

ABSTRACT

Title of thesis: IDENTIFICATION OF SEASONAL VARIATIONS IN VOLATILE SULFUR COMPOUND PRODUCTION AND RELEASE IN THE SECONDARY TREATMENT SYSTEM OF A WASTEWATER TREATMENT PLANT

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This research was motivated by the need to control odor emission from the District of Columbia Water and Sewer Authority. Ever-increasing urbanization has created a situation where residential communities exist in close proximity to wastewater treatment plants. Offensive odor emissions associated with the treatment process causes a nuisance to the public. Odor mitigation has become a priority for many wastewater treatment authorities. The purpose of this study is to quantify the odorous compounds associated with the secondary treatment system of an advanced wastewater treatment plant. Determine the significant odor source locations in the secondary treatment system. Identify significant parameters which affect both the formation and release of odorants/odors from the secondary system and provide useful baseline information for the selection of appropriate treatment technologies for odor reduction.

IDENTIFICATION OF SEASONAL VARIATIONS IN VOLATILE SULFUR COMPOUND
PRODUCTION AND RELEASE IN THE SECONDARY TREATMENT
SYSTEM OF A TREATMENT PLANT

by

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DEDICATION

This thesis is dedicated to my loving family, **Wg Cdr N.V. Sekyiamah, Mrs. V Sekyiamah, Esi Nana Sekyiamah and Papa Victor Hammond Sekyiamah.**

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LIST OF ACRONYMS

| | |
|------|----------------------------------|
| VSC | - Volatile Sulfur Compounds |
| VNC | - Volatile Nitrogenous Compounds |
| VFA | - Volatile Nitrogenous Compounds |
| MM | - Methyl Mercaptan |
| EM | - Ethyl Mercaptan |
| PM | - Propyl Mercaptan |
| BM | - Butyl Mercaptan |
| DMS | - Dimethyl Sulfide |
| DES | - Diethyl Sulfide |
| DMDS | - Dimethyl disulfide |
| DEDS | - Diethyl disulfide |
| CDS | - Carbon Disulfide |
| COS | - Carbonyl Sulfide |
| MA | - Methylamine |
| DMA | - Dimethylamine |
| TMA | - Trimethylamine |
| EA | - Ethylamine |
| DEA | - Diethylamine |
| n-PA | - Propylamine |
| AWWT | - Advance Wastewater Treatment |
| WWT | - Wastewater Treatment |
| WWC | - Wastewater Collection |

| | |
|--------|------------------------------------|
| PCT | - Primary Collection Treatment |
| STS | - Secondary Treatment Collection |
| SAT | - Secondary Aeration Treatment |
| SST | - Secondary Sedimentation Tank |
| BNR | - Biological Nitrogen Removal |
| BNRT | - Biological Nitrogen Removal Tank |
| Ft | - Feet |
| Min | - Minute |
| Hr/hrs | - Hour |
| AS | - Activated Sludge |
| Lbs | - Pounds |
| mL | - Milliliters |
| L | - Liters |
| ppb | - Parts Per Billion |
| ppm | - Parts Per Million |
| VP | - Vapor Pressure |
| HLC | - Henry's Law Constant |
| MW | - Molecular Weight |
| SRB | - Sulfide Reducing Bacteria |
| pKa | - Acidic Partitioning Constant |
| MB | - Methanogenic Bacteria |
| AB | - Acidogenic Bacteria |
| SBL | - Sludge Blanket Level |

CHAPTER 1 - SUMMARY

1.1 Introduction

Odors are the principle source of complaints for wastewater treatment plant (WWTP) biosolids land application programs. Most WWTP unit processes, preliminary treatment, primary clarifiers, activated sludge basins, secondary clarifiers, sludge thickening, conditioning and holding processes and the dewatering process, are to differing extents potential sources of odor (*Kim et al, 2002*). Odorants can develop as by-products in each unit process. These odorants are then concentrated in solids and cause solids thickening and handling facilities to be major onsite odor sources. Inevitably, the land application of biosolids faces stiff opposition from the public, largely due to the offensive biosolids odor. Volatile Sulfur Compounds (VSCs) are one of the most prevalent odorants associated with wastewater treatment (*Nural Islam et al, 1998, Langehove et al, 1985, Huang et al, 1979*). The identification and quantification of VSCs serves as a basis for a larger discussion on odor reduction at WWTPs. *Camp Dresser & McKee, 2003*, performed a comprehensive odor study at the District of Columbia Water and Sewer Authority (DCWASA) found that the secondary aeration tank was a major source of VSCs, including hydrogen sulfide (H_2S), methyl mercaptan (MM), dimethyl sulfide (DMS), carbon disulfide (CS_2) and carbonyl sulfide (COS). In this study the secondary treatment system was ranked second (34.5%) after the grit and screening facilities in odor emissions under current operations. If the grit removal facilities are fitted with new odor control structures as planned by DC WASA, the secondary system

would account for 53.6% of the total odor emission from WWTP. Another observation of this study was that the highest odor emissions were from the front end of the aeration tanks where the return activated solids are feed.

The presence of VSCs in odor emissions from the aeration tanks is counter-intuitive since anaerobic conditions are required for their formation and secondary treatment is ideally an aerobic process. There are a several explanations for VSC gas emissions from these tanks; firstly, low aeration efficiency causing inadequate mass transfer of oxygen and hence the development of anaerobic zones, secondly methylation of the H₂S from the upstream processes and thirdly the stripping of VSCs in the recycled sludge from the secondary sedimentation tanks. It is proposed that the adequate understanding of VSC generation and release patterns and their dependence on various plant parameters and/or environmental conditions will assist in better control of odor production and/or release.

1.2 Scope and Objectives

1.2.1 Background

DC WASA operates the Blue Plains Advanced Wastewater Treatment Plant (AWWTP) located to the south of DC on the banks of the Potomac River. This plant is the largest AWWTP in the world, serves more than two million people in the Washington Metropolitan area and has the capacity to treat 370 million gallons of sewage a day. Several high profile residential communities are located within a four mile radius of the Blue Plains AWWTP, therefore the issue of on-site odor and odor incident mitigation is of added importance. Another area of concern is the public acceptance of the land application of biosolids. Biosolids, a by-product of the WWTP process, are high in organic content and nutrient value and are useful in restoring nutrients/organic matter to soils. The land application of biosolids directly benefits WWTP by negating a large portion of their operational budget (i.e. biosolids utilization fees). Offensive odor from biosolids hinders the societal acceptance of its land application.

1.2.2 Problem Statement

Secondary treatment at DC WASA – Blue Plains AWWTP is the second highest odor emission source (34.5%) at current process conditions. After complete construction of the on going grit/screenings housing buildings, the secondary will account for 53.6% of the total odor emission from the plant. It is desirable to find on-site process modification strategies to reduce odor emissions from this system. A first step to solving

this problem is a better understanding of the odorant production and odor release patterns of the secondary system and the relationship between odorant formation and operating/environmental conditions.

1.2.3 Overall Research Goals

The principle goals of this study were to provide a better understanding of the production and release of VSCs in the secondary system as an initial step in the formulation of on-site odor control strategies at a WWTP. In addition, this study aimed at providing tools to predict odor incident and mitigate odor release.

1.2.4 Specific Research Goals

These goals will be achieved by evaluating the secondary treatment process for:

- Seasonal variation in the production of VSCs;
- Seasonal variation in the release of VSCs;
- Conditions conducive for VSC production; and
- Conditions conducive for VSC emissions.

The production of VSCs is the actual formation of these compounds and the release of VSCs describes their partitioning into the atmosphere. Chemical analytical measurements were used to establish VSC production dependence on various plant and environmental parameters. Both chemical and sensory analytical measurements are used to establish significant relationships between the release of VSCs and the dependence of this release on certain environmental parameters.

CHAPTER 2

NUISANCE ODORS ASSOCIATED WITH THE MUNICIPAL WASTEWATER TREATMENT PROCESS

2.1 Introduction

Wastewater treatment plants (WWTPs) are a necessary part of public health protection in any society. The collection of potentially harmful wastewater and its subsequent treatment to benign effluent water, fit for disposal into waterways, is an important municipal endeavor. Initially WWTPs were built a distance away from residential areas so as to avoid potential health risks. Ever-increasing urbanization, however, has created a situation where residential communities now exist in close proximity to WWTPs. Unpleasant odors from these plants are the major cause of complaints from the public. Complaints about odor emissions have been increasing due to; encroachment of housing on land surrounding sewage treatment works, the operation of the WWT system at or near capacity due to the lag of plant development and expansion of the service area and increased awareness of consumer rights (*Metcalf and Eddy, 2003*). Currently, WWT systems are required to achieve significant and satisfactory reductions in organic matter, toxic substances, metals and nutrients. On the other hand the issue of odor has not been successfully regulated or addressed. WWTPs have to develop a system-wide odor control strategy. This strategy may include the continuous monitoring of odor released from the treatment process, controlling odorants either released into or formed in the wastewater collection system, fine tuning unit

processes in a WWTP so as to minimize odorants generation and/or release, and the installation of odor containment and treatment facilities.

Here a distinction is made between odor and odorants. Odor is the perceived effect of odorants as interpreted by the human olfactory system. An odorant is a compound causing odors. The resolution of the odor problem demands accurate detection and quantification of both odor and odorants. Mitigation can then be achieved by the appropriate choice of specific unit processes, process modifications, process substitutions and process control methods. To this end, the participation of plant designers, plant operators and legislations is required.

Health symptoms attributed to odors and odorants include eye, nose and throat irritation, headache, nausea, diarrhea, hoarseness, sore throat, cough, chest tightness, nasal congestion, palpitations, shortness of breath, stress, drowsiness, annoyance, upsetting of appetite and alterations in mood (*Schiffman et al, 2001, Wilkens et al, 1994*). A discussion on the effects of odors from biosolids on public health concluded that there were three potential hypotheses. The first hypothesis suggests that symptoms are induced by irritant properties of the odorants, which for a wide range of odorants, occurs at a concentration of about 3- 10 times that of threshold odor. Even though in many cases, individual compounds do not exceed their irritant threshold, the synergism exhibited by compounds as a group results in this occurrence. The second hypothesis suggests that health symptoms occur at concentrations that are above detection thresholds but fall far below the levels that cause irritation. Sulfur containing compounds and organic amines are typical of this group (*Wilkens et al, 1994*). The third hypothesis suggests that odorous gases may contain co-pollutants such as endotoxins which cause the initial health effect.

Subsequent exposure to the odorous gas in the absence of the co-pollutant can produce similar health effects (*Schiffman et al, 2001*). The psychological basis by which these compounds exert adverse health effects is rooted in the fact that the olfactometric system is hardwired to the brain.

2.4 The Olfactometry System

The olfactometry system consists of the olfactory epithelium, the olfactory bulb and the olfactory cortex. In humans the olfactory epithelium is located in a 3 cm² area in the nasal cavity. The olfactory epithelium consists of the tens of millions of olfactory neuron-receptors which ensure direct contact and reception of odorous substances. Contact with the external environment is via inhalation and exhalation. The olfactory nerve fibers (neurons) act as a conduit of information to the brain via the olfactory bulb where preliminary processing of the electrical outputs from the neurons takes place (*Martin and Laffort, 1994*). The information is then sent to the central nervous system in the brain for further processing. Human beings are able to perceive a wide range of olfactometry stimuli, even at very low concentrations, some at ppb/ppt levels.

A rudimentary model for odor perception can be expressed in two stages, physiological reception and psychological interpretation. There are various factors that affect the physiological reception of odors. Reception wanes with age, is poorer in smokers than non- smokers and declines with both general and dental health. Sensitivity is also affected by familiarity in two contradictory ways. With continued exposure to an odor, sensitivity to that odor decreases due to adaptation or olfactometric fatigue. On the other hand non continuous exposure increases sensitivity to a particular compound since

familiarity with the compound enables easier detection and identification. Psychological interpretation results in judgment about the perceived odor and mental impressions become associated with the odor (*Martin and Laffort, 1994*). There are four general dimensions of an odor, concentration, intensity (the strength of smell), character (verbal descriptors) and hedonic tone (the degree of pleasantness). It would seem that the important function of the human sense of smell is to provoke an emotional response that is largely determined by individual experience. All human senses, be it sight, touch, hearing, smelling or tasting, aid our human interaction with the environment. Odor and its perception likewise affect human behavior. It is evident that reliable and accurate information about odors and human exposure to odors is important for the health and safety of the public.

2.5 Typical Odorants

The offensive odor associated with WWT plants is primarily caused by a complex mixture of odorants such as volatile sulfur compounds (VSCs), volatile nitrogenous compounds (VNCs) and volatile fatty acids (VFAs). Both inorganic and organic odorants are common to WWTPs. H₂S and ammonia (NH₃) are the major inorganic compounds (*Nural Islam et al, 1998*). H₂S is the most notorious odorant associated with the wastewater collection system and is the principal reason for the premature structural failure of concrete sewer structures (Hao et al, 1996). Ammonia is mainly formed as a by-product of microbial decomposition of organic matter containing nitrogen (e.g. urea to NH₃ and CO₂). Urea (an end product in human metabolism) is present in domestic wastes in significant concentrations. Urine has an average composition of 25 g/L of urea.

Common organic odorants include mercaptans, sulfides, amines, indole / skatole, organic acids, aldehydes, and ketones. Organic acids, aldehydes and ketones are intermediaries in the breakdown of hydrocarbons and are thus very common in domestic and industrial food wastes. Mercaptans, amines and ketones are major odorants produced as a result of industrial activity (*Martin and Laffort, 1994*). Mercaptans are formed by the demethylation of lignin in the Kraft pulp operation process and the decomposition of various sulfur containing compounds during the petroleum refining process (*Lens et al, 1998*). Mercaptans are also by-products of various chemical manufacturing processes attributed to industries such as pharmaceuticals, insecticides, plastic and rubber production.

2.3.1 Volatile Sulfur Compounds

VSCs have adverse organoleptic characteristics (Table 2-1). A distinct property is their unpleasant smell, low olfactory detection thresholds and limited solubility such that even at very low concentration, wastewater containing these compounds generates offensive odors. Due to the highly reactive nature of VSCs, these compounds are prone to cause operational problems in wastewater collection and treatment systems by poisoning catalysts and corroding pumps and pipes. VSCs although present in trace levels are responsible for the taste and odor problems associated with different waters, foods and beverages. Dimethyl disulfide is responsible for the off flavoring associated with broccoli storage. The undesirable flavors in dairy products can be attributed to dimethyl sulfide, yet the desirable flavor of Swiss cheese is also attributed to dimethyl sulfide (*Bentley et al, 2004*). VSCs prevalent at a WWT plant include hydrogen sulfide (H₂S), carbon

disulfide (CS_2), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), methyl mercaptan (MM) and ethyl mercaptan (EM).

2.3.2 Volatile Nitrogenous Compounds

Volatile Nitrogenous Compounds are a family of compounds with a nitrogenous functional group, examples of which would be ammonia, amines, indole and scatole. These compounds have a high vapor pressure, a high polarity, high toxicity (*Yoshiro et al, 1996*), a strong basic character and a high solubility in water (Table 2-1). In domestic waste, ammonia (NH_3) is produced from the oxidation of urea ($\text{CO}-(\text{NH}_2)_2$) to carbon dioxide (CO_2) (*Henry and Gehr, 1980*). Ammonia is also used in various cleaning agents. Ammonia irritates the skin, respiratory tract and mucous membranes. Aliphatic primary and secondary amines are endogenously synthesized as metabolites and excreted by living organisms. Indole, scatole and indole / scatole type compounds can be produced from the metabolism of the essential amino acid tryptophane. The lower molecular weight aliphatic amines such as methylamine (MA), dimethylamine (DMA), ethylamine (EA), diethylamine (DEA) and n-prop-propylamine (n-PA), are also discharged into the wastewater collection system since they serve as raw materials and intermediates in the manufacture of various industrial chemicals such as pesticides, medicines, dyestuffs, polymers, surfactants and cosmetics (*Verschueren, 1996*). In a WWTP, aliphatic and aromatic amines are also formed as by-products of the biodegradation of proteins, amino acids and other such nitrogen containing organic compounds. Volatile amines have been detected at the part per billion (ppb) and part per million (ppm) levels at various locations in WWTPs (*Nural Islam et al, 1998, Abalos et al, 1999*).

2.3.3 Volatile Fatty Acids

Volatile fatty acids (VFAs) are important metabolites and intermediaries of carbohydrate fermentation in anaerobic conditions (eqn – 1). VFAs are produced from humic substances during the water treatment process. Anaerobic sludge digestion results in VFA, aldehydes and ketone production. The thermal treatment of sludge encourages the volatilization of VFAs and once they have been produced by microbial synthesis. Small chain (C₂ – C₅) free fatty acids are strongly hydrophobic compounds (*Lin Pan et al, 1995*) and readily partition out of aqueous environments

Carbohydrates ----- Carboxylic acids ----- Aldehydes ----- Ketones (eqn - 1)

Table 2-1: Physical and Olfactory Properties of Odorants

| Odorant | Symbol | Chemical Formula | Mw | Mp | Bp | Vapor | Sol | H | log | Odor | Odor Character |
|----------------------|--------|---|-------|--------|-------|----------|----------------------|----------------------|-------|-----------|---|
| | | | | | | Pressure | | | Pow | Threshold | |
| | | | | | | 25°C | 25°C | 25°C | | OTC | |
| | | | g | °C | °C | mm Hg | mg/L | atm-m3/mol | | (ug/L) | |
| Inorganic | | | | | | | | | | | |
| Hydrogen sulfide | HS | H ₂ S | 34.1 | -85.4 | -60.3 | | 410 ¹ [5] | | | 0.4[6] | Rotten egg [10][11] |
| Ammonia | N | NH ₃ | 17 | -77.7 | -33.4 | 7510 | 482000 ² | 0.0000161 | 0.23 | 37 [6] | Sharp, pungent, irritating [7][11] |
| Organic | | | | | | | | | | | |
| Sulfides | | | | | | | | | | | |
| Dimethyl sulfide | DMS | (CH ₃) ₂ S | 62.1 | -83 | 38 | 502 | 22000 | 0.0016 | 0.92 | 9.0 [6] | Decayed vegetables [10][11] |
| Diethyl sulfide | DES | (CH ₃ CH ₂) ₂ S | 90.2 | -103 | 92 | 60.2 | 3130 | 0.0009 | 1.95 | 0.25[6] | Garlic like, nauseating, ether [10][11] |
| Di n-propyl sulfide | DPS | (CH ₃ CH ₂ CH ₂) ₂ S | 118 | 102 | 142 | 6.45 | 351 | 0.0024 | 2.88 | | Hedonic tone, foul, nauseating [10] |
| Polysulfides | | | | | | | | | | | |
| Carbon disulfide | CDS | CS ₂ | 76.1 | -109 | 46 | 359 | 1180 | 0.0144 ² | 1.94 | 2.6 [6] | Vegetable sulfide, slight pungent [10] |
| Dimethyl disulfide | DMDS | CH ₃ SSCH ₃ | 94.2 | -85 | 112 | 28.7 | 3000 | 0.00121 ¹ | 1.77 | 1 [6] | Vegetable sulfide, putrid [11] |
| Diethyl disulfide | DEDS | CH ₃ CH ₂ SSCH ₂ CH ₃ | 122 | -102 | 154 | 4.28 | 300 | 0.00215 ¹ | 2.86 | 0.25 [7] | |
| Mercaptans | | | | | | | | | | | |
| Methyl mercaptan | MM | CH ₃ SH | 48.1 | -123 | 6 | 1510 | 15400 | 0.0031 | 0.78 | 1.1[6] | Sulfidly, pungent, decayed cabbage [10][11] |
| Ethyl mercaptan | EM | CH ₃ CH ₂ SH | 62 | -148 | 35 | 529 | 15600 | 0.00453 ¹ | 1.27 | 0.19 [6] | Decayed cabbage, earthy, sulfidly [10][11] |
| n-Propyl mercaptan | PM | CH ₃ CH ₂ CH ₂ SH | 76 | -113 | 68 | 154 | 1900 | 0.0081 | 1.81 | 0.5 [6] | Hedonic tone, unpleasant [10] |
| n-Butyl Mercaptan | BM | CH ₃ CH ₂ CH ₂ CH ₂ SH | 90.2 | -115.7 | 98.5 | 45.5 | 597 | 0.00908 | 2.28 | 1[8] | Strong, unpleasant [10] |
| Amines | | | | | | | | | | | |
| Methylamine | MA | CH ₃ NH ₂ | 31.1 | -93.4 | -6.3 | 2650 | 1080000 | 0.0000111 | -0.57 | 20 [6] | Putrid, rotten fish [11] |
| Ethylamine | EA | CH ₃ CH ₂ NH ₂ | 45.1 | -80.5 | 16.5 | 1050 | 1000000 | 0.0000123 | -0.13 | 39 [6] | Pungent, ammonical [1] |
| n-Propylamine | PA | CH ₃ CH ₂ CH ₂ NH ₂ | 59.1 | -83 | 47.2 | 310 | 1000000 ¹ | 0.0000148 | 0.48 | 7.0 [6] | |
| n-Butylamine | BA | CH ₃ CH ₂ CH ₂ CH ₂ NH ₂ | 73.1 | -49.1 | 77 | 92.9 | 1000000 ¹ | 0.0000174 | 0.97 | | Sour, ammonia like |
| Polyamines | | | | | | | | | | | |
| Dimethylamine | DMA | (CH ₃) ₂ NH ₂ | 45.1 | -92.2 | 6.8 | 1520 | 1630000 ⁴ | 0.0000177 | -0.38 | 47 [6] | Putrid, rotten fish [11] |
| Trimethylamine | TMA | (CH ₃) ₃ NH ₂ | 59.1 | -117.1 | 2.8 | 1610 | 890000 ³ | 0.000104 | 0.16 | 0.2 [6] | Ammonical [12] |
| Organic acids | | | | | | | | | | | |
| Acetic acid | AA | CH ₃ COOH | 60.1 | 16.6 | 117.9 | 15.7 | 1000000 | 0.0000001 | -0.17 | 145 | Vinegar like [12][11] |
| Propionic acid | PA | CH ₃ CH ₂ COOH | 74.1 | -20.7 | 141.1 | 3.53 | 1000000 | 0.00000044 | 0.33 | 28[9] | Slight sweetish odor [12] |
| Butyric acid | BA | CH ₃ CH ₂ CH ₂ SH COOH | 88.1 | -5.7 | 163.7 | 1.65 | 60000 | 0.00000054 | 0.79 | 0.5[9] | Pungent, rancid butter [12][11] |
| Valeric acid | VA | CH ₃ CH ₂ CH ₂ CH ₂ COOH | 102.1 | -34 | 186.1 | 0.196 | 24000 | 0.00000047 | 1.39 | 4.8 | Unpleasant, sweat, perspiration [12][11] |

(¹ = 20 °C, ² = 24 °C, ³ = 30 °C, ⁴ = 40 °C) [5] Merck Index – 12 edition, [6] Nural Islam, 1999, [7] Dague, 1972, [8] Henry & Gehr, 1980, [9] Kim, 2002, [10] Verschuieren, 1996, [11] Martin & Laffort, 1994 [12] www.chemfinder.com

2.4 Odor Sources

Odorants are either released into the wastewater collection system or are formed at specific points along the collection and/or treatment process. Depending on varying ambient conditions and the various parameters associated with unit processes at a WWTP, each unit process differentially contributes to the production and/or release of odorants. This leads to the importance of understanding the nature of environmental influences and controlling operational parameters to minimize reducing conditions.

2.4.1 Wastewater

Influent wastewater is variable in nature. This variability depends on the diurnal and seasonal nature of human activity and the environment. Intermittent and/or accidental industrial discharges also contribute to this variability. Sources of odor can be classified into two categories; sources which promote the mass transfer of odorants and sources which promote the formation of odorants. Wastewaters both domestic and industrial are a notorious source of nuisance odors. Domestic wastewaters, high in organic matter, nitrogenous compounds, sulfur compounds and phosphorous are prime potential odor causing matrices during septic events. Sulfur compounds are present in both the collection system and the treatment process whereas nitrogenous compounds are usually insignificant in the collection system. In elevated temps during extended residence times, ammonia may be produced as a by-product of the hydrolysis of nitrogen containing organic compounds in the collection system.

The energy industry is a significant source of odor causing compounds emitting high concentrations of H₂S, EM and sulfur dioxide (SO₂). With the food industries not

only VSC but amines, alcohols and ketones are present at significant concentrations. Industrial wastewaters from the paper mill industries contain significant concentrations of sulfates in part due to the oxidation of other sulfur compounds (*Lens et al, 1998*). Wastewater from industrial activities may or may not be pretreated before discharging into the collection network. The combination and composition of both industrial and domestic wastewater will in part determine the extent of odor events associated with the collection and treatment of wastewater. The sulfate ion, a major precursor for the production of H₂S is one of the most prevalent anions found naturally in the environment and thus easily enters the collection system by infiltration. Domestic wastewater consists of substantial sulfate concentrations from household detergent products.

2.4.2 Wastewater Collection as a Source of Odors

Slime growth on sewer walls and stagnant sludge deposits in the sewer lines support the growth of sulfate reducing bacteria (SRB). These bacteria are essentially responsible for the production of H₂S in the sewer system. The amounts of H₂S produced and released into the sewer atmosphere is influenced by the wastewater detention time, the longitudinal gradation of the sewer lines, the water temperature, dissolved oxygen and pH of the sewage in the system (*Langehove et al, 1985, USEPA, 1985*). H₂S eventually attacks sewer concrete by the formation of sulfuric acid in slime layers coating the sewer walls, poisons catalyst in the WWT process and can be toxic to WWT plant operators at excessive concentrations. The discharge of industrial wastewater pre-treated or otherwise, also serves as a source of odorants to the WWC system. The Kraft paper production process results in VSC concentrations in the low parts per million (ppm) in the waste

effluent liquid and H₂S emissions are associated with the petroleum refining process (*Smet et al, 1998*). Odorous gases accumulate in the sewer atmosphere and are released at air release valves, cleanouts, manholes and house vents. A good correlation was found between odor units (SOU/m³) and H₂S concentration (ppm) at the intake of a WWTP that served a domestic sewage network (*Gostelow et al, 2001*).

2.4.3 Wastewater Treatment Process Description

Wastewater treatment is achieved by a series of unit treatment processes. The treatment schematic can be looked at as two simultaneous treatment operations; (1) a liquid treatment process and (2) a simultaneous solids concentration process. Wastewater essentially undergoes physical and then biological treatment. The wastewater treatment process includes the production and concentration of a large amount of biosolids. Safe handling, treatment and/or disposal of biosolids are essential for public health safety.

2.4.3.1 Physical Treatment

Bar screens, Grit Chambers and Primary Clarification Tanks make up part of the physical treatment process. Organic matter also adheres and accumulates on screens and forms anaerobic zones within the organic matter clusters which lead to offensive odor production. The aeration of the grit settling tanks causes severe odor problems in the grit chamber. The aerated grit chamber has a high potential for the release of odors due to the high turbulence of the incoming wastewater and the constant aeration achieved. Excessive detention times can result in anaerobic zones in the settled sludge at the bottom of the primary tanks. This may result in the formation and subsequent release of various

odorants, namely H₂S and NH₃ (*Nural Islam et al, 1998*). It has been noted that total VSCs were higher in primary effluent than in the influent. This was suggested to be either due to the production of VSCs in anaerobic zones at the bottom of the clarification tanks or from the return wash water from the sludge processing facilities (*Hwang et al, 1995*). The return wastewater has been shown to contain high concentrations of odorants, especially TMA, EA, NH₃, DMS and MM (*Nural Islam et al, 1998*). The potential odor release from these backflows depends not only on odorant concentration but also on how freely the return wastewater falls into the tank and hence interacts intimately with the atmosphere.

2.4.3.2 Biological Treatment

Biological treatment may involve BOD removal and nitrogen and/or phosphorous removal. Treatment takes place in aerobic, anoxic and/or anaerobic environments. Generally under aerobic conditions, odorants are not produced and may actually be decomposed (e.g. SAT) (*Nural Islam et al, 1998*). Over 95% of VSCs in primary effluents were eliminated by the secondary aeration process (*Hwang et al, 1995*), due to both biological degradation and the effect of stripping. The odor emission rate of the aeration tanks is highest near the influent or front end of the process and decreases toward the back end where the influent flows to the sedimentation tanks (*Camp Dresser & McKee, 2003*). On occasion, especially around the immediate area where return activated sludge (RAS) is returned, poor mixing has been noted to be the cause of permanent sludge deposits (*Bhatla, 1975*). The accumulation of sludge deposits coupled with a limited oxygen supply, results in anaerobic zones and may lead to odor production.

The odors associated with any aerated process is heightened by the very nature of the process, that is, the intense mixing achieved by the aeration and hence intimate contact between all phases, the sludge, the waste liquid and the compressed air. The method of aeration used, significantly affects the intensity of the odors. Mechanical aeration, coarse bubble diffusers and fine bubble diffusers differ in the intensity of associated odor. Fine bubble diffusers are noted to achieve 50% less air emission than coarse bubble diffusers (*Camp Dresser & McKee, 2003*). The secondary sedimentation tank releases very little odor as compared to the primary clarifiers and the secondary aeration tanks (*Nural Islam et al, 1998*). The major factors here are the low odorant concentration in the surface wastewater of the sedimentation tanks and the minimal interaction between the aqueous phase and the gaseous phase. Even though limited release of VSCs occurs from the tanks, studies show significant production potential in anaerobic zones at the bottom of the SST (*Langehove et al, 1985*). The Biological Nitrogen Removal (BNR) process is carried out under aerobic and anoxic conditions. The BNR process has been observed to release small amounts of DMS (~ 2 ppbv) (Kim et al, 2002).

2.4.3.3 Biosolids Processing Facilities

A significant source of odorants in biosolids can in part be attributed to anaerobic conditions that develop in the upstream treatment processes. Biosolids are simply a concentration of separated suspended solids from the various unit processes and therefore there is a similar concentration of odorants in these solids. Biosolids often undergo anaerobic storage and/or treatment, extreme turbulence, pH adjustments and/or thermal treatment. The nature of the biosolids stream and the specific treatment used will

determine the production and release of odors. Biosolids thickening facilities, anaerobic digesters and sludge load-out facilities have an extremely high potential for the release of odors. The highest potential for odor release occurs when unstabilized biosolids are handled. Dewatering significantly increases the surface area available for the release of pre-formed odorants. TMA, DMDS and DMS are the main odorants released from lime stabilized biosolids (*Kim et al, 2002, Murthy et al, 2003*]. Significant concentrations of DMS (820 ppbv) have been detected in the ambient air during sludge loading (*Nielsen and Jonsson, 2002*).

2.5 Fundamental Mechanisms for Controlling Odorant Production and Destruction

There are several reported biotic and abiotic mechanisms for the production and degradation of VSCs in aerobic, anoxic and anaerobic environments. The significant mechanisms associated with the production of VSCs in a wastewater treatment plant are; (1) the production of H₂S by sulfate reducing bacteria (SRB), (2) the degradation of sulfur containing amino acids, (3) the methylation of H₂S and MM and (4) the abiotic oxidation of MM to DMDS (*Lomans et al, 2002, Yarosz et al, 2003*). The major formation pathways of VNCs are the; (1) decarboxylation of amino acids, amination of carbonyl compounds and (2) the degradation of nitrogen containing compounds (*Kataoka, 1996*). VFAs have been identified at various locations in WWTPs (*Kim et al, 2002, Langehove et al, 1985*). Short chain aliphatic carboxylic acids (C₂ – C₇) are formed from carbohydrate metabolism whilst branched chain carboxylic acids (isobutyric and isovaleric) are formed as a result of the fermentation of the branched chain amino acids (valine and leucine) (*Willig et al, 2004*). VFA speciation is strongly pH dependent and volatility is higher at lower pHs. Considering domestic sewage with a pH ~ 7, VFA do not play a major role in odor emission. VSCs are the most prevalent family of odorants in a domestic wastewater collection and treatment system (*Hao et al, 1996, Smet et al, 1998, Jenkins et al, 1980*]; therefore further discussion on production mechanisms will concentrate on these odorants.

2.5.1 The Oxidation states of sulfur compounds

Considering the biochemical cycling of sulfur, transformations occur due to its oxidation state and physical status. In oxidizing conditions the most stable sulfur species is sulfate, whilst in reducing conditions elemental sulfur and sulfide are the most stable. There are numerous other sulfur species which are formed in natural environments (sulfite, polysulfide and/or thiosulfate), however these species are considered unstable (Tichy *et al*, 1998, Bentley *et al*, 2004). The conversion from one sulfur species to the other is a combination of biological, chemical and geochemical processes and is strongly affected by other species like carbon, oxygen, nitrogen and iron (Lomans *et al*, 2002).

Table 2-2: Oxidation states of sulfur compounds

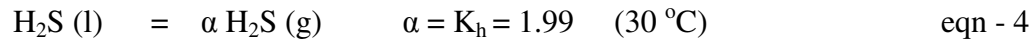
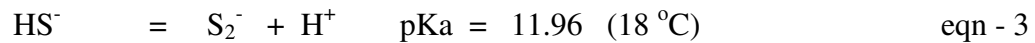
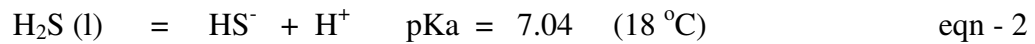
| Component | Appearance | Oxidation State |
|----------------------------------|---|-----------------|
| Hydrogen sulfide | H ₂ S/HS ⁻ | -2 |
| Reduced organic sulfur compounds | Mercaptans | -2 |
| | Carbonyl | -2 |
| | Methyl sulfides | -2 |
| | | |
| Metal sulfides | FeS | -2 |
| Pyretic sulfur | S ₂ ²⁻ | -1 |
| Elemental sulfur | S | 0 |
| Thiosulfate | S ₂ O ₃ ²⁻ | +2 |
| Sulfur dioxide | SO ₂ | +4 |
| Sulfate | SO ₄ ²⁻ | +6 |

2.5.2 Mechanisms of Volatile Sulfur Compound Production

2.5.2.1 Production of hydrogen sulfide by sulfate reducing bacteria

The reduction of the sulfate ion (SO_4^{2-}) is the most significant mechanism for the production of H_2S in wastewater environments. Sulfates are the major stock of mobile sulfur compounds and due to their high solubility considerable amounts are easily transported in the environment. Domestic sewage typically contains 20 to 500 mg/L of sulfate but some industrial wastewaters contain higher concentrations of sulfate, sulfite or other sulfur compounds (*Lens et al, 1998*). Bioavailability of sulfates in part depends on the hardness of the water due to the formation of CaSO_4 and/or MgSO_4 [5]. In anaerobic environments rich in oxidized sulfur compounds (sulfate, sulfite or thiosulfate), sulfate reduction (in addition to methanogenesis) occurs as an end step in the anaerobic mineralization process (Redox Eh < -150 mV) (*Smet et al, 1998*). SRB plays an important role in the mineralization process by using sulfate as the terminal electron acceptor (Figure 2-1). SRB will uptake proprionate, butyrate, higher and branched fatty acids, lactate and higher alcohols as an electron donor or carbon source. In the presence of sulfate, SRB will compete with Methanogenic bacteria (MB) and obligatory hydrogen producing Acidogenic bacteria (AB) for the available substrates. The importance of this competition increases with a decrease in the chemical oxygen demand (COD)/sulfate ratio where the amount organic matter present is insufficient for the complete reduction of the sulfate present. This competition will determine to what extent sulfide and/or methane are produced. The optimal pH range for SRB anaerobic digestion is 6.00 - 8.00 but methanogens are more efficient at a pH range of 6.75 - 7.55 (*Lens et al, 1998*).

Temperature plays an important role in H₂S generation, the highest production rate occurs at 30 °C [28]. Sulfide is a weak acid in solution and once produced, speciation is strongly dependant on pH (eqn 2 & eqn 3). At a neutral pH approximately 50% is in the H₂S_(aq) form. The equilibrium between H₂S in solution and in the gas phase is governed by Henry's law (eqn 4), which is strongly temperature dependent. SRB activity is known to have a high demand for iron but an accurate assessment of the role of iron concentration remains difficult in sulfidogenic systems because precipitation of iron sulfide (FeS) and complex ion formation reduce its bioavailability (*Lens et al, 1998*).



2.5.2.2 Degradation of sulfur-containing amino acids

The degradation of sulfur containing amino acids has considerable odor generation implications. Proteins are made up of single units of amino acids and both cysteine and methionine have been shown to be present in protein extracts from activated and anaerobically digested sludge (*Yarosz et al, 2003*). Sulfur occurs in a reduced form in some amino acids, namely cystine, cysteine, methionine and taurine. It is thought to provide a structural link between molecules. This degradation involves the sequential break down of proteins to form free amino acids of which cysteine and methionine are then broken down to form S₂⁻, MM, DMS, DMDS, NH₃ and other smaller sized amino acids (Figure 2-8) (*Lomans et al, 2002* , *Smet et al, 1998* , *Yarosz et al, 2003*). This

protein breakdown occurs in oxygen deficient environments by the action of proteolytic (hydrolysis) bacteria such as *E. coli*, *Proteus vulgaris* and *pseudomonas aeruginosa*.

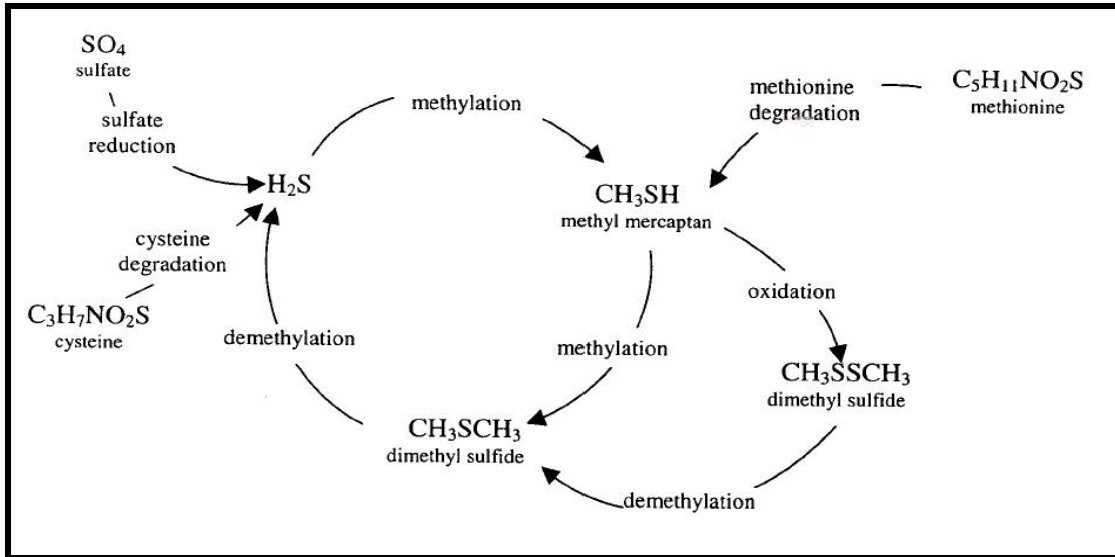
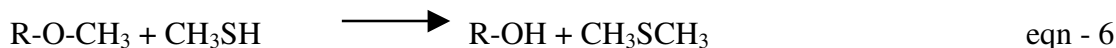
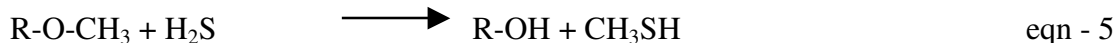


Figure 2-1: Suggested VSC formation pathways in sludge (excerpted from *Yarosz et al, 2003*)

2.5.2.3 Methylation of hydrogen sulfide and methyl mercaptan

The methylation of H_2S and MM to MM and DMS respectively by heterotrophic bacteria occurs in sulfide rich environments and may occur as a sulfide detoxifying mechanism (*Lomans et al, 2002, Stets et al, 2003, Bak et al, 1992*). This methylation reaction is thought to proceed in two sequential steps with methyl mercaptan as an intermediate (eqn – 5 & eqn 6, Figure 2-1). The carbon for this reaction is from the methyl group in methoxylated compounds (*Yarosz et al, 2003*). The loss of methyl groups from methoxylated compounds is a general reaction and occurs naturally in terrestrial environments (*Bentley et al, 2004*). The precursors for these reactions are H_2S ,

MM and methyl donating groups. Methoxylated compounds are found in abundance in the wastewater environment.



2.5.2.4 Abiotic reactions

DMDS production is partly a result of the oxidation and dimerization of MM (eqn- 7). This reaction occurs in the presence of oxygen and is catalyzed by several agents including metal surfaces and light (*Yarosz et al, 2003, Bentley et al, 2004*).



2.5.3 Mechanics of VSC Destruction

The mechanics of VSC destruction include biotic degradation, atmospheric degradation and chemical oxidation. Aerobic and/or anaerobic biological ecosystems have mechanisms by which VSCs are degraded (*Lomans et al, 2002*). In aerobic systems, VSCs serve as a carbon source in microbial metabolic processes. In anaerobic environments, VSCs are degraded by various adaptive microbial consortia. Various atmospheric oxidants will oxidize VSCs in air.

2.5.3.1 Biotic degradation

Before VSCs are released into the atmosphere, considerable quantities have undergone degradation by microbial populations. Under aerobic and anoxic conditions, bacteria such as *Hyphomicrobium* and *Thiobacillus sp.* convert DMS to MM and formaldehyde. The MM produced is also oxidized to form formaldehyde and sulfides [Bentley *et al.*, 2004, Lomans *et al.*, 2002]. The obligate bacterium *Methylophaga sulfidovorans* is a specialist in the preferential aerobic oxidation of H₂S and DMS [40]. In anaerobic environments, degradation of DMS and MM is mainly attributed to methanogens, SRBs and denitrifying bacteria. Methanogenic bacteria can demethylate MM, DMS and DMDS to form MM and H₂S. In sulfate rich environments, SRB can also demethylate MM and DMS to form H₂S [14]. The extent to which methanogens or sulfate reducers participate and/or compete in the degradation of MM and DMS depends on the concentrations of sulfate in the system. High concentrations of sulfate favor the activity of SRBs. These reactions can be very significant in maintaining low levels of VSCs in anaerobic environments and therefore preventing the inhibition of methanogens and eventually sulfate reducers. Demethylation of DMS by denitrifiers using NO₃⁻ as the terminal electron acceptor (anoxic conditions) has been observed, followed by further oxidation of the resulting methyl groups to CO₂ (Lomans *et al.*, 2002, Visscher *et al.*, 1995).

2.5.3.2 Atmospheric chemical degradation

The atmospheric lifetime of MM, H₂S and DMS is very short and may be from a few minutes to hours for MM, to a day or two for DMS and H₂S (Smet *et al.*, 1998).

Atmospheric degradation proceeds mainly by hydroxyl radical (OH^\cdot) attack during the day and nitrate radical (NO_3^\cdot) attack at night. The OH^\cdot radical attack during the day initiates the degradation but it is the NO_3^\cdot radical attack at night that substantially reduces DMS production (*Bentley et al, 2004*). The daylight oxidation of nitrogen oxides is a source for the NO_3^\cdot radical.

2.6 Odor Control Technologies and Strategies

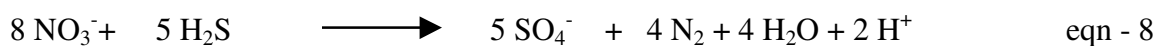
To avoid odorous off gassing, sewerage should be maintained in a completely aerobic state throughout its transit in the sewage network and during the treatment process. This scenario though ideal, is very costly to achieve. Due to the prohibitive costs WWTP authorities are more likely to favor the *in situ* treatment and/or the collection and treatment of odorous gases.

2.6.1 The Collection Network

Industrial wastewaters should be strongly regulated and enforced to eliminate odorants before discharge into the sewer network. The adoption of inline flow equalization basins to avoid slug deposits into the collection system is a useful measure (*Martin and Laffort, 1994*). Slug deposits are solid waste and should be disposed of in a solids disposal system. On entering the collection system, slug deposits generally become immobile and form anaerobic zones that encourage odor production. By maintaining aerobic conditions in the sewer network, complete metabolic hydrolysis of organic material occurs and thereby negates the production of odorants. Unless a process

requirement necessitates the need, all anaerobic zones should be avoided by good system design, maintenance and housekeeping (*Metcalf and Eddy, 2003*). This goal can be achieved in part by; the addition of hydrogen peroxide (H_2O_2), ozone and/or air at specific points along the collection system to maintain aerobic wastewater streams, controlling microbial populations in the sewer network by disinfection (Cl_2 , H_2O_2) and/or pH control, oxidizing and/or precipitating sulfides, designs that minimize turbulence in collection systems and off-gas treatment at selected locations in the sewer network (*Gostelow et al, 2001*).

