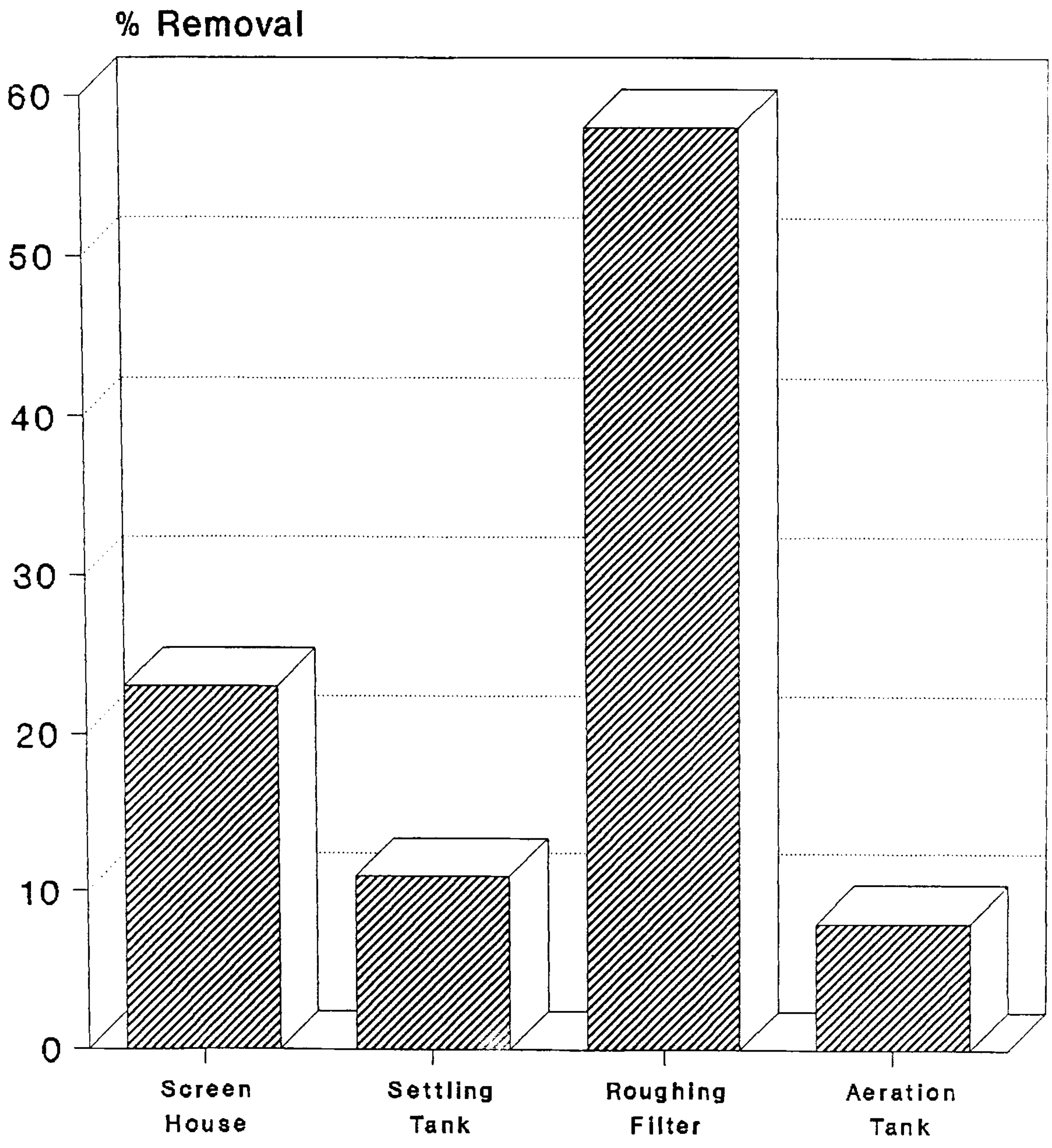
Roughing Filter: The main removal mechanisms in this section were air stripping and biodegradation. Wastewater was pumped to the top of the packed tower and was sprayed through a rotating arm system onto the tower bed. This operation, with its efficient air water contact was expected to remove large quantities of volatiles. The major losses here were the nonpolar components such as benzene, carbon tetrachloride, toluene, etc.. The concentrations in the water at the outlet well of the roughing filter subtracted from those at the top showed that most of the remaining volatiles were removed from the water during the transit down through the tower. The air flow up through the filter bed stripped volatiles. Also, the bacterial action in the bed can remove significant amounts of degradable material, if it remains in the liquid phase for a sufficient amount of time. Apparently, much of the loss of the nonpolar compounds in the roughing filter was due to air stripping , while the more soluble polar compounds were probably removed principally by biodegradation. This unit accounted for 58% of total VOC removal.

Aeration Tank: The removal mechanisms here were biodegradation and air stripping. This unit accounted for about 8% of total VOC removal, with no detectable VOCs in the effluent.

The VOCs lost in the four areas of the plant are shown graphically in Figure 5.3. Of the total removal rate, it was assumed that 70% of the non-polar compounds and 10% of the polar compounds were emitted to the air [34].

The measurement of removal indicated that the roughing filter and the screen house operation units were the major emission sources in the LRSA sewerage plant. These two sections accounted for 81% of total VOC removal.

Figure 5.3: Removal of Total VOCs from LRSA Plant



Chapter 6

Conclusions

The concentrations of 28 volatile organic compounds (VOCs) in air and water samples from the screen house, primary settling tank, roughing filter, and aeration tank operation units in the Linden Roselle Sewerage Authority wastewater treatment plant were measured by high resolution gas chromatography. The removal rates of these VOCs at each treatment unit were calculated by determining the difference between the concentration in water at each stage and the previous stage, but the estimation of emission rates of these VOCs at each treatment unit depends on their removal mechanisms.

In order to more accurately estimate emission of VOCs specifically for some units (since their removal mechanisms are more complex) the emission rates of VOCs were evaluated with concentration in water by using the fraction of saturation β which was the experimental constant calculated from

Table 6.1: The Removal rates of VOCs in LRSA Plant

Operation Unit	Removal Rate (kg/day)	R_i/R_{total} (%)
Screen House	736	23
Settling Tanks	356	11
Roughing Filters	1893	58
Aeration Tanks	266	8
Total	3251	100

vapor-liquid equilibrium. In this project, the β ranged from 0.001 to 0.976 for all of four treatment units.

The removal rates of VOCs at the four sections in LRSA wastewater treatment plant are presented in Table 6.1. It was assumed that 70% of the nonpolar compounds and 10% of the polar compounds were emitted to the air.

Chapter 7

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