The oxidation process involves the addition of a strong oxidizing agent to the wastewater stream. Many non-odorous compounds are also oxidized resulting in the inefficient use of the oxidizing agents. H_2O_2 is more useful as an oxidant than Cl_2 , only 1 kg H_2O_2 /kg – S is needed as compared to 8.4 kg Cl_2 /kg – S. H_2O_2 does not form toxic chlorophenols through the reaction with phenol, and will increase the dissolved oxygen (DO) content of the wastewater. Iron salts oxidize and/or precipitate sulfides. Ferric chloride will oxidize sulfide to sulfur while being reduced to ferrous (II). Subsequently ferrous (II) will precipitate sulfide as $Fe(II)S$. The bioxide process makes use of the addition of nitrates to biochemically oxidize sulfide to sulfate (eqn – 8). A biocide, antraquinone can be added to wastewater to interrupt the sulfate-reduction process in anaerobic environments by interacting with the cytoplasmic membrane of the SRB, effectively disrupting sulfide production.

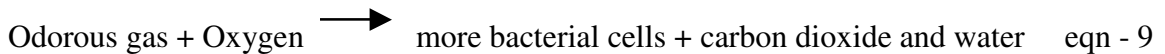


2.6.2 Treatment Technologies

There are two main categories of odorous gas treatment, biochemical and physiochemical treatment. Biochemical treatment includes biofilters, tricking filters, bioscrubbers and activated sludge reactors. Physiochemical treatment includes chemical scrubbers, thermal oxidation, catalytic oxidation, ozonation and adsorption (activated carbon).

2.6.3 Biochemical Treatment

There has been a dramatic increase in the use of biochemical treatment methods to address odor problems. These methods have gained in popularity due to their ability to significantly destroy the pollutants and not just serve as a phase transfer remediation. The biological transformation process can simply be expressed by; (eqn – 9)



Acclimated microorganisms can oxidize sulfide to non odorous sulfur species such as sulfate or elemental sulfur, once provided with an oxygen source. Phototrophic, heterotrophic and autotrophic bacteria have all been successfully used for the desulphurization of odorous gas (*Burgess et al, 2001*). Biochemical treatment has several advantages over physicochemical processes which include; the economic gain due to low capital outlay, lower operation and maintenance costs since money is saved by not purchasing oxidants and catalysts, sale of recovered sulfur, no production of chemical sludge and a generally lower energy consumption cost.

Biofilters contain microbes present in the bulk media (simple-soil, peat, and compost and/or engineered-specific combination of materials) which is immobilized by support structures. The bulk media and the odorous gas are moistened to facilitate microbial activity and to provide a source of nutrients (nitrogen, phosphorus, potassium) and carbon (*Burgess et al, 2001*). The odorous gas provides the carbon source and is passed through the media from the bottom up so as to allow as much contact time with the microbes in the bulk media. Biofilters have no liquid phase and the relative solubility of odorants is of relatively little significance. Biofilters are effective at treating odorants with an air/water partition coefficient of 1 or less. Biofilters are very effective at removing sulfur based odor compounds (H_2S , organic sulfides and mercaptans) but are not as efficient at removing nitrogen based compounds (NH_3 and amines) (*Harshman and Barnette, 2000*).

Biotrickling filters are operated on the same concept as the biofilters but in this case the action of the microbes is designed to take place in the liquid phase. A myriad of microbial colonies form biofilms on the support media (foam cubes, ceramic, plastic, activated carbon and/or various combinations). The humidifying liquid which supplies nutrients also serves as the primary medium for the elimination of the odorants. Unlike biofilters, the solubility of the odorants is very significant and therefore the air/water partitioning of the odorants is one of the major drawbacks of this method (*Lens et al, 1998*). Biotrickling filters are effective at treating odorants with an air/water partition coefficient of 0.1 or less (*Burgess et al, 2001*). Bioreactors containing foam cubes as the support media, were successfully used to support microbes which oxidized various

odorants (mainly H₂S), to odorless sulfate. After two years of continuous operation, H₂S removal efficiency was still at 98%.

Bioscrubbers are a liquid based odor control system. Bioscrubbers differ from media based processes in that the treatment of the odorants occurs wholly in the liquid phase. Therefore the system is largely dependant on the air/water partitioning of the gaseous odorants into the aqueous medium in a gas/liquid exchange column (*Smet et al, 1998*). The aqueous medium is advantageous in that it affords operators better control over pH, temperature, nutrient balance and the removal of metabolic products (*Lens et al, 1998*). On the other hand a significant amount of odorants are volatile and have poor solubility.

The activated sludge (AS) treatment system is a wholly liquid based odor control system. Odorous gases are transferred from their source via blowers to a submerged pipe network in the activated sludge basin. Odorants are removed from the gaseous phase by a combination of mechanisms; (1) absorption into the mixed liquor, (2) adsorption onto microbial flocs and (3) condensation of odorants (*Hwang et al, 1995*). The absorption of odorous gases into the mixed liquor is limited by bubble size and gas residence time. The adsorption onto microbial flocs is the dominant mechanism for higher molecular weight compounds with low solubility. Condensation occurs when the warm gaseous air streams contact with the cooler mixed liquor. Odorants are subsequently destroyed by microbial degradation in the liquid phase. Pilot activated sludge plant systems have to varying extents effectively removed low concentrations of H₂S, amines, ammonia and mercaptans. These odorants were treated to below 0.1 ppm (*Burgess et al, 2001*). It has been noted that longer SRT provide for the degradation of indole and scatole. Emissions

from the activated sludge aeration tank may increase due to the effect of stripping especially when the system is overloaded but the overall emission from the plant would decrease.

2.6.4 Physiochemical Treatment

2.6.4.1 Scrubbing

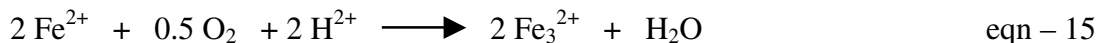
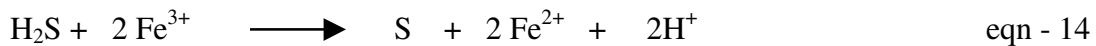
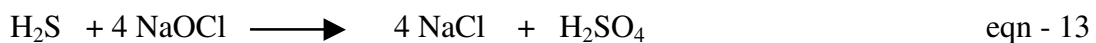
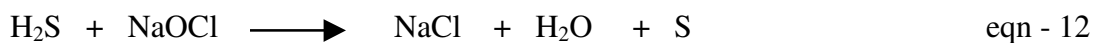
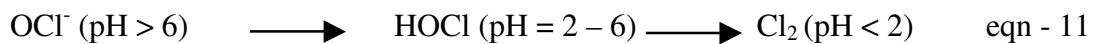
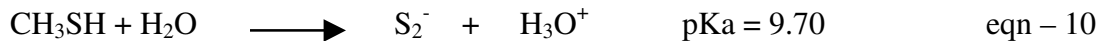
Essentially, scrubbing transfers odorants from the gas phase to the liquid phase by intimate contact of odorous air with the aqueous phase. Efficiency depends on the odorant concentration in the gas phase, air/water partitioning coefficient of odorant, the mass transfer resistance of the scrubbing system and chemical scrubbing solution. The removal mechanism is purely chemical and not prone to upsets as are biological systems. The main types of scrubbing are alkaline scrubbing, oxidative Scrubbing and catalytic Scrubbing.

Alkaline Scrubbing makes use of an increase in alkalinity to improve removal efficiencies (e.g. H₂S and MM, eqn – 10). There is an added alkaline cost in the presence of high CO₂ concentration. When pH is greater than 10, precipitation of CaCO₃ and MgCO₃ from the scrubbing water occurs. This clogs up the scrubber and increases maintenance costs.

Alkaline oxidative scrubbing makes use of an oxidant and alkaline addition to control pH (e.g. hypochlorite eqn 12 & 13) (*Smet et al, 1998*). CO₂ adsorption is insignificant at pH range 9 – 10 and therefore there is no precipitation of CaCO₃ and/or MgCO₃. Unlike the Alkaline scrubbing, oxidative alkaline scrubbing can be used to treat various other volatile organic sulfur compounds (VOSCs). For VOSCs, HOCl has a more

potent oxidative power than OCl^- and therefore systems to treat gas predominated by VOSCs would operate at a pH of 6.5 (eqn – 11). A two stage wet scrubber using a OCl^- solution of 0.1 – 0.23%, and a NaOH solution of pH 10.5 – 11.6, proved to be 85 – 95% effective at reducing odor (*Basher and Shahalam, 1982*). Potassium permanganate (KMnO_4) is efficient as an oxidant in the treatment of a wide range of VSCs (e.g. DMS, DMDS, PM and BM) but it is more expensive than hypochlorite.

Catalytic scrubbing utilizes the catalytic properties of certain metals (e.g. iron (III), eqn – 14 & 15) to harness the oxidative potential of molecular oxygen. A removal efficiency of 96% has been achieved with an optimal pH of 8.5 – 9.0 and with an iron concentration of 200 - 250 ppm (*Smet et al, 1998*). In addition an accompanying step may be added where the action of *Thiobacillus ferrooxidans* bacteria may be used to oxidize the ferrous iron back to the ferric form either in a fixed bed or suspended cell reactor.



2.6.4.2 Adsorption, Incineration and Masking

Adsorption is based on the transfer of odorants from a mobile gaseous phase onto active sites on a stationary solid phase. Efficiency depends on the surface area per unit volume of the solid phase and adsorption properties of the odorants. Activated carbon (AC) is the most typical adsorbent material used for the removal of VSCs. VNC removal is not as efficient (*Hwang et al, 1994*). A pilot study by (*Huang et al, 1979*), showed a 91% removal efficiency of H₂S by an activated carbon column before breakthrough.

Incineration is a very efficient but expensive method when treating low level pollutant concentrations. Thermal incineration requires temperatures up to 700 – 1000 °C with a gas residence time of 0.5 - 1s. For catalytic incineration the temperature can be lower. For 90% removal efficiency of H₂S and CS₂ by catalytic combustion with platinumized ceramic honey comb catalyst, an inlet temperature of 375 - 425 °C. SO₂ emission may result from the incineration of sulfur compounds. This would require post-treatment to avoid the potential for acid rain formation.

Masking agents (e.g. terpenes) can be used to overcome the nuisance of discontinuous and/or small odor emissions. Applications where these agents mask toxic concentrations of odorants can be dangerous (*Smet et al, 1998*). Some agents act as acid/base reactions and are effective against H₂S and MM, other agents act with enzymatic properties.

2.7 Efficacy of Treatment Technologies

2.7.1 Procedure for Odor Abatement

When odor has been determined as being a nuisance, steps should be taken to minimize or eliminate the frequency and intensity of the odor event. There is an initial discovery period where the exact source of the odor is determined. Physical and process conditions are checked and altered to mitigate the odor problem by good housekeeping and/or appropriate process changes. If unsuccessful, the next step would be to identify the major odorants associated with the odor. Both sensory and chemical analytical methods should be applied at this stage. After identification, suitable remediation methods should be tested on a bench scale. Once all conditions to minimize the odor release are identified, full scale design and construction would be the final step. Even after odor control structures have been constructed, the treatment system should be fine tuned and frequently monitored to achieve optimal efficiency. To appropriately monitor odor release from the system, plant operators should have a good understanding of WWT processes and analytical measurement procedures.

2.7.2 Useful Analytical Methods

Frequent odor/odorant monitoring techniques at a WWT plant may include the use of Draeger tubes, an H₂S Data logger, a Jerome meter and a Nasal ranger. Draeger tubes are used to measure the concentration of specific odorants almost instantaneously. The majority of Draeger tubes are scaled tubes, operating on a defined sample volume drawn through the tube. The concentration of the odorant is read directly from the

calibrated scale by assessing the length of the discoloration. Currently, about 160 short term Draeger tubes are available for determining and measuring more than 350 different gases, vapors and aerosols, to include H₂S, DMS, DMDS, MM, EM, MA, DMA and TMA. The H₂S Data logger (Odialog) was designed specifically for the wastewater industry based on valuable input and feedback from actual plants. The Odialog automatically logs H₂S concentrations in the 10ppb - 200 ppm range. Typical applications include locating and monitoring the source of H₂S gas emissions from sewage pumping stations and receiving manholes.

A Jerome meter is also used to measure the concentration of H₂S gas but this instrument is also sensitive to other VSCs, especially DMDS, MM, EM, PM and BM. It offers an analysis range of 0.003 - 50 ppm for H₂S and corrosion control. The Nasal ranger is a portable field olfactometer used for detecting, measuring and quantifying odor strength in ambient air. The Nasal ranger operates on the principle of diluting odorous air with odor free carbon filtered air in specific volume ratios, i.e. dilution to threshold (D/T) ratios. Ambient weather conditions need to be recorded and accounted for so as to be able to compare data collected under different conditions.

Intermittent odor/odorant monitoring techniques include GC and/or olfactometric analysis. These methods are extremely sensitive and accurate at determining levels of odors and/or odorants but are notably more time consuming and expensive. Therefore, they are not suited for real-time continuous field monitoring operations. These infrequent monitoring techniques can be useful in calibrating or validating the more frequent monitoring methods. Suitable sampling, pre-concentration, isolation and detection procedures would have to be identified and appropriately applied to achieve the desired

level of accuracy and confidence. Analysis may be carried out in a remote laboratory. Further discussion of these methods can be found in chapter 3.

Sensory array systems (electronic noses) offer an alternative to the analytical and olfactometric measurement of odors/odorants. Both analytical and olfactometric methods have their merits and demerits. Although olfactometric methods give a true human evaluation of odor, it is subjective. On the other hand, quantification of odorants by a chemical analytical method (e.g. GC) provides accurate concentrations of each constituent odorant but no link to total olfactory perception. The electronic nose offers a solution to some of these problems and may form a useful link between analytical and sensory methods (*Romain et al, 2000*). The electronic nose consists of three functional structures, an odor sensor array, a data pre-processor and a pattern recognition system (*Dewettinick et al, 2001*). The overlapping response from an array of non-specific sensors results in an odor specific response pattern. This response pattern is then processed by a pattern recognition system which objectively detects, quantifies and even characterizes odorous gases. Electronic noses have potential for general continuous online monitoring and early warning of undesirable industrial discharges into a WWC network (*Bourgeois and Steutz, 2002, Bourgeois et al, 2003*). Non invasive outdoor continuous monitoring of the air above a process stream is a valuable option, for early detection of undesirable process changes (*Nake et al, 2004*).

CHAPTER 3

SEASONAL VARIATION IN VSC PRODUCTION AND RELEASE IN THE SECONDARY TREATMENT SYSTEM OF A WASTEWATER TREATMENT PLANT

3.1 Introduction

Offensive odors associated with the wastewater treatment process are a nuisance to the public. Communities near WWTPs are in constant contention with the management of these plants. Odor mitigation has become a priority for many treatment authorities. The most common odor control strategies have involved the on-site collection and treating of odorous gas. This method though effective is not always the most appropriate and cost effective strategy. The notion that the odor from a treatment plant is homogenous in nature is erroneous. Each unit process in the treatment scheme has a unique contribution to the total odor generated from the plant. To effectively reduce total odor generation and prioritize treatment strategies, the contribution and hence importance of each unit process needs to be determined. To achieve this, environmental conditions and process parameters which affect the formation of odorants and the release of odorants and therefore odors need to be understood for each unit process. Identification and quantification of odorous compounds provide a baseline for selecting and monitoring appropriate treatment strategies.

The purpose of this study is to quantify the odorous compounds associated with the secondary treatment system of an advanced wastewater treatment plant (AWWTP), determine the significant odor source locations in the secondary system, identify

significant parameters which affect both the formation and release of odorants/odors from the system and provide useful baseline information for the selection of appropriate treatment technologies for odor reduction in the secondary system.

3.4 Scope and Objectives

3.2.1 Background Information

Plant odor minimization is a priority for the District of Columbia Water and Sewer Authority (DCWASA) at Blue Plains. This plant is the largest advanced AWWTP in the world and has the capacity to treat 370 MGD of sewage. As part of DCWASA's odor control strategy, a plant wide odor study was conducted by *Camp Dresser & McKee, 2003*. It was found that the secondary treatment system ranked second (34.5%) in odor emissions after the grit and screens facility (36.1%) and had the potential to be the highest odor source once the grit and screening facilities were fitted with planned odor control structures.

The secondary system at DCWASA is essentially a rapid aerated activated system for the treatment of carbonaceous biological oxygen demand (CBOD). The system consists of a secondary aeration tank and secondary sedimentation tanks. Wastewater is treated for CBOD in the aeration tanks and separation of water and solids is achieved in the sedimentation tanks. Several researchers have found varying concentrations of volatile organic compounds (VOCs) across the secondary treatment system of various WWTPs, notably reduced sulfur compounds. *Nurul Islam et al, 1998*, recorded concentrations of ~ 20 ppmv – 80 ppbv for dimethyl sulfide (DMS) and Methyl mercaptan (MM) across the secondary treatment system. *Kim et al, 2002*, measured concentrations of DMS ~ 3 ppbv and dimethyl disulfide (DMDS) ~ 2 ppbv in return activated sludge (RAS). *Jenkins et al, 1980*, quantified MM ~ 44 ppbv from mixed liquor sampled from the front end of an aeration tank.

Reduced volatile sulfur compounds (VSCs) are formed primarily as a result of anaerobic metabolic activity by sulfur reducing bacteria (SRB). Anaerobic conditions are created in the sedimentation tanks due to the inherent quiescent, non turbulent nature of the separation process in the sedimentation tanks. The mixed liquor in the aeration tanks which is ideally an aerobic process may turn anaerobic due to inefficient mixing and/or oxygen transfer. *Bhatla M, 1975*, discovered that sludge deposits at the bottom of the front end of an aeration tank were the root cause of usually high odor emissions from the aeration tanks.

3.2.2 General Objectives

The general objectives of this study are to improve our understanding of VSCs as odorant sources across the secondary treatment system at DCWASA. Identify and quantify VSCs in the secondary treatment system and understand the environmental conditions and process parameters that affect VSC odorant formation and emission from the secondary treatment system.

3.2.3 Specific Objectives

The specific objectives of this study were to evaluate the secondary treatment process through:

- Quantification of VSCs.
- Identification of production and release locations.
- Determination of seasonal trends in VSC production.
- Determination of seasonal trends in VSC release.

3.5 Literature Review

In this section, techniques to identify and quantify VSCs are discussed. Both chemical analytical and sensory analytical measurements are examined in relationship to the measurement of odorant/odors, especially the VSCs associated with a WWTP.

3.3.1 Chemical Analytical Measurements

There has been great advancement in the use of analytical methods in the quantification of VSCs but some challenges still remain. There are problems associated with each stage in the analytical procedure: sampling, pre-concentration, isolation and detection. These problems can be attributed to the very nature of the VSCs. Most VSCs are highly reactive in nature and known to have absorptive, adsorptive, photo-oxidative and metal catalytic oxidative. These VSCs exist at wide concentration ranges in complex matrices including several compounds present at several orders of magnitude (*Wilkins, 1994*).

3.3.1.1 Sampling and sample preparation

Sampling techniques differ with the different matrices (gaseous or liquid) being sampled. To maintain the integrity of gaseous samples, inert sampling vessels and connectors should be used. These include various glass sampling vessels, stainless steel canisters, polymer bags and tubing made of inert material. The use of aluminum foil to cover exposed vessels helps to prevent losses through photo-oxidation. Atmospheric oxidants such as SO₂, O₃ and NO_x contribute to VSC loss and the use of in-line scrubbing systems is in common practice. Tygon shavings and various substrates (e.g. glass beads)

coated with Na_2CO_3 have proven to be useful (*Wardenski, 1997*). With liquid matrices the main concern would be losses due to adsorption onto the walls of the sampling containers. Inert polymeric bottles made of Teflon and/or polyethylene are useful. Dark collection vials can be used to prevent photo biochemical reactions from taking place.

Pre-concentration and isolation of gaseous samples include headspace equilibrium, purge and trap methods (*Hwang et al, 1995*), sorption onto certain metals, sorption onto solid sorbents, cryogenic trapping (*Simo et al, 1993*) and solid phase micro-extraction (SPME). Certain metals, namely gold, palladium and platinum are known to chemisorb sulfur gases (*Wardenski, 1997*). Therefore techniques which use metal fiber/foil adsorption and subsequent flash desorption are common. Adsorption onto solid sorbents at low temperatures is a popular pre-concentration step. Solids sorbents include activated carbon, silica gel, aluminium oxide and various porous polymers. Porous polymers are more commonly used because sample collection is less restricted by water vapor. Tenax exhibits high thermal stability and has low water affinity. Tenax trapping is a widely used pre-concentration procedure (*Langehove et al, 1985, Tangerman 1986*). Cryogenic trapping is a cold trapping procedure for the concentration of VSCs at low concentrations. This usually involves open or packed (glass beads or fiber wool, Tenax or activated carbon) and U-shape adsorption tubes, immersed in liquid nitrogen or argon (*Hwang et al, 1995*). Detecting low molecular weight VSCs is a challenge due to their high water solubility and volatility. Direct analysis of aqueous samples minimizes sample preparation and therefore reduces analysis time, reduces systematic errors and minimizes sample contamination. A down side of concentration methods is that impurities may also be concentrated and lead to false positives and/or high results.

3.3.1.2 Solid phase micro-extraction

Solid phase micro-extraction (SPME) is an alternative to the traditional sampling and pre-concentration/isolation methods. SPME is a quick and easy solvent free method for partitioning target compounds from their matrices onto an absorbent, thereby achieving sampling and pre-concentration/isolation into one step which in took up to 80% of the overall time for analysis. Field sampling is also simplified with the use of the SPME portable field samplers. By using a suitable coolant (e.g. dry ice), volatile and semi-volatile compounds extracted in the field remain on the SPME fiber significantly longer. The extraction process is essentially governed by the kinetics of diffusion in the sample matrix and/or adsorption on the polymer fiber coating. This method relies on the equilibration of target analytes between the sample matrix and the SPME fiber. SPME procedure consists of two steps, firstly the extraction step where the coated fiber is exposed to the analytes in the matrix (liquid or gaseous). Secondly, the fiber bearing the analytes is desorbed in the injection port of an analytical instrument (usually a Gas Chromatograph – GC) where separation and quantification takes place. GC-MS-SIM has been used with the 75um SPME car-PDMS fiber for the detection of VSCs at a WWTP in the low ppb to ppt range (*Nielsen and Jonsson, 2000, Kim et al, 2002, Haberhauer-Troyer et al, 1999, Abalos, 2002*).

A variety of coated fibers with different polarities and film thicknesses are commercially available. Essentially the SPME fiber is made up of fused silica fiber covered by a specific coating (poly-dimethylsiloxane (PDMS), Carboxen – PDMS etc) to enhance adsorption properties for target analytes. The unique pore structure of carboxen - 1006 enables the extraction of a wide range of target compounds, including VSCs

without significant displacement of lighter weight analytes. The highly retentive carboxen/PDMS coating ensures that the VSCs remain on the fiber for up to 3 days after sampling at $-4\text{ }^{\circ}\text{C}$, if appropriately stored. Competition for the finite adsorption sites on a SPME fiber leads to competitive adsorption. The effect of competitive adsorption among VSCs is strongly molecular weight/size dependant. Whilst DMDS is hardly affected by the presence of other lower molecular weight VSCs, MM and DMS have shown a net difference in concentration of about 20% (*Visan, 2004*). On the other hand under dynamic flow conditions and limited exposure times, the effect of competitive adsorption may not be noticeable (*Kim et al, 2002*). Humidity has a significant effect on the extraction efficiency of a SPME fiber due to competitive adsorption (*Visan, 2004*). This phenomenon affects to a greater extent lower molecular weight compounds. The effect of this competition can be up to 50% of expected values for both MM and DMS. Stability of the extraction response is also greatly reduced by high relative humidity (*Haberhauer-Troyer et al, 1999*). To minimize the effect of humidity, calibration either has to be done at the same relative humidity of the sample air or the sample air has to be efficiently dried before SPME fiber exposure. Numerous drying agents have been used (MgSO_4 , Na_2SO_4 and Na_2CO_3) and CaCl_2 is known to be the most suitable for VSC sampling (*Tangerman 1986, Nielsen and Jonsson, 2002*). Equilibrium time in SPME varies depending on analytes and the sample matrix. Literature sites a range of exposure times for both dynamic and static equilibrium methods. These range from 5 min to 90 min (*Visan, 2004, Lestremau et al, 2003*). Acceptable SPME storage may be achieved at low temperatures for most VSCs but (*Haberhauer-Troyer et al, 1999*) found out that PM and BM showed significant losses at $-23\text{ }^{\circ}\text{C}$ over a 48 hr period.

3.2.2 Sensory Analytical Measurement

There is very limited work that has been done on the relationship between chemical analytical and sensory data due to the difficulty in relating odorant concentrations to the odor intensity. Various reasons exist including the synergistic and antagonistic interactions between odorants and the limited knowledge of the sense of olfaction (*Martin and Laffort, 1994*). Although chemical analytical measurements are very useful due to its repeatability and sensitivity, it says very little about the actual odor sensed by the human nose. Sensory analytical measurements are therefore a needed part of an ultimate odor reduction strategy.

There are two main methods in current use; subjective measurements (rely entirely on the human nose) and objective measurements (incorporate a dilution apparatus - olfactometer). Subjective sensory measurements are quick and cheap but interpretation of the results is difficult. Odor character, intensity and hedonic tone are parameters that may be measured subjectively. 'Subjective' here refers to a personal and individualistic mental experience. A typical numbered scale for the order of intensity would be 0 - no odor perceivable, 1 - barely perceivable, 2 - faintly perceivable, 3 - clearly perceivable, 4 - strong and very strong. The intensity scale is relative and differences between these values are not necessarily equal and thus the distinction is not clearly evident (*Turk et al, 1980*). On the other hand, there are two categories of dilution related measurement techniques for objective sensory odor measurements; threshold olfactometry and suprathreshold olfactometry.

For threshold olfactometry, the odor sample is diluted with odor free air till the odor is barely detectable. Both static (eqn - 1) and dynamic (eqn - 2) dilution methods can be used. With static olfactometry, dilution of the odorous sample is achieved with a known volume of odor free air (i.e. the syringe method or the scentometer). Static methods suffer from concentration distortions due to adsorption and desorption effects on the surface area (plastics, glass etc) of the containment used for dilution. Catalytic reactions may also take place. Techniques with high surface area to volume ratios are especially susceptible to concentration distortions. Dynamic olfactometry offers the potential to achieve a dynamic state of equilibrium and hence avoid such adsorption desorption problems.

$$C = (Q_o + Q_r) / Q_o \quad (\text{Static}) \quad \text{eqn - 1}$$

$$C = (V_o + V_f) / V_o \quad (\text{Dynamic}) \quad \text{eqn - 2}$$

C = odor concentration

Q_o = is the flow of the odorous sample

Q_f = is the flow of odor free air required to reduced the sample to threshold

V_o = volume of odorous sample

V_f = volume of odor free air required to reduce the sample to threshold

Suprathreshold olfactometry is a measure of odor intensity rather than concentration. Dose/response curves are produced by measuring intensity at several different dilutions. Suprathreshold olfactometry presents fewer problems with the methodology and therefore minimizes variations in the observed data. The essential

principle is the dilution of a sample until its intensity matches that of a reference gas or the vice versa where a reference gas is diluted till it matches the intensity of the sample. The common reference odorant is n-butanol.

The odor threshold concentration (OTC) is a measure of the relative strength of an odor. OTC is defined as the concentration of odorous gas that can no longer be detected when the gas is diluted with odor free air (*Huang et al, 1979*). Two types of OTCs are in common use, detection and recognition thresholds. Arguments to use recognition threshold as opposed to detection thresholds would be that an odor cannot be distinguished as offensive or not if it has not been recognized. At dilution to detection the presence of an odor can be detected but its character cannot be recognized. Recognition can only be achieved at higher concentrations than detection, usually a factor of 1.5 to 10^5 (*Dravicks et al, 1980*). The dimensionless OTC units may be termed threshold odor numbers (TON) or dilution to threshold (D/T). Some scientists express these units as odor units per cubic meter (OU / m³). The choice of a cubic meter is arbitrary.

3.4 Experimental Approach, Materials and Methodology

In this section, the experimental approach and materials are described. Since the main focus of this work was to study *in situ* production and release patterns of volatile sulfur compounds (VSCs) in the secondary treatment system, a full-scale experimental approach was developed. This approach included a study of the VSC production and release patterns in the secondary aeration tank, the secondary sedimentation tank and in part the primary clarification tank.

3.4.1 Wastewater Treatment Process Description at DCWASA

Successive unit processes are used in the treatment of the wastewater. The wastewater undergoes screening and grit removal in the head-works. Primary clarification removes suspended matter from the waste stream. Dissolved organic matter is treated in the secondary aeration tanks, secondary sedimentation tanks and the biological nutrient removal (BNR) tanks. Sand filtering achieves phosphorous removal and chlorination is for disinfection. Gravity thickeners receive solids from the primary clarification tanks and dissolved air flotation (DAF) thickeners receive solids from the secondary sedimentation and the BNR tanks. Gravity and DAF thickened solids are subsequently, blended in a blend tank and dewatered using either high speed centrifuges or a belt press. Liming is the last step in the treatment of the biosolids.

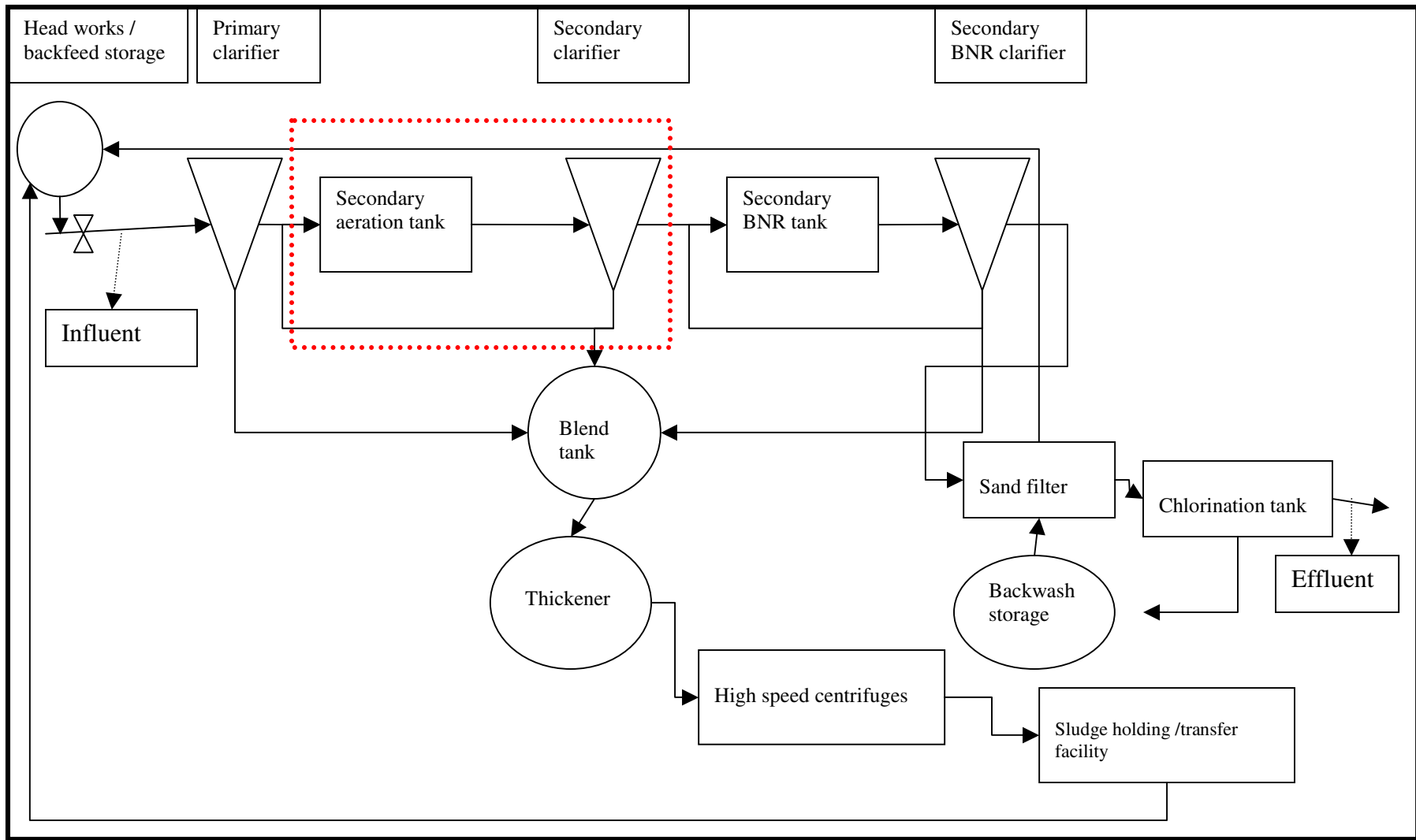


Figure 3-1: A schematic representation of the DCWASA advanced wastewater treatment system.

3.4.1.1 The secondary treatment system

The secondary treatment system in a WWTP plant is designed to reduce BOD in the wastewater. At Blue Plains AWWTP, this system precedes the BNR system but follows immediately after the primary sedimentation process (shown in box - Figure 3-1). The secondary treatment system comprises of aeration and sedimentation tanks (figures 3-2 & 3-3). Wastewater flow patterns, sampling locations and methods are also indicated in the figures. Effluent from the primary clarification tanks enters the secondary aeration tanks in a step feed mode. Primary effluent/Secondary influent enters the secondary treatment system through gates on opposite ends of the 1st, 2nd, 3rd and 4th passes. Due to a malfunctioning gate in pass 1, no influent entered through gate 1. Therefore the wastewater at this point was solely aerated return activated sludge (RAS). After treatment in a single aeration tank, wastewater flows through channels to six sedimentation tanks. Separation of water and solids occurs in these tanks. Clear wastewater flows over weirs into troughs and is subsequently gathered and transported to the BNR tanks. The settled solids is either wasted (waste activated sludge -WAS), or pumped back to the front end of the 1st pass in the aeration tank RAS. WAS is pumped to the DAF units where it is concentrated.

3.4.2 General Approach

3.4.2.1 Sampling approach

Both liquid wastewater samples and off-gas air samples were strategically collected from various locations associated with the secondary treatment process so as to investigate VSC production and release patterns across the secondary treatment system. Sampling locations included the primary effluent (location A - Prim), the 1st and 3rd passes of the aeration tank (location B - Sec 1, location C – Sec 3), the top and bottom of the sedimentation tanks (location D - Sed T, Location E – Sed B). Liquid wastewater samples were analyzed using the headspace - SPME method and an examination of this concentration profile gives a clear picture of VSC production locations and parametric influences. The off-gas air samples were collected and analyzed with the use of a flux chamber (constructed in-house) and the tedlar bag – SPME method was used for the analysis. Likewise an analysis of the off-gas concentration profile establishes VSC release locations and environmental influences.

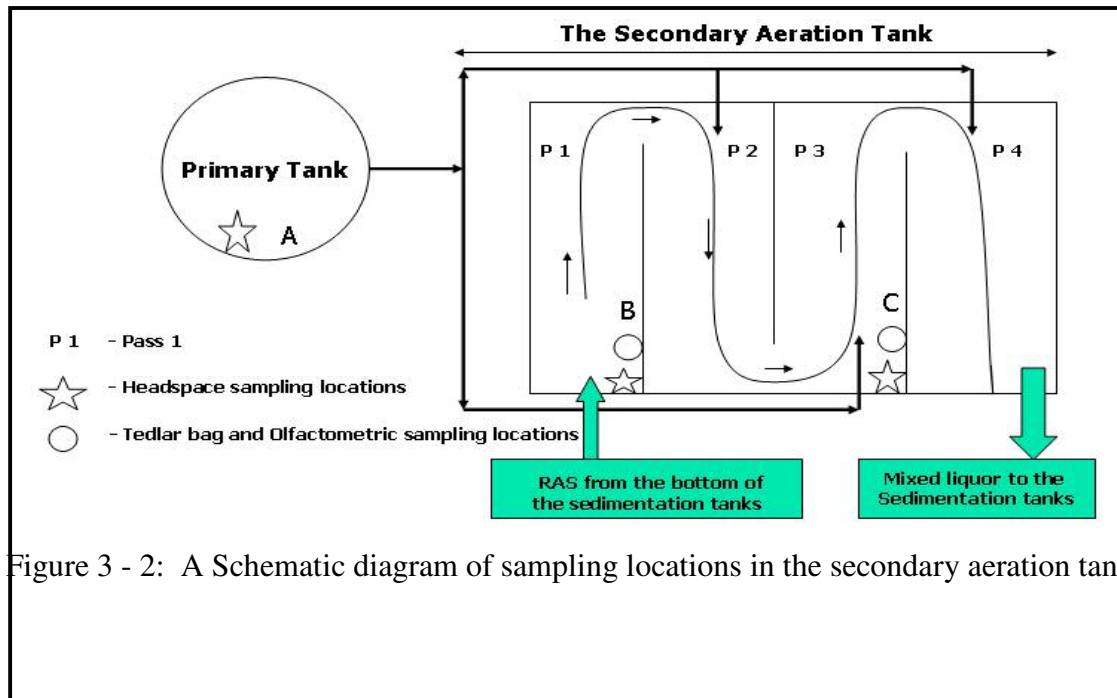


Figure 3 - 2: A Schematic diagram of sampling locations in the secondary aeration tank

3.4.2.2 Headspace - Procedure

The headspace method was used to analyze odorants in wastewater samples from various locations; the primary clarification tank, the secondary aeration tank (1st & 3rd passes) and the secondary sedimentation tanks (Figure 3-2 & Figure 3-3). Wastewater samples were collected from the surface of the various tanks was collected, including a sample from the bottom of the sedimentation tank (approx. 0-2 ft high from the tank floor). All wastewater samples were stored in multi-purpose polyethylene (20 oz) containers. Wastewater samples were capped in 20 ml glass vials. After the approximate 5 – 10 minutes of sample preparation, SPME fibers were then exposed to the headspace of the aqueous samples for an hour (Appendix IV-5). Field storage and transportation of fibers was carried out in a cooler with dry ice. At the lab SPME fibers were stored in a freezer (– 40 °C) until they were analyzed.

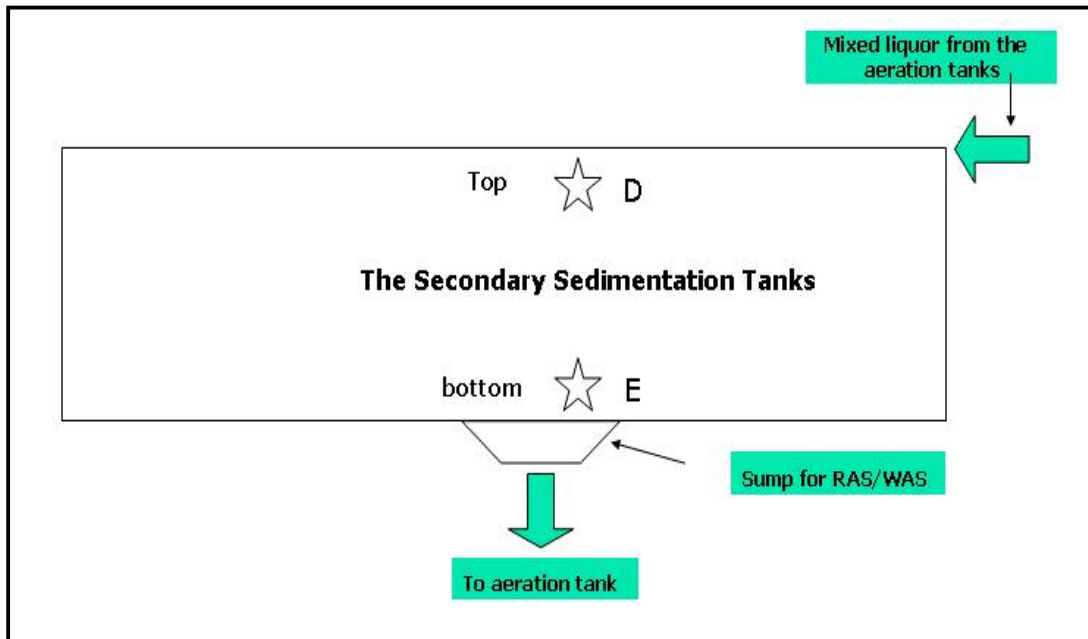


Figure 3 - 3: A Schematic diagram of sampling locations in the secondary sedimentation tank

3.4.2.3 Flux chamber - procedure

A flux chamber designed and fabricated solely from stainless steel (bottom section) and Plexiglas (top dome W/stack) was used to isolate the gases from the 1st and 3rd passes of the SAT (Appendix IV-8) (Eklund, 1992, EPA, 1999). Teflon tubing, a vacuum chamber, a CaCl₂ humidity trap and a pump (operated at 4 L/min) were used to trap the off gases into 1 L and 10 L tedlar bags (Appendix IV-8). SPME fibers were then exposed to the gaseous sample in the 1 L tedlar bags for an hour prior to GC/MS/SIM analysis (Appendix IV-6). Similar conditions used in the headspace method were applied to the storage and transportation of SPME fibers both in the field and at the lab. The 10 L tedlar bag with sample gases were freighted (approx 18 hr) for olfactometric analysis at St Croix Sensory Inc, MN.

3.4.2.3 Sampling regime

A minimum of six sampling events were carried out for each season in 2004. During all of the winter and for 4 of the 7 spring sampling sessions, only one out of six sedimentation tanks that fed into the aeration tank was analyzed.

Table 3-1: Sampling events by season.

| | Season | | | |
|---|----------------------|----------------------|----------------------|----------------------|
| | Winter | Spring | Summer | Fall |
| 1 | 23 rd Feb | 13 th May | 22 nd Jul | 11 th Oct |
| 2 | 5 th Mar | 24 th May | 29 th Jul | 13 th Oct |
| 3 | 12 th Mar | 27 th May | 6 th Aug | 15 th Oct |
| 4 | 19 th Mar | 3 rd Jun | 9 th Aug | 18 th Oct |
| 5 | 22 nd Mar | 7 th Jun | 16 th Aug | 20 th Oct |
| 6 | 29 th Mar | 10 th Jun | 18 th Aug | 22 nd Oct |
| | | | | |

For olfactometric analysis at St. Croix Sensory Inc, 1 set of samples was sent during the winter, 3 during spring, 4 during summer and 6 during the fall.

3.4.3 Materials

SPME fibers (23GA, manual, W/75um carboxen-PDMS coating, Merlin micro seal) and holders were purchased from Supelco, Bellefonte, PA. Tedlar bags (1 L) and portable air sampling pumps (airchek sampler model 224-PCXR4) were obtained from SKC, Eighty Four, PA. Tedlar bags (10 L) and vacuum chambers were obtained from St Croix Sensory, Lake Elmo, MN. Teflon tubing (Tube 870PFA 1/4*1/6), multi-purpose polyethylene containers (16oz – w/lid) and a polyethylene sampling dipper (6 ft) were purchased from Fisher Scientific Company, Fair Lawn, NJ. CaCl₂ (4-20 mesh anhydrous) was also purchased from Fisher Scientific Company, Fair Lawn, NJ. In-line tubing connectors (Teflon PFA union tees and straight connectors, polypropylene & stainless steel straight connectors and panel mount hose barbs) were purchased from Cole palmer Instrument Company, Vernon Hills, IL. Glass vials (23 * 75 mm 20 ml rounded bottom) were purchased from Fisher Scientific Company, Fair Lawn, NJ. Seal caps (20mm TFE/SIL W/retain ING ring) were obtained from Sun Sri, Duluth, GA. Field DO/Temperature probe (YSI 550A) was purchased from YSI Environmental, Yellow Springs, OH. An electrode meter (accumet AR60 pH/mv/ion/cond/DO), an ORP probe (electrode platinum combo BNC) and a pH probe (electrode accuphast W/ATC) were purchase from Fisher Scientific Company, Fair Lawn, NJ. A Sludge Judge (Corepro Sr. 15' sampler) was purchase from USAbluebook, Gurnee, IL. A suitable Flux Chamber was designed and partially constructed in house at the DCWASA AWWTP. The 24"

diameter cylindrical stainless steel bottom was fabricated in the metal and machine workshops at DCWASA from 16 gauge stainless sheet purchase from Samuel Specialty Metals, Baltimore, MD. The 1/4" Plexiglas dome (24" diameter with a 1" flange) was built by Capital Plastics Company, Beltsville, MD (Appendix IV-2).

3.4.4 Analytical Methodology

In this section, both the chemical analytical and the sensory analytical methods used in this study are described in detail.

3.4.4.1 Chemical analytical measurement

Analytical chemical measurement was carried out on a gas chromatograph (GC) system, composed of two Agilent 6890N GCs connected in series using solid phase micro-extraction (SPME) fibers as the sampling and pre-concentration method. The first GC (GC-1) is equipped with a Merlin microseal (Appendix III) septum (Supelco, Bellefonte, PA) and a 0.75 mm injection port liner which is designed for SPME fibers. GC-1 is connected to a Flame Ionization Detector (FID). The two GCs are connected by a cryo trap system (Gerstel CTS1, Baltimore, MD) in which a 1m long HP-5 column with a 0.32 mm inner diameter and a phase thickness of 0.25 μm is placed. The second GC (GC-2) is connected to an Agilent 5973 Mass Spectrometry Detector (MSD) (figure 3-4) (Appendix III). The MSD is set to the Select Ion Monitoring (SIM) mode. A similar analytical set up, GC/MS/SIM, was used in a study of the gas phase analysis of various odorous compounds associated with wastewater treatment (*Abalos, 2002, Haberhauerroyer et al, 1999, Nielsen and Jonsson, 2000, Kim et al, 2002*). More

information about the GC set up and SPME method can be found elsewhere (Arispe et al, pending).

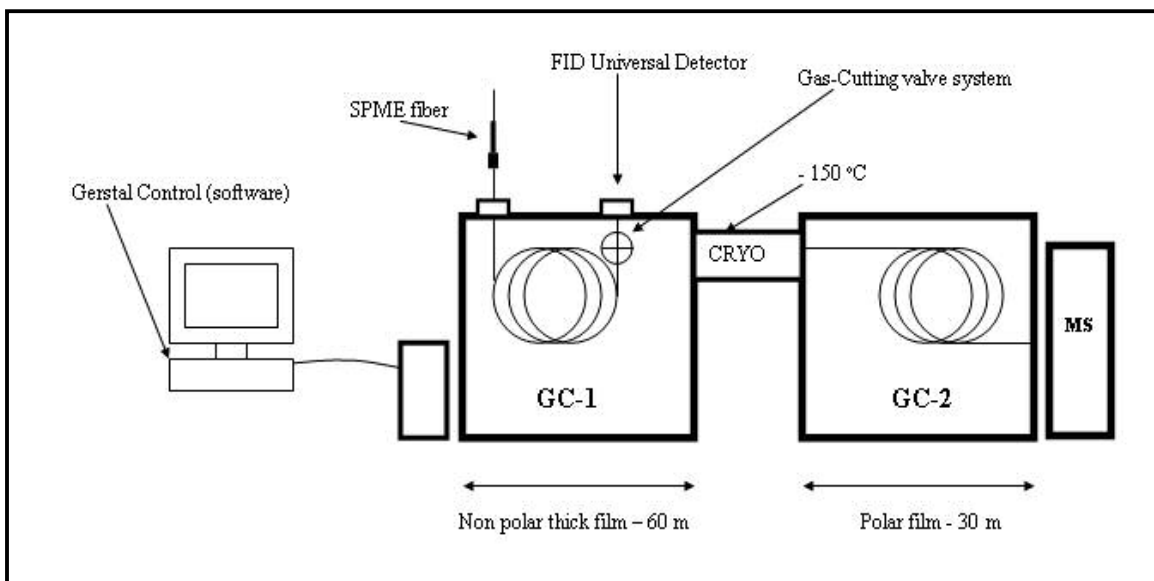


Figure 3 – 4: A schematic diagram of the coupled Gas Chromatographic system

Calibration Procedure

Certified Teflon membrane permeation devices (NIST traceable, VICI Metronics, Inc. California, USA) and a gas generating instrument (dynacalibrator – model 320, VICI Metronics, Inc.) were used to prepare standard gases of each compound. The permeation devices were placed in a thermostated glass chamber in the dynacalibrator with a base flow of high purity nitrogen gas of 72mL/min. Gas from this chamber is diluted with nitrogen gas at different flow rates to achieve the desired standard gas concentrations. The standard gas is then passed through a cylindrical Teflon collection chamber (i.d. = 4.1 cm, Savillex, Co., Mennetonka, Minnesota) with two injection ports for SPME fiber exposure and a temperature probe (Traceable 4085, Control Com., Houston Texas). The standard gas is allowed to achieve equilibrium with the Teflon chamber before valves on

both ends of the chamber are closed at the same time, to trap the standard gas in the chamber. The SPME fiber (75µm carboxen coating) was exposed to the standard gas in the Teflon chamber for 1 hour before injection into the GC-1 for the GC-MS analysis. Septa were replaced after each injection to avoid leakage of gas. A detailed description of this procedure is described in VSC standard calibration work carried out by Arispe et al, pending.

The measurable target VSCs include MM, EM, PM, BM, DMS and DMDS.

Standard calibration curves for these compounds exhibited a linear curve fit (r^2) greater than 0.99. Limits of calibration (LOCs) were identified using the standard experimental procedure as detailed by Arispe et al., pending. Limits of quantification (LOQs) were set at + / - 10 % of the LOCs. The standard curves for MM were still under development at the time of data analysis and therefore the standard curve of EM was used as a surrogate. A description of the difficulty in developing calibration curves for MM relates to the fact that MM readily oxidizes in air to form its dimer, DMDS. Preliminary investigation of this phenomenon is detailed in sub-section 3.4.5.4.

| | LOCs | | LODs | | Trendline | |
|------|---------------|---------------|---------------|---------------|--------------------------------|----------------|
| | Upper ppbv | Lower ppbv | Upper ppbv | Lower ppbv | Equation | R ² |
| DMS | 2615 | 5.7 | 2877 | 5.2 | $Y = 3 \times 10^7 X$ | 0.9974 |
| DMDS | 677 | 0.82 | 745 | 0.74 | $Y = 1 \times 10^8 X$ | 0.9961 |
| EM | 427 | 0.48 | 469 | 0.43 | $Y = 2 \times 10^7 X$ | 0.9955 |
| PM | 236 | 23 | 280 | 22 | $Y = 2 \times 10^6 X - 18839$ | 0.9957 |
| BM | 214 | 17 | 234 | 17 | $Y = 2 \times 10^7 X - 168207$ | 0.9907 |

Table 3-2: Calibration curves for volatile sulfur compounds.

LOC - Limit of calibration, LOD - Limit of detection - set at +/- 10% of LOCs

3.4.4.2 Analytical Sensory Measurement

Analytical olfactometric measurement was facilitated by the use of 10 L tedlar sampling bags and analyzed by St Croix Sensory Inc, Lake Elmo, MN. St Croix Sensory analyzed the samples to determine the detection and recognition thresholds (ASTM E679 & EN13725:2003), using odor panel assessors on a AC'SCENT olfactometer. Data on intensity (ASTM E544), hedonic tone and odor descriptors (ASTM E58) were also measured.

3.4.4.3 Process Parameters

The variables measured can be broken down into primary and supplementary parameters. Primary parameters consist of variables that were immediately measured and/or calculated from measured variables during sampling events. Primary parameters include pH, oxidative-reductive potential (ORP), water temperature, dissolved oxygen (DO), sludge blanket level (SBL), sulfides concentration (S^{2-}), soluble iron concentration ($Fe^{2+} + Fe^{3+}$) and spiked oxygen uptake rate (Spiked OUR). Supplementary parameters refer to variables that were collected from the PCH system (the DCWASA database that stores all the process parameters monitored at the plant) and/or from other external sources. Supplementary parameters include the food-microorganism ratio (F/M), initial settling velocity (ISV), settled sludge volume – 60 (SSV₆₀), sludge retention time (SRT) and volatile suspended solids (VSS).

Measurement of Primary Variables

Both **pH** and **ORP** were measured in the field using an electrode meter (accumet AR60 pH/mv/ion/cond/DO) with a pH probe (electrode accuphast W/ATC) and an ORP probe (electrode platinum combo BNC) respectively. All samples (~ 300ml) were collected in polyethylene containers and were thoroughly shaken before measurement. In-situ field measurements of **DO** and **water temperature** were carried out using a field DO/Temperature probe (YSI 550A). pH, ORP, DO and water temperature values were recorded only after the readings had stabilized. In the event of continued variability, the average of three spot readings was taken after a three minute wait period. The **SBL** was measured using a sludge judge (Corepro Sr. 15' sampler). The sludge judge was immersed in two locations in each tank and an average was recorded.

OUR and **SOUR** were calculated from wastewater samples taken from the head of the 1st pass of the secondary aeration tank. The samples were collected in polyethylene containers and immediately transported to the lab for analysis. Air was initially introduced into the wastewater sample (300 ml) for ~ 2 minutes and DO uptake was measured using a DO probe, and a digital stop clock. For the **Spiked OUR** calculations, primary effluent (60ml) was added to the wastewater sample (300ml) in a ratio of 1:5 after it had been saturated with DO.

Sulfide concentration was determined in the USDA labs. The wastewater samples were collected and transported to the lab in sealed polyethylene containers. The samples were then transferred into capped labeled polyethylene bottles, making sure that

there were no air pockets between the liquid surface and the cap. These samples were stored in a – 4 degree freezer till they were analyzed. **Soluble iron** was determined at an external lab. The wastewater samples collected were also stored in a - 4 degree freezer in capped polyethylene containers till they were analyzed.

3.4.5 Sensitivity of Method

In this section, results of in house laboratory studies to determine the errors associated with the sampling procedures used are described.

3.4.5.1 Equilibrium studies

To better understand the importance of wastewater / headspace air equilibration before SPME exposure in the headspace method, a study was performed to investigate the variability of the headspace VSC concentration due to equilibration time between the wastewater samples and the headspace air. Wastewater samples were thoroughly mixed and poured into all the vials. Three SPME fibers were exposed after each equilibration time period (0, 30 & 60 minutes). Fibers were stored in a (-40 °C) freezer before analysis. There is no obvious trend or significant variation in VSC concentration with equilibration time at both high and low VSC concentration ranges (Figure 3-5).

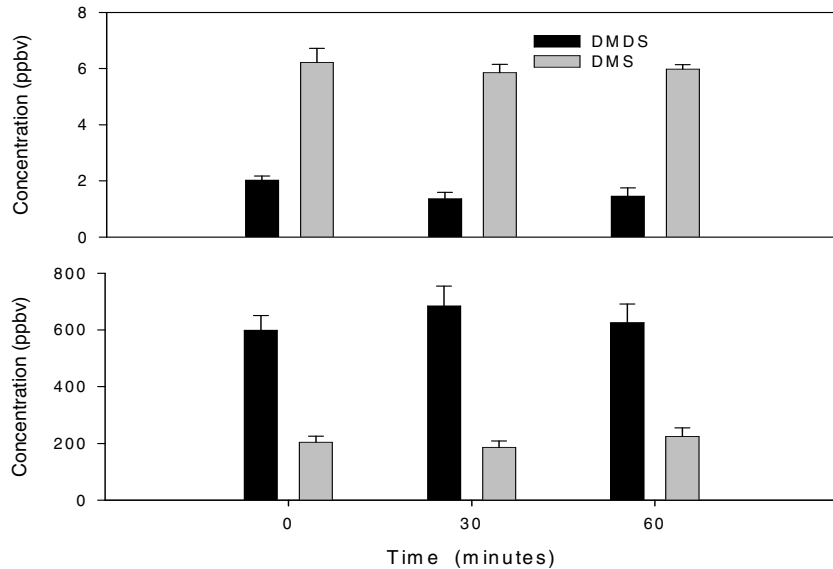


Figure 3-5: Variability of headspace samples with equilibration time before SPME exposure

Variability for the time for equilibration was 7.3- 12 % for DMDS and 3.0 – 9.5% for DMS. It would seem that the inherent variability in this active biological system outweighs any significant influence due to the headspace equilibration time.

3.4.5.2 Storage Studies

A typical sampling day would take 30 hrs to complete GC-MS-SIM analysis of all fibers. To investigate the effect of storage time on VSC losses from the SPME fiber, 18 fairly new SPME fibers were exposed for 1 hour to standard gas (DMDS & DMS) in preconditioned tedlar bags. Three SPME fibers were run in succession at specific intervals (0, 6, 12, 24 and 30) for a 30 hr period. Fibers were stored in a (- 40 °C) freezer while they were queued for GC-MS-SIM analysis just like on a regular sampling day. The first 12 hrs shows decrease in DMS concentration of 14.5% and a similar decrease in DMDS concentration of 16.7% (figure 3 – 6).

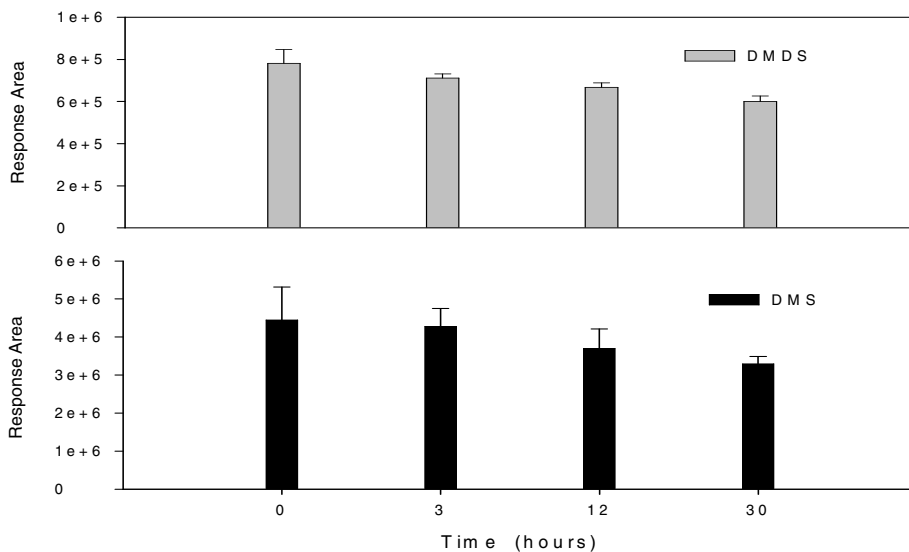


Figure 3-6: Variability of headspace samples with time of storage

3.4.5.3 Tedlar Bag Studies

Tedlar bags, although inert have been known to give off volatile organic compounds (VOCs). A study was carried out to determine whether tedlar bags gave off significant amounts of the VSCs studied. This study was carried out in four stages. Stage 1 - SPME fibers were exposed for 1 hour to nitrogen filled tedlar bags and immediately analyzed. Stage 2 - After flashing the tedlar bags with nitrogen gas three times, the same procedure as in the first stage was used to check VSC concentration in the bags. Stage 3 - The bags were baked and VSC concentration checked and finally the tedlar bags were again flushed with nitrogen gas twice and checked for VSC concentration. It is clear that the preconditioning method used effectively cleaned the Tedlar bags of any detectable VSCs (Table 3-3).

Table 3-3: Testing the Tedlar bag preconditioning method

| Stage 1 | A | | | | Stage 2 | B + A | | |
|---------|-----------|-------|-------|--|---------|---------|-------|---|
| Fibers | DMDS | BM | other | | DMDS | BM | other | |
| 1 | 0 | 50639 | 0 | | 1 | 0 | 0 | 0 |
| 2 | 14794 | 0 | 0 | | 2 | 0 | 0 | 0 |
| 3 | 0 | 0 | 0 | | 3 | 0 | 0 | 0 |
| 4 | 0 | 0 | 0 | | 4 | 0 | 0 | 0 |
| Stage 3 | C + B + A | | | | Stage 4 | D+C+B+A | | |
| 1 | 0 | 0 | 0 | | 1 | 0 | 0 | 0 |
| 2 | 0 | 0 | 0 | | 2 | 0 | 0 | 0 |
| 3 | 0 | 0 | 0 | | 3 | 0 | 0 | 0 |
| 4 | 0 | 0 | 0 | | 4 | 0 | 0 | 0 |

All units are in response areas

A = expose SPME fiber to 1 L Tedlar bag filled with nitrogen gas

B = 3 clean out procedures

C = Oven bake the nitrogen filled tedlar bag at 100 oC

D = 2 clean out procedures

* clean out procedure = flushing the tedlar bag with nitrogen gas

3.4.5.4 Methyl Mercaptan Calibration

Background

The calibration of MM using the method described in section 3.4.4.1, provided inconclusive results. There was always an abnormally high DMDS peak identified in the MM standard gas. The question to be answered was whether the MM permeation device and/or the gas generating dynacalibrator were contaminated with DMDS. An alternative explanation could be that there was oxidation of MM taking place on the surface of the SPME fiber and/or on the surface of the permeation device. To investigate this issue, one of the dynacalibrators was thoroughly cleaned by removing all permeation devices, ramping up the temperature to the maximum allowable and purging the whole system with nitrogen gas. This treatment was stopped only when GC-MS-SPME runs no longer identified DMDS. All stainless steel valves, Teflon tubes, connectors and chambers

where replaced. The calibration procedure described for other VSCs was followed with GC-MS identification and quantification. Preliminary results showed continued identification of an abnormally high DMDS peak. This initial work prompted an investigation into the possibility of oxidation either on the SPME fiber or on the permeation device.

Procedure

Fresh MM permeation devices, prepared under nitrogen where ordered from an alternative manufacturer (Kin-Tek, Inc) and shipped in an air tight PVC container. Dichloromethane was used as a cleaning solvent to thoroughly clean the exterior of the MM permeation device with a soft brittle brush for 2 minutes. The permeation device was then placed in a conical vacuum flask covered with foil paper to block out light. Excess solvent was stripped off by vacuum suction for 30 minutes. The MM device was then placed in an air tight Teflon jar, also covered in foil, with two injection ports for sample collection. To exclude SPME fiber oxidation, gas samples were collected using a gas tight syringe (also covered in foil), and injected directly into the injector port for GC-MS analysis. Gas samples were analyzed over a period of 105 hours (~ 4 days). The ratio of MM to DMDS was plotted a shown below and these results were indicative of the oxidation of MM to DMDS on the surface of the permeation device.

Initially, the concentration of MM is about 10 times that of DMDS but within the first 6 hours, there is a sustained and substantial production of DMDS thereby reducing the ratio of MM to DMDS. The remaining time 99 hours can be described as the process of establishing a dynamic equilibrium. These results also give an insight into the

possibility of oxidation of MM during wastewater sample collection and preparation as both these stages were not designed to exclude the presence of oxygen.

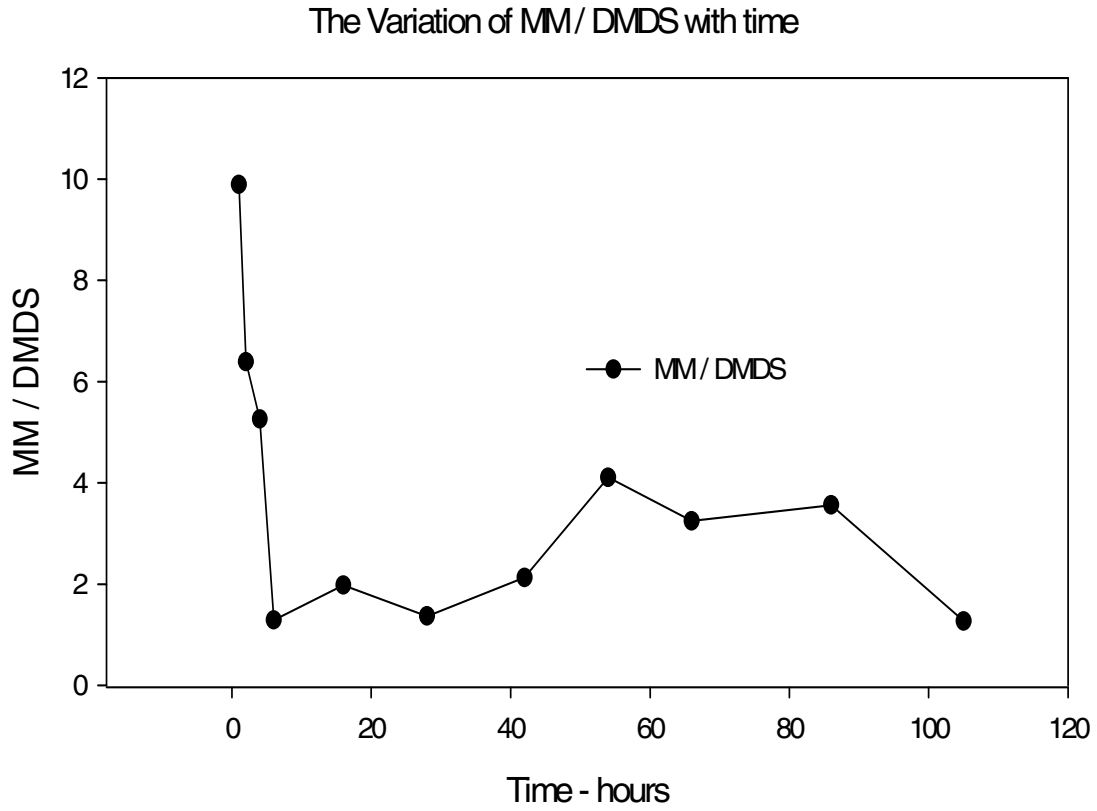


Figure 3-7: Variation of MM/DMDS ratio with time.

3.5 Results and Discussion

3.5.1 General Approach

There were two general approaches used in this work, the headspace approach and the tedlar bag approach. The headspace approach was designed to determine the concentration of VSCs in the wastewater. This approach gave insight into the seasonal and locational variability of VSCs in the wastewater across the secondary treatment system. In concert with primary parametric data, deductions as to VSC source/production locations could be made. The tedlar bag approach was designed to determine the release of VSCs from the secondary treatment system. Seasonal and locational VSC and odor release patterns gave an indication as to the influence of plant parameters over odor release patterns. Both methods had the potential for bias by the oxidation of MM to DMDS since there was no attempt made to exclude the presence of oxygen (Section 2.5.2.4 & 3.4.5.4). VSCs that were detected below LOQs were assigned a numeric value of $\frac{1}{2}$ their respective LOQs. For the effective interpretation of this data, box plots graphs, trend-line graphs and tables of data have been used. The box plots provide information on mean and median values, 25th to 75th percentile values and in cases where the data series is greater than 9, box plots also provide the 5th and 95th percentiles values and outliers. The percentile values give an indication as to the spread associated with a particular data series. Comparing the mean and median values gives an indication of the possible bias of the mean value due to outliers. The trend-line graphs have been used to distinguish locational VSC trends over the entire sampling period. Tables of data have been used to support the graphs and the various discussions in this sub-section.

3.5.2 Headspace Approach

Of the six target VSCs (MM, EM, PM, BM, DMS and DMDS) analyzed in the headspace approach, only MM, DMS and DMDS were identified. The concentrations of MM were considerably lower than that of DMS and DMDS (~ 8.1% of DMDS and 8.5% of DMS). This observation is contradictory to our knowledge of anaerobic metabolic activity. We would expect that the concentration of MM would be substantially higher than that of DMDS since MM is a consistent by-product of microbial anaerobic metabolic process in wastewater environments. It is known that MM is readily abiotically oxidized in air to form DMDS (*Yarosz et al, 2003, Lomans et al, 2002, Smet et al, 1998*). In-house lab experiments have shown that there is oxidation of MM to DMDS on the certified MM permeation tubes (Kin-Tek) during the calibration process (Section 3.4.5.4). It is more than likely that MM in the wastewater samples was oxidized to DMDS during the sample collection and preparation procedures.

A look at the annual box plots of VSC concentration for the various sampling locations, DMDS, DMS and MM all show that the highest mean concentrations and the largest variability was observed at the bottom of the sedimentation tanks (Figure 3-8, Appendix II Table A1). Annual means of 110 ppbv, 83 ppbv and 8.7 ppbv were recorded for DMDS, DMS and MM respectively at the bottom of the sedimentation tanks (Appendix II - Table 1A). Wastewater samples at the top of the sedimentation tanks showed the least variability and smallest measurable quantities of VSCs. It should be noted that the mean annual VSC concentrations of the 1st pass are higher than that of the 3rd pass.

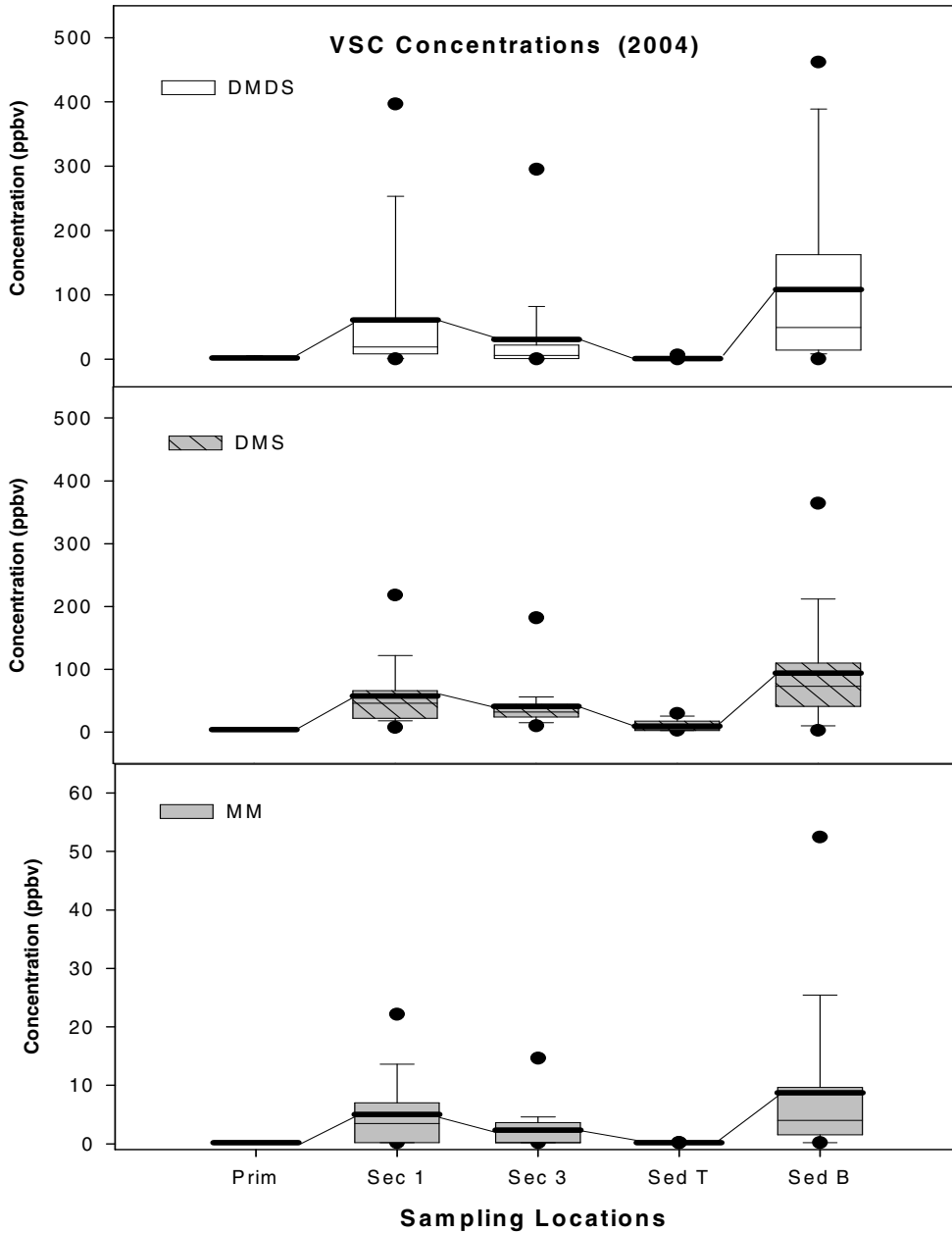


Figure 3 – 8: Annual VSC wastewater concentrations across the secondary treatment system.

An examination of the annual variation in ORP gives an indication as to the septicity and therefore the odor production potential of the wastewater at the various sampling locations (Figure 3-9). Results indicate that the wastewater at the bottom of the sedimentation tank was septic (anaerobic) with very little variability. The conditions in both the 1st and 3rd passes of the aeration tank and the top of the sedimentation tanks are largely aerobic. It is noted that, the 1st pass is less aerobic than the 3rd pass. The concentration of sulfides in wastewater is indicative of the activity of SRBs. These bacteria are the primary cause of VSC production in a largely domestic sewage system which is most often high in sulfate concentration. The sulfide levels at the bottom of the sedimentation tanks are much greater than at the top. This coincides with greater septicity at the bottom of the sedimentation tank. High levels of sulfides in the 3rd pass of the aeration tanks are most likely a result of the addition of primary effluent, high in sulfide concentration. Wastewater from the collection system and thus the primary clarifier are usually high in sulfide concentration due to septicity associated with the collection system.

VSC data analyzed seasonally across the secondary system provides some useful information. The bottom of the sedimentation tank during the winter period showed not only the highest mean concentrations of DMDS, DMS and MM but also the largest variability of these respective compounds (Figures 3-10, 3-11 & Appendix I-5 and Appendix II - Table 1B). The mean seasonal values of DMDS, DMS and MM recorded during the winter sampling session were 200 ppbv, 110 ppbv and 19 ppbv respectively. Interestingly, the summer and fall sampling events showed lower mean seasonal VSC concentrations across the secondary treatment system.

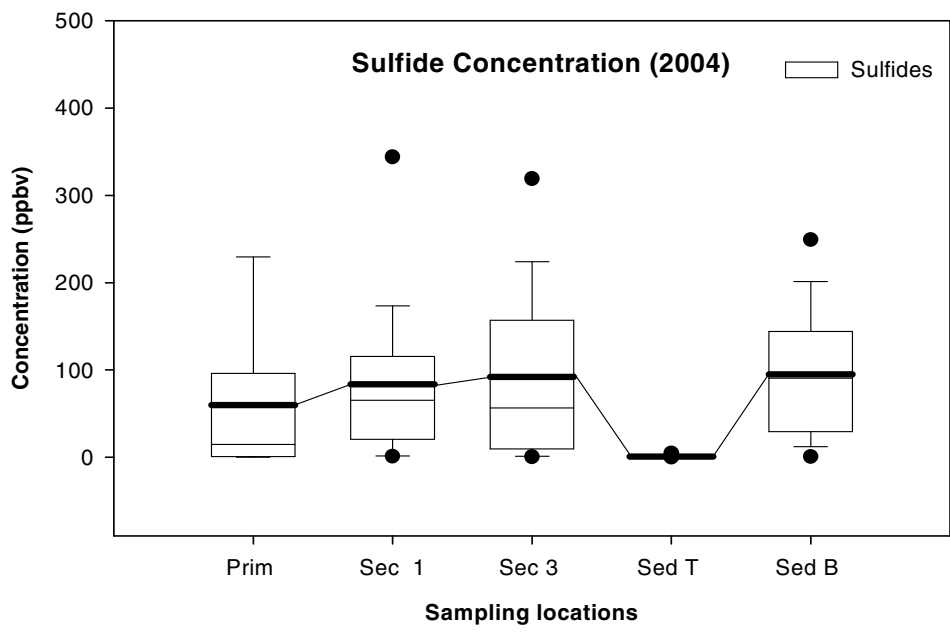
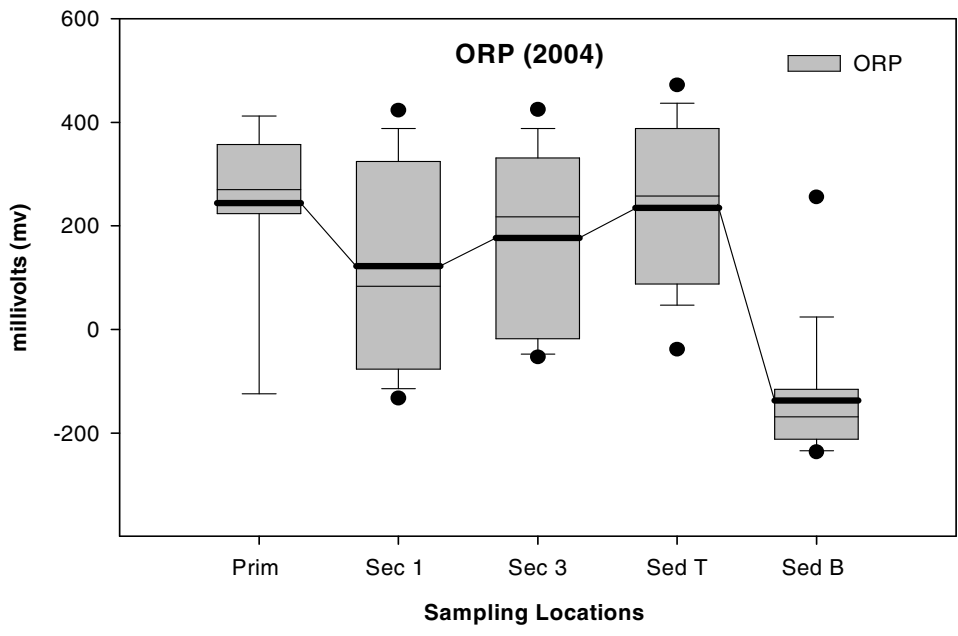


Figure 3 – 9: Annual ORP and Sulfide wastewater concentrations across the secondary treatment system.

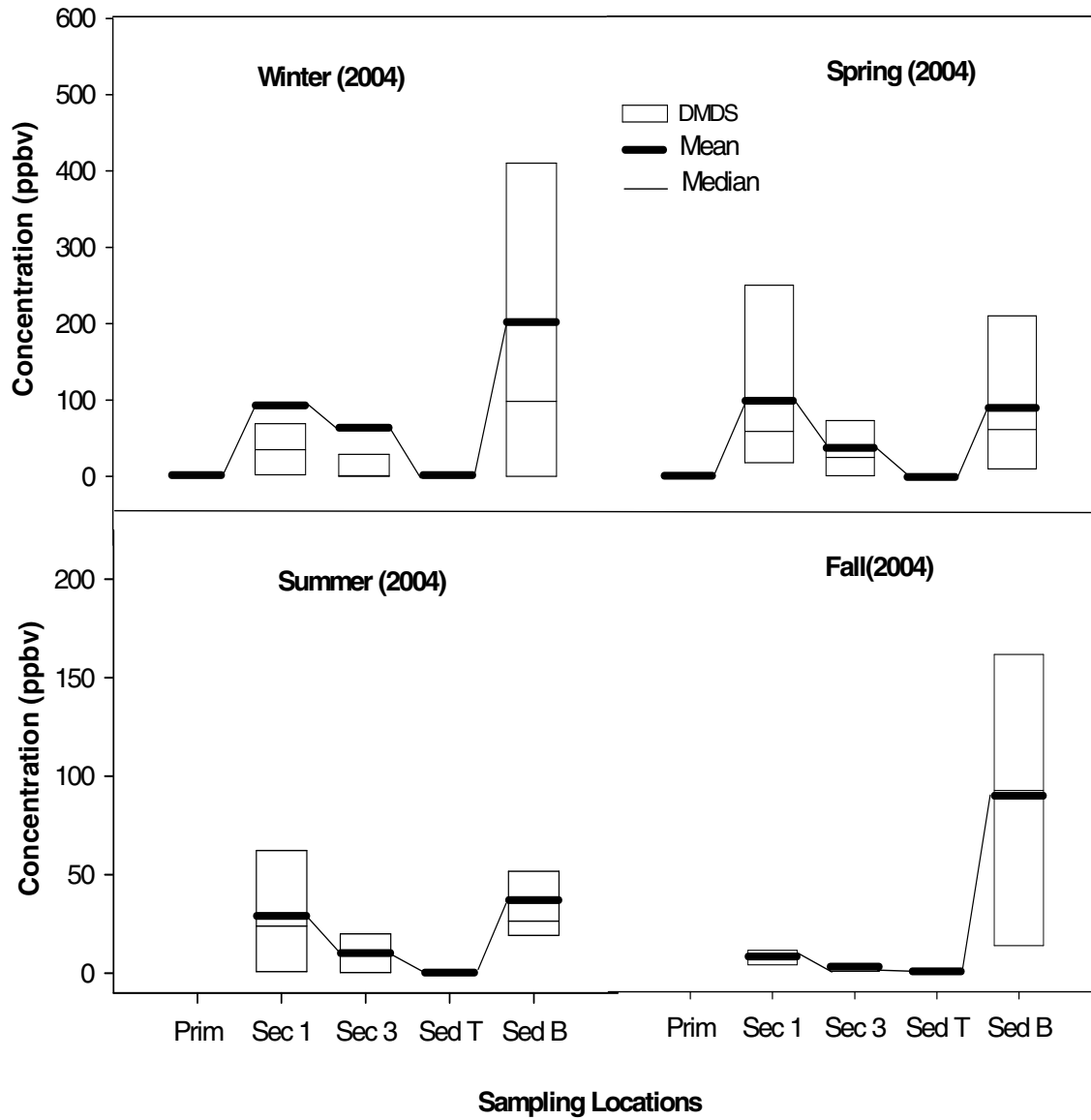


Figure 3 – 10: Seasonal DMS wastewater concentrations across the secondary treatment system.

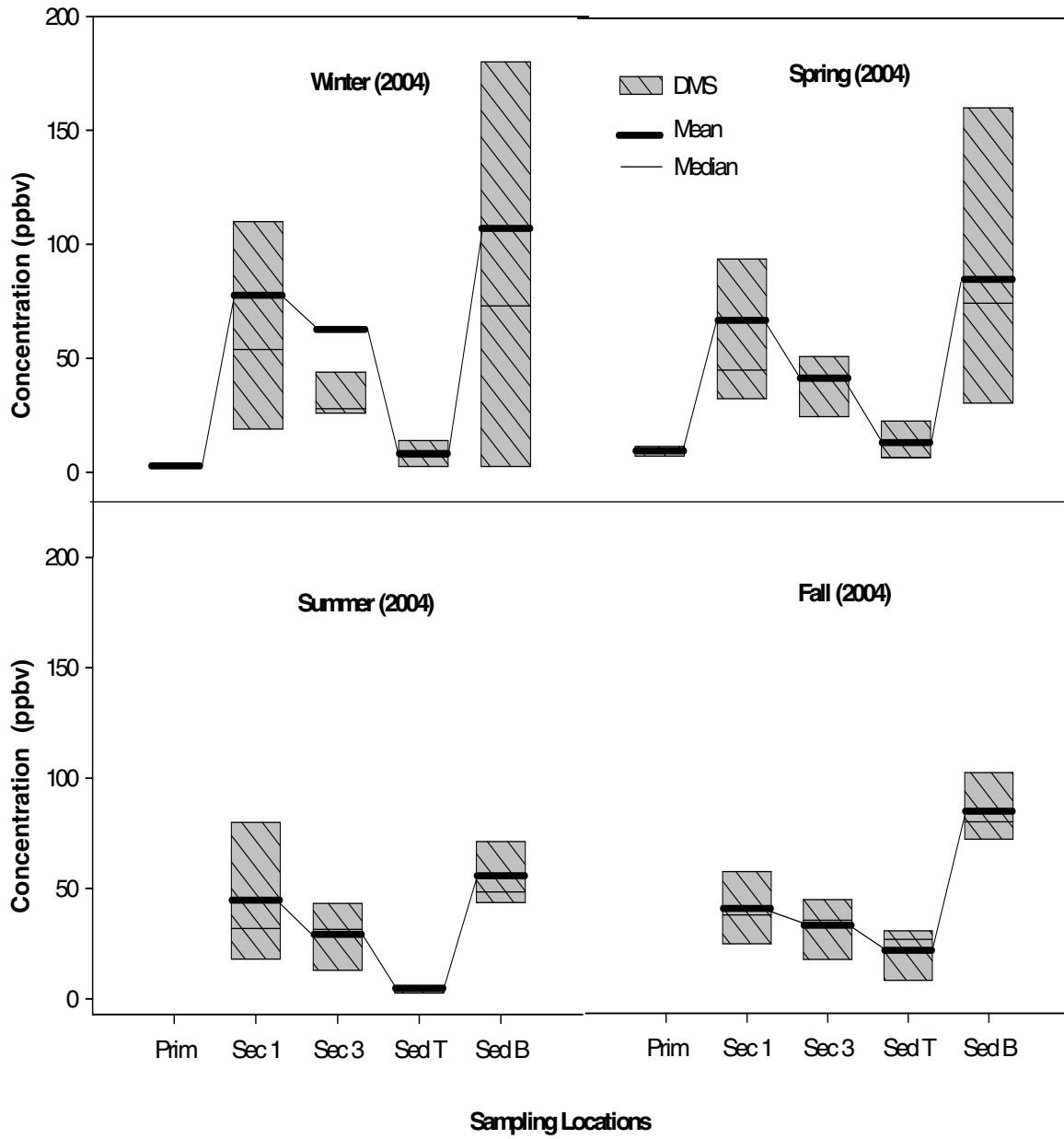


Figure 3 – 11: Seasonal DMS wastewater concentrations across the secondary treatment system.

These observations would seem to be an anomaly because under normal conditions, microbial metabolic activity increases with an increase in temperature. It is likely then that there are other more influential factors which may be driving the observed variations in the seasonal VSC concentrations. The observed locational annual trends are also present in the data analyzed seasonally. The mean seasonal VSC concentrations at the bottom of the sedimentation tank are consistently the highest. The top of the same sedimentation tank recorded the lowest VSC concentrations. The mean seasonal VSC concentrations in the 1st pass of the secondary aeration tank are higher than that of the 3rd pass.

The locational trends in the VSC concentrations across the secondary treatment system, as described above, are again observed when considering the individual sampling events throughout the year. The VSC concentrations at the bottom of the sedimentation tank are generally the highest and concentrations at the top are consistently the lowest (Figure 3-11). This distinct concentration gradient between the top and the bottom of the sedimentation tank is a clear indication that VSCs are either settling with the flocs in the sedimentation process or are produced at the bottom of the sedimentation tanks. The concentrations of VSCs in the 1st pass of the aeration tanks are largely greater than that of the 3rd (Appendix I - 7). DMDS, DMS and MM concentrations in the 1st pass range from 470 - 0.37 ppbv, 250 - 2.6 ppbv and 26 - 0.17 ppbv respectively.

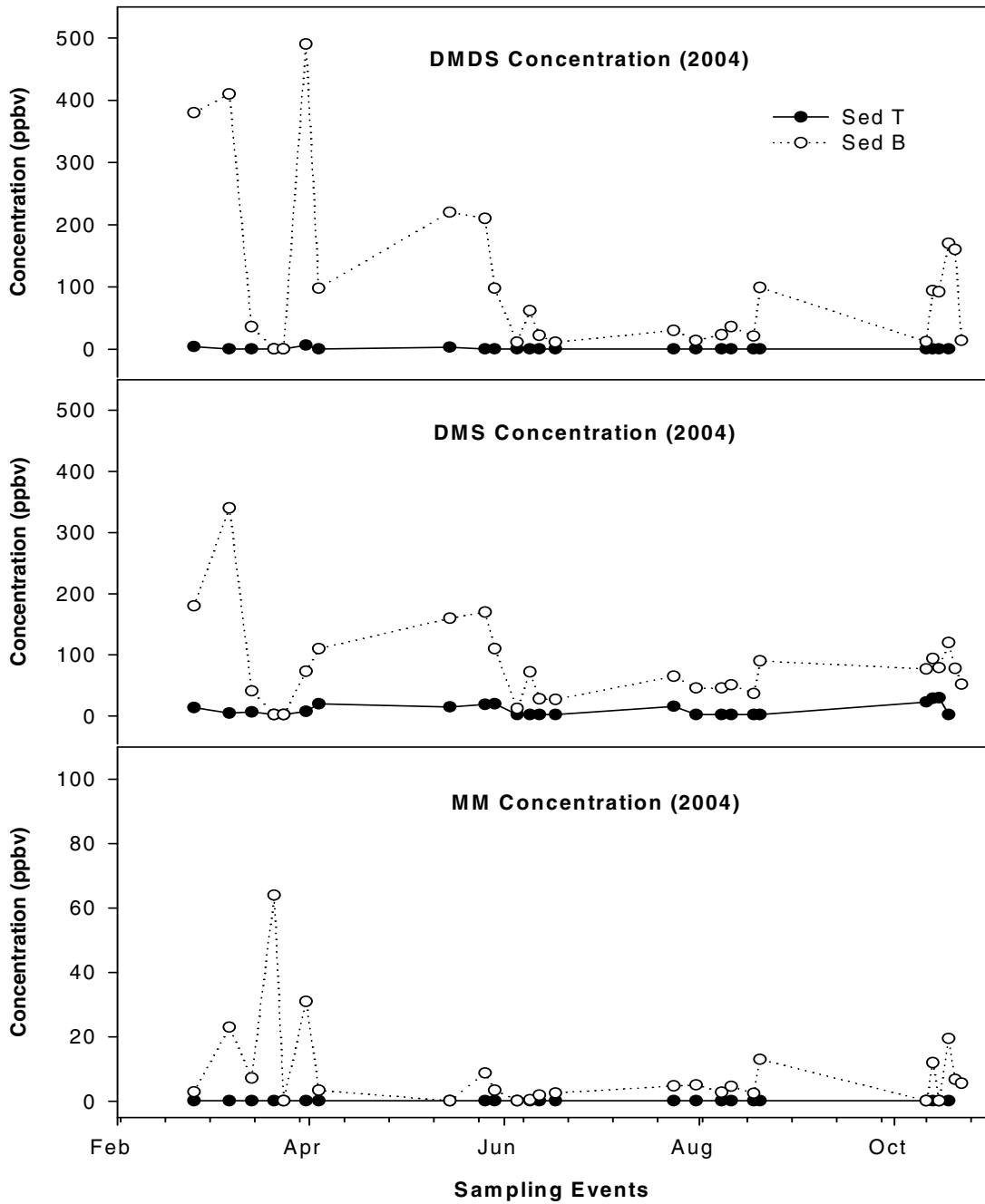


Figure 3 – 11: VSC wastewater concentrations per sampling event in the secondary sedimentation basin.

Kim et al, 2002, measured DMDS (~ 3ppbv) and DMS (~2ppbv) in RAS samples from the same WWTP (DCWASA – Blue Plains). *Nurul Islam et al, 1998*, also measured MM (~ 2500 – 30 ppbv) and DMS (~ 1200 – 20 ppbv) concentrations from the aeration and sedimentation tanks at 4 WWTPs. *Jenkins et al, 1980*, likewise measured MM concentrations of ~ 44 ppbv from mixed liquor sampled at the head of a secondary aeration tank. The measured VSCs from the secondary treatment system in these studies are similar in compound type and concentration range to the values determined by this study.

There are a few conclusions that can be made when the wastewater flow patterns in the secondary treatment system are considered in the analysis of the VSC locational and seasonal trends as described above. Reviewing the flow patterns, wastewater is fed into the secondary treatment system from the primary clarification tanks in step-feed mode to alternate ends, at the head of each of the 4 passes in the secondary aeration tank (Section 3.4.2.1). Due to a malfunctioning sluice gate, no influent was introduced into the 1st pass. Therefore RAS from the bottom of the sedimentation tank that was returned to the head of the 1st pass was unaltered by the addition of primary effluent. The observed VSC trends as described above suggests that the source of VSCs in the secondary system is from microbial metabolic activity at the bottom of the secondary sedimentation tank and thus the high VSC concentrations at this location.

A closer look at the DMDS and DMS concentrations at the bottom of the sedimentation tanks, provide useful insights into the factors that influence VSC production. MM has been excluded from this analysis because most of the measured concentrations were close to or below the LOQ.

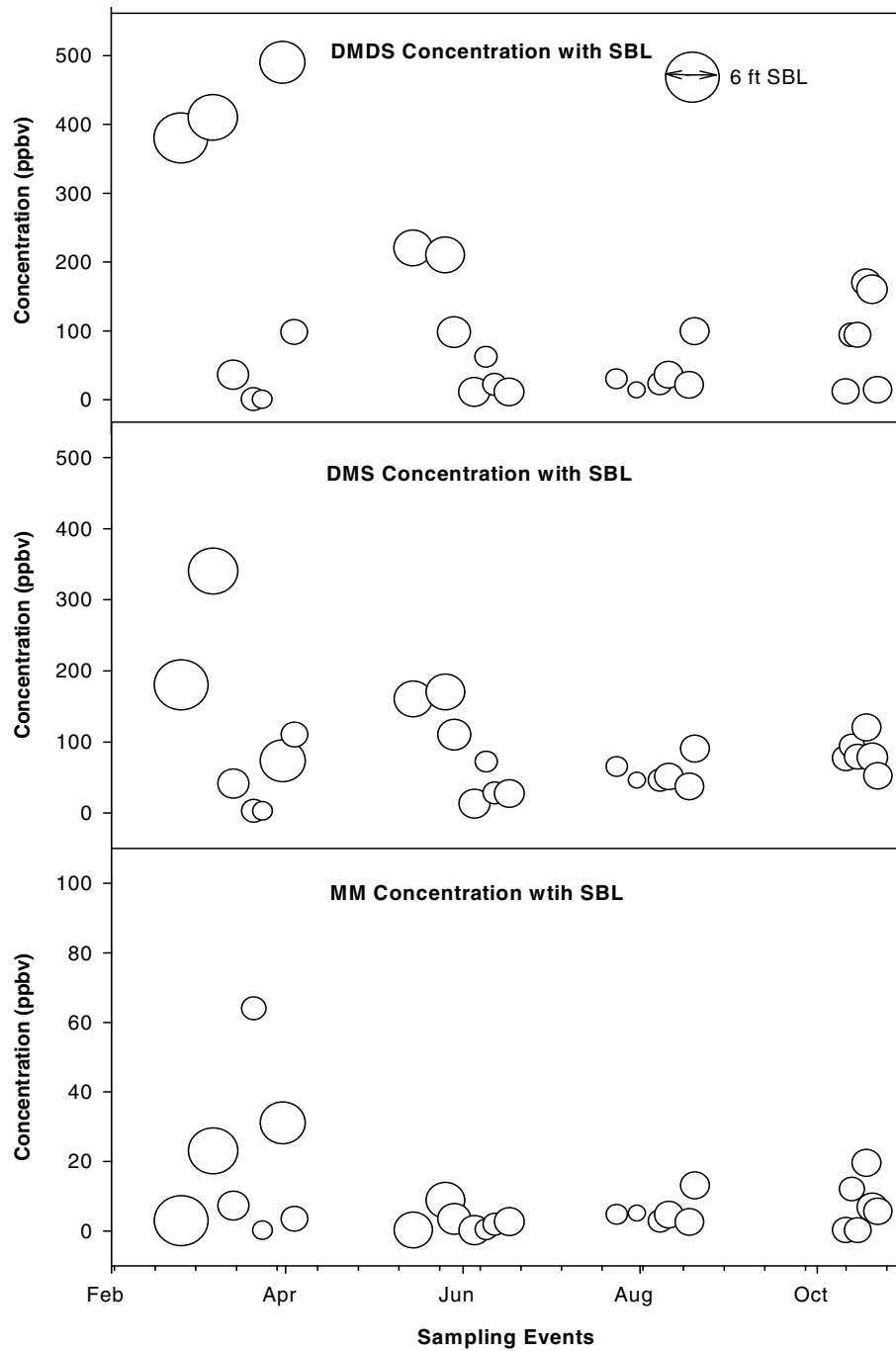


Figure 3 – 12: VSC wastewater concentrations with sludge blanket levels per sampling event at the bottom of the secondary sedimentation basin.

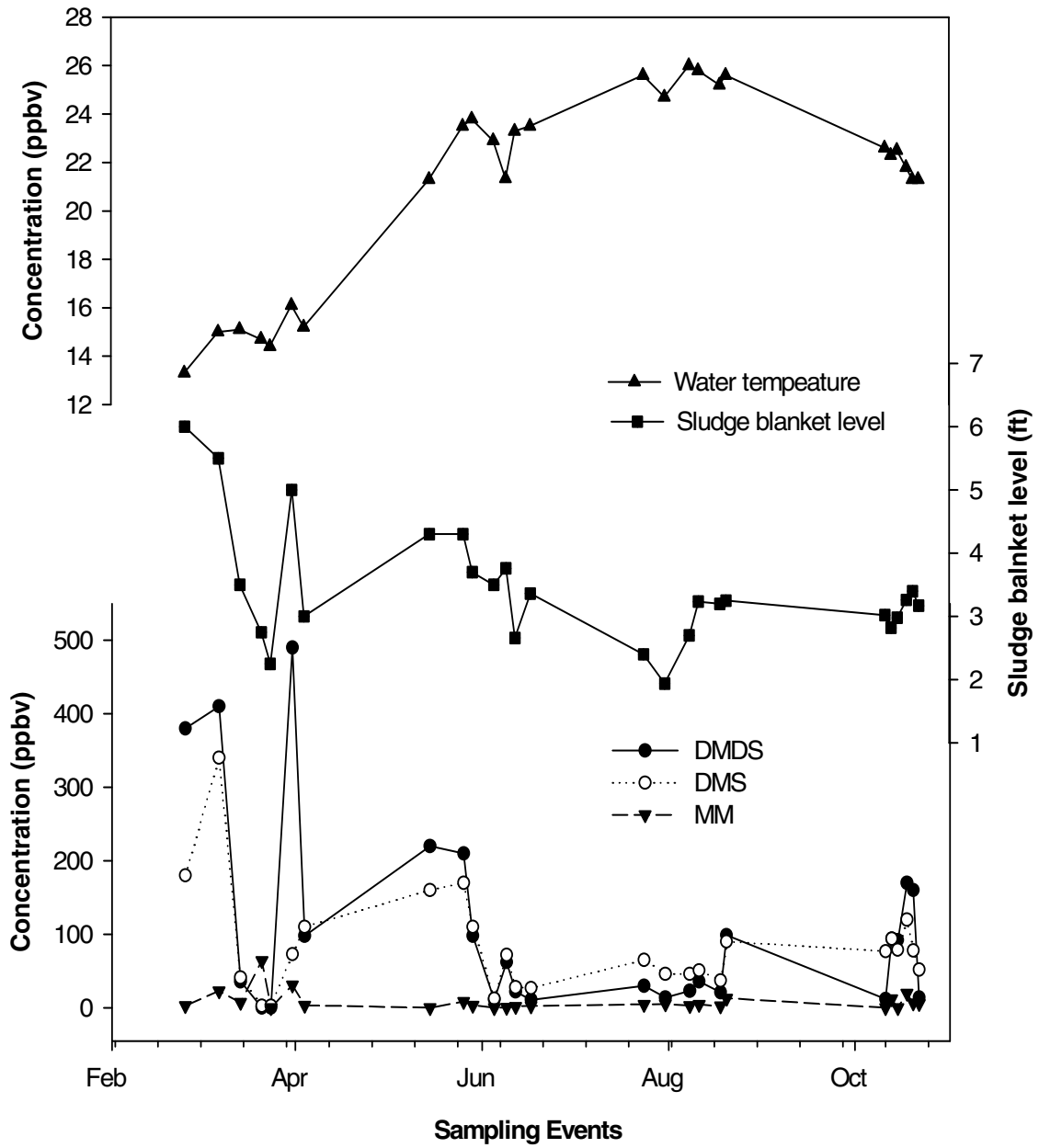


Figure 3 – 13: VSC wastewater concentrations per sampling event at the bottom of the secondary sedimentation basin compared with sludge blanket levels and water temperature.

Graphically, results indicate that the VSC concentrations at the bottom of the secondary treatment system are strongly dependent on the sludge blanket levels (SBLs) (Figure 3-12 & 3-13). The higher the SBLs the greater the production of VSCs. This is especially noticeable during the winter months when high SBLs were recorded. Bubble plots illustrate this relationship (Figure 3-12) where the size of each circular plot represents the respective SBL measured at the bottom of the sedimentation tank for each respective sampling event. The trend-lines in Figure 3-13, reveal that water temperature does not have a significant influence on the production of VSCs at the bottom of the sedimentation tank. This is contrary to what we would expect of normal microbial metabolic activity.

Statistically, DMDS and DMS at the bottom of the sedimentation tanks displayed strong positive correlation with SBLs (e.g. DMDS/SBL - correlation = 0.86, p-value < 0.001 and df = 25, Table 3-4). Water temperature has a moderate negative correlation with VSC concentration at the bottom of the sedimentation tank; this is counter intuitive and is likely as a result of a negative bias created by the higher sludge blanket levels in the winter (Table 3-4). ORP shows a moderate negative correlation with DMS (correlation = - 0.35, p-value = 0.003). Sulfides concentration does not statistically correlate well with VSC concentration.

Table 3 – 4: Statistical analysis of VSC concentration and plant parameters

| | DMDS Correlation | DMS Correlation | DMDS P-value | DMS P-value |
|------------------------------|----------------------------|---------------------------|------------------------|-----------------------|
| Sludge level | 0.86 | 0.72 | < 0.001 | < 0.001 |
| Water temperature | -0.45 | -0.26 | < 0.001 | < 0.001 |
| ORP | -0.32 | -0.35 | 0.33 | 0.003 |
| Sulfide concentration | 0.05 | 0.08 | < 0.001 | 0.31 |
| Degrees of freedom | 25 | 25 | 25 | 25 |

3.5.2 Flux Chamber - Approach

In this part of the study, gas emissions from the secondary aeration tank were analyzed for VSCs. Of the six target VSCs (MM, EM, PM, BM, DMS and DMDS) analyzed; only MM, DMS and DMDS were identified. An average of 79 % of MM peaks identified was below quantification limits. Unlike with the headspace method, the concentrations of DMDS were also considerably lower than that of DMS (~ 15.1% of DMS). An average of 37 % of DMDS peaks identified was below quantification limits. MM was not included in the data analysis of the gaseous emissions from the tedlar bag approach.

Annual box plots of VSC concentration for the 1st and 3rd passes of the secondary aeration tank show that DMS is over 6 times greater in concentration than DMDS. Annual means of DMS and DMDS for the 1st pass were 24 ppbv and 3.3 ppbv respectively. There were large variations in VSC concentrations measured throughout the year (Figure 3-14, Appendix II - Table 2A). DMS and DMDS released from the aeration tank varied significantly throughout the year. Winter and Spring VSC concentrations were the least with winter means of 4.7 ppbv and 0.85 ppbv for DMS and DMDS respectively for the 1st pass of the aeration tank. Fall VSC concentrations were the highest with means of 9.3 ppbv and 66 ppbv for DMS and DMDS respectively (Figure 3-15 & Appendix 1 – 12 and Appendix II - Table 2B).

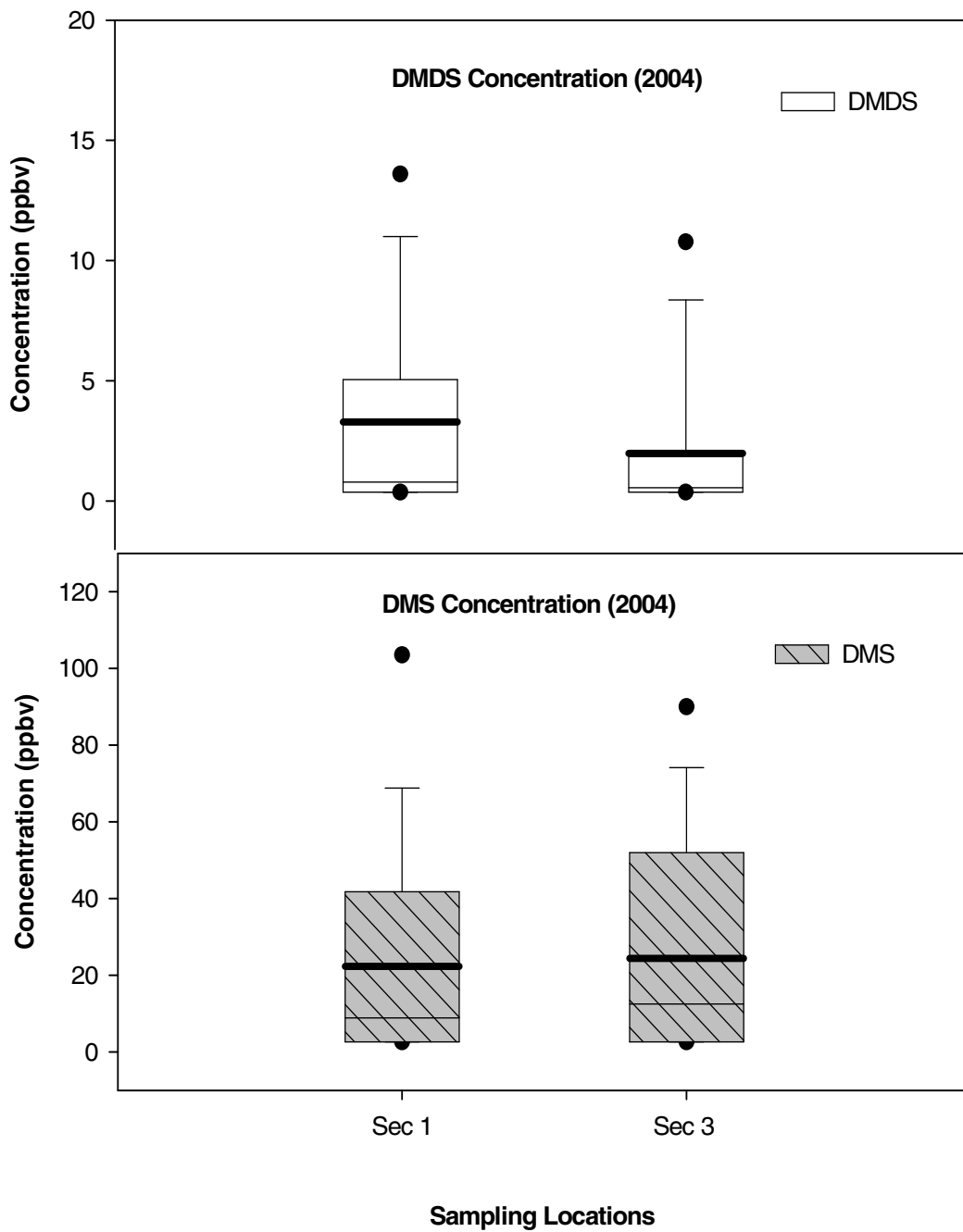


Figure 3 – 14: Annual VSC gas emission concentrations along the secondary aeration tanks.

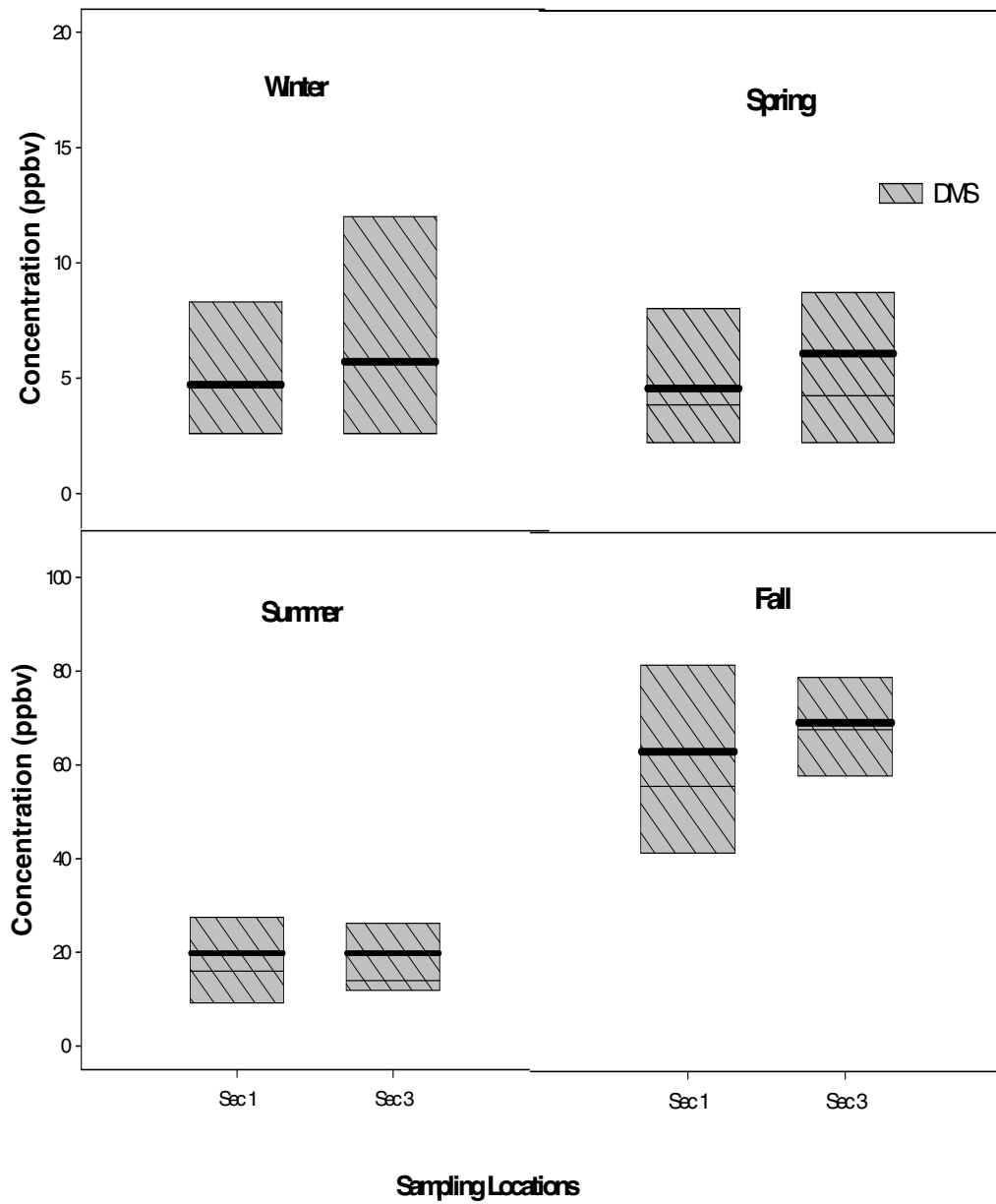


Figure 3 – 15: Seasonal DMS gas emission concentrations along the secondary aeration tanks.

This observed seasonal trend would explain why warmer months experience a larger number of odor incidents than do colder months. *Camp Dresser & McKee, 2003*, carried out an odor study at DC WASA and measured a concentration of 110 ppbv and 13 ppbv for MM and DMS respectively, using a flux chamber to trap off-gases from the head of the 1st pass of the secondary aeration tank.

Samples collected for the summer and fall range from 2.6 – 120 ppbv for DMS and 0.37 – 15 ppbv for DMDS (Appendix II – Table 7&8). These concentration ranges are proximate to published odor recognition concentration for each compound; ~ 9 ppb for DMS and ~ 1 ppb for DMDS (Table 2-1). Considering the VSC concentrations, DMS was consistently greater than DMDS in both passes of the aeration tank. However an examination of their odor index values would suggest that both compounds play a significant role in the intensity of perceived odor (Appendix II – Table 2C). There is no distinct difference in VSC odor index between the 1st and 3rd passes of the aeration tank (Appendix II – Table 2C). Recognition odor intensity values (OU/m³) show a similar seasonal trend. The fall sampling sessions exhibited the highest mean odor concentration (2254 OU/m³), and the winter the least (33 OU/m³) (Figure 3-15 & Appendix Table 2B). A visual inspection of Figure 3-15, reveals a distinct correlation between VSC concentrations and odor unit values. Statistically, a strong relationship does exist between both VSCs and odor intensity (DMS: p – value < 0.001, correlation = 0.81 and a df = 13 – Table 3-5).

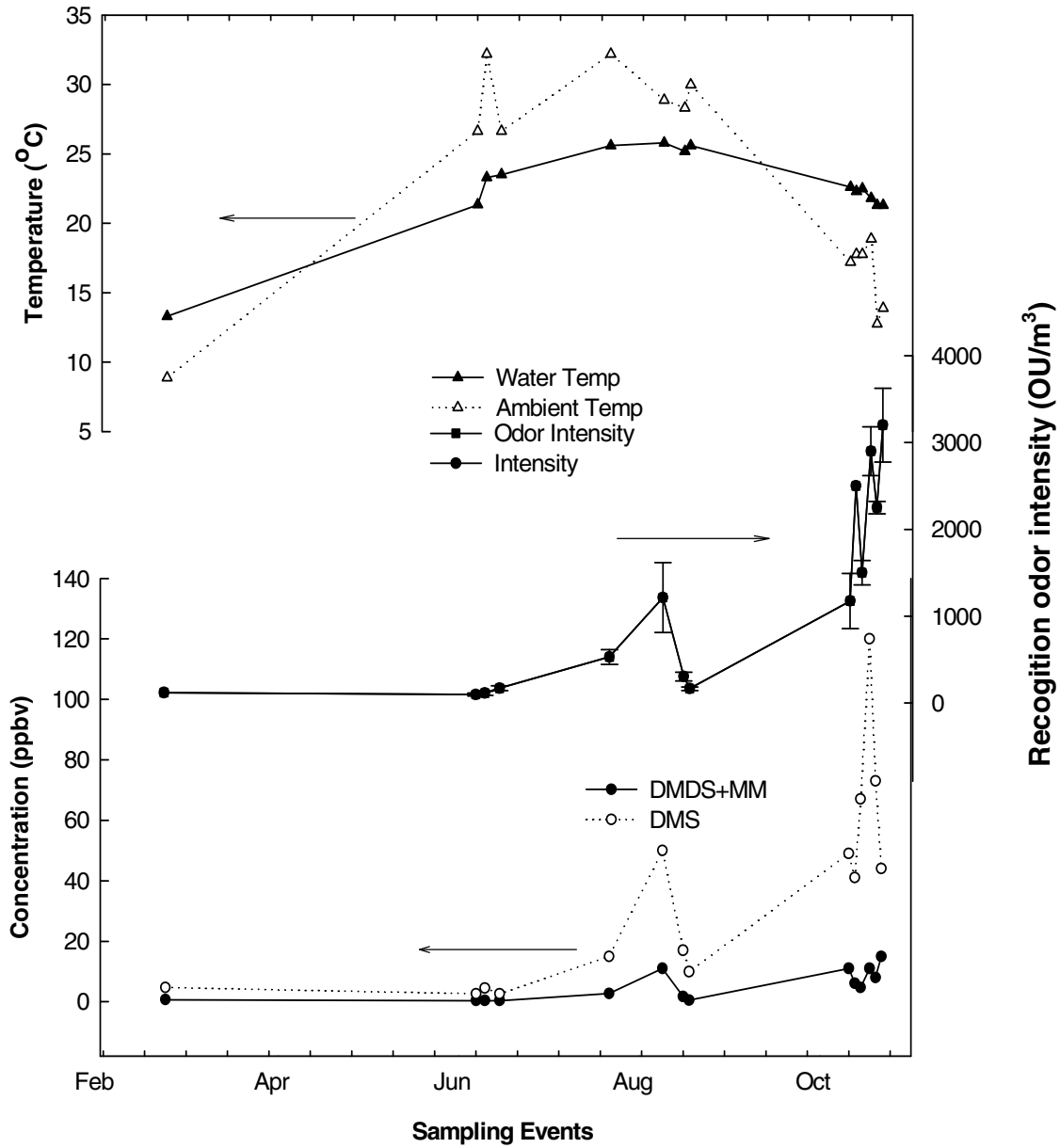


Figure 3 – 15: Seasonal VSC and odor gas emission concentrations along the secondary aeration tanks compared with temperature.

Statistically, the relationship between VSC concentration and odor concentration with wastewater temperature is very poor (Table 3 - 5). In the 1st pass of the aeration tank, the fall VSC concentrations and odor unit values increased from their previous values in the summer even as wastewater temperature dropped (Figure 3-15). Odor concentration from the 3rd pass shows a similar trend (Appendix II – Table 2B). Statistically by excluding the fall data, the relationship between VSC concentration and odor units with water temperature greatly improves (Table 3 - 5). The analysis of the data from the flux chamber procedure shows very strong correlation between GC-MS and olfactometry analytical data. DMS and DMDS concentrations correlate extremely well with recognition odor threshold concentration (Odor intensity/DMDS values – correlation = 0.85, p < 0.001) (Table 3 - 5).

Table 3-5: Statistical relationship between VSCs, water temperature and odor concentration for the 1st pass of the aeration tank.

| | Intensity | | Water Temperature | | Water Temperature (excluding fall data) | |
|---------------------------|-----------|-------------|-------------------|-------------|--|-------------|
| | P- value | Correlation | P- value | Correlation | P-value | Correlation |
| DMDS | < 0.001 | 0.85 | 0.047 | 0.04 | 0.36 | 0.35 |
| DMS | < 0.001 | 0.81 | < 0.001 | < 0.001 | 0.001 | 0.43 |
| Intensity | 1 | 1 | < 0.001 | - 0.074 | < 0.001 | 0.43 |
| Degrees of freedom | 13 | 13 | 13 | 13 | 7 | 7 |

Further evidence of the good correlation between analytical and olfactometric measurements is provided by odor character descriptors. Olfactometric analysis has an odor characterization dimension. Samples were scaled on various odor descriptors which include; floral, fruity, vegetable, earthy, offensive, fishy, chemical and medicinal (Figure

3-16). The positive X and Y axis represent the wholesomeness / pleasantness of the sample, whilst the negative X and Y axis represent the offensiveness / clinical nature of the odor sample. Each sample has two points in these diagrams, this is each sample has a point in both the X-Y quadrant and the -X and -Y quadrant. Since all diagrams are on the same vertical and horizontal scale, cross comparison is easier. An analysis of clusters of points for a specific location, shows that the odor from the 1st pass increased in intensity on the -X and -Y scale (offensiveness) from the spring (~ -0.6), to the summer (~ -0.8) and the fall (~ -1.3). These odor descriptors correlate extremely well with both the GC-MS and odor unit data. The odor intensity was higher in the summer than in the spring/winter and even as water temperatures decreased in the fall, odor intensity in the fall was higher than it was in the summer.

The fall odor anomaly goes against conventional wisdom which would otherwise suggest that odor/odorant concentration would decrease in the fall with a decrease in water temperature. To get a better picture this anomaly, VSC emission rates were calculated based on air flow rates (L/s) in the individual passes (1 & 3) (Table 3 - 6). The mass of VSC emission rates support the contention that odorants and odor released in the fall was higher than in all the other seasons.

Table 3 - 6: Mass flow rate for VSCs emitted from the secondary aeration tank

| Aeration Tank Emissions | | Winter | Spring | Summer | Fall |
|---|-------------|--------|--------|--------|------|
| Air flow rate (10⁶ L/s) (1st pass) | | 1.5 | 2.8 | 3.1 | 3.2 |
| Mass flow / pass (1) (kg/ day-pass) | DMDS | 0.5 | 0.8 | 2.6 | 8.8 |
| | DMS | 2.2 | 3.8 | 17.5 | 61.7 |
| Air flow rate (10⁶ L/s) (3rd pass) | | 2.2 | 2.3 | 3.5 | 3.2 |
| Mass flow / pass (3) (kg/ day-pass) | DMDS | 0.5 | 0.6 | 2.2 | 4.2 |
| | DMS | 3.5 | 4.1 | 20.7 | 67.9 |

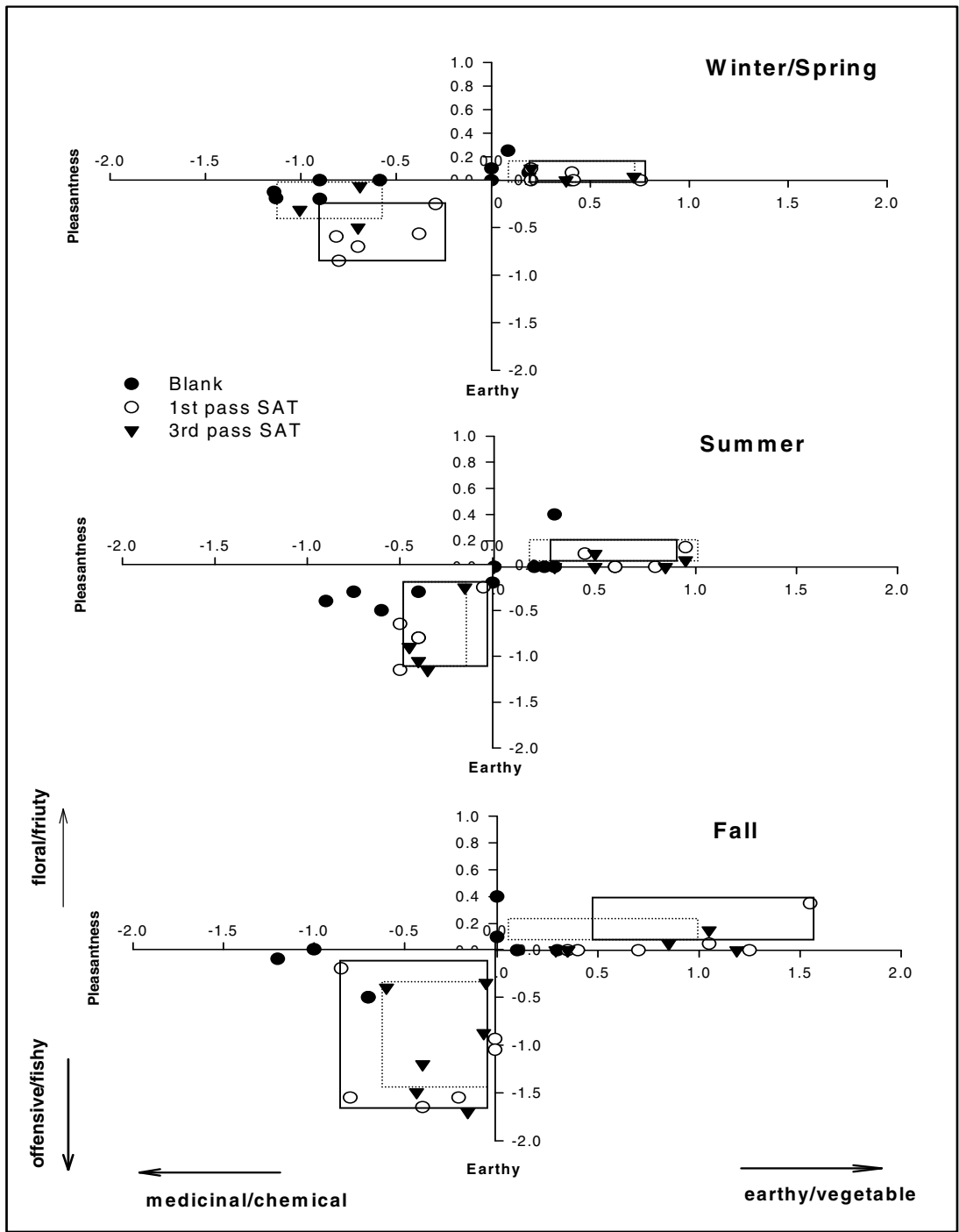


Figure 3-16: Seasonal variations in scaled odor description along the secondary treatment system.

Summary

The observations from the headspace approach support the assertion that VSCs are produced in the anaerobic wastewater environment that exists at the bottom of the secondary sedimentation basins. Concentrations of VSCs produced in the sedimentation basins are strongly dependant on the sludge blanket levels in these basins. In addition, the wastewater in the 1st pass of the aeration tank is solely aerated RAS from the bottom of the sedimentation tanks and on average the concentration of VSCs in the 1st pass was higher than that from the 3rd pass. Assuming that the aeration tank is sufficiently aerated and thus efficiently mixed, these observations indicate that VSCs are systematically stripped from and/or degraded in the aeration tanks resulting in a negative concentration gradient along the length of the tanks.

Results from the tedlar bag approach, illustrate that VSCs are released in the aeration tanks of the secondary treatment system. The release of VSCs is seasonally dependent with little release in colder wastewater temperatures and much greater release in warmer wastewater temperatures. Release rates are less dependent on wastewater concentrations than on wastewater temperature. VSCs play a significant role in the perceived odor from the secondary treatment system as confirmed by olfactometric data. The mass flux of VSCs from the surface of the aeration tanks is seasonally dependent, higher in the summer and fall and lower in the winter and spring. The mass flux of VSCs does not vary significantly along the length of the secondary aeration tank.

3.5.3 Statistical Modeling of VSC Concentration

In this section, a statistical model to predict levels of VSCs at the bottom of the sedimentation basin is presented. The results from the full scale plant study have shown that VSCs formed at the bottom of the sedimentation basin are subsequently released from the aeration tanks and therefore perceived as odor. This statistical predictive model will be useful to plant operators and plant managers to control the incidents of plant odor.

3.5.3.1 Process Parameters

Primary process parameters were measured and recorded and/or sampled on site during each sampling event. The primary parameters included in the statistical modeling include ORP, water temperature, sludge blanket level (SBL), sulfide concentration, spiked oxygen uptake rate (spiked OUR) and soluble iron concentration. Relevant secondary parameters (process variables) were collected for the secondary treatment process from the PCH system at the DCWASA – Blue Plains AWWTP. The PCH system is a digital database of all plant parameters, adjusted daily by the plant operators and the department of wastewater laboratory staff. The relevant plant process parameters included initial settling velocity (ISV), food to microorganism ratio (F/M), settled sludge volume (SSV₆₀) and sludge retention time (SRT). A calculated parameter, *density, was also included to account for the density of the settled sludge at the bottom of the sedimentation tank. Chlorine addition to the secondary system to treat the issue of foaming caused by filamentous bacteria was accounted for by the use of a dummy variable.

3.5.3.2 Description of Process Parameters

Sludge Blanket Level

SBL is a measure of the depth of the sludge blanket at the bottom of the secondary sedimentation tank, in feet. A high SBL means poor settleability and/or high solids inventory in the sedimentation tank. High SBL should result in the increased concentration of VSCs at the bottom of the secondary sedimentation tank.

Oxidation Reduction Potential

ORP is a general measure of the relative concentrations of oxidants (oxygen nitrates etc) and reductants (sulfides, ammonia and organics) in a system. A high ORP indicates a high concentration of oxidants compared to reductants and the vice versa is also true. A lack of oxidants results in the incomplete metabolic oxidation of organic matter and produces a variety odorous by products. The lower the ORP, the higher the concentration of VSCs are likely to be at the bottom of the sedimentation basin.

Water Temperature

Water temperature not only directly affects the metabolic activity of microorganisms but also affects gas transfer rates and sludge settling characteristics. Higher waste water temperature increases the metabolic activity of microorganisms and therefore depletes available oxidants faster, resulting in the development of anaerobic conditions. It would be expected that higher wastewater temperatures would result in an increase in VSC concentration at the bottom of the sedimentation basin.

Spiked Oxygen Uptake Rate

Spiked OUR relates directly to the rate of organic consumption and microbial growth in an activated sludge system. High Spiked OUR is indicative of a high metabolic sludge and would result in increases the concentration of VSCs at the bottom of the sedimentation basin.

Sulfide Concentration

Sulfide concentration in the sludge blanket is an indication of the extent of anaerobic metabolic activity at the bottom of the sedimentation basin. High sulfide concentration would coincide with a high production of VSCs.

Soluble Iron Concentration

Ferric chloride (FeCl_3) and waste pickle liquor are added to wastewater streams to help with coagulation and flocculation of suspended matter in the primary and secondary processes and thus improve settleability and phosphorous removal. The concentration of soluble iron in biosolids is negatively correlated with odor from lime stabilized biosolids. High soluble iron concentration in the SBL should coincide with lower VSC concentration at the bottom of the sedimentation basin.

Solids Retention Time

SRT represents the average period of time during which the biosolids remain in the secondary treatment system. If the solids spent a time constant ratio between the aeration tanks and the sedimentation tanks, then the higher the SRT the longer the time spent in the sedimentation basin. The secondary sedimentation process is an inherently

anaerobic process, therefore the higher the SRT and hence the longer the time spent in the sedimentation basin, the greater the potential to produce VSCs at the bottom of the sedimentation basin.

Initial Setting Velocity

ISV is a measure of how well a sludge sample settles in the first few minutes of settling and thus captures the true nature of the settling sludge (i.e. fast settling or slow settling). ISV is the settling velocity of the sludge/water interface at the beginning of a sludge settleability test and is measured in ft/min. An advantage of ISV is that it inherently accounts for the effect of high mixed liquor suspended solids (MLSS) concentrations, this is, ISV decreases with an increase in MLSS. Low ISV is indicative of poorly settled sludge and/or high MLSS concentrations and therefore a decrease in ISV should result in an increase in VSC production.

Food to Micro-organism ratio

The f/m ratio compares the amount of food (BOD or COD) in the influent of an activated sludge system to the amount of microorganisms available in the system. The food is measured in lbs/day of BOD whilst the microorganisms are lbs – VSS in aeration tanks. A high f/m ratio may encourage the growth of filamentous bacteria and hence poor settleability in the sedimentation tanks. A low f/m ratio is indicative of a large solids inventory in the aeration tanks which may lead to nitrification and excess DO consumption. Therefore a low f/m ratio should result in a high VSC concentration at the bottom of the sedimentation tank.

Settled Sludge Volume

SSV₆₀ is a measure of how well a sludge sample settles in 60 minutes. SSV₆₀ is measured in milliliters of settled sludge per liter of mixed liquor. A high SSV₆₀ is indicative poor sludge settleability characteristics and/or a high suspended solids concentration in the mixed liquor. High SSV₆₀ should result in the increased production of VSCs at the bottom of the sedimentation tank.

****Density***

Settled volume index (SVI₆₀) is the volume of 1g of sludge after 60 minutes of settling. The inverse of SVI₆₀ is the mass per unit volume of settled sludge after 60 minutes. The density parameter is a product of the VSS of sludge and the inverse of the SSV₆₀. This density term gives an indication of the density of the settled sludge after 60 minutes and therefore the higher the density term the higher the VSC concentration at the bottom of the sedimentation tank.

$$*Density = VSS / SSV_{60} = mg/L / ml/L = mg/ml$$

Chlorine addition

Chlorine is intermittently added directly to the RAS from the sedimentation tank. Chlorine is a powerful oxidant and is not only useful in the wastewater environment as a bactericide and/or a microorganism inhibitor but also as a chemical oxidizing agent. If added in sufficient concentrations, chlorine should decrease VSC production. At DC WASA – blue plains, the effective dosing concentration of chlorine when it is added is 2 mg/L. This concentration is not intended to act as an oxidant but as a bactericide. A

dummy variable was used to account for the addition (+1) or non addition (-1) of chlorine.

3.5.3.3 Procedure

Single Linear and quadratic regression analysis was used to distinguish between parameters with a strong correlation with VSCs. DMS was used to represent VSCs concentration at the bottom of the sedimentation tank in this analysis (Table 3 – 7 & Appendix V – Table 1A). DMS was chosen instead of DMDS because DMS is directly indicative of anaerobic microbial activity. From this initial analysis, sludge level, ISV, SSV and *density were used in their quadratic form in the multiple regression analysis to determine a predictive model for VSC concentration at the bottom of the sedimentation tank.

Table 3 – 7: Correlation between DMS and process parameters.

| Description | Correlation | | |
|--------------------------|-------------|---------|-----------|
| | | Linear | Quadratic |
| Chlorine | A | / | / |
| Sludge level | B | 0.5154 | 0.5329 |
| ORP | C | 0.1244 | 0.1244 |
| Water temperature | D | 0.0672 | 0.0689 |
| Sulfide | E | 0.0061 | 0.0745 |
| Spiked OUR | F | 0.0138 | 0.0258 |
| Soluble Iron | G | 0.4089 | 0.7447 |
| ISV | H | 0.38 | 0.55 |
| F/M | I | 0.0072 | 0.008 |
| SSV | J | 0.3646 | 0.5222 |
| SRT | K | 0.00007 | 0.0276 |
| *Density | L | 0.208 | 0.302 |

All the parameters discussed above were used in either linear or quadratic form in the development of the statistical model. Numerous stepwise statistical models were tried. Various statistical factors were used to evaluate the quality of the various models. These include; the p-values for the model as a whole and the individual parameters, adjusted R^2 values, standard error of estimate (St err), the mean residual sum of squares (MS), the confidence intervals of the estimated parameters, the signs of the coefficients of the independent variables and the F-ratio. The adjusted R^2 which measures the amount of variation in the dependent variable explained by the model should be as high as possible. The p-values which measures the statistical distinction from zero should be as low as possible. The standard error of estimate of the model should be as low as possible. The mean residual sum of squares which is a measure of the variation which is not explained by the model should be as low as possible. The confidence intervals of the estimated parameters should not include zero, since this is an indication that the true value of the parameter is most likely zero. The signs of the coefficients of the parameters should make sense in the wastewater environment. The F-ratio which is a measure of the significance of a reduction in the regression sum of squares between two models should be as high as possible. After numerous series of models were tried, remembering that the goal of the statistical modeling process was to seek the simplest adequate model, model #13 was found to be the best (Appendix III – Table 1C).

$$\text{Model \#13: } Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2^2 + \beta_3 X_3 + \beta_4 X_3^2 \quad \text{eqn - 3}$$

Where

Y = DMS concentration (ppbv) at the bottom of the sedimentation tank

X₁ = food to microorganism ratio

X₂ = sludge blanket level

X₃ = settled sludge volume (60 minutes)

Therefore Model #13 =

$$\text{Model \#13: } Y = 149.8 - 51.3 X_1 + 6.8 X_2^2 - 1.43 X_3 + 3.5 \times 10^{-3} X_3^2 \quad \text{eqn - 4}$$

$$\text{Residual error (e) = Actual DMS conc. - Predicted DMS conc.} \quad \text{eqn - 5}$$

An evaluation of the scatter of the residual error associated with the DMS prediction model, shows that the residuals are evenly scattered with no obvious bias (Figure 3 – 16, Appendix 3 – Table 1D). Model #13 is not affected by systematic bias. The DMS predictive model confirms that solids inventory in the secondary sedimentation basin is the key to controlling the production of VSCs at the bottom of the sedimentation basin. Therefore solids inventory is the key to controlling the odor associated with the secondary treatment system.

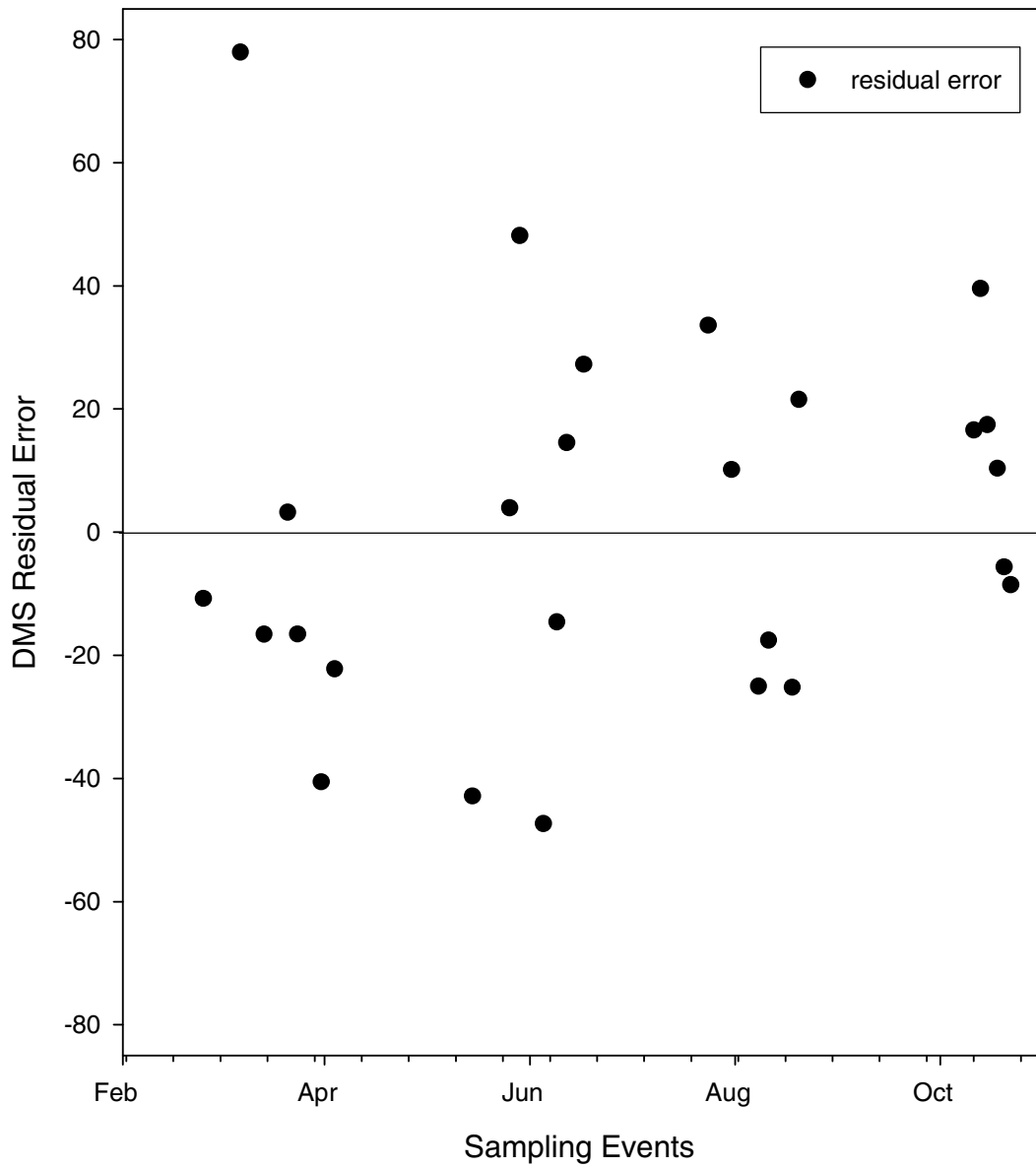


Figure 3 – 17: Variation of the residual error associated with DMS prediction

3.5.4 Error Analysis

There are systematic and random errors associated with the sample collection techniques and with the GC-MS-SPME analytical method which results in uncertainty associated with the concentration values measured in this study. The errors associated with the GC-MS-SPME analytical method are exemplified by the variance associated with the calibration curves. Each data point in the calibration curve has an associated standard deviation. The collective average of the percent standard deviation may be used as a surrogate for the percent error associated with the GC-MS-SPME analytical method. The percent deviation associated with the DMDS, DMS and EM calibration curves is 6.6%, 9.4% and 7.4% respectively. Collectively the error associated with the calibration of these VSCs is 7.8%.

The errors associated with the field sampling techniques may be estimated by the variance associated results from duplicate samples. The percent deviation associated with DMDS, DMS and MM concentrations in the duplicates are 21%, 18.3% and 24.2% for the head space method and 17.6 %, 18.3% and 15.4% for the tedlar bag method respectively. Therefore the collective errors associated with the field sampling of VSCs are 21.2% for the headspace method and 17.1% for the tedlar bag method.

Considering the errors associated with both the GC-MS-SPME analytical method and the field sampling procedures, the errors in VSC concentrations associated with this study are ~ 27%. This % error for on-site environmental studies is relative good. Due to this associated error, two significant figures were used in reporting VSC concentrations.

3.6 Conclusions and Further Research

This study set out to quantify variations in VSC concentration across the secondary treatment system at DC WASA, determine seasonal trends in the production and release of VSCs and identify the dominant environmental conditions and plant process parameters which control the trends observed. These objectives were achieved by GC-MS measurements of VSC concentrations in the wastewater across the secondary treatment system (using a headspace-SPME method), and measurements of VSC gas emissions from the secondary aeration tanks (using a flux chamber – SPME method). Olfactometric analysis of the odorous gas emissions from the aeration tank were also carried out in an effort to relate odor to odorant gas emission levels.

The results from this study have determined that, the predominant VSCs produced in and/or emitted from the secondary treatment system are DMDS, DMS and MM. The highest measured VSC wastewater concentration for DMDS, DMS and MM were 490 ppbv, 340 ppbv and 64 ppbv respectively and were measured from wastewater samples collected from the bottom of the secondary sedimentation tank. Similar compounds and compound concentration values have been determined by *Kim et al, 2002*, *Nurul Islam et al, 1998* and *Jenkins et al, 1980* from previous studies of VSCs associated with the secondary treatment system. The wastewater VSC concentration profiles across the secondary treatment system, determined that VSC production takes place in the sludge blanket at the bottom of the secondary sedimentation tank and is positively correlated to the depth of the sludge blanket. Statistically, VSC production is strongly dependant on the sludge blanket level (DMDS: correlation = 0.86, $p < 0.001$ for $df = 25$ and DMS:

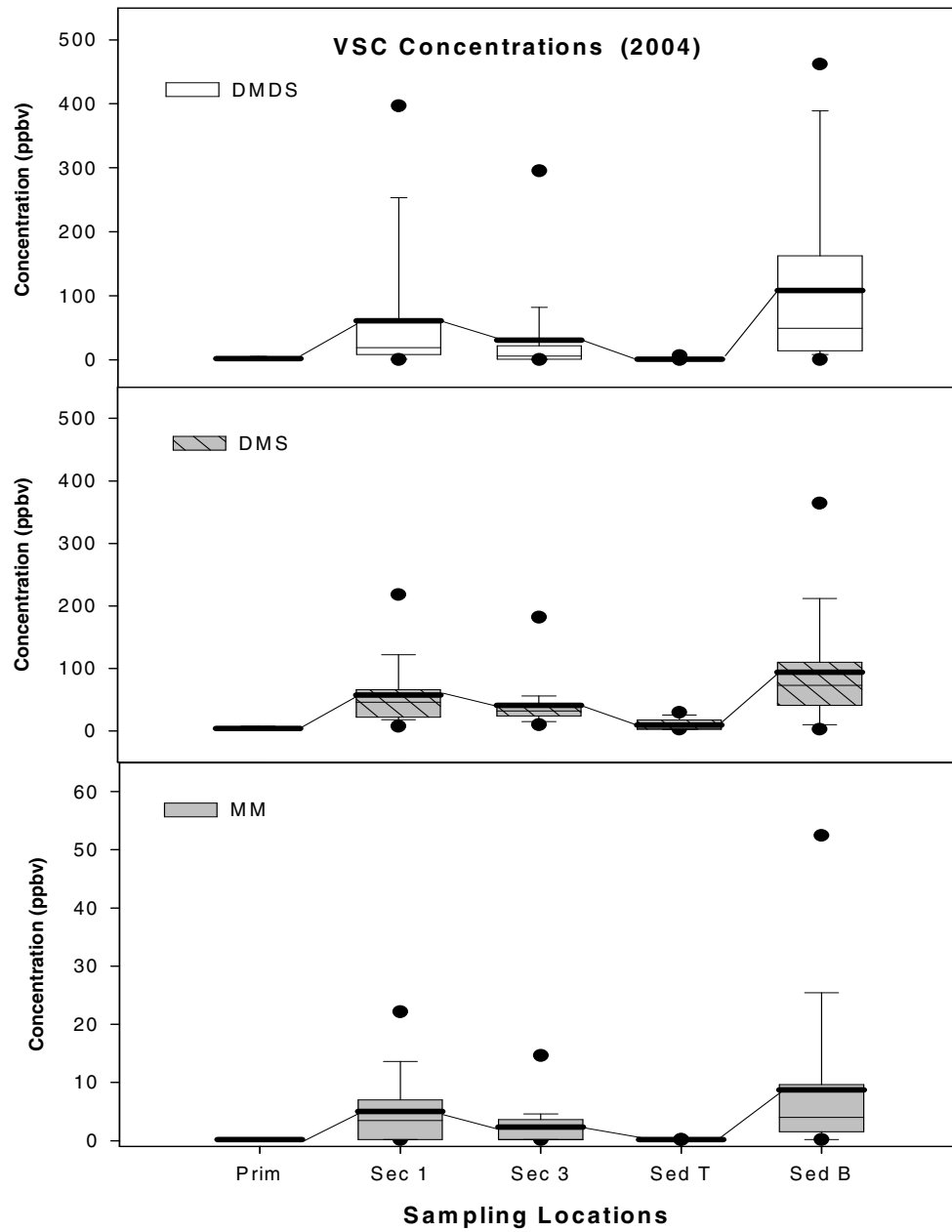
correlation = 0.72, $p < 0.001$ for $df = 25$). The concentration of VSCs at the bottom of the sedimentation tank is however poorly correlated with wastewater temperature.

The off-gas VSC concentration profile of the secondary aeration tanks indicates that both the 1st and the 3rd passes give off DMDS, DMS and MM. DMS has the highest concentration of VSCs in the gas emitted from the aeration tanks. However a look at using an odor approach, based on OTC values of DMDS = 1 and DMS = 9, indicates that both odorants play a significant role in the intensity of perceived odor. VSC gas emissions concentrations are the least in the winter followed by the spring. The summer and the fall record the highest VSCs, the fall being higher than the summer. Sensory analysis shows that recognition intensity values (OU/m^3) confirm this trend. The actual VSC emissions ($kg / (pass - day)$), based on mass air flow rate (L/s) in each pass also shows a similar seasonal trend. Statistical modeling of the VSC production potential in the secondary sedimentation basin has shown that the most influential plant process parameters are sludge blanket level, settled sludge volume and food to microorganism ratio. An analysis of scatter associated with this model shows no obvious systematic bias.

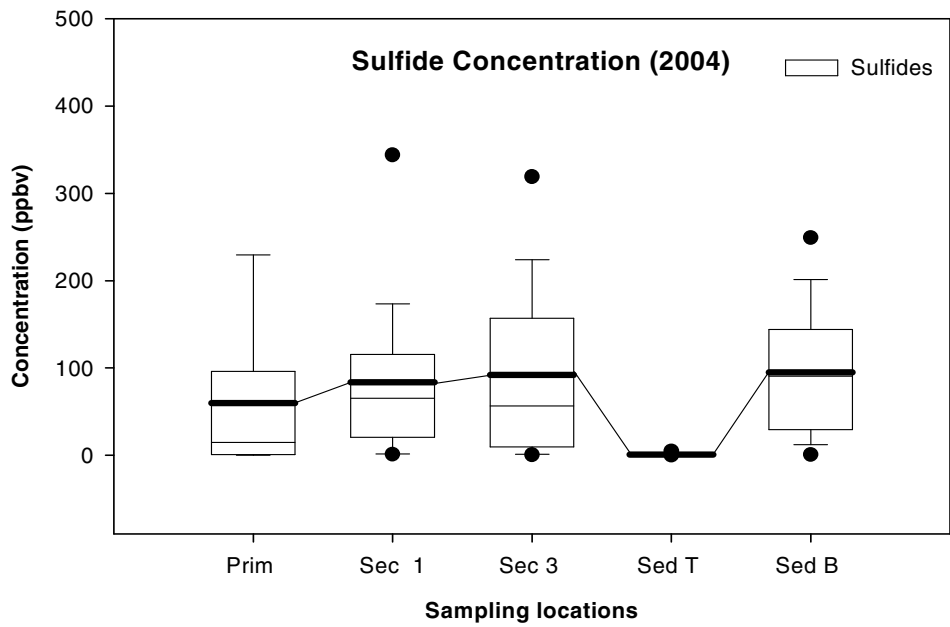
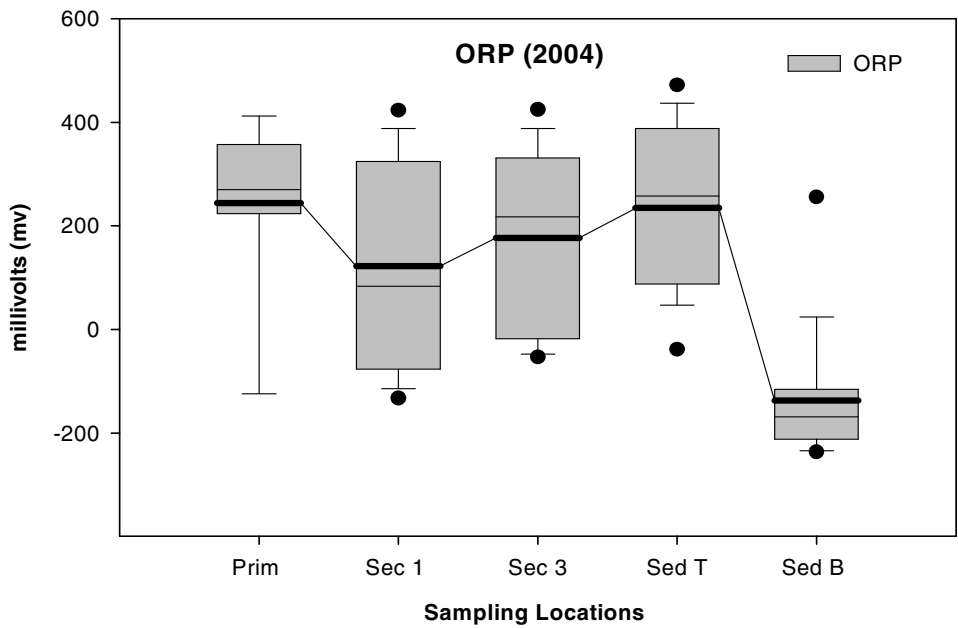
Results from this work strongly indicate that solids inventory in the sedimentation basin is responsible for the production of VSCs in the secondary treatment system. Emissions of VSCs across this system occur in the aeration tank and are reasonably related to water temperature. Wastewater treatment plants should strive to effectively control the solids inventory in the secondary sedimentation basin so as not to create conditions conducive for the production of VSCs. The solids must be quickly settled and moved out of the sedimentation basins before substantial production of VSCs begins. Therefore a broader discussion on the settleability of solids in the sedimentation basin

indirectly affects the production of VSCs. Settleability indices such as sludge volume index (SVI), initial settling velocity (ISV) and settled sludge volume (SSV) may also be good surrogates for VSC production potential in the secondary sedimentation basin. Further research to validate and fine tune the VSC predictive model would provide plant managers and operators with tools to predict and therefore control VSC/odor production in the secondary treatment system. As wastewater treatment plants move to automate their various unit processes and enhance computer aided control systems, adequate predictive models are an invaluable tool in the effective control of the odor incidents associated with the wastewater treatment process.

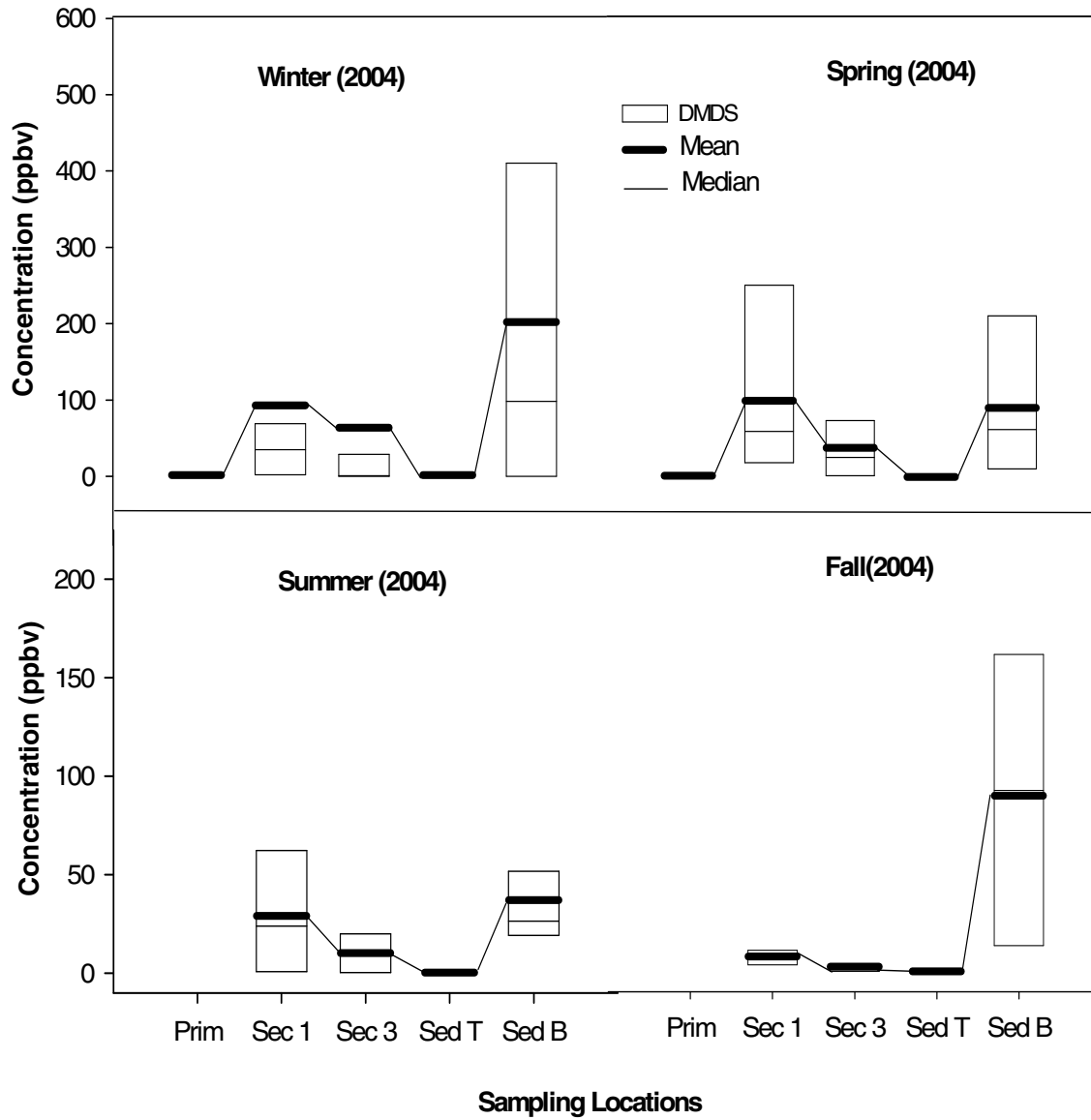
Appendix I



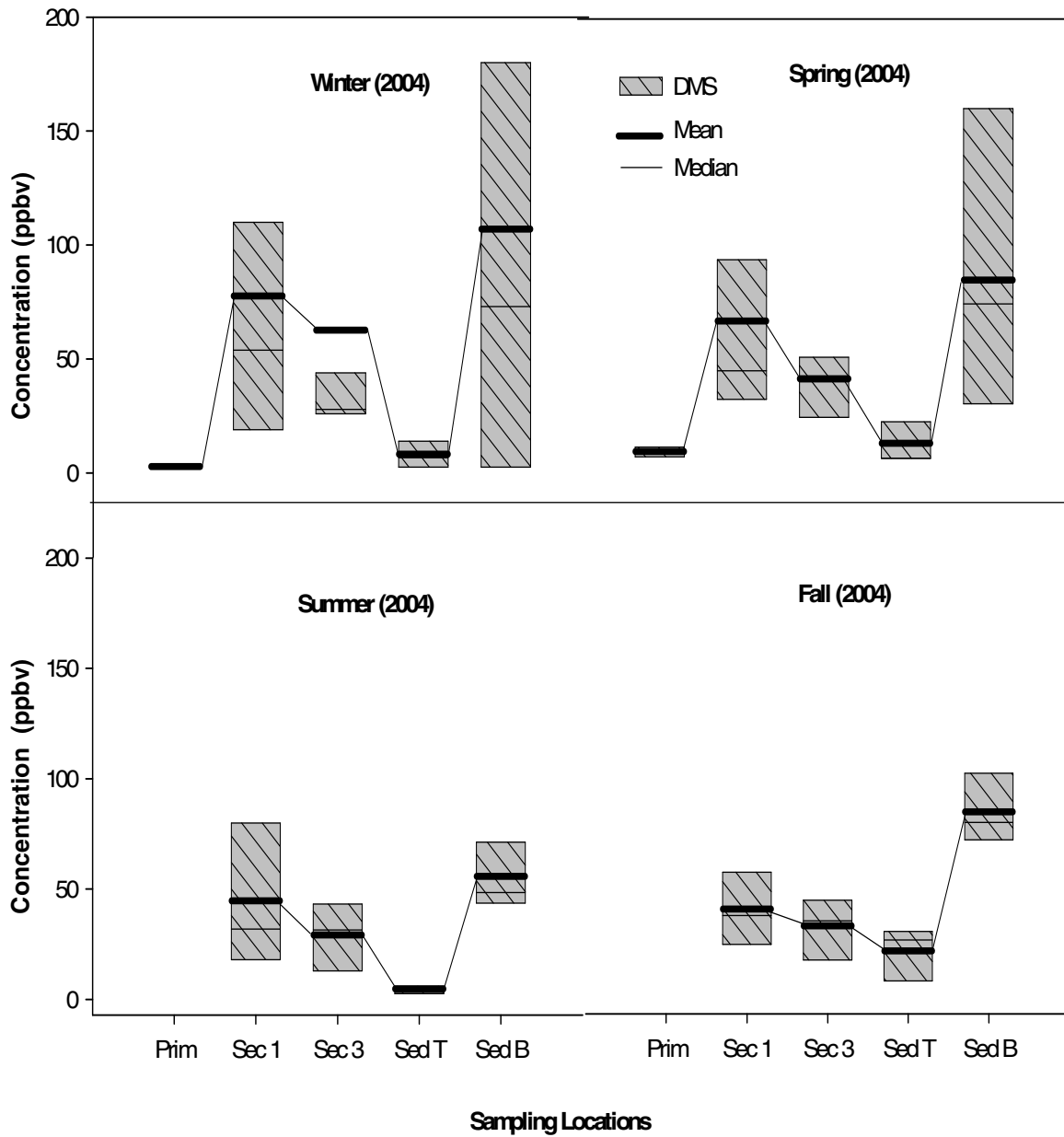
Appendix I – 1: Annual VSC wastewater concentrations across the secondary treatment system.



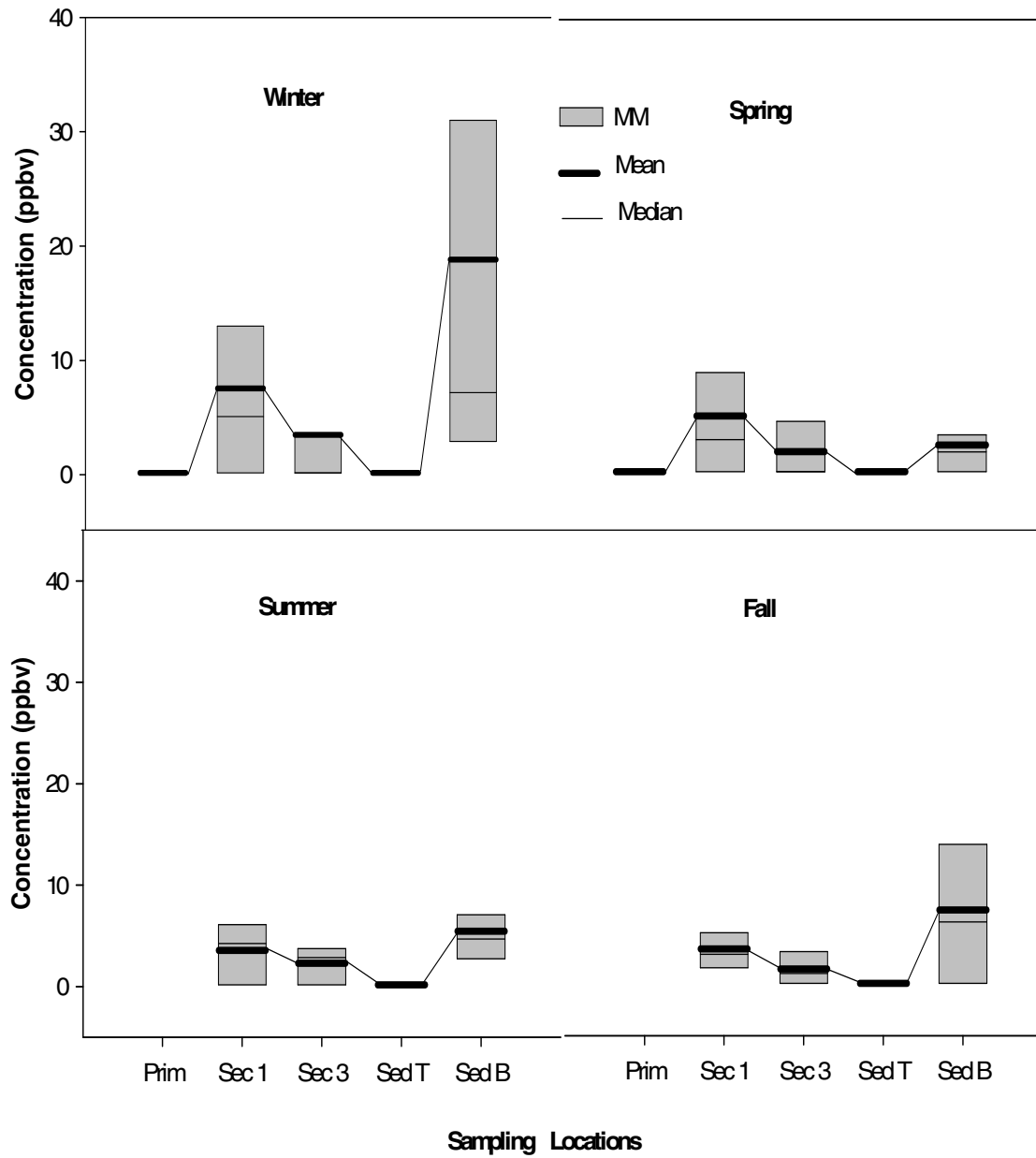
Appendix I – 2: Annual ORP and Sulfide wastewater concentrations across the secondary treatment system.



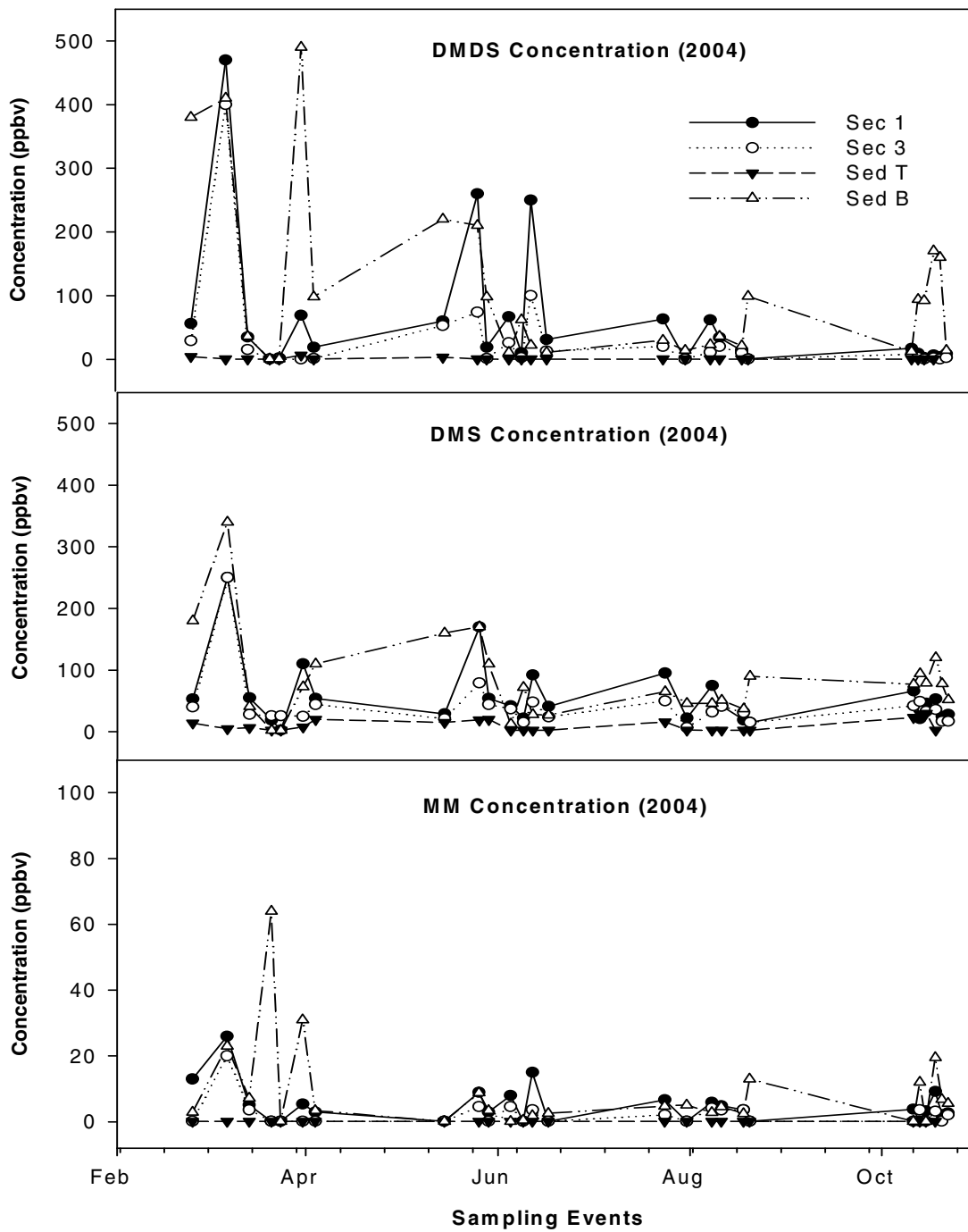
Appendix I– 3: Seasonal DMDS wastewater concentrations across the secondary treatment system.



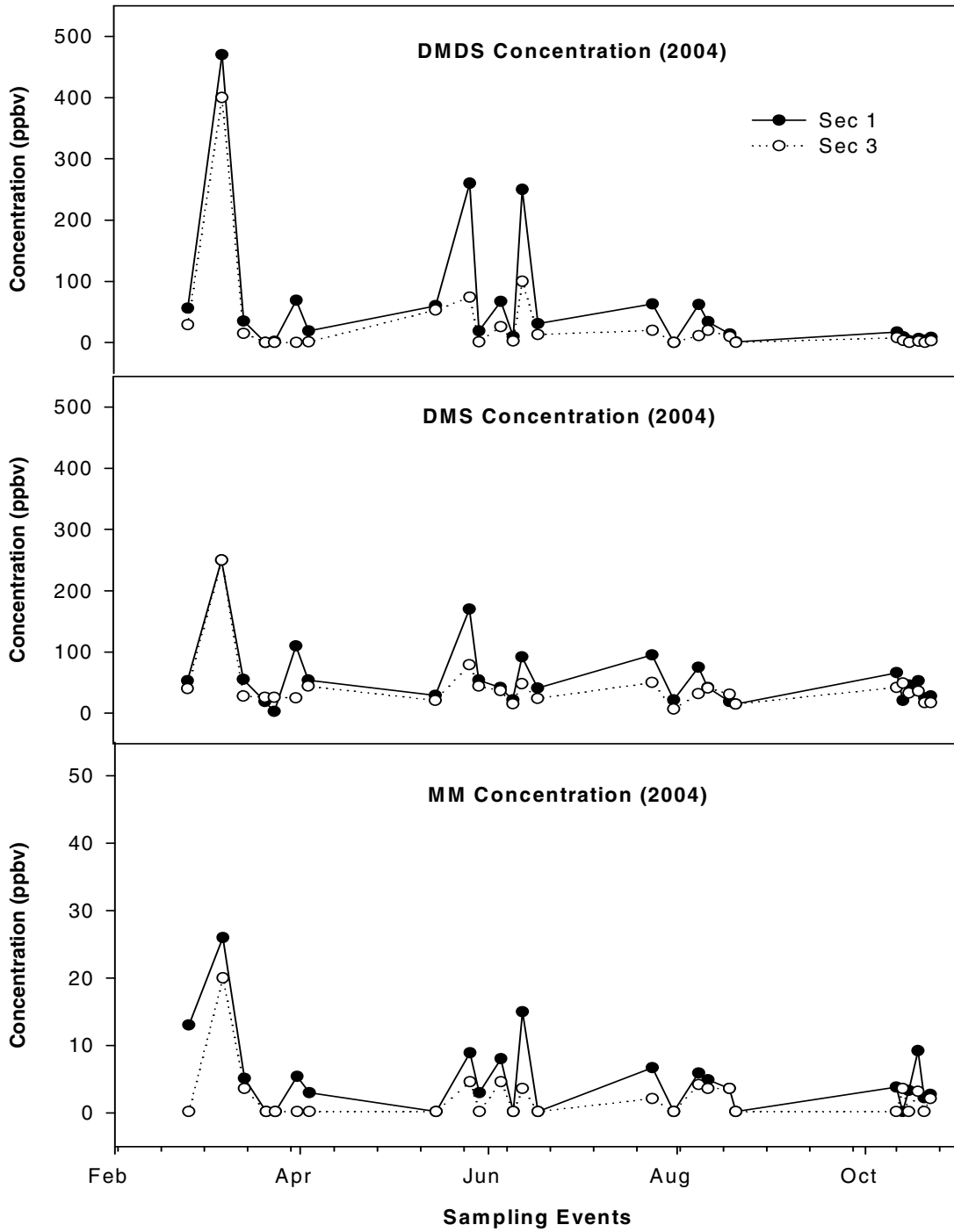
Appendix I – 4: Seasonal DMS wastewater concentrations across the secondary treatment system.



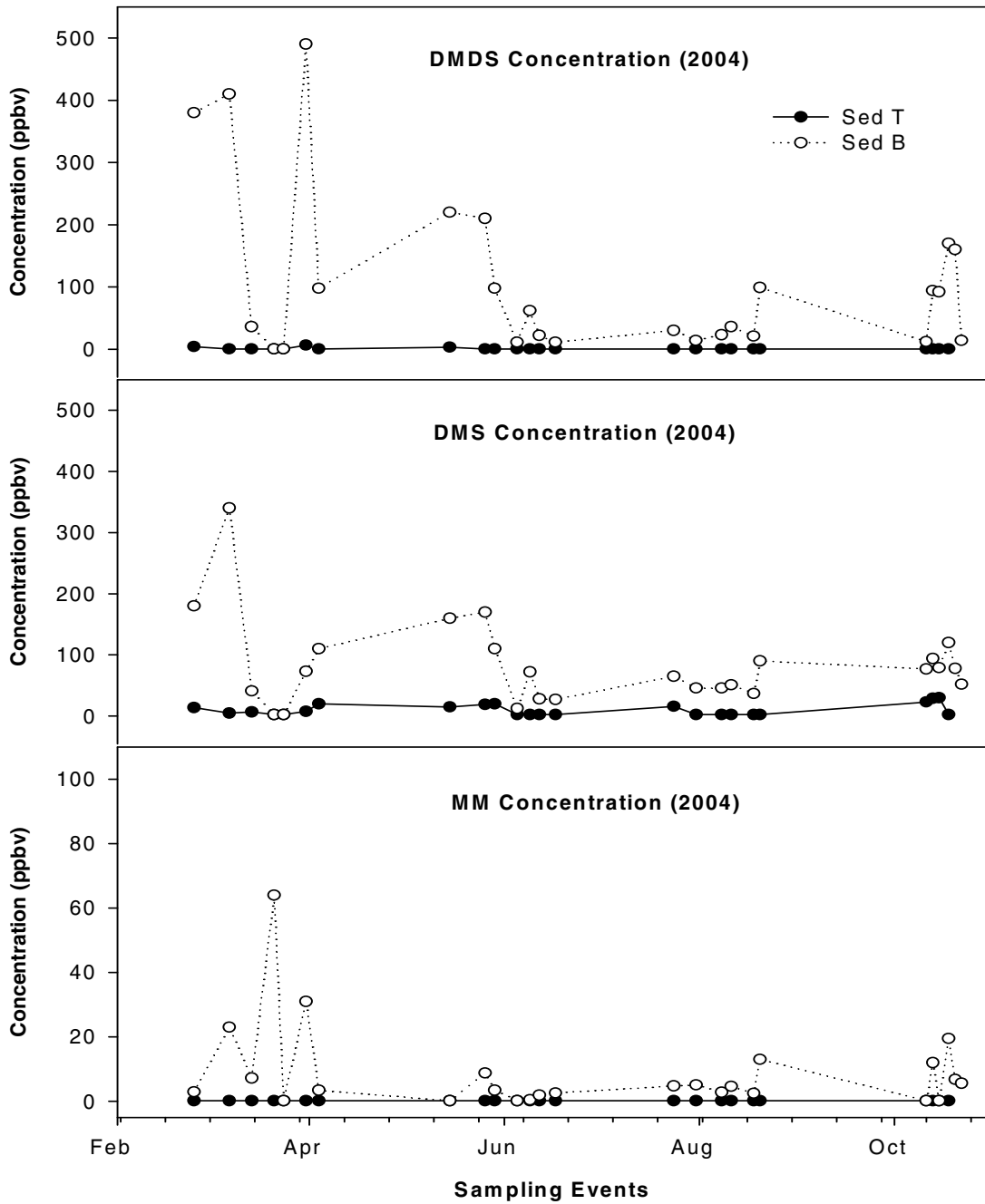
Appendix I – 5: Seasonal MM wastewater concentrations across the secondary treatment system.



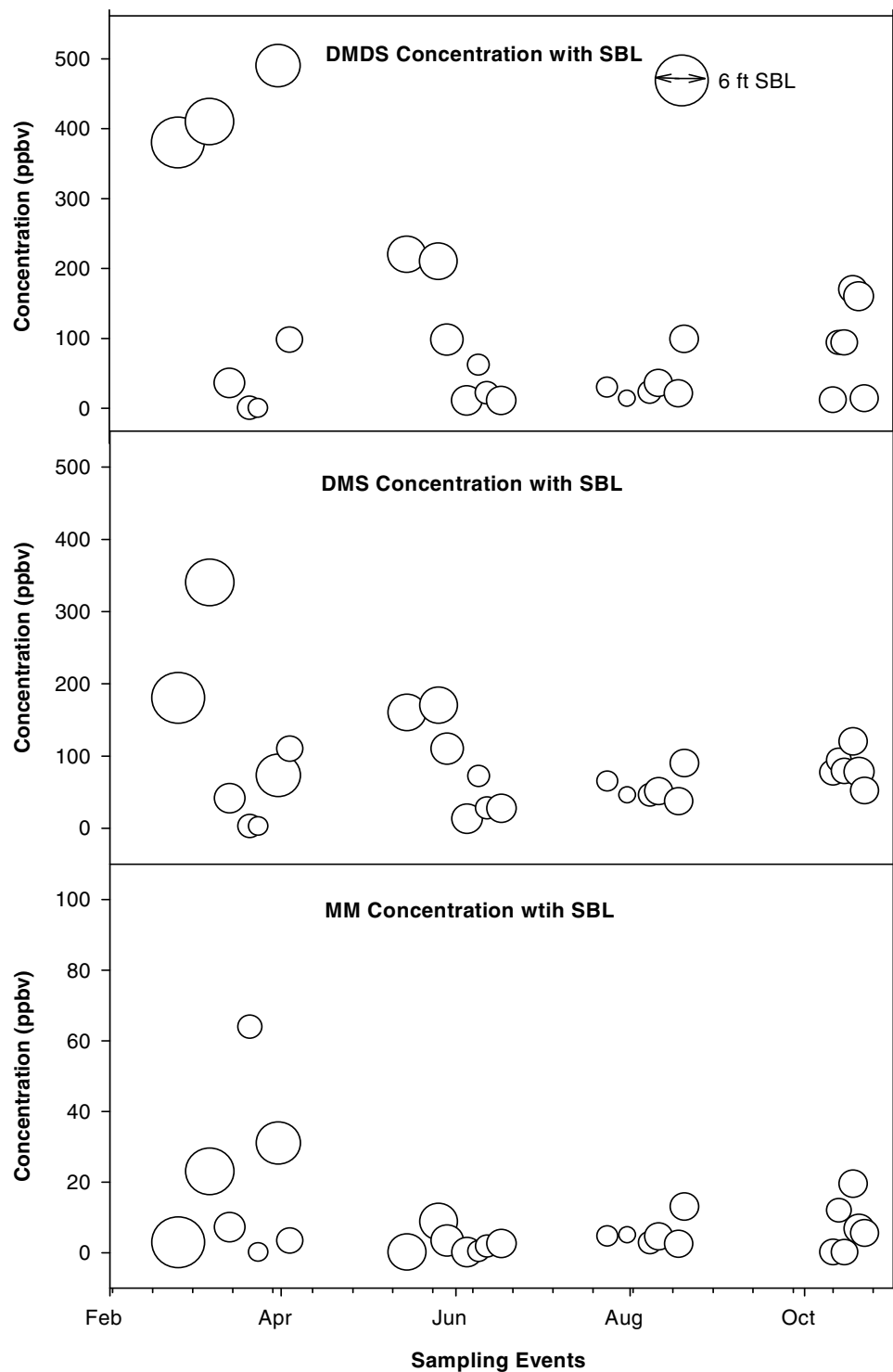
Appendix I– 6: VSC wastewater concentrations per sampling event across the secondary treatment system.



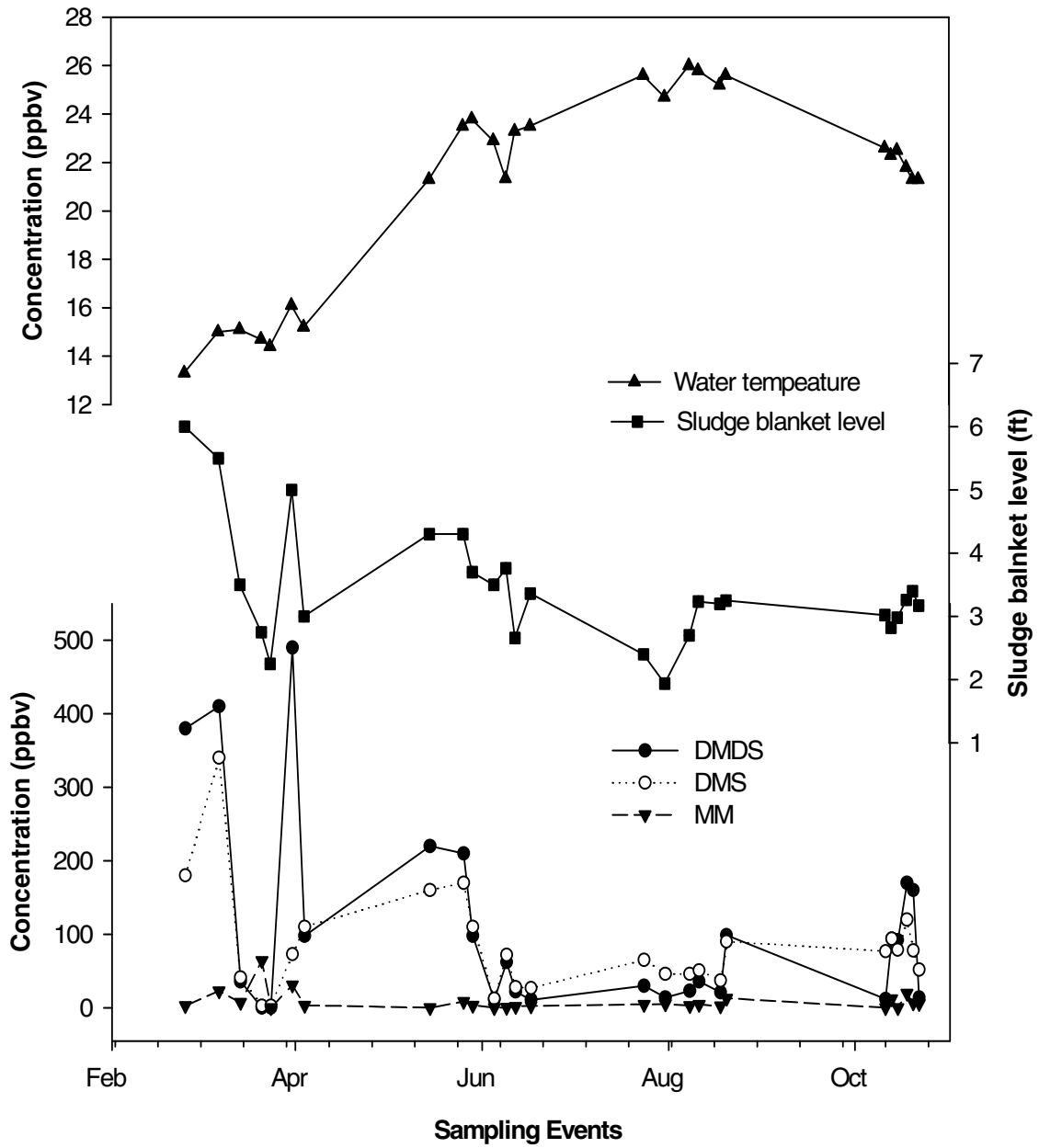
Appendix I– 7: VSC wastewater concentrations per sampling event along the secondary aeration tank.



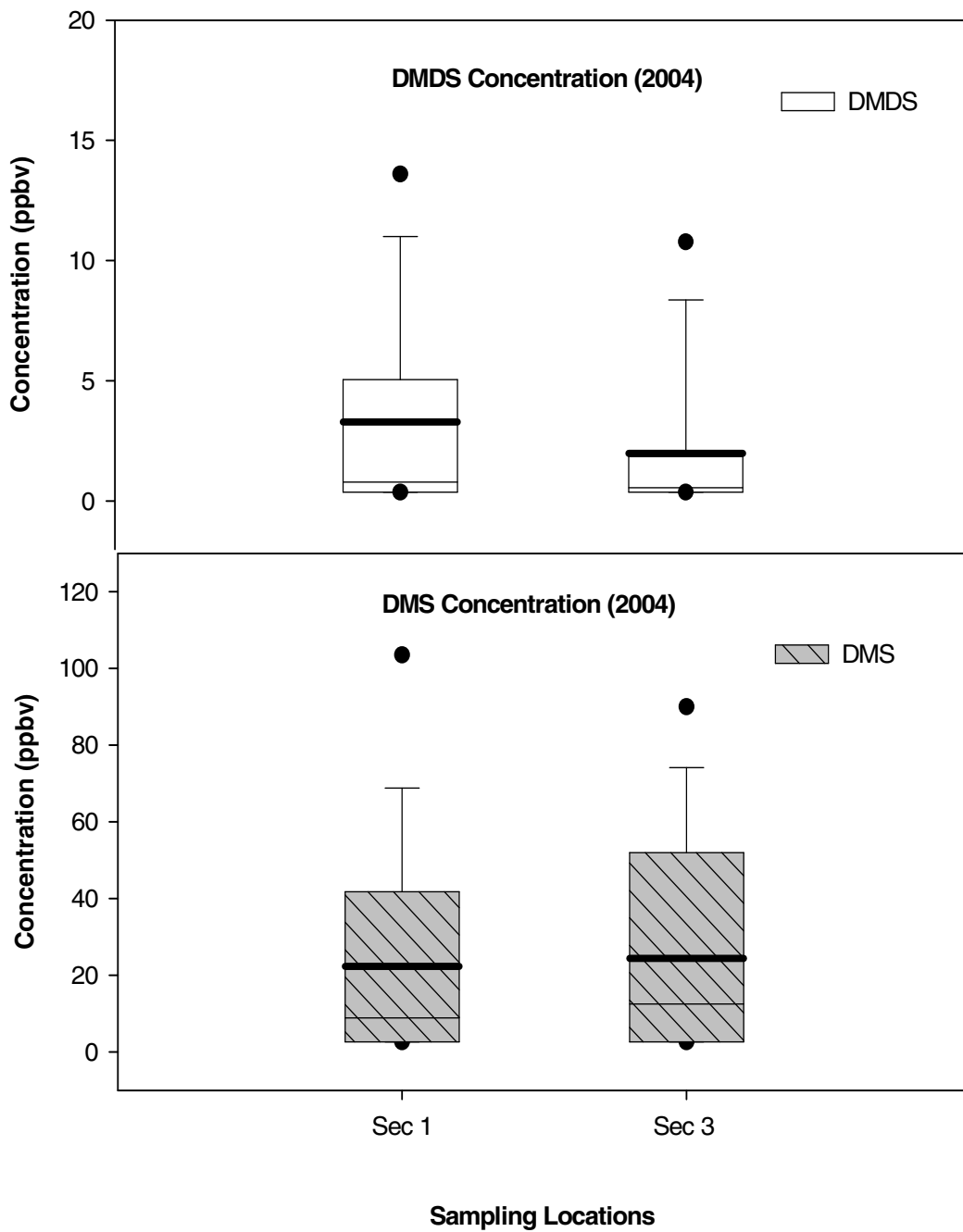
Appendix I – 8: VSC wastewater concentrations per sampling event in the secondary sedimentation basin.



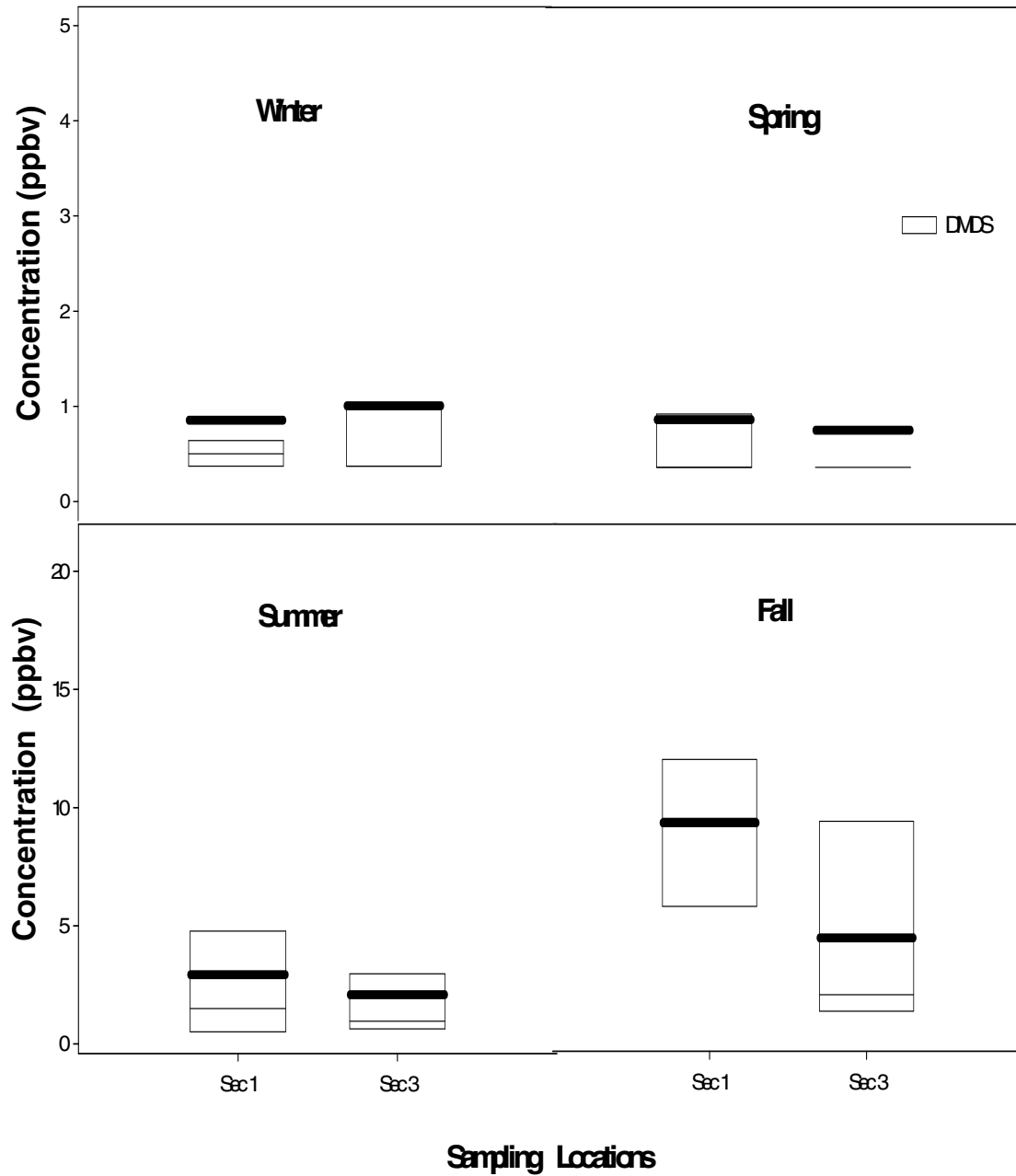
Appendix I – 9: VSC wastewater concentrations with SBLs per sampling event at the bottom of the secondary sedimentation basin.



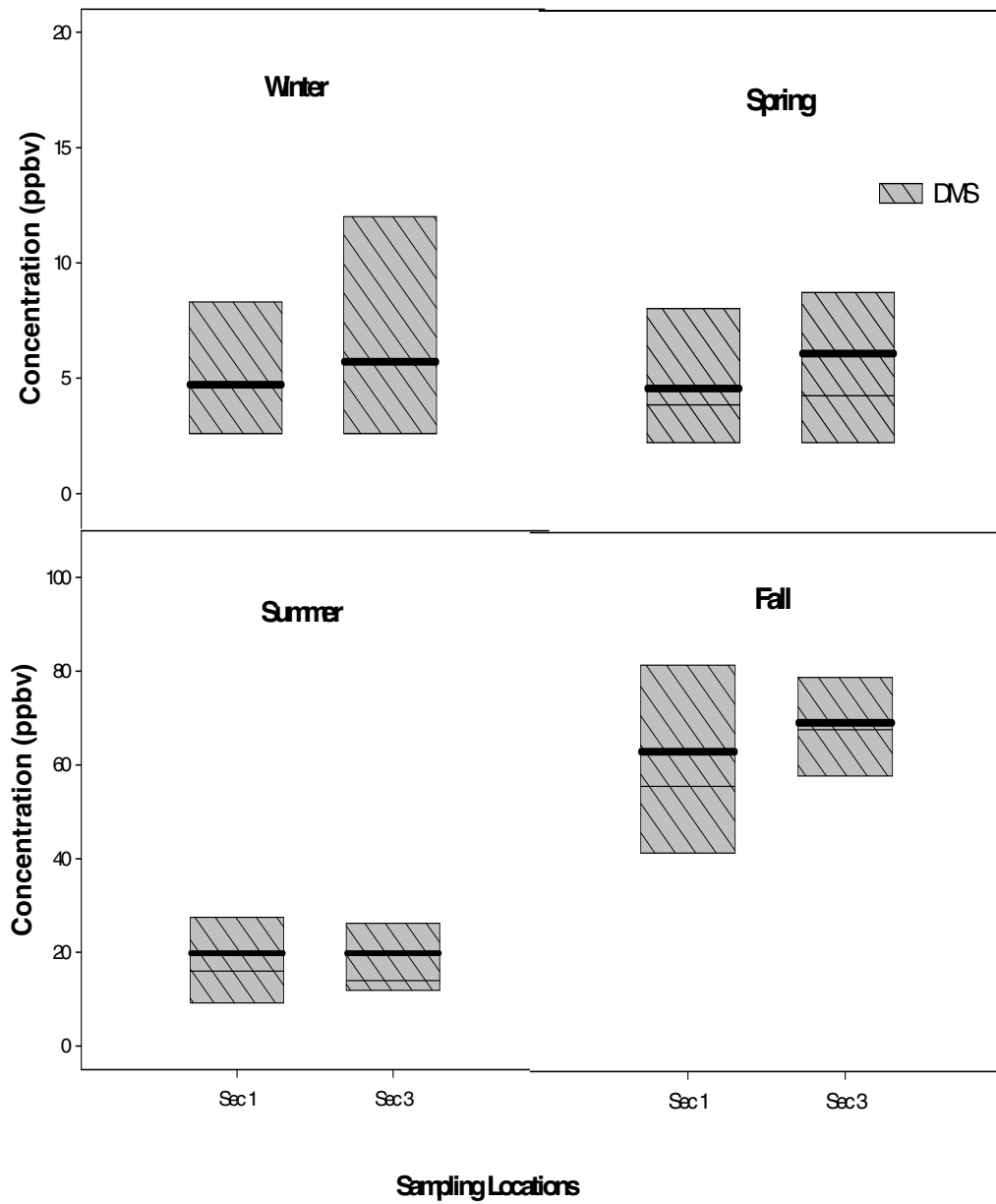
Appendix I – 10: VSC wastewater concentrations per sampling event at the bottom of the secondary sedimentation basin compared with SBLs and water temperature.



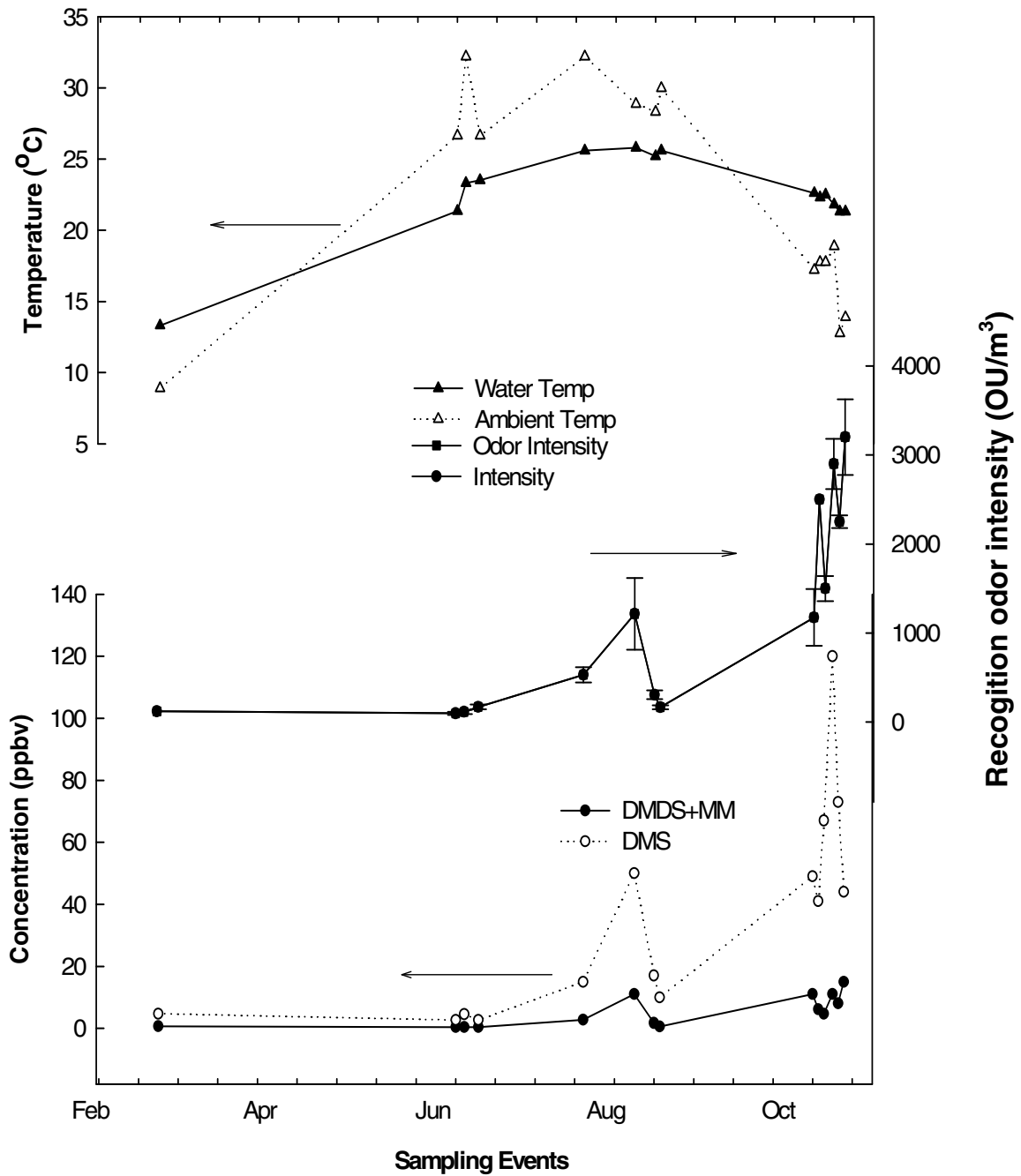
Appendix I– 11: Annual VSC gas emission concentrations along the secondary aeration tanks.



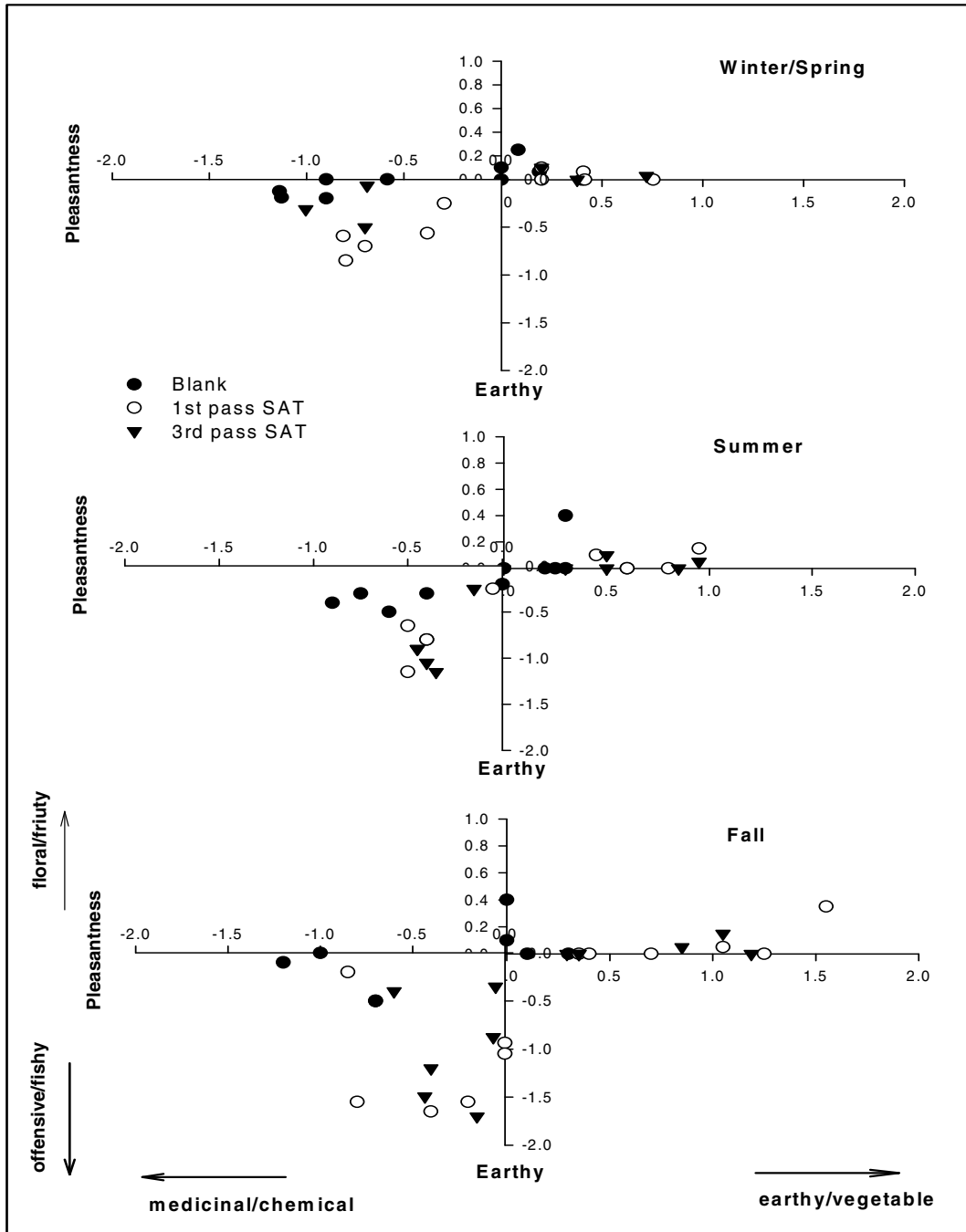
Appendix I – 12: Seasonal DMS gas emission concentrations along the secondary aeration tanks.



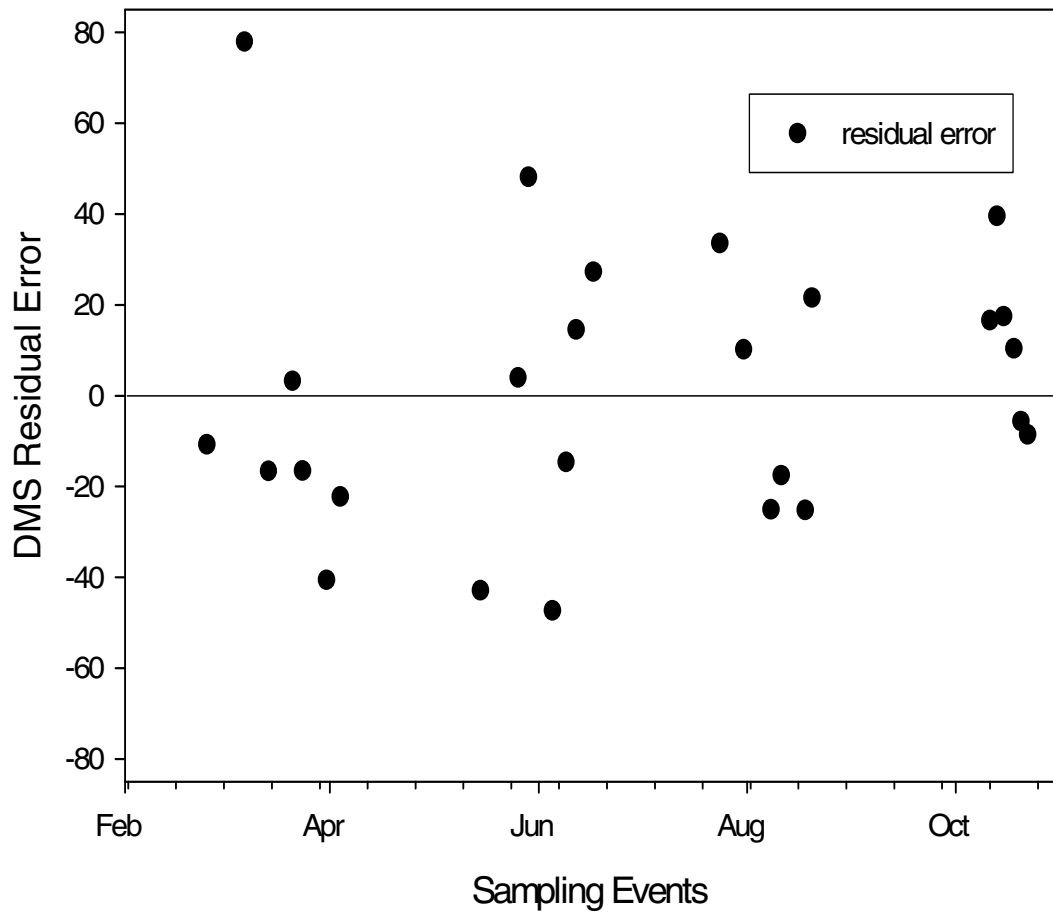
Appendix I– 13: Seasonal DMS gas emission concentrations along the secondary aeration tanks.



Appendix I – 14: Seasonal VSC and odor gas emission concentrations along the secondary aeration tanks compared with temperature.



Appendix I– 15: Seasonal variations in scaled odor descriptors along the secondary aeration tanks.



Appendix I – 16: Variation of the residual error associated with DMS prediction

APPENDIX II

Calibration Tables for Volatile Sulfur Compounds

| DMS | Concentration (ppmv) | Area | Flow (ml/min) | error | error amount | Limits | % deviation |
|--------|----------------------|--------|---------------|---------|--------------|--------|-------------|
| | 0.0025 | 172279 | 1100 | 0.11 | 18950 | 155051 | 11.0% |
| 0.0034 | 257388 | 805 | 0.07 | 18017 | | 7.0% | |
| 0.0073 | 437298 | 380 | 0.15 | 65594 | | 15.0% | |
| 0.0197 | 902742 | 140 | 0.14 | 126383 | | 14.0% | |
| 0.0367 | 1491830 | 75 | 0.09 | 134264 | | 9.0% | |
| 0.5382 | 17535865 | 395 | 0.1 | 1753586 | | 10.0% | |
| 1.4764 | 40781958 | 144 | 0.04 | 1631278 | | 4.0% | |
| 2.9943 | 78453184 | 71 | 0.05 | 3922659 | 86298502 | 5.0% | |

Table 1 : Calibration data for DMS average **9.4%**

| DMDS | Concentration (ppmv) | Area | Flow (ml/min) | error | error amount | Limits | % deviation |
|--------|----------------------|----------|---------------|--------|--------------|----------|-------------|
| | 0.5852 | 67734306 | 71 | 0.09 | 6096087 | 74507737 | 9.0% |
| 0.2885 | 35370783 | 144 | 0.01 | 353707 | | 1.0% | |
| 0.1052 | 15258758 | 395 | 0.05 | 762937 | | 5.0% | |
| 0.0335 | 4447802 | 1240 | 0.05 | 222390 | | 5.0% | |
| 0.0223 | 4367794 | 70 | 0.07 | 305745 | | 7.0% | |
| 0.0104 | 2027238 | 150 | 0.07 | 141906 | | 7.0% | |
| 0.0052 | 1454010 | 300 | 0.11 | 159941 | | 11.0% | |
| 0.0015 | 384474 | 1050 | 0.07 | 26913 | | 7.0% | |
| 0.0004 | 81841 | 4010 | 0.07 | 5728 | 73656 | 7.0% | |

Table 2 : Calibration data for DMDS average **6.6%**

| PM | Concentration (ppmv) | Area | Flow (ml/min) | error | error amount | Limits |
|--------|----------------------|------|---------------|-------|--------------|--------|
| | 0.0102 | 4282 | 945 | 0.07 | 300 | 3426 |
| 0.0260 | 18995 | 370 | 0.09 | 1710 | | |
| 0.0371 | 45071 | 260 | 0.05 | 2254 | | |
| 0.1285 | 193932 | 75 | 0.05 | 9697 | | |
| 0.1338 | 217246 | 72 | 0.07 | 15207 | 260695 | |

Table 3 : Calibration data for PM

| BM | Concentration (ppmv) | Area | Flow (ml/min) | error | error amount | Limits |
|--------|----------------------|------|---------------|--------|--------------|--------|
| | 0.0041 | 2192 | 1990 | 0.09 | 197 | 1973 |
| 0.0086 | 41623 | 945 | 0.07 | 2914 | | |
| 0.0220 | 156469 | 370 | 0.07 | 10953 | | |
| 0.0313 | 377058 | 260 | 0.05 | 18853 | | |
| 0.1085 | 1972017 | 75 | 0.1 | 197202 | 2169219 | |

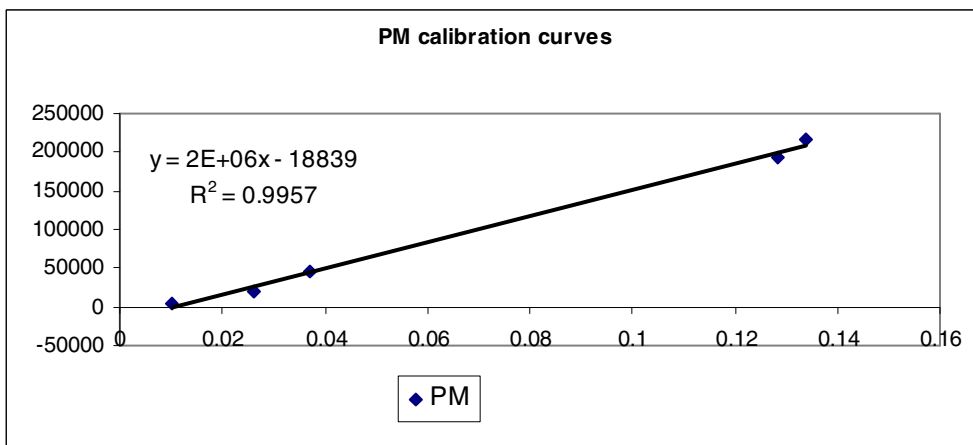
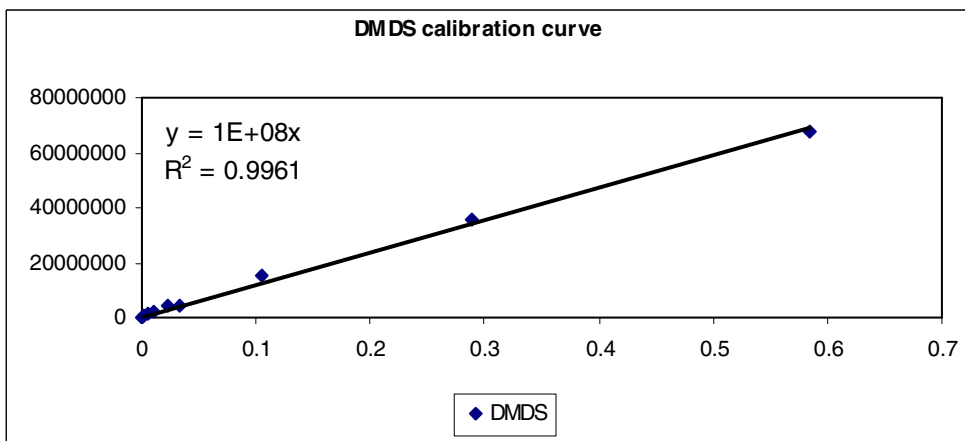
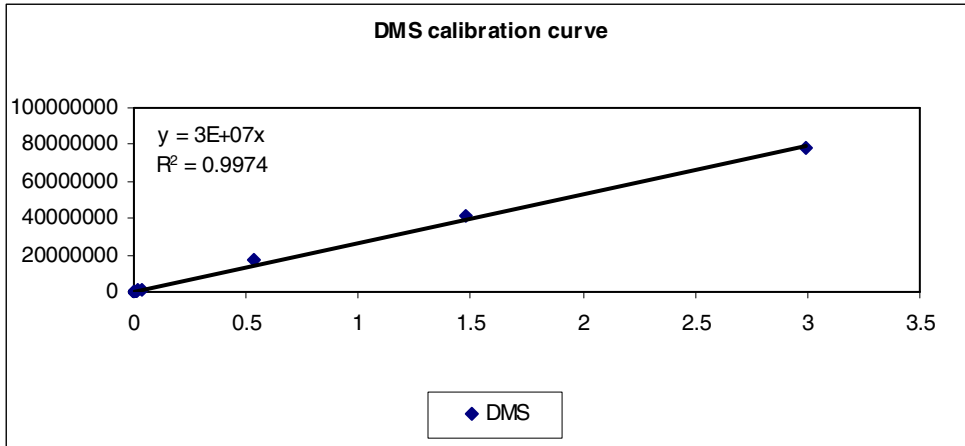
Table 4 : Calibration data for BM

| EM | Concentration (ppmv) | Area | Flow (ml/min) | error | error amount | Limits | % deviation |
|--------|----------------------|------|---------------|--------|--------------|--------|-------------|
| | 0.0127 | 4801 | 2320 | 0.05 | 240 | 4321 | 5.0% |
| 0.0189 | 22056 | 1560 | 0.12 | 2646 | | 12.0% | |
| 0.0603 | 538358 | 490 | 0.1 | 53835 | | 10.0% | |
| 0.1136 | 1114469 | 260 | 0.05 | 55723 | | 5.0% | |
| 0.4101 | 4265026 | 72 | 0.05 | 213251 | 4691529 | 5.0% | |

Table 5 : Calibration data for EM average **7.4%**

Average % deviation per VSC per sampling event (% Error)

| | Headspace | | | Tedlar bag | | |
|-----------|-----------|------|------|------------|------|------|
| | DMS | DMS | MM | DMS | DMS | MM |
| 23-Feb-04 | 16.3 | 14 | 22.6 | 42.6 | / | / |
| 05-Mar-04 | 7.7 | 9 | 1.3 | / | 40.9 | / |
| 12-Mar-04 | 23.2 | 15.1 | 28 | 15.1 | / | / |
| 19-Mar-04 | / | 37.7 | / | 25.4 | / | / |
| 22-Mar-04 | / | 31.1 | / | / | / | / |
| 29-Mar-04 | 15.7 | 9.4 | 19.7 | 26.4 | / | / |
| 02-Apr-04 | 32.4 | 19.3 | 22.7 | / | 22.5 | / |
| 13-May-04 | 19.7 | 24.5 | / | / | / | / |
| 24-May-04 | 8.2 | 30.4 | / | 10.1 | 17.6 | / |
| 27-May-04 | 16.1 | 5.4 | / | / | / | / |
| 03-Jun-04 | 15.4 | 22.8 | 13.2 | / | / | / |
| 7-Jun-04 | 20 | 6.9 | 20.5 | 41.7 | 40.6 | / |
| 10-Jun-04 | 23.8 | 18.8 | 29.9 | / | / | / |
| 15-Jun-04 | 27.5 | 15.6 | 16.9 | 4.1 | 35.8 | / |
| 22-Jul-04 | 26 | 16.7 | 19.4 | / | 17.5 | / |
| 29-Jul-04 | 20.1 | 19.9 | 20.9 | 30.4 | 27.6 | / |
| 6-Aug-04 | 24.2 | 16.5 | 45.3 | / | 8.4 | / |
| 9-Aug-04 | 27.7 | 17.4 | 24.7 | 14.2 | 21.3 | / |
| 16-Aug-04 | 21.8 | 17.3 | 26.7 | 4.6 | 7.5 | / |
| 18-Aug-04 | 16.8 | 13.4 | 23.6 | 15 | / | / |
| 11-Oct-04 | 27.8 | 7 | 32.3 | 7 | 4 | 3.2 |
| 13-Oct-04 | 29.9 | 27.1 | 27.1 | 17.6 | 6.4 | 29.8 |
| 15-Oct-04 | 20.9 | 25.8 | / | 31.6 | 10.5 | / |
| 18-Oct-04 | 22.1 | 14.1 | 43.1 | 4.4 | 17.4 | 13.1 |
| 20-Oct-04 | 19.1 | 22.1 | 16.2 | 1 | 8.5 | / |
| 22-Oct-04 | 22.7 | 19.6 | 30.6 | 7.6 | 5.8 | / |
| Average | 21.0 | 18.3 | 24.2 | 17.6 | 18.3 | 15.4 |



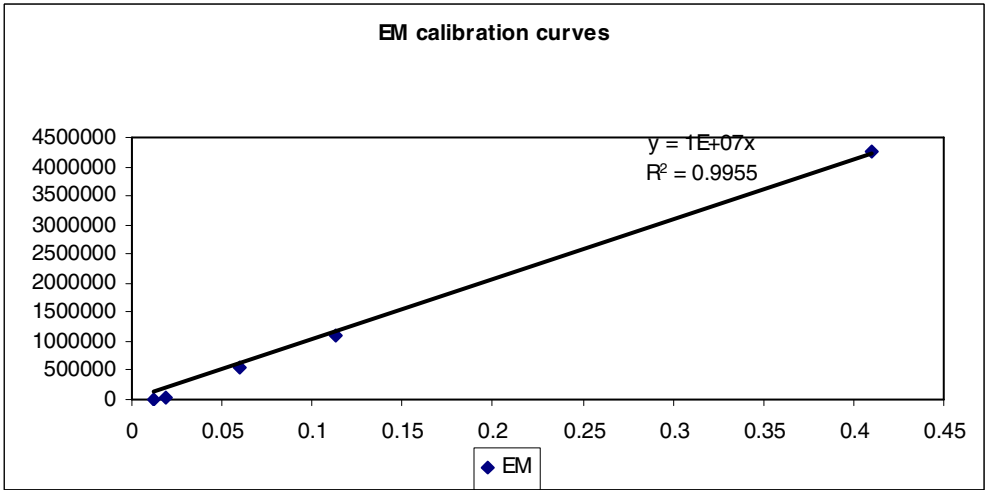
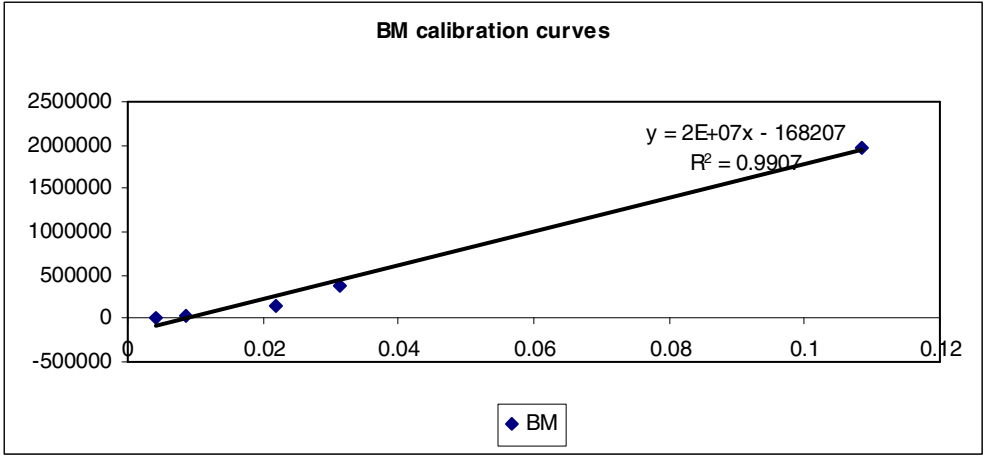


Table 1A: Headspace Method: Annual VSC concentrations in the secondary treatment system.

| | | Annual | | | |
|-------------|--------------|--------------|----------------|------|-------|
| | | mean ppbv | median ppbv | stdv | % dev |
| DMDS | Prim | 1.9 | 0.75 | 1.9 | 103 |
| | Sec 1 | 60 | 19 | 110 | 177 |
| | Sec 3 | 30 | 5.5 | 79 | 260 |
| | Sed T | 0.91 | 0.37 | 1.5 | 170 |
| | Sed B | 110 | 49 | 130 | 124 |
| DMS | Prim | 3.9 | 2.6 | 1.8 | 48 |
| | Sec 1 | 58 | 44 | 53 | 91 |
| | Sec 3 | 41 | 33 | 45 | 109 |
| | Sed T | 9.8 | 3.7 | 9.3 | 95 |
| | Sed B | 83 | 73 | 71 | 85 |
| MM | Prim | 0.17 | 0.17 | 0.00 | 0 |
| | Sec 1 | 5.0 | 3.5 | 5.9 | 118 |
| | Sec 3 | 2.3 | 0.09 | 4.0 | 175 |
| | Sed T | 0.17 | 0.17 | 0.00 | 0 |
| | Sed B | 8.7 | 4.0 | 14 | 157 |

Table 1B: Headspace Method: Seasonal VSC concentrations in the secondary treatment system.

| | | Seasonal | | | | | | | | | | | | | | | |
|-------------|--------------|----------|--------|------|-----|--------|--------|------|-----|--------|--------|------|-----|------|--------|------|-----|
| | | Winter | | | | Spring | | | | Summer | | | | Fall | | | |
| | | mean | median | stdv | % | mean | median | stdv | % | mean | median | stdv | % | mean | median | stdv | % |
| | | ppbv | ppbv | | dev | | ppbv | ppbv | | ppbv | ppbv | | dev | ppbv | ppbv | | dev |
| DMDS | Prim | 1.5 | 0.37 | 2.0 | 133 | 2.5 | 2.5 | 1.9 | 74 | n | n | n | n | n | n | n | n |
| | Sec 1 | 93 | 35 | 170 | 181 | 100 | 60 | 110 | 109 | 29 | 24 | 29 | 99 | 8.0 | 7.5 | 5.1 | 64 |
| | Sec 3 | 64 | 1.1 | 150 | 233 | 39 | 26 | 38 | 99 | 10 | 10 | 8.8 | 87 | 2.8 | 2.6 | 2.7 | 97 |
| | Sed T | 1.8 | 0.37 | 2.6 | 141 | 0.77 | 0.37 | 1.1 | 138 | 0.37 | 0.37 | 0 | 0 | 0.37 | 0.37 | 0 | 0 |
| | Sed B | 200 | 98 | 220 | 106 | 91 | 62 | 91 | 100 | 37 | 27 | 31 | 84 | 90 | 93 | 68 | 75 |
| DMS | Prim | 2.9 | 2.6 | 0.62 | 21 | 5.5 | 5.9 | 2.2 | 40 | n | n | n | n | n | n | n | n |
| | Sec 1 | 78 | 54 | 83 | 107 | 64 | 42 | 52 | 81 | 45 | 32 | 33 | 74 | 40 | 37 | 18 | 45 |
| | Sec 3 | 63 | 28 | 83 | 132 | 38 | 37 | 22 | 57 | 29 | 32 | 16 | 55 | 32 | 35 | 13 | 40 |
| | Sed T | 8.3 | 6.7 | 6.5 | 77 | 9.2 | 2.6 | 8.4 | 91 | 4.8 | 2.6 | 5.5 | 114 | 21 | 26 | 13 | 60 |
| | Sed B | 110 | 73 | 120 | 112 | 83 | 72 | 65 | 79 | 56 | 49 | 19 | 34 | 83 | 79 | 22 | 27 |
| MM | Prim | 0.17 | 0.17 | 0 | 0 | 0.17 | 0.17 | 0 | 0 | n | n | n | n | n | n | n | n |
| | Sec 1 | 7.5 | 5.1 | 9.2 | 122 | 5.0 | 3.00 | 5.8 | 115 | 3.6 | 4.3 | 2.8 | 79 | 3.6 | 3.0 | 3.0 | 85 |
| | Sec 3 | 3.5 | 0.17 | 7.4 | 212 | 1.9 | 0.17 | 2.2 | 118 | 2.3 | 2.9 | 1.8 | 78 | 1.6 | 1.1 | 1.6 | 103 |
| | Sed T | 0.17 | 0.17 | 0 | 0 | 0.17 | 0.17 | 0 | 0 | 0.17 | 0.17 | 0 | 0 | 0.17 | 0.17 | 0 | 0 |
| | Sed B | 19 | 7.2 | 23 | 122 | 2.5 | 1.9 | 3.1 | 122 | 5.5 | 4.7 | 3.8 | 71 | 7.4 | 6.2 | 7.4 | 101 |

Table 2B: Tedlar bag method: Seasonal VSC concentrations in the secondary treatment system

| | | Seasonal | | | | | | | | | | | | | | | |
|------------------------------|----------------|-----------------|--------|------|-------|---------------|--------|------|-------|---------------|--------|------|-------|-------------|--------|------|-------|
| | | Winter | | | | Spring | | | | Summer | | | | Fall | | | |
| | | mean | median | stdv | % dev | mean | median | stdv | % dev | mean | median | stdv | % dev | mean | median | stdv | % dev |
| | | ppbv | ppbv | | | ppbv | ppbv | | | ppbv | ppbv | | | ppbv | ppbv | | |
| DMDS | Sec 1 | 0.85 | 0.50 | 1.0 | 122 | 0.87 | 0.37 | 1.0 | 120 | 2.9 | 1.5 | 4.0 | 137 | 9.3 | 9.5 | 3.8 | 41 |
| | Sec 3 | 1.0 | 0.37 | 1.4 | 142 | 0.76 | 0.37 | 1.0 | 136 | 2.1 | 0.97 | 3.1 | 146 | 4.4 | 2.0 | 4.7 | 106 |
| DMS | Sec 1 | 4.7 | 2.6 | 3.0 | 64 | 4.9 | 4.2 | 2.9 | 58 | 20 | 16 | 15 | 78 | 66 | 58 | 30 | 45 |
| | Sec 3 | 5.7 | 2.6 | 5.4 | 94 | 6.4 | 4.6 | 4.7 | 73 | 20 | 14 | 16 | 79 | 72 | 71 | 15 | 20 |
| Recognition Threshold | | | | | | | | | | | | | | | | | |
| | Sec 1 | 120 | 120 | 0 | 0 | 127 | 113 | 38 | 30 | 554 | 418 | 466 | 84 | 2254 | 2375 | 788 | 35 |
| | Sec 3 | 33 | 33 | 0 | 0 | 143 | 155 | 29 | 20 | 533 | 493 | 224 | 42 | 1080 | 820 | 1130 | 105 |
| Temperature | | | | | | | | | | | | | | | | | |
| | Water | 13.3 | 13.3 | 0.0 | 0 | 22.7 | 23.3 | 1.2 | 5 | 25.6 | 25.6 | 0.3 | 1 | 21.3 | 22.1 | 0.6 | 3 |
| | Ambient | 8.9 | 8.9 | 0.0 | 0 | 28.5 | 26.6 | 3.2 | 11 | 29.8 | 29.4 | 1.7 | 6 | 16.4 | 17.5 | 2.5 | 15 |

Table 2A: Tedlar bag method: Annual VSC concentrations in the secondary treatment system.

| | | Annual | | | |
|-------------|--------------|--------|--------|------|-------|
| | | mean | median | stdv | % dev |
| | | ppbv | ppbv | | |
| DMDS | Sec 1 | 3.3 | 0.79 | 4.3 | 131 |
| | Sec 3 | 2.0 | 0.55 | 3.0 | 153 |
| DMS | Sec 1 | 22 | 8.9 | 29 | 131 |
| | Sec 3 | 24 | 13 | 29 | 119 |

Table 2C: Tedlar bag method: Mean seasonal VSC concentrations and respective odor index

| VSC concentration | | | | | | | | | |
|-------------------|--------|-----|--------|-----|--------|------|------|------|--|
| | Winter | | Spring | | Summer | | Fall | | |
| | DMDS | DMS | DMDS | DMS | DMDS | DMS | DMDS | DMS | |
| Sec 1 | 0.85 | 4.7 | 0.87 | 4.9 | 2.9 | 20.0 | 9.3 | 66.0 | |
| Sec 3 | 1.0 | 5.7 | 0.76 | 6.4 | 2.1 | 20.0 | 4.4 | 72.0 | |
| VSC Odor Index | | | | | | | | | |
| | Winter | | Spring | | Summer | | Fall | | |
| | DMDS | DMS | DMDS | DMS | DMDS | DMS | DMDS | DMS | |
| Sec 1 | 0.9 | 0.5 | 0.9 | 0.5 | 2.9 | 2.2 | 9.3 | 7.3 | |
| Sec 3 | 1.0 | 0.6 | 0.8 | 0.7 | 2.1 | 2.2 | 4.4 | 8.0 | |

VSC emission rates (1st pass SAT)

| Tedlar bag | DMDS ppbv ug/l | DMS ppbv ug/l | air flow L/day *10 | air flow L/day | DMDS g/day | DMS g/day | DMDS kg/pass- day | DMS kg/pass-day |
|------------|----------------------|---------------------|--------------------------|-------------------|---------------|--------------|-------------------------|--------------------|
| 23-Feb-04 | 0.6 | 4.7 | 97853 | 978532 | 0.6 | 4.6 | 0.2 | 1.4 |
| 5-Mar-04 | 0.4 | 9.6 | 159011 | 1590114 | 0.6 | 15.3 | 0.2 | 4.5 |
| 12-Mar-04 | 0.5 | 2.6 | 145557 | 1455566 | 0.8 | 3.8 | 0.2 | 1.1 |
| 19-Mar-04 | 0.4 | 2.6 | 89699 | 896988 | 0.3 | 2.3 | 0.1 | 0.7 |
| 22-Mar-04 | 0.4 | 2.6 | 122316 | 1223165 | 0.5 | 3.2 | 0.1 | 0.9 |
| 29-Mar-04 | 3.2 | 2.6 | 240556 | 2405557 | 7.7 | 6.3 | 2.3 | 1.9 |
| 2-Apr-04 | 0.5 | 8.3 | 195706 | 1957064 | 1.0 | 16.2 | 0.3 | 4.8 |
| Mean | | | | 1500998 | 1.6 | 7.4 | 0.5 | 2.2 |
| 13-May-04 | 3.2 | 4.2 | 322100 | 3221001 | 10.3 | 13.5 | 3.1 | 4.0 |
| 24-May-04 | 0.9 | 9.5 | 232401 | 2324013 | 2.2 | 22.1 | 0.6 | 6.6 |
| 27-May-04 | 0.5 | 8.3 | 220170 | 2201697 | 1.1 | 18.3 | 0.3 | 5.4 |
| 3-Jun-04 | 0.4 | 2.6 | 354718 | 3547178 | 1.3 | 9.2 | 0.4 | 2.7 |
| 7-Jun-04 | 0.4 | 2.6 | 428108 | 4281077 | 1.6 | 11.1 | 0.5 | 3.3 |
| 10-Jun-04 | 0.4 | 4.5 | 228324 | 2283241 | 0.8 | 10.3 | 0.3 | 3.1 |
| 15-Jun-04 | 0.4 | 2.6 | 220170 | 2201697 | 0.8 | 5.7 | 0.2 | 1.7 |
| Mean | | | | 2865700 | 2.6 | 12.9 | 0.8 | 3.8 |
| 22-Jul-04 | 2.7 | 15.0 | 346563 | 3465634 | 9.4 | 52.0 | 2.8 | 15.5 |
| 29-Jul-04 | 0.4 | 7.2 | 357572 | 3575718 | 1.3 | 25.7 | 0.4 | 7.7 |
| 6-Aug-04 | 1.3 | 20.0 | 318023 | 3180228 | 4.1 | 63.6 | 1.2 | 18.9 |
| 9-Aug-04 | 11.0 | 50.0 | 285405 | 2854051 | 31.4 | 142.7 | 9.3 | 42.5 |
| 16-Aug-04 | 1.7 | 17.0 | 212015 | 2120152 | 3.6 | 36.0 | 1.1 | 10.7 |
| 18-Aug-04 | 0.6 | 9.9 | 326177 | 3261773 | 1.8 | 32.3 | 0.5 | 9.6 |
| Mean | | | | 3076259 | 8.6 | 58.7 | 2.6 | 17.5 |
| 11-Oct-04 | 11.0 | 49.0 | 326177 | 3261773 | 35.9 | 159.8 | 10.7 | 47.6 |
| 13-Oct-04 | 6.1 | 41.0 | 330254 | 3302545 | 20.1 | 135.4 | 6.0 | 40.3 |
| 15-Oct-04 | 4.7 | 67.0 | 285405 | 2854051 | 13.4 | 191.2 | 4.0 | 56.9 |
| 18-Oct-04 | 11.0 | 120.0 | 313946 | 3139456 | 34.5 | 376.7 | 10.3 | 112.1 |
| 20-Oct-04 | 8.0 | 73.0 | 326177 | 3261773 | 26.1 | 238.1 | 7.8 | 70.9 |
| 22-Oct-04 | 15.0 | 44.0 | 322100 | 3221001 | 48.3 | 141.7 | 14.4 | 42.2 |
| Mean | | | | 3173433 | 29.7 | 207.2 | 8.8 | 61.7 |

VSC emission rates (3rd pass SAT)

| Tedlar bag | DMS | DMS | Air flow | Air flow | DMS | DMS | DMS | DMS |
|------------|------|------|----------|----------------|-------------|--------------|-------------|-------------|
| | ppbv | ppbv | L/day | L/day | ppbv | ppbv | kg/pass-day | kg/pass-day |
| | | | | | g/day | g/day | | |
| | | | | | | | | |
| 23-Feb-04 | 4.2 | 2.6 | 97853 | 978532 | 4.1 | 2.5 | 1.2 | 0.8 |
| 5-Mar-04 | 0.37 | 12.0 | 159011 | 1590114 | 0.6 | 19.1 | 0.2 | 5.7 |
| 12-Mar-04 | 1.0 | 2.6 | 371027 | 3710267 | 3.7 | 9.6 | 1.1 | 2.9 |
| 19-Mar-04 | 0.37 | 2.6 | 81544 | 815443 | 0.3 | 2.1 | 0.1 | 0.6 |
| 22-Mar-04 | 0.37 | 2.6 | 207938 | 2079380 | 0.8 | 5.4 | 0.2 | 1.6 |
| 29-Mar-04 | 0.37 | 2.6 | 428108 | 4281077 | 1.6 | 11.1 | 0.5 | 3.3 |
| 2-Apr-04 | 0.37 | 15.0 | 212015 | 2120152 | 0.8 | 31.8 | 0.2 | 9.5 |
| Mean | | | | 2224995 | 1.7 | 11.7 | 0.5 | 3.5 |
| | | | | | | | | |
| 13-May-04 | 3.1 | 2.6 | 289482 | 2894823 | 9.0 | 7.5 | 2.7 | 2.2 |
| 24-May-04 | 0.37 | 2.6 | 285405 | 2854051 | 1.1 | 7.4 | 0.3 | 2.2 |
| 27-May-04 | 0.37 | 15.0 | 248710 | 2487102 | 0.9 | 37.3 | 0.3 | 11.1 |
| 3-Jun-04 | 0.37 | 2.6 | 289482 | 2894823 | 1.1 | 7.5 | 0.3 | 2.2 |
| 7-Jun-04 | 0.37 | 4.6 | 118239 | 1182393 | 0.4 | 5.4 | 0.1 | 1.6 |
| 10-Jun-04 | 0.37 | 8.4 | 203861 | 2038608 | 0.8 | 17.1 | 0.2 | 5.1 |
| 15-Jun-04 | 0.37 | 9.0 | 159011 | 1590114 | 0.6 | 14.3 | 0.2 | 4.3 |
| Mean | | | | 2277416 | 2.0 | 13.8 | 0.6 | 4.1 |
| | | | | | | | | |
| 22-Jul-04 | 1.2 | 13.0 | 550424 | 5504242 | 6.6 | 71.6 | 2.0 | 21.3 |
| 29-Jul-04 | 0.4 | 8.7 | 357572 | 3575718 | 1.3 | 31.1 | 0.4 | 9.3 |
| 6-Aug-04 | 1.1 | 13.0 | 318023 | 3180228 | 3.5 | 41.3 | 1.0 | 12.3 |
| 9-Aug-04 | 8.3 | 51.0 | 358795 | 3587950 | 29.8 | 183.0 | 8.9 | 54.5 |
| 16-Aug-04 | 0.83 | 15.0 | 212015 | 2120152 | 1.8 | 31.8 | 0.5 | 9.5 |
| 18-Aug-04 | 0.73 | 18.0 | 326177 | 3261773 | 2.4 | 58.7 | 0.7 | 17.5 |
| Mean | | | | 3538344 | 7.6 | 69.6 | 2.2 | 20.7 |
| | | | | | | | | |
| 11-Oct-04 | 1.7 | 55.0 | 326177 | 3261773 | 5.5 | 179.4 | 1.7 | 53.4 |
| 13-Oct-04 | 12.0 | 62.0 | 330254 | 3302545 | 39.6 | 204.8 | 11.8 | 60.9 |
| 15-Oct-04 | 1.6 | 73.0 | 285405 | 2854051 | 4.6 | 208.3 | 1.4 | 62.0 |
| 18-Oct-04 | 2.3 | 77.0 | 313946 | 3139456 | 7.2 | 241.7 | 2.1 | 71.9 |
| 20-Oct-04 | 0.37 | 68.0 | 326177 | 3261773 | 1.2 | 221.8 | 0.4 | 66.0 |
| 22-Oct-04 | 8.5 | 97.0 | 322100 | 3221001 | 27.4 | 312.4 | 8.1 | 93.0 |
| Mean | | | | 3173433 | 14.3 | 228.1 | 4.2 | 67.9 |
| | | | | | | | | |

Summary of Winter Sampling Events

| Headspace | | | | Tedlar bag | | | | | |
|------------------|--------|-------|-------|------------|------------------|-------|------|------|-----|
| | DMDS | DMS | MM | | DMDS | DMS | MM | | |
| | ppbv | ppbv | ppbv | | ppbv | ppbv | ppbv | | |
| Detection Limit | 0.74 | 5.2 | 0.34 | | 0.74 | 5.2 | 0.34 | | |
| 23-Feb-04 | prim | 2.6 | 2.6 | 1.7 | 23-Feb-04 | blank | 0.74 | 2.6 | 1.7 |
| | sec1 | 56.0 | 53.0 | 13.0 | | Prim | 3.2 | 2.6 | 1.7 |
| | sec3 | 29.0 | 40.0 | 1.7 | | sec1 | 0.64 | 2.6 | 6.6 |
| | sedT | 4.2 | 14.0 | 1.7 | | sec3 | 4.2 | 2.6 | 7.6 |
| | sed B2 | 380.0 | 180.0 | 1.7 | | | / | / | / |
| 05-Mar-04 | prim | 0.75 | 2.6 | 1.7 | 05-Mar-04 | blank | 0.37 | 2.6 | 1.7 |
| | sec1 | 470.0 | 250.0 | 26.0 | | Prim | 0.37 | 2.6 | 1.7 |
| | sec3 | 400.0 | 250.0 | 20.0 | | sec1 | 0.37 | 9.6 | 1.7 |
| | sedT | 0.37 | 2.6 | 1.7 | | sec3 | 0.37 | 12.0 | 1.7 |
| | sed B2 | 410.0 | 340.0 | 23.0 | | sedT | 0.37 | 2.6 | 1.7 |
| 12-Mar-04 | prim | 5.6 | 2.6 | 1.7 | 12-Mar-04 | blank | 0.37 | 2.6 | 1.7 |
| | sec1 | 35.0 | 55.0 | 5.1 | | Prim | 0.37 | 2.6 | 1.7 |
| | sec3 | 15.0 | 28.0 | 3.6 | | sec1 | 0.37 | 2.6 | 1.7 |
| | sedT | 0.37 | 6.7 | 1.7 | | sec3 | 0.37 | 2.6 | 1.7 |
| | sed B2 | 36.0 | 41.0 | 7.2 | | sedT | 0.37 | 2.6 | 1.7 |
| 19-Mar-04 | prim | 0.37 | 2.6 | 1.7 | 19-Mar-04 | blank | 0.37 | 2.6 | 1.7 |
| | sec1 | 0.37 | 19.0 | 1.7 | | Prim | 0.37 | 2.6 | 1.7 |
| | sec3 | 0.37 | 26.0 | 1.7 | | sec1 | 0.37 | 2.6 | 1.7 |
| | sedT | 0.37 | 2.6 | 1.7 | | sec3 | 0.37 | 2.6 | 1.7 |
| | sed B2 | 0.37 | 2.6 | 1.7 | | sedT | / | / | / |
| 22-Mar-04 | prim | 0.37 | 2.6 | 1.7 | 22-Mar-04 | blank | 0.37 | 2.6 | 1.7 |
| | sec1 | 2.0 | 2.6 | 1.7 | | Prim | 0.37 | 2.6 | 1.7 |
| | sec3 | 0.37 | 26.0 | 1.7 | | sec1 | 0.37 | 2.6 | 1.7 |
| | sedT | 0.37 | 2.6 | 1.7 | | sec3 | 0.37 | 2.6 | 1.7 |
| | sed B2 | 0.37 | 4.6 | 1.7 | | | 0.37 | 2.6 | 1.7 |
| 29-Mar-04 | prim | 0.37 | 2.6 | 1.7 | 29-Mar-04 | blank | 0.37 | 2.6 | 1.7 |
| | sec1 | 69.0 | 110.0 | 5.4 | | Prim | 0.37 | 2.6 | 1.7 |
| | sec3 | 0.37 | 25.0 | 1.7 | | sec1 | 3.2 | 2.6 | 1.7 |
| | sedT | 6.6 | 7.7 | 1.7 | | sec3 | 0.37 | 2.6 | 1.7 |
| | sed B2 | 490.0 | 73.0 | 31.0 | | sedT | 0.89 | 2.6 | 1.7 |
| 02-Apr-04 | prim | 0.37 | 2.6 | 1.7 | 02-Apr-04 | blank | 0.37 | 2.6 | 1.7 |
| | sec1 | 19.0 | 54.0 | 3.0 | | Prim | 0.37 | 2.6 | 1.7 |
| | sec3 | 1.1 | 44.0 | 1.7 | | sec1 | 0.37 | 8.3 | 1.7 |
| | sedT | 0.37 | 20.0 | 1.7 | | sec3 | 0.37 | 15.0 | 1.7 |
| | sed B2 | 98.0 | 110.0 | 3.4 | | sedT | 0.37 | 2.6 | 1.7 |

Summary of Spring Sampling Events

| Headspace | | | | Tedlar bag | | | | | |
|------------------|--------------|-------|-------|------------|------------------|-------|------|------|-----|
| | DMS | DMS | MM | | DMS | DMS | MM | | |
| | ppbv | ppbv | ppbv | | ppbv | ppbv | ppbv | | |
| Detection Limit | 0.74 | 5.2 | 0.34 | | 0.74 | 5.2 | 0.34 | | |
| 13-May-04 | blank | 2.8 | 2.6 | 1.7 | 13-May-04 | blank | 3.5 | 2.6 | 1.7 |
| | prim | 3.2 | 7.7 | 1.7 | | Prim | 2.8 | 2.6 | 1.7 |
| | sec1 | 60.0 | 29.0 | 1.7 | | sec1 | 3.2 | 4.2 | 1.7 |
| | sec3 | 53.0 | 21.0 | 1.7 | | sec3 | 3.1 | 2.6 | 1.7 |
| | sedT | 3.2 | 15.0 | 1.7 | | sedT | 3.0 | 2.6 | 1.7 |
| | sed B2 | 220.0 | 160.0 | 1.7 | | | | | |
| 24-May-04 | blank | 0.37 | 2.6 | 1.7 | 24-May-04 | blank | 0.37 | 2.6 | 1.7 |
| | prim | 1.8 | 5.1 | 1.7 | | Prim | 0.37 | 2.6 | 1.7 |
| | sec1 | 260.0 | 170.0 | 8.9 | | sec1 | 0.93 | 9.5 | 1.7 |
| | sec3 | 74.0 | 79.0 | 4.6 | | sec3 | 0.37 | 2.6 | 1.7 |
| | sedT | 0.37 | 19.0 | 1.7 | | sedT | 0.83 | 2.6 | 1.7 |
| | sed B2 | 210.0 | 170.0 | 8.8 | | | | | |
| 27-May-04 | prim | 0.37 | 2.6 | 1.7 | 27-May-04 | blank | 0.37 | 2.6 | 1.7 |
| | sec1 | 19.0 | 54.0 | 3.0 | | Prim | 0.37 | 2.6 | 1.7 |
| | sec3 | 1.1 | 44.0 | 1.7 | | sec1 | 0.37 | 8.3 | 1.7 |
| | sedT | 0.37 | 20.0 | 1.7 | | sec3 | 0.37 | 15.0 | 1.7 |
| | sed B2 | 98.0 | 110.0 | 3.4 | | sedT | / | / | / |
| 03-Jun-04 | prim | 4.7 | 6.7 | 1.7 | 03-Jun-04 | blank | / | / | / |
| | sec1 | 67.0 | 42.0 | 8.0 | | sec1 | 0.37 | 2.6 | 1.7 |
| | sec3 | 26.0 | 37.0 | 4.6 | | sec3 | 0.37 | 2.6 | 1.7 |
| | sedT | 0.37 | 2.6 | 1.7 | | sedT | 0.37 | 2.6 | 1.7 |
| | sed B2 | 11.0 | 12.6 | 1.7 | | | 0.37 | 2.6 | 1.7 |
| 7-Jun-04 | sec1 | 10.0 | 22.0 | 1.7 | 7-Jun-04 | blank | 1.8 | 2.6 | 1.7 |
| | sec3 | 2.5 | 15.3 | 1.7 | | sec1 | 0.37 | 2.6 | 1.7 |
| | sedT | 0.37 | 2.6 | 1.7 | | sec3 | 0.64 | 2.6 | 1.7 |
| | sedB avge | 62.0 | 72.0 | 1.7 | | sedT | 0.37 | 2.6 | 1.7 |
| 10-Jun-04 | sec1 | 250.0 | 92.0 | 15.0 | 10-Jun-04 | blank | 1.4 | 2.6 | 1.7 |
| | sec3 | 100.0 | 48.0 | 3.6 | | sec1 | 0.37 | 4.5 | 1.7 |
| | sedT | 0.37 | 2.6 | 1.7 | | sec3 | 0.37 | 8.4 | 1.7 |
| | sedB avge | 22.0 | 28.0 | 1.9 | | sedT | 0.37 | 2.6 | 1.7 |
| 15-Jun-04 | sec1 | 31.0 | 41.0 | 1.7 | 15-Jun-04 | blank | 0.90 | 2.6 | 1.7 |
| | sec3 | 13.0 | 24.0 | 1.7 | | sec1 | 0.37 | 2.6 | 1.7 |
| | sedT | 0.37 | 5.0 | 1.7 | | sec3 | 0.37 | 9.0 | 1.7 |
| | sedB avge | 11.0 | 27.0 | 2.6 | | sedT | / | / | / |

Summary of Summer Sampling Events

| Headspace | | | | Tedlar bag | | | | | |
|------------------|------------|------|------|------------|------------------|-------|------|------|------|
| | DMDS | DMS | MM | | DMDS | DMS | MM | | |
| | ppbv | ppbv | ppbv | | ppbv | ppbv | ppbv | | |
| Detection Limit | 0.74 | 5.2 | 0.34 | | 0.74 | 5.2 | 0.34 | | |
| 22-Jul-04 | prim | 6.4 | 6.6 | 0.17 | 22-Jul-04 | blank | 0.83 | 2.6 | 0.17 |
| | sec1 | 63.0 | 95.0 | 6.7 | | Prim | 1.0 | 2.6 | 1.3 |
| | sec3 | 20.0 | 50.0 | 2.1 | | sec1 | 2.7 | 15.0 | 2.0 |
| | sedT | 0.37 | 16.0 | 0.17 | | sec3 | 1.2 | 13.0 | 0.17 |
| | sedB avge | 30.0 | 65.0 | 4.8 | | | | | |
| 29-Jul-04 | prim | 1.4 | 6.4 | 0.17 | 29-Jul-04 | blank | 0.52 | 2.6 | 0.17 |
| | sec1 | 0.37 | 22.0 | 0.17 | | Prim | 0.37 | 2.6 | 0.17 |
| | sec3 | 0.37 | 6.7 | 0.17 | | sec1 | 0.37 | 7.2 | 0.17 |
| | sedT | 0.37 | 2.6 | 0.17 | | sec3 | 0.37 | 8.7 | 0.17 |
| | sedB avge | 14.0 | 46.0 | 5.1 | | | | | |
| 6-Aug-04 | sec1 | 62.0 | 75.0 | 5.9 | 6-Aug-04 | blank | 0.37 | 2.6 | 0.17 |
| | sec3 | 11.0 | 32.0 | 4.2 | | sec1 | 1.3 | 20.0 | 0.17 |
| | sedT | 0.37 | 2.6 | 0.17 | | sec3 | 1.1 | 13.0 | 0.17 |
| | sedB avge | 23.0 | 46.0 | 2.8 | | | | | |
| 9-Aug-04 | sec1 | 34.0 | 42.0 | 4.9 | 9-Aug-04 | blank | 0.37 | 2.6 | 0.17 |
| | sec3 | 20.0 | 41.0 | 3.6 | | sec1 | 11.0 | 50.0 | 0.17 |
| | sedT | 0.37 | 2.6 | 0.17 | | sec3 | 8.3 | 51.0 | 0.17 |
| | sedB avge | 36.0 | 51.0 | 4.6 | | | | | |
| 16-Aug-04 | sec1 | 14.0 | 19.0 | 3.6 | 16-Aug-04 | blank | 0.37 | 2.6 | 0.17 |
| | sec3 | 9.7 | 31.0 | 3.6 | | sec1 | 1.7 | 17.0 | 0.17 |
| | sedT | 0.37 | 2.6 | 0.17 | | sec3 | 0.83 | 15.0 | 0.17 |
| | sedB avge | 21.0 | 37.0 | 2.5 | | | | | |
| 18-Aug-04 | sec1 | 0.91 | 15.0 | 0.17 | 18-Aug-04 | blank | 0.37 | 2.6 | 0.17 |
| | sec3 | 0.37 | 15.0 | 0.17 | | sec1 | 0.37 | 9.9 | 0.17 |
| | sedT | 0.37 | 2.6 | 0.17 | | sec3 | 0.73 | 18.0 | 0.17 |
| | sed B avge | 99.0 | 90.0 | 13.0 | | | | | |

Summary of Fall Sampling Events

| Headspace | | DMDS | DMS | MM | Tedlar bag | | DMDS | DMS | MM |
|-----------------|-----------|-------|-------|------|------------|-------|------|-------|------|
| | | ppbv | ppbv | ppbv | | | ppbv | ppbv | ppbv |
| Detection Limit | | 0.74 | 5.2 | 0.34 | | | 0.74 | 5.2 | 0.34 |
| 11-Oct-04 | sec1 | 17.0 | 66.0 | 3.8 | 11-Oct-04 | sec1 | 11.0 | 49.0 | 3.0 |
| | sec3 | 7.8 | 42.0 | 0.17 | | sec3 | 1.7 | 55.0 | 0.17 |
| | sedT | 0.37 | 23.0 | 0.17 | | | | | |
| | sedB avge | 12.0 | 77.0 | 0.17 | | | | | |
| 13-Oct-04 | sec1 | 9.3 | 21.0 | 0.17 | 13-Oct-04 | blank | 0.37 | 2.6 | 0.17 |
| | sec3 | 3.2 | 49.0 | 3.6 | | sec1 | 6.1 | 41.0 | 6.6 |
| | sedT | 0.37 | 29.0 | 0.17 | | sec3 | 12.0 | 62.0 | 14.0 |
| | sedB avge | 94.0 | 94.2 | 12.0 | | | | | |
| 15-Oct-04 | sec1 | 2.6 | 46.0 | 3.3 | 15-Oct-04 | sec1 | 4.7 | 67.0 | 3.3 |
| | sec3 | 0.37 | 33.0 | 0.17 | | sec3 | 1.6 | 73.0 | 0.17 |
| | sedT | 0.37 | 30.0 | 0.17 | | | | | |
| | sedB avge | 92.0 | 79.0 | 0.17 | | | | | |
| 18-Oct-04 | sec1 | 6.5 | 53.0 | 9.2 | 18-Oct-04 | sec1 | 11.0 | 120.0 | 9.6 |
| | sec3 | 2.3 | 36.0 | 3.2 | | sec3 | 2.3 | 77.0 | 18.0 |
| | sedB avge | 172.9 | 120.0 | 19.5 | | | | | |
| 20-Oct-04 | sec1 | 4.0 | 25.0 | 2.2 | 20-Oct-04 | blank | 0.37 | 2.6 | 0.17 |
| | sec3 | 0.37 | 17.0 | 0.17 | | sec1 | 8.0 | 73.0 | 5.6 |
| | sedB avge | 160.0 | 78.0 | 6.8 | | sec3 | 0.37 | 68.0 | 0.17 |
| 22-Oct-04 | sec1 | 8.5 | 28.0 | 2.7 | 22-Oct-04 | sec1 | 15.0 | 44.0 | 4.0 |
| | sec3 | 2.8 | 17.0 | 2.1 | | sec3 | 8.5 | 97.0 | 0.17 |
| | sedT | 0.37 | 2.6 | 0.17 | | | | | |
| | sedB avge | 14.0 | 52.0 | 5.6 | | | | | |

Tedlar bags Summary blank samples

| Tedlar bag | | | DMDS ppbv 0.74 | DMS ppbv 5.2 | MM ppbv 0.34 |
|-------------------|-------------|-------|-------------------------------|-----------------------------|-----------------------------|
| | LOQs | | | | |
| Winter | 23-Feb-04 | blank | 0.74 | 2.6 | 0.17 |
| | 5-Mar-04 | blank | 0.37 | 2.6 | 0.17 |
| | 12-Mar-04 | blank | 0.37 | 2.6 | 0.17 |
| | 19-Mar-04 | blank | 0.37 | 2.6 | 0.17 |
| | 22-Mar-04 | blank | 0.37 | 2.6 | 0.17 |
| | 29-Mar-04 | blank | 0.37 | 2.6 | 0.17 |
| | 2-Apr-04 | blank | 0.37 | 2.6 | 0.17 |
| Spring | 13-May-04 | blank | 3.5 | 2.6 | 0.17 |
| | 24-May-04 | blank | 0.37 | 2.6 | 0.17 |
| | 27-May-04 | blank | 0.37 | 2.6 | 0.17 |
| | 3-Jun-04 | blank | 0.37 | 2.6 | 0.17 |
| | 7-Jun-04 | blank | 1.8 | 2.6 | 0.17 |
| | 10-Jun-04 | blank | 1.4 | 2.6 | 0.17 |
| | 15-Jun-04 | blank | 0.90 | 2.6 | 0.17 |
| Summer | 22-Jul-04 | blank | 0.83 | 2.6 | 0.17 |
| | 29-Jul-04 | blank | 0.37 | 2.6 | 0.17 |
| | 6-Aug-04 | blank | 0.37 | 2.6 | 0.17 |
| | 9-Aug-04 | blank | 0.37 | 2.6 | 0.17 |
| | 16-Aug-04 | blank | 0.37 | 2.6 | 0.17 |
| | 18-Aug-04 | blank | 0.37 | 2.6 | 0.17 |
| Fall | 11-Oct-04 | | | | |
| | 13-Oct-04 | blank | 0.37 | 2.6 | 0.17 |
| | 15-Oct-04 | | | | |
| | 18-Oct-04 | | | | |
| | 20-Oct-04 | blank | 0.37 | 2.6 | 0.17 |
| | 22-Oct-04 | | | | |

Summary Primary Clarification Tank Samples

| Headspace | | | DMS | DMS | MM |
|---------------|-----------|------|------|------|------|
| | | | ppbv | ppbv | ppbv |
| LOQ | | | 0.74 | 5.2 | 0.34 |
| Winter | 23-Feb-04 | prim | 2.6 | 2.6 | 0.17 |
| | 5-Mar-04 | prim | 0.75 | 4.0 | 0.17 |
| | 12-Mar-04 | prim | 5.6 | 2.6 | 0.17 |
| | 19-Mar-04 | prim | 0.37 | 2.6 | 0.17 |
| | 22-Mar-04 | prim | 0.37 | 2.6 | 0.17 |
| | 29-Mar-04 | prim | 0.37 | 3.7 | 0.17 |
| | 2-Apr-04 | prim | 0.37 | 2.6 | 0.17 |
| Spring | 13-May-04 | prim | 3.2 | 7.7 | 0.17 |
| | 24-May-04 | prim | 1.8 | 5.1 | 0.17 |
| | 27-May-04 | prim | 0.37 | 2.6 | 0.17 |
| | 3-Jun-04 | prim | 4.7 | 6.7 | 0.17 |
| Summer | 22-Jul-04 | prim | | | |
| | 29-Jul-04 | prim | | | |

| Tedlar bag | | | DMS | DMS | MM |
|---------------|-----------|------|------|------|------|
| | | | ppbv | ppbv | ppbv |
| LOQ | | | 0.74 | 5.2 | 0.34 |
| Winter | 23-Feb-04 | Prim | 3.2 | 2.6 | 0.17 |
| | 5-Mar-04 | Prim | 0.37 | 2.6 | 0.17 |
| | 12-Mar-04 | Prim | 0.37 | 2.6 | 0.17 |
| | 19-Mar-04 | Prim | 0.37 | 2.6 | 0.17 |
| | 22-Mar-04 | Prim | 0.37 | 2.6 | 0.17 |
| | 29-Mar-04 | Prim | 0.37 | 2.6 | 0.17 |
| | 2-Apr-04 | Prim | 0.37 | 2.6 | 0.17 |
| Spring | 13-May-04 | Prim | 2.8 | 2.6 | 0.17 |
| | 24-May-04 | Prim | 0.37 | 2.6 | 0.17 |
| | 27-May-04 | Prim | 0.37 | 2.6 | 0.17 |
| Summer | 22-Jul-04 | Prim | 1.0 | 2.6 | 1.3 |
| | 29-Jul-04 | Prim | 0.37 | 2.6 | 0.17 |

Summary Secondary Aeration Tank Samples (1st pass)

| Headspace | | | DMS | DMS | MM |
|-----------|-----------|------|-------|-------|------|
| | | | ppbv | ppbv | ppbv |
| LOQ | | | 0.74 | 5.2 | 0.34 |
| Winter | 23-Feb-04 | sec1 | 56.0 | 53.0 | 13.0 |
| | 05-Mar-04 | sec1 | 470.0 | 250.0 | 26.0 |
| | 12-Mar-04 | sec1 | 35.0 | 55.0 | 5.1 |
| | 19-Mar-04 | sec1 | 0.37 | 19.0 | 0.17 |
| | 22-Mar-04 | sec1 | 2.0 | 2.6 | 0.17 |
| | 29-Mar-04 | sec1 | 69.0 | 110.0 | 5.4 |
| | 02-Apr-04 | sec1 | 19.0 | 54.0 | 3.0 |
| Spring | 13-May-04 | sec1 | 60.0 | 29.0 | 0.17 |
| | 24-May-04 | sec1 | 260.0 | 170.0 | 8.9 |
| | 27-May-04 | sec1 | 19.0 | 54.0 | 3.0 |
| | 03-Jun-04 | sec1 | 67.0 | 42.0 | 8.0 |
| | 7-Jun-04 | sec1 | 10.0 | 22.0 | 0.17 |
| | 10-Jun-04 | sec1 | 250.0 | 92.0 | 15.0 |
| | 15-Jun-04 | sec1 | 31.0 | 41.0 | 0.17 |
| Summer | 22-Jul-04 | sec1 | 63.0 | 95.0 | 6.7 |
| | 29-Jul-04 | sec1 | 0.37 | 22.0 | 0.17 |
| | 6-Aug-04 | sec1 | 62.0 | 75.0 | 5.9 |
| | 9-Aug-04 | sec1 | 34.0 | 42.0 | 4.9 |
| | 16-Aug-04 | sec1 | 14.0 | 19.0 | 3.6 |
| | 18-Aug-04 | sec1 | 0.91 | 15.0 | 0.17 |
| Fall | 11-Oct-04 | sec1 | 17.0 | 66.0 | 3.8 |
| | 13-Oct-04 | sec1 | 9.3 | 21.0 | 0.17 |
| | 15-Oct-04 | sec1 | 2.6 | 46 | 3.3 |
| | 18-Oct-04 | sec1 | 6.5 | 53.0 | 9.2 |
| | 20-Oct-04 | sec1 | 4.0 | 25.0 | 2.2 |
| | 22-Oct-04 | sec1 | 8.5 | 28.0 | 2.7 |

Summary Secondary Aeration Tank Samples (1st pass)

| Tedlar bag | | | DMDS | DMS | MM |
|------------|-----------|------|------|-------|------|
| | | | ppbv | ppbv | ppbv |
| LOQ | | | 0.74 | 5.2 | 0.34 |
| Winter | 23-Feb-04 | sec1 | 0.64 | 4.7 | 6.6 |
| | 05-Mar-04 | sec1 | 0.37 | 9.6 | 0.17 |
| | 12-Mar-04 | sec1 | 0.53 | 2.6 | 0.17 |
| | 19-Mar-04 | sec1 | 0.37 | 2.6 | 0.17 |
| | 22-Mar-04 | sec1 | 0.37 | 2.6 | 0.17 |
| | 29-Mar-04 | sec1 | 3.2 | 2.6 | 0.17 |
| | 02-Apr-04 | sec1 | 0.50 | 8.3 | 0.17 |
| Spring | 13-May-04 | sec1 | 3.2 | 4.2 | 0.17 |
| | 24-May-04 | sec1 | 0.93 | 9.5 | 0.17 |
| | 27-May-04 | sec1 | 0.50 | 8.3 | 0.17 |
| | 03-Jun-04 | sec1 | 0.37 | 2.6 | 0.17 |
| | 7-Jun-04 | sec1 | 0.37 | 2.6 | 0.17 |
| | 10-Jun-04 | sec1 | 0.37 | 4.5 | 0.17 |
| | 15-Jun-04 | sec1 | 0.37 | 2.6 | 0.17 |
| Summer | 22-Jul-04 | sec1 | 2.7 | 15.0 | 2.0 |
| | 29-Jul-04 | sec1 | 0.37 | 7.2 | 0.17 |
| | 6-Aug-04 | sec1 | 1.3 | 20.0 | 0.17 |
| | 9-Aug-04 | sec1 | 11.0 | 50.0 | 0.17 |
| | 16-Aug-04 | sec1 | 1.7 | 17.0 | 0.17 |
| | 18-Aug-04 | sec1 | 0.56 | 9.9 | 0.17 |
| Fall | 11-Oct-04 | sec1 | 11.0 | 49.0 | 3.0 |
| | 13-Oct-04 | sec1 | 6.1 | 41.0 | 6.6 |
| | 15-Oct-04 | sec1 | 4.7 | 67.0 | 3.3 |
| | 18-Oct-04 | sec1 | 11.0 | 120.0 | 9.6 |
| | 20-Oct-04 | sec1 | 8.0 | 73.0 | 5.6 |
| | 22-Oct-04 | sec1 | 15.0 | 44.0 | 4.0 |

Summary Secondary Aeration Tank Samples (3rd pass)

| Headspace | | | DMS | DMS | MM |
|-----------|-----------|------|-------|-------|------|
| | | | ppbv | ppbv | ppbv |
| LOQs | | | 0.74 | 5.2 | 0.34 |
| Winter | 23-Feb-04 | sec3 | 29.0 | 40.0 | 0.17 |
| | 05-Mar-04 | sec3 | 400.0 | 250.0 | 20.0 |
| | 12-Mar-04 | sec3 | 15.0 | 28.0 | 3.6 |
| | 19-Mar-04 | sec3 | 0.37 | 26.0 | 0.17 |
| | 22-Mar-04 | sec3 | 0.37 | 26.0 | 0.17 |
| | 29-Mar-04 | sec3 | 0.37 | 25.0 | 0.17 |
| | 02-Apr-04 | sec3 | 1.1 | 44.0 | 0.17 |
| Spring | 13-May-04 | sec3 | 53.0 | 21.0 | 0.17 |
| | 24-May-04 | sec3 | 74.0 | 79.0 | 4.6 |
| | 27-May-04 | sec3 | 1.1 | 44.0 | 0.17 |
| | 03-Jun-04 | sec3 | 26.0 | 37.0 | 4.6 |
| | 7-Jun-04 | sec3 | 2.5 | 15.3 | 0.17 |
| | 10-Jun-04 | sec3 | 100.0 | 48.0 | 3.6 |
| | 15-Jun-04 | sec3 | 13.0 | 24.0 | 0.17 |
| Summer | 22-Jul-04 | sec3 | 20.0 | 50.0 | 2.1 |
| | 29-Jul-04 | sec3 | 0.37 | 6.7 | 0.17 |
| | 6-Aug-04 | sec3 | 11.0 | 32.0 | 4.2 |
| | 9-Aug-04 | sec3 | 20.0 | 41.0 | 3.6 |
| | 16-Aug-04 | sec3 | 9.7 | 31.0 | 3.6 |
| | 18-Aug-04 | sec3 | 0.37 | 15.0 | 0.17 |
| Fall | 11-Oct-04 | sec3 | 7.8 | 42.0 | 0.17 |
| | 13-Oct-04 | sec3 | 3.2 | 49.0 | 3.6 |
| | 15-Oct-04 | sec3 | 0.37 | 33 | 0.17 |
| | 18-Oct-04 | sec3 | 2.3 | 36.0 | 3.2 |
| | 20-Oct-04 | sec3 | 0.37 | 17.0 | 0.17 |
| | 22-Oct-04 | sec3 | 2.8 | 17.0 | 2.1 |

Summary Secondary Aeration Tank Samples (3rd pass)

| Tedlar bag | DMS | DMS | MM |
|-------------------|-------------|-------------|-------------|
| | ppbv | ppbv | ppbv |
| LOQs | 0.74 | 5.2 | 0.34 |
| 23-Feb-04 | 4.2 | 2.6 | 7.6 |
| 05-Mar-04 | 0.37 | 12.0 | 0.17 |
| 12-Mar-04 | 1.0 | 2.6 | 0.17 |
| 19-Mar-04 | 0.37 | 2.6 | 0.17 |
| 22-Mar-04 | 0.37 | 2.6 | 0.17 |
| 29-Mar-04 | 0.37 | 2.6 | 0.17 |
| 02-Apr-04 | 0.37 | 15.0 | 0.17 |
| 13-May-04 | 3.1 | 2.6 | 0.17 |
| 24-May-04 | 0.37 | 2.6 | 0.17 |
| 27-May-04 | 0.37 | 15.0 | 0.17 |
| 03-Jun-04 | 0.37 | 2.6 | 0.17 |
| 7-Jun-04 | 0.37 | 4.6 | 0.17 |
| 10-Jun-04 | 0.37 | 8.4 | 0.17 |
| 15-Jun-04 | 0.37 | 9.0 | 0.17 |
| 22-Jul-04 | 1.2 | 13.0 | 0.17 |
| 29-Jul-04 | / | 8.7 | 0.17 |
| 6-Aug-04 | 1.1 | 13.0 | 0.17 |
| 9-Aug-04 | 8.3 | 51.0 | 0.17 |
| 16-Aug-04 | 0.83 | 15.0 | 0.17 |
| 18-Aug-04 | 0.73 | 18.0 | 0.17 |
| 11-Oct-04 | 1.7 | 55.0 | 0.17 |
| 13-Oct-04 | 12.0 | 62.0 | 14.0 |
| 15-Oct-04 | 1.6 | 73.0 | 0.17 |
| 18-Oct-04 | 2.3 | 77.0 | 18.0 |
| 20-Oct-04 | 0.37 | 68.0 | 0.17 |
| 22-Oct-04 | 8.5 | 97.0 | 0.17 |

Summary Secondary Sedimentation Tank (Top)

| Headspace | | | DMS | DMS | MM |
|---------------|-----------|------|------|------|------|
| | | | ppbv | ppbv | ppbv |
| LOQs | | | 0.74 | 5.2 | 0.34 |
| Winter | 23-Feb-04 | sedT | 4.2 | 14.0 | 0.17 |
| | 05-Mar-04 | sedT | 0.37 | 4.8 | 0.17 |
| | 12-Mar-04 | sedT | 0.37 | 6.7 | 0.17 |
| | 19-Mar-04 | sedT | 0.37 | 2.6 | 0.17 |
| | 22-Mar-04 | sedT | 0.37 | 2.6 | 0.17 |
| | 29-Mar-04 | sedT | 6.6 | 7.7 | 0.17 |
| | 02-Apr-04 | sedT | 0.37 | 20.0 | 0.17 |
| Spring | 13-May-04 | sedT | 3.2 | 15.0 | 0.17 |
| | 24-May-04 | sedT | 0.37 | 19.0 | 0.17 |
| | 27-May-04 | sedT | 0.37 | 20.0 | 0.17 |
| | 03-Jun-04 | sedT | 0.37 | 2.6 | 0.17 |
| | 7-Jun-04 | sedT | 0.37 | 2.6 | 0.17 |
| | 10-Jun-04 | sedT | 0.37 | 2.6 | 0.17 |
| | 15-Jun-04 | sedT | 0.37 | 2.6 | 0.17 |
| Summer | 22-Jul-04 | sedT | 0.37 | 16.0 | 0.17 |
| | 29-Jul-04 | sedT | 0.37 | 2.6 | 0.17 |
| | 6-Aug-04 | sedT | 0.37 | 2.6 | 0.17 |
| | 9-Aug-04 | sedT | 0.37 | 2.6 | 0.17 |
| | 16-Aug-04 | sedT | 0.37 | 2.6 | 0.17 |
| | 18-Aug-04 | sedT | 0.37 | 2.6 | 0.17 |
| Fall | 11-Oct-04 | sedT | 0.37 | 23.0 | 0.17 |
| | 13-Oct-04 | sedT | 0.37 | 29.0 | 0.17 |
| | 15-Oct-04 | sedT | 0.37 | 30 | 0.17 |
| | 22-Oct-04 | sedT | 0.37 | 2.6 | 0.17 |

Summary Secondary Sedimentation Tank (Top)

| Tedlar bag | DMS | DMS | MM |
|-------------------|-------------|-------------|-------------|
| | ppbv | ppbv | ppbv |
| LOQs | 0.74 | 5.2 | 0.34 |
| 23-Feb-04 | n | n | n |
| 05-Mar-04 | 0.37 | 2.6 | 0.17 |
| 12-Mar-04 | 0.37 | 2.6 | 0.17 |
| 19-Mar-04 | 0.37 | 2.6 | 0.17 |
| 22-Mar-04 | 0.37 | 2.6 | 0.17 |
| 29-Mar-04 | 0.89 | 2.6 | 0.17 |
| 02-Apr-04 | 0.37 | 2.6 | 0.17 |
| 13-May-04 | 3.0 | 2.6 | 0.17 |
| 24-May-04 | 0.83 | 2.6 | 0.17 |
| 27-May-04 | 0.37 | 2.6 | 0.17 |
| 03-Jun-04 | 0.37 | 2.6 | 0.17 |
| 7-Jun-04 | 0.37 | 2.6 | 0.17 |
| 10-Jun-04 | 0.37 | 2.6 | 0.17 |
| 15-Jun-04 | 0.37 | 2.6 | 0.17 |

Summary Secondary Sedimentation Tank (Bottom)

| Headspace | | DMS | DMS | MM |
|------------------|-----------|-------------|-------------|-------------|
| LOQs | | ppbv | ppbv | ppbv |
| | | 0.74 | 5.2 | 0.34 |
| 23-Feb-04 | sed B2 | 380.0 | 180.0 | 2.9 |
| 05-Mar-04 | sed B2 | 410.0 | 340.0 | 23.0 |
| 12-Mar-04 | sed B2 | 36.0 | 41.0 | 7.2 |
| 19-Mar-04 | sed B2 | 0.37 | 2.6 | 64.0 |
| 22-Mar-04 | sed B2 | 0.37 | 2.6 | 0.17 |
| 29-Mar-04 | sed B2 | 490.0 | 73.0 | 31.0 |
| 02-Apr-04 | sed B2 | 98.0 | 110.0 | 3.4 |
| 13-May-04 | sed B2 | 220.0 | 160.0 | 0.17 |
| 24-May-04 | sed B2 | 210.0 | 170.0 | 8.8 |
| 27-May-04 | sed B2 | 98.0 | 110.0 | 3.4 |
| 03-Jun-04 | sed B2 | 11.0 | 12.6 | 0.17 |
| 7-Jun-04 | sedB avge | 62.0 | 72.0 | 0.45 |
| 10-Jun-04 | sedB avge | 22.0 | 28.0 | 1.9 |
| 15-Jun-04 | sedB avge | 11.0 | 27.0 | 2.6 |
| 22-Jul-04 | sedB avge | 30.0 | 65.0 | 4.8 |
| 29-Jul-04 | sedB avge | 14.0 | 46.0 | 5.1 |
| 6-Aug-04 | sedB avge | 23.0 | 46.0 | 2.8 |
| 9-Aug-04 | sedB avge | 36.0 | 51.0 | 4.6 |
| 16-Aug-04 | sedB avge | 21.0 | 37.0 | 2.5 |
| 18-Aug-04 | sedB avge | 99.0 | 90.0 | 13.0 |
| 11-Oct-04 | sedB avge | 12.0 | 77.0 | 0.17 |
| 13-Oct-04 | sedB avge | 94.0 | 94.0 | 12.0 |
| 15-Oct-04 | sedB avge | 92 | 79 | 0.17 |
| 18-Oct-04 | sedB avge | 170.0 | 120.0 | 19.5 |
| 20-Oct-04 | sedB avge | 160.0 | 78.0 | 6.8 |
| 22-Oct-04 | sedB avge | 14.0 | 52.0 | 5.6 |

Process Parameters

| | pH | | | | | | | | | | |
|----------------------|------|-------|-------|-------------|-------|------|------|------|------|------|-------------|
| | Prim | Sec 1 | Sec 3 | Sed T | Sed B | 4 | 6 | 8 | 10 | 12 | |
| 23-Feb-04 | 6.47 | 6.38 | 6.55 | 6.53 | 6.95 | | | | | | 6.95 |
| 05-Mar-04 | 6.60 | 6.91 | 6.73 | 6.61 | 6.59 | | | | | | 6.59 |
| 12-Mar-04 | 6.67 | 6.74 | 6.54 | 6.15 | 6.32 | | | | | | 6.32 |
| 19-Mar-04 | 6.42 | 6.42 | 6.32 | 6.38 | 6.42 | | | | | | 6.42 |
| 22-Mar-04 | 6.26 | 6.21 | 6.23 | 6.25 | 6.44 | | | | | | 6.44 |
| 29-Mar-04 | 6.35 | 6.62 | 6.17 | 6.35 | 6.62 | | | | | | 6.62 |
| 02-Apr-04 | 6.35 | 6.88 | 6.60 | 6.60 | 6.92 | | | | | | 6.92 |
| Seasonal avge | 6.45 | 6.59 | 6.45 | 6.41 | 6.61 | | | | | | 6.61 |
| 13-May-04 | 6.61 | 6.62 | 6.57 | 6.93 | 6.54 | | | | | | 6.54 |
| 24-May-04 | 6.55 | 6.63 | 6.61 | 6.82 | 6.58 | | | | | | 6.58 |
| 27-May-04 | 6.61 | 6.65 | 6.59 | 6.62 | 6.55 | | | | | | 6.55 |
| 03-Jun-04 | 6.75 | 6.70 | 6.63 | 6.84 | 6.61 | | | | | | 6.61 |
| 7-Jun-04 | | 6.66 | 6.64 | 6.65 | 6.29 | | 6.66 | 6.81 | 6.95 | 6.97 | 6.74 |
| 10-Jun-04 | | 6.62 | 6.64 | 6.52 | 6.30 | | 6.82 | 6.74 | 7.00 | 7.26 | 6.82 |
| 15-Jun-04 | | 6.67 | 6.68 | 6.52 | 6.69 | | 6.67 | 6.74 | 6.67 | 7.26 | 6.81 |
| Seasonal avge | 6.63 | 6.65 | 6.62 | 6.70 | 6.51 | | 6.72 | 6.76 | 6.87 | 7.16 | 6.66 |
| 22-Jul-04 | 6.67 | 6.97 | 6.87 | 6.94 | 7.00 | 7.04 | | 7.09 | 7.00 | 7.03 | 7.03 |
| 29-Jul-04 | 6.80 | 6.80 | 6.87 | 6.91 | 7.02 | 6.91 | 6.99 | 7.04 | | 6.99 | 6.99 |
| 6-Aug-04 | | 6.88 | 6.55 | 6.82 | 6.96 | 6.93 | 7.09 | 7.03 | 6.97 | 7.04 | 7.00 |
| 9-Aug-04 | | 6.97 | 6.78 | 6.80 | 6.84 | 6.92 | 6.97 | 6.99 | 6.96 | 6.85 | 6.92 |
| 16-Aug-04 | | 6.50 | 6.61 | 6.81 | 7.02 | 7.04 | 7.06 | 6.87 | 6.77 | 6.59 | 6.89 |
| 18-Aug-04 | | 6.55 | 6.67 | 6.75 | 6.96 | 6.96 | 7.04 | 6.89 | 6.84 | 6.66 | 6.89 |
| Seasonal avge | 6.74 | 6.78 | 6.73 | 6.84 | 6.97 | 6.97 | 7.03 | 6.99 | 6.91 | 6.86 | 6.96 |
| 11-Oct-04 | | 6.40 | 6.40 | 6.59 | 6.69 | 6.65 | 6.68 | 6.60 | | 6.54 | 6.63 |
| 13-Oct-04 | | 6.70 | 6.68 | 6.72 | 6.86 | 6.76 | 6.43 | 6.78 | | 6.55 | 6.68 |
| 15-Oct-04 | | 6.73 | 6.62 | 6.81 | 6.89 | 6.85 | 6.40 | 6.80 | 6.76 | 6.61 | 6.72 |
| 18-Oct-04 | | 6.55 | 6.50 | n | 6.81 | 6.64 | 6.40 | 6.88 | n | 6.57 | 6.66 |
| 20-Oct-04 | | 6.38 | 6.35 | n | 6.60 | 6.52 | 6.32 | n | 6.54 | 6.52 | 6.50 |
| 22-Oct-04 | | 6.55 | 6.67 | 6.75 | 6.96 | 6.96 | 7.04 | 6.89 | 6.84 | 6.66 | 6.89 |
| Seasonal avge | | 6.55 | 6.54 | 6.72 | 6.80 | 6.73 | 6.55 | 6.79 | 6.71 | 6.58 | 6.68 |

| ORP | | | | | | | | | | | |
|---------------|-------|--------|-------|--------------|--------|--------|--------|--------|--------|--------|---------------|
| | Prim | Sec 1 | Sec 3 | SedT | Sed B | 4 | 6 | 8 | 10 | 12 | Sed Bavg |
| 23-Feb-04 | 428.4 | 365.7 | 329.5 | 448.7 | -222.7 | | | | | | -222.7 |
| 05-Mar-04 | 387.8 | 317.6 | 335.8 | 424.7 | -210.1 | | | | | | -210.1 |
| 12-Mar-04 | 367.8 | 345.1 | 352.9 | 388.6 | -119.8 | | | | | | -119.8 |
| 19-Mar-04 | 313.7 | 289.7 | 305.3 | 333.5 | 280.1 | | | | | | 280.1 |
| 22-Mar-04 | 346.1 | 353.6 | 364.4 | 409.0 | 211.2 | | | | | | 211.2 |
| 29-Mar-04 | 339.4 | -119.1 | 304.2 | 309.4 | -233.6 | | | | | | -233.6 |
| 02-Apr-04 | 265.4 | 265.4 | 211.6 | 386.7 | -188.4 | | | | | | -188.4 |
| Seasonal avge | 349.8 | 259.7 | 314.8 | 385.8 | -69.0 | | | | | | -69.0 |
| stdv | 52.4 | 170.8 | 50.7 | 49.3 | 219.0 | | | | | | 219.0 |
| 13-May-04 | 270.3 | 170.4 | 419.9 | 479.9 | -236.4 | | | | | | -236.4 |
| 24-May-04 | 256.3 | 436.0 | 427.1 | 422.1 | -191.3 | | | | | | -191.3 |
| 27-May-04 | 248.9 | 304.9 | 314.9 | 375.0 | -114.9 | | | | | | -114.9 |
| 03-Jun-04 | 198.2 | 383.1 | 249.8 | 261.1 | -236.5 | | | | | | -236.5 |
| 7-Jun-04 | | 229.5 | 223.4 | 254.6 | -140.8 | -166.8 | -147.5 | -182.5 | -175.7 | | -162.7 |
| 10-Jun-04 | | 399.2 | 374.2 | 352.1 | -224.5 | -260.2 | -198.4 | -274.3 | -169.2 | | -225.3 |
| 15-Jun-04 | | 276.1 | 234.6 | 162.9 | -228.5 | -201.3 | -162.2 | -218.5 | -186.1 | | -199.3 |
| Seasonal avge | 243.4 | 314.2 | 320.6 | 329.7 | -196.1 | -209.4 | -169.4 | -225.1 | -177.0 | | -195.2 |
| stdv | 31.4 | 96.8 | 87.5 | 109.4 | 49.6 | 47.2 | 26.2 | 46.3 | 8.5 | | 44.4 |
| 22-Jul-04 | 127.8 | -140.0 | -30.5 | 48.6 | -230.8 | -218.7 | | -216.6 | -222.3 | -200.7 | -217.8 |
| 29-Jul-04 | 119.3 | -4.0 | 132.9 | 56.6 | -150.4 | -181.2 | -182.2 | -176.6 | | -180.8 | -174.2 |
| 6-Aug-04 | | -109.3 | -13.9 | -66.5 | -139.6 | -186.6 | -180.9 | -159.5 | -153.0 | -196.6 | -169.4 |
| 9-Aug-04 | | -100.9 | -24.9 | 45.7 | -149.5 | -166.2 | -206.2 | -157.5 | -168.1 | -179.1 | -171.1 |
| 16-Aug-04 | | -72.6 | -15.5 | 90.5 | -147.5 | -174.5 | -199.2 | -133.5 | -134.4 | -130.0 | -153.2 |
| 18-Aug-04 | | -57.3 | -47.5 | 87.9 | -140.5 | -176.3 | -206.4 | -107.9 | -170.6 | -204.0 | -167.6 |
| Seasonal avge | 123.5 | -80.7 | 0.1 | 43.8 | -159.7 | -183.9 | -195.0 | -158.6 | -169.7 | -181.9 | -175.5 |
| stdv | 6.0 | 47.4 | 66.2 | 57.4 | 35.1 | 18.3 | 12.6 | 37.1 | 32.7 | 27.4 | 21.9 |
| 11-Oct-04 | | -7.4 | 160.9 | 116.4 | -161.9 | -133.6 | -154.6 | -51.8 | | -28.0 | -106.0 |
| 13-Oct-04 | | -38.0 | 72.8 | 75.8 | -124.5 | -125.9 | -133.6 | -117.3 | | -107.9 | -121.8 |
| 15-Oct-04 | | -112.6 | -30.5 | 89.9 | -122.9 | -130.4 | -142.9 | -108.5 | -61.5 | -126.4 | -115.4 |
| 18-Oct-04 | | -88.8 | -56.4 | n | -80.4 | -56.4 | -107.0 | -1.2 | n | -38.4 | -56.7 |
| 20-Oct-04 | | -48.1 | 41.7 | n | -92.2 | -92.0 | -143.1 | n | -93.0 | -55.0 | -95.1 |
| 22-Oct-04 | | -57.3 | -47.5 | 87.9 | -140.5 | -176.3 | -206.4 | -107.9 | -170.6 | -204.0 | -167.6 |
| Seasonal avge | | -58.7 | 23.5 | 92.5 | -120.4 | -119.1 | -147.9 | -77.3 | -108.4 | -93.3 | -110.4 |
| stdv | | 37.4 | 84.8 | 17.1 | 30.1 | 40.8 | 32.8 | 49.9 | 56.1 | 66.8 | 36.3 |

| SL | | | | | | | | |
|----------------------|-----|-----|-----|-----|-----|-----|------------|------|
| | 2 | 4 | 6 | 8 | 10 | 12 | SL avge | stdv |
| 23-Feb-04 | 6.0 | | | | | | 6.0 | |
| 05-Mar-04 | 5.5 | | | | | | 5.5 | |
| 12-Mar-04 | 3.5 | | | | | | 3.5 | |
| 19-Mar-04 | 2.8 | | | | | | 2.8 | |
| 22-Mar-04 | 2.3 | | | | | | 2.3 | |
| 29-Mar-04 | 5.0 | | | | | | 5.0 | |
| 02-Apr-04 | 3.0 | | | | | | 3.0 | |
| Seasonal avge | | | | | | | 4.0 | |
| stdv | | | | | | | | |
| 13-May-04 | 4.3 | | | | | | 4.3 | |
| 24-May-04 | 4.3 | | | | | | 4.3 | |
| 27-May-04 | 3.7 | | | | | | 3.7 | |
| 03-Jun-04 | 3.5 | | | | | | 3.5 | |
| 7-Jun-04 | 1.8 | | 3 | 2.5 | 2.5 | 2.8 | 2.5 | 0.5 |
| 10-Jun-04 | 2.5 | | 3 | 2.3 | 3.2 | 2.3 | 2.7 | 0.4 |
| 15-Jun-04 | 4 | | 3 | 3 | 4.5 | 2.3 | 3.4 | 0.9 |
| Seasonal avge | 3.4 | | 3.0 | 2.6 | 3.4 | 2.5 | 3.5 | 0.4 |
| stdv | | | | | | | | |
| 22-Jul-04 | 3.3 | 2.7 | | 2.2 | 2 | 1.8 | 2.4 | 0.6 |
| 29-Jul-04 | 1.8 | 2.3 | 2.2 | 2.1 | | 1.3 | 1.9 | 0.4 |
| 6-Aug-04 | 2 | 3 | 3.5 | 2.3 | 2 | 3.4 | 2.7 | 0.7 |
| 9-Aug-04 | 3.8 | 3 | 3.8 | 1.8 | 3.2 | 3.8 | 3.2 | 0.8 |
| 16-Aug-04 | 3.5 | 3.3 | 4.2 | 2.2 | 2.8 | 3.2 | 3.2 | 0.7 |
| 18-Aug-04 | 3.2 | 4 | 4.2 | 2 | 3 | 3.1 | 3.3 | 0.8 |
| Seasonal avge | 2.9 | 3.1 | 3.6 | 2.1 | 2.6 | 2.8 | 2.8 | 0.5 |
| stdv | | | | | | | | |
| 11-Oct-04 | 3 | 3.5 | 4 | 1.8 | | 2.8 | 3.0 | 0.8 |
| 13-Oct-04 | 3.5 | 2.5 | 4 | 1.6 | | 2.5 | 2.8 | 0.9 |
| 15-Oct-04 | 3 | 3.5 | 4.5 | 1.9 | 1.7 | 3.3 | 3.0 | 1.0 |
| 18-Oct-04 | 3.5 | 3.3 | 5.3 | 1.2 | | 3 | 3.3 | 1.5 |
| 20-Oct-04 | 3.4 | 3.3 | 4.6 | | 2.6 | 3.1 | 3.4 | 0.7 |
| 22-Oct-04 | 3.6 | 3.5 | 4.2 | 2.2 | 2.2 | 3.3 | 3.2 | 0.8 |
| Seasonal avge | 3.3 | 3.3 | 4.4 | 1.7 | 2.2 | 3.0 | 3.1 | 1.0 |
| stdv | | | | | | | | |

Sulfides

| | blank | Prim | Sec 1 | Sec 3 | Sed T | Sed 2 | 4 | 6 | 8 | 10 | 12 | Sed Bavg |
|---------------|-------|----------|--------|--------|-------|--------|--------|--------|--------|--------------|--------------|----------|
| 23-Feb-04 | | 0.19 | 27.54 | 26.37 | 0.21 | 92.38 | | | | | | |
| 05-Mar-04 | | 0.11 | 27.67 | 31.46 | 0.23 | 80.31 | | | | | | |
| 12-Mar-04 | 0.09 | 35.61 | 1.89 | 1.32 | 0.38 | 58.08 | | | | | | |
| 19-Mar-04 | 0.09 | 14.80 | 0.89 | 0.40 | 0.51 | 2.23 | | | | | | |
| 22-Mar-04 | 0.11 | 13.73 | 1.17 | 0.84 | 0.67 | 1.33 | | | | | | |
| 29-Mar-04 | 0.14 | 3.32 | 17.26 | 5.37 | 0.38 | 105.40 | | | | | | |
| 02-Apr-04 | 0.19 | 0.42 | 16.60 | 16.25 | 0.14 | 76.73 | | | | | | |
| Seasonal avge | | | | | | | | | | | | |
| stdv | | | | | | | | | | | | |
| 13-May-04 | 0.41 | 64.12 | 90.28 | 92.48 | 0.76 | 102.66 | | | | | | |
| 24-May-04 | 1.12 | 35.26 | 87.69 | 67.26 | 1.43 | 89.05 | | | | | | |
| 27-May-04 | 1.32 | 145.26 | 60.66 | 10.84 | 2.00 | 74.04 | | | | | | |
| 03-Jun-04 | 0.21 | 96.27 | 16.95 | 3.08 | 0.40 | 16.95 | | | | | | |
| 7-Jun-04 | | | 70.35 | 2.79 | 0.43 | 102.32 | 108.51 | 74.94 | 93.81 | 71.80 | 90.28 | |
| 10-Jun-04 | | | 111.66 | 134.36 | n | 105.75 | 89.78 | 84.70 | 87.45 | 86.30 | 90.80 | |
| 15-Jun-04 | | | 86.02 | 34.49 | 5.17 | 90.72 | 93.76 | 75.60 | 96.43 | 97.17 | 90.74 | |
| Seasonal avge | | | | | | | | | | | | |
| stdv | | | | | | | | | | | | |
| 22-Jul-04 | | 0.86 | 168.66 | 217.13 | 0.7 | 177.0 | 165.0 | n | 211.0 | 168.7 | 159.6 | 176.27 |
| 29-Jul-04 | | 1.61 | 169.77 | 240.22 | 1.2 | 305.9 | 212.4 | 215.7 | 207.3 | n | 157.2 | 219.71 |
| 6-Aug-04 | | n | 182.54 | 208.26 | 1.1 | 160.3 | 193.3 | 235.0 | 194.1 | 162.5 | 214.3 | 193.25 |
| 9-Aug-04 | | n | 127.04 | 144.30 | 1.2 | 108.5 | 189.5 | 211.5 | 127.9 | 101.3 | 116.4 | 142.49 |
| 16-Aug-04 | | n | 103.79 | 122.11 | 0.9 | 103.1 | 163.6 | 165.0 | 124.3 | 148.8 | 140.5 | 140.88 |
| 18-Aug-04 | | 310.6289 | 45.64 | 101.54 | 0.6 | 57.4 | 44.0 | 44.4 | 49.4 | 78.0 | 67.5 | 56.76 |
| Seasonal avge | | | | | | | | | | | | |
| stdv | | | | | | | | | | | | |
| 11-Oct-04 | | n | 36.96 | 12.93 | 0.60 | 16.54 | 38.79 | 30.94 | 18.75 | n | 22.35 | 25.47 |
| 13-Oct-04 | | n | 48.96 | 195.40 | 0.74 | 27.18 | 141.48 | 195.40 | 164.63 | n | 157.90 | 137.32 |
| 15-Oct-04 | | n | 21.58 | 46.04 | 0.71 | 89.78 | 71.44 | 243.41 | 0.86 | 13.84 | 201.95 | 103.55 |
| 18-Oct-04 | | n | 430.92 | 361.47 | n | 342.15 | 333.98 | 309.95 | 182.54 | n | 157.56 | 265.24 |
| 20-Oct-04 | | n | 99.11 | 198.00 | n | 143.35 | 108.45 | 248.82 | n | 113.08 | 131.58 | 149.06 |
| 22-Oct-04 | | 175.85 | 129.57 | 125.37 | 0.19 | 138.10 | 177.79 | 186.18 | 125.93 | 138.71 | 139.62 | 151.05 |
| Seasonal avge | | | | | | | | | | | | |
| stdv | | | | | | | | | | | | |

APPENDIX III

Table 1 A: Correlation between DMS and process parameters

| | Correlation | |
|--------------------------|-------------|-----------|
| | Linear | Quadratic |
| | | |
| pH | 0.0034 | 0.078 |
| SL | 0.5154 | 0.5329 |
| ORP | 0.1244 | 0.1244 |
| Water temperature | 0.0672 | 0.0689 |
| Sulfide | 0.0061 | 0.0745 |
| Spiked OUR | 0.0138 | 0.0258 |
| Soluble Iron | 0.4089 | 0.7447 |
| ISV | 0.38 | 0.55 |
| F/M | 0.0072 | 0.008 |
| SSV | 0.3646 | 0.5222 |
| SRT | 0.00007 | 0.0276 |
| *Density | 0.208 | 0.302 |

Table 1B: Plant Process parameters 2004

| | Parameters | | | | | | | | | | | | | | | | VSC Concentration | |
|-----------|------------|--------|----------|----------|------------|----------|-----------|------|----------|------|----------|-----------|---------------------|--------|--------|---------|-------------------|------|
| | Primary | | | | | | Secondary | | | | Dummy | Composite | Quadratic Variables | | | | DMDS | DMS |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | ppbv | ppbv |
| | SL | ORP | wat temp | sulfides | Spiked OUR | sol iron | ISV | F/M | SSV (60) | SRT | Chlorine | den | SL 2 | ISV2 | SSV2 | Dens2 | | |
| 23-Feb-04 | 6.0 | -222.7 | 13.3 | 92.4 | 132.0 | 250 | 0.08 | 1.52 | 270 | 6.28 | 0 | 58.29 | 36.0 | 0.0064 | 72900 | 3397.92 | 380 | 180 |
| 05-Mar-04 | 5.5 | -210.1 | 15.0 | 80.3 | 149.0 | 310 | 0.04 | 0.59 | 350 | 2.04 | 0 | 45.18 | 30.3 | 0.0016 | 122500 | 2040.92 | 410 | 340 |
| 12-Mar-04 | 3.5 | -119.8 | 15.1 | 58.1 | 192.0 | 190 | 0.15 | 0.63 | 200 | 1.84 | 0 | 28.26 | 12.3 | 0.0225 | 40000 | 798.74 | 36 | 41 |
| 19-Mar-04 | 2.8 | 280.1 | 14.7 | 2.2 | 145.0 | 94 | 0.14 | 1.17 | 220 | 0.89 | 0 | 38.88 | 7.6 | 0.0196 | 48400 | 1511.47 | 0.38 | 2.6 |
| 22-Mar-04 | 2.3 | 211.2 | 14.4 | 1.33 | 149.0 | 60 | 0.21 | 0.49 | 170 | 1.72 | 0 | 26.45 | 5.1 | 0.0441 | 28900 | 699.62 | 0.38 | 2.6 |
| 29-Mar-04 | 5.0 | -233.6 | 16.1 | 105.4 | 208.0 | 210 | 0.13 | 1.29 | 230 | 0.7 | 0 | 25.13 | 25.0 | 0.0169 | 52900 | 631.38 | 490 | 73 |
| 02-Apr-04 | 3.0 | -188.4 | 15.2 | 76.7 | 159.0 | 53 | 0.09 | 0.41 | 355 | 0.95 | 0 | 33.78 | 9.0 | 0.0081 | 126025 | 1140.81 | 98 | 110 |
| 13-May-04 | 4.3 | -236.4 | 21.3 | 102.7 | 359.0 | 200 | 0.07 | 0.4 | 360 | 3.47 | 0 | 50.47 | 18.5 | 0.0049 | 129600 | 2546.76 | 220 | 160 |
| 24-May-04 | 4.3 | -191.3 | 23.5 | 89 | 337.0 | 230 | 0.05 | 0.34 | 320 | 1.88 | 0 | 30.93 | 18.5 | 0.0025 | 102400 | 956.38 | 210 | 170 |
| 27-May-04 | 3.7 | -114.9 | 23.8 | 74.04 | 300.0 | 170 | 0.1 | 0.91 | 250 | 0.86 | 0 | 24.16 | 13.7 | 0.0100 | 62500 | 583.51 | 98 | 110 |
| 03-Jun-04 | 3.5 | -236.5 | 22.9 | 16.9 | 293.0 | 160 | 0.22 | 0.64 | 170 | 1.15 | 1 | 16.50 | 12.3 | 0.0484 | 28900 | 272.29 | 11 | 13 |
| 7-Jun-04 | 3.8 | -162.7 | 21.3 | 90.3 | 213.6 | 0.6 | 0.24 | 0.49 | 150 | 0.8 | 1 | 30.90 | 14.1 | 0.0576 | 22500 | 955.05 | 62 | 72 |
| 10-Jun-04 | 2.7 | -225.3 | 23.3 | 90.8 | 301.0 | 1.6 | 0.17 | 0.98 | 150 | 0.8 | 1 | 29.85 | 7.1 | 0.0289 | 22500 | 891.29 | 22 | 28 |
| 15-Jun-04 | 3.4 | -199.3 | 23.5 | 90.7 | 268.0 | 2.8 | 0.11 | 1.63 | 200 | 1.0 | 1 | 31.89 | 11.3 | 0.0121 | 40000 | 1016.83 | 11 | 27 |
| 22-Jul-04 | 2.4 | -217.8 | 25.6 | 176.3 | 733.0 | 16.4 | 0.16 | 0.28 | 200 | 1.5 | 0 | 33.75 | 5.8 | 0.0256 | 40000 | 1138.92 | 30 | 65 |
| 29-Jul-04 | 1.9 | -174.2 | 24.7 | 219.7 | 348.0 | 50.2 | 0.07 | 1.11 | 70 | 0.5 | 1 | 9.22 | 3.8 | 0.0049 | 4900 | 85.06 | 14 | 46 |
| 6-Aug-04 | 2.7 | -169.4 | 26.0 | 193.3 | 486.0 | 14.2 | 0.22 | 0.41 | 100 | 14.0 | 0 | 20.90 | 7.3 | 0.0484 | 10000 | 436.86 | 23 | 46 |
| 9-Aug-04 | 3.2 | -171.1 | 25.8 | 142.5 | 337.0 | 25.5 | 0.1 | 0.35 | 250 | 8.5 | 0 | 39.22 | 10.5 | 0.0100 | 62500 | 1537.98 | 36 | 51 |
| 16-Aug-04 | 3.2 | -153.2 | 25.2 | 140.9 | 244.0 | 30.5 | 0.17 | 0.28 | 210 | 8.0 | 0 | 28.06 | 10.2 | 0.0289 | 44100 | 787.57 | 21 | 37 |
| 18-Aug-04 | 3.3 | -167.6 | 25.6 | 56.8 | 528.0 | 21.2 | 0.07 | 0.37 | 150 | 3.2 | 1 | 14.28 | 10.6 | 0.0049 | 22500 | 203.80 | 99 | 90 |
| 11-Oct-04 | 3.0 | -106.0 | 22.6 | 25.5 | 333.0 | 29.8 | 0.14 | 0.27 | 240 | 16.7 | 0 | 29.41 | 9.1 | 0.0196 | 57600 | 865.12 | 12 | 77 |
| 13-Oct-04 | 2.8 | -121.8 | 22.3 | 137.3 | 262.0 | 11.0 | 0.15 | 0.15 | 180 | 4.5 | 0 | 34.44 | 8.0 | 0.0225 | 32400 | 1186.03 | 94 | 94 |
| 15-Oct-04 | 3.0 | -115.4 | 22.5 | 103.5 | 230.0 | 38.7 | 0.16 | 0.17 | 170 | 12.8 | 0 | 21.46 | 8.9 | 0.0256 | 28900 | 460.73 | 92 | 79 |
| 18-Oct-04 | 3.3 | -56.7 | 21.8 | 265.2 | 357.0 | 14.2 | 0.15 | 0.1 | 100 | 14.7 | 1 | 10.38 | 10.6 | 0.0225 | 10000 | 107.72 | 170 | 120 |
| 20-Oct-04 | 3.4 | -95.1 | 21.3 | 149.1 | 180.0 | 38.3 | 0.12 | 0.14 | 240 | 15.0 | 1 | 25.10 | 11.6 | 0.0144 | 57600 | 630.08 | 160 | 78 |
| 22-Oct-04 | 3.2 | -167.6 | 21.3 | 151.1 | 270.0 | 41.8 | 0.1 | 0.28 | 200 | 11.8 | 1 | 19.94 | 10.0 | 0.0100 | 40000 | 397.72 | 14 | 52 |

* Limit of quantification

Table 1C: VSC statistical modeling

| Multiple Regression Statistical Analysis | | | | | | | | | | | | | | | | Statistical Parameters | | | | | | | |
|--|--------------------------|---|---|---|---|---|---|---|---|---|---|---|---|----------------|----------------|------------------------|----------------|---------|-------|---------|---------|--------|---------|
| Model | Plant Process Parameters | | | | | | | | | | | | | | | Ad R ² | St err | P-value | R SS | MS | F-ratio | | |
| 1 | b0 | A | B | C | D | E | F | G | H | I | J | K | L | B ² | H ² | J ² | L ² | 0.777 | 33.41 | 0.0038 | 10046 | 1116.2 | 6.4456 |
| 2 | b0 | A | B | C | D | E | F | G | H | I | J | K | L | B ² | H ² | J ² | L ² | 0.798 | 31.80 | 0.0013 | 10113 | 1011.4 | 7.5838 |
| 3 | b0 | A | B | C | D | E | F | G | H | I | J | K | L | B ² | H ² | J ² | L ² | 0.816 | 30.34 | 0.0004 | 10124 | 920.4 | 8.9281 |
| 4 | b0 | A | B | C | D | E | F | G | H | I | J | K | L | B ² | H ² | J ² | L ² | 0.812 | 30.65 | 0.002 | 11270 | 939.2 | 9.3284 |
| 5 | b0 | A | B | C | D | E | F | G | H | I | J | K | L | B ² | H ² | J ² | L ² | 0.824 | 29.72 | <0.0001 | 11479 | 883.0 | 10.7290 |
| 6 | b0 | A | B | C | D | E | F | G | H | I | J | K | L | B ² | H ² | J ² | L ² | 0.8358 | 28.67 | <0.0001 | 11511 | 822.2 | 12.5661 |
| 7 | b0 | A | B | C | D | E | F | G | H | I | J | K | L | B ² | H ² | J ² | L ² | 0.8398 | 28.32 | <0.0001 | 12029 | 801.9 | 14.1073 |
| 8 | b0 | A | B | C | D | E | F | G | H | I | J | K | L | B ² | H ² | J ² | L ² | 0.8433 | 28 | <0.0001 | 12551 | 784.5 | 15.9503 |
| 9 | b0 | A | B | C | D | E | F | G | H | I | J | K | L | B ² | H ² | J ² | L ² | 0.8440 | 27.95 | <0.0001 | 13280 | 781.2 | 17.9022 |
| 10 | b0 | A | B | C | D | E | F | G | H | I | J | K | L | B ² | H ² | J ² | L ² | 0.8411 | 28.20 | <0.0001 | 14318 | 795.5 | 19.9068 |
| 11 | b0 | A | B | C | D | E | F | G | H | I | J | K | L | B ² | H ² | J ² | L ² | 0.8142 | 30.50 | <0.0001 | 17669 | 929.9 | 19.2647 |
| 12 | b0 | A | B | C | D | E | F | G | H | I | J | K | L | B ³ | H ³ | J ³ | L ³ | 0.8185 | 30.15 | <0.0001 | 18178 | 908.9 | 23.5420 |
| 13 | b0 | A | B | C | D | E | F | G | H | I | J | K | L | B ⁴ | H ⁴ | J ⁴ | L ⁴ | 0.7902 | 32.41 | <0.0001 | 22054 | 1050.2 | 24.5459 |

Table 1D: Variation in the residual error associated with DMS prediction

| Analysis of model residuals | | | | | |
|------------------------------------|-----------|-----------------|----------------------|-------------------|-----------------|
| F/M | SL | SSV (60) | Predicted DMS | Actual DMS | Residual |
| 1.52 | 6.0 | 270 | 190.8 | 180 | -10.8 |
| 0.59 | 5.5 | 350 | 262.1 | 340 | 77.9 |
| 0.63 | 3.5 | 200 | 57.6 | 41 | -16.6 |
| 1.17 | 2.8 | 220 | -0.6 | 2.6 | 3.2 |
| 0.49 | 2.3 | 170 | 19.2 | 2.6 | -16.6 |
| 1.29 | 5.0 | 230 | 113.6 | 73 | -40.6 |
| 0.41 | 3.0 | 355 | 132.2 | 110 | -22.2 |
| 0.4 | 4.3 | 360 | 202.9 | 160 | -42.9 |
| 0.34 | 4.3 | 320 | 166.1 | 170 | 3.9 |
| 0.91 | 3.7 | 250 | 61.8 | 110 | 48.2 |
| 0.64 | 3.5 | 170 | 60.3 | 13 | -47.3 |
| 0.49 | 3.8 | 150 | 86.6 | 72 | -14.6 |
| 0.98 | 2.7 | 150 | 13.5 | 28 | 14.5 |
| 1.63 | 3.4 | 200 | -0.2 | 27 | 27.2 |
| 0.28 | 2.4 | 200 | 31.4 | 65 | 33.6 |
| 1.11 | 1.9 | 70 | 35.8 | 46 | 10.2 |
| 0.41 | 2.7 | 100 | 71.0 | 46 | -25.0 |
| 0.35 | 3.2 | 250 | 68.6 | 51 | -17.6 |
| 0.28 | 3.2 | 210 | 62.2 | 37 | -25.2 |
| 0.37 | 3.3 | 150 | 68.5 | 90 | 21.5 |
| 0.27 | 3.0 | 240 | 60.4 | 77 | 16.6 |
| 0.15 | 2.8 | 180 | 54.4 | 94 | 39.6 |
| 0.17 | 3.0 | 170 | 61.5 | 79 | 17.5 |
| 0.1 | 3.3 | 100 | 109.6 | 120 | 10.4 |
| 0.14 | 3.4 | 240 | 83.7 | 78 | -5.7 |
| 0.28 | 3.2 | 200 | 60.6 | 52 | -8.6 |

Model 1

| StatTools (Core Analysis Pack) | | | | | | |
|---------------------------------------|---------------------------|-----------------------|--------------------------|--------------------------|--------------------|--------------------|
| Analysis: Regression | | | | | | |
| Performed By: ksekyiamah | | | | | | |
| Summary | Multiple R | R-Square | Adjusted R-Square | StErr of Estimate | | |
| | 0.9590 | 0.9197 | 0.7770 | 33.41059095 | | |
| ANOVA Table | Degrees of Freedom | Sum of Squares | Mean of Squares | F-Ratio | p-Value | |
| Explained | 16 | 115119.4333 | 7194.964578 | 6.4456 | 0.0038 | |
| Unexplained | 9 | 10046.40829 | 1116.267587 | | | |
| Regression Table | Coefficient | Standard Error | t-Value | p-Value | Lower Limit | Upper Limit |
| Constant | 219.9145029 | 133.2246755 | 1.6507 | 0.1332 | -81.46065091 | 521.2896568 |
| SL | -115.3102207 | 82.58388072 | -1.3963 | 0.1961 | -302.127938 | 71.50749664 |
| ORP | 0.121741854 | 0.103690505 | 1.1741 | 0.2705 | -0.112822365 | 0.356306073 |
| wat temp | 4.898368745 | 4.495557087 | 1.0896 | 0.3042 | -5.271287919 | 15.06802541 |
| Sulfides | -0.214121955 | 0.212359383 | -1.0083 | 0.3396 | -0.694512253 | 0.266268344 |
| Spiked OUR | 0.020463546 | 0.083233034 | 0.2459 | 0.8113 | -0.167822658 | 0.208749751 |
| sol iron | 0.017924704 | 0.193589692 | 0.0926 | 0.9283 | -0.420005603 | 0.455855011 |
| ISV | 1239.439059 | 1544.378167 | 0.8025 | 0.4429 | -2254.187074 | 4733.065192 |
| F/M | -91.57666203 | 30.01280964 | -3.0513 | 0.0138 | -159.4703543 | -23.68296972 |
| SSV (60) | -2.915830304 | 1.131358445 | -2.5773 | 0.0298 | -5.475140913 | -0.356519695 |
| SRT | -0.981898647 | 2.143603496 | -0.4581 | 0.6578 | -5.831066649 | 3.867269355 |
| Chlorine | 25.85393283 | 26.72805514 | 0.9673 | 0.3587 | -34.60912856 | 86.31699421 |
| Den | 11.39693809 | 5.450410169 | 2.0910 | 0.0661 | -0.932746317 | 23.72662249 |
| SL 2 | 26.4593402 | 12.19317133 | 2.1700 | 0.0581 | -1.123529658 | 54.04221007 |
| ISV2 | -5820.987995 | 5168.323401 | -1.1263 | 0.2892 | -17512.5478 | 5870.571806 |
| SSV2 | 0.006055237 | 0.002275906 | 2.6606 | 0.0260 | 0.000906779 | 0.011203695 |
| Dens2 | -0.166007294 | 0.077292025 | -2.1478 | 0.0603 | -0.340854002 | 0.008839415 |

Model 2

| StatTools | (Core Analysis Pack) | | | | | |
|-------------------------|---------------------------|-----------------------|--------------------------|--------------------------|--------------------|--------------------|
| Analysis: | Regression | | | | | |
| Performed By: | ksekylamah | | | | | |
| Summary | Multiple R | R-Square | Adjusted R-Square | StErr of Estimate | | |
| | 0.9587 | 0.9192 | 0.7980 | 31.80233109 | | |
| ANOVA Table | Degrees of Freedom | Sum of Squares | Mean of Squares | F-Ratio | p-Value | |
| Explained | 15 | 115051.9589 | 7670.130594 | 7.5838 | 0.0013 | |
| Unexplained | 10 | 10113.88263 | 1011.388263 | | | |
| Regression Table | Coefficient | Standard Error | t-Value | p-Value | Lower Limit | Upper Limit |
| Constant | 223.9638477 | 125.8389313 | 1.7798 | 0.1055 | -56.42276429 | 504.3504597 |
| SL | -118.177002 | 77.82110667 | -1.5186 | 0.1598 | -291.5732333 | 55.21922928 |
| ORP | 0.119115468 | 0.098174054 | 1.2133 | 0.2529 | -0.099629955 | 0.337860892 |
| wat temp | 5.382730133 | 3.846378872 | 1.3994 | 0.1919 | -3.187536072 | 13.95299634 |
| Sulfides | -0.213940149 | 0.202135977 | -1.0584 | 0.3148 | -0.664327173 | 0.236446876 |
| sol iron | 0.018603997 | 0.184252245 | 0.1010 | 0.9216 | -0.39193559 | 0.429143583 |
| ISV | 1267.839045 | 1465.919821 | 0.8649 | 0.4074 | -1998.433862 | 4534.111953 |
| F/M | -93.42260094 | 27.6597368 | -3.3776 | 0.0070 | -155.0523351 | -31.79286675 |
| SSV (60) | -2.91653569 | 1.076895653 | -2.7083 | 0.0220 | -5.316008733 | -0.517062647 |
| SRT | -1.129414199 | 1.95885924 | -0.5766 | 0.5770 | -5.494024578 | 3.23519618 |
| Chlorine | 24.85049196 | 25.14310451 | 0.9884 | 0.3463 | -31.17183605 | 80.87281998 |
| Den | 11.22926146 | 5.147272374 | 2.1816 | 0.0541 | -0.239576101 | 22.69809901 |
| SL 2 | 26.80195599 | 11.53018831 | 2.3245 | 0.0424 | 1.111095448 | 52.49281652 |
| ISV2 | -5923.507641 | 4903.501903 | -1.2080 | 0.2548 | -16849.19074 | 5002.17546 |
| SSV2 | 0.006047941 | 0.002166169 | 2.7920 | 0.0191 | 0.001221417 | 0.010874466 |
| Dens2 | -0.163279146 | 0.072809345 | -2.2426 | 0.0488 | -0.325508477 | -0.001049815 |

Model 3

| StatTools (Core Analysis Pack) | | | | | | |
|---------------------------------------|---------------------------|-----------------------|--------------------------|--------------------------|--------------------|--------------------|
| Analysis: Regression | | | | | | |
| Performed By: ksekyiamah | | | | | | |
| Summary | Multiple R | R-Square | Adjusted R-Square | StErr of Estimate | | |
| | 0.9587 | 0.9191 | 0.8162 | 30.33778581 | | |
| ANOVA Table | Degrees of Freedom | Sum of Squares | Mean of Squares | F-Ratio | p-Value | |
| Explained | 14 | 115041.6478 | 8217.260558 | 8.9281 | 0.0004 | |
| Unexplained | 11 | 10124.19372 | 920.3812477 | | | |
| Regression Table | Coefficient | Standard Error | t-Value | p-Value | Lower Limit | Upper Limit |
| Constant | 226.9894729 | 116.5907126 | 1.9469 | 0.0775 | -29.6249554 | 483.6039012 |
| SL | -117.5565549 | 74.00553529 | -1.5885 | 0.1405 | -280.4416398 | 45.32853005 |
| ORP | 0.119759727 | 0.093454979 | 1.2815 | 0.2264 | -0.085933295 | 0.325452748 |
| wat temp | 5.354795906 | 3.659743642 | 1.4632 | 0.1714 | -2.70024554 | 13.40983735 |
| Sulfides | -0.215690272 | 0.192117076 | -1.1227 | 0.2855 | -0.638537105 | 0.20715656 |
| ISV | 1253.995242 | 1392.281989 | 0.9007 | 0.3871 | -1810.396754 | 4318.387237 |
| F/M | -93.26670186 | 26.34482219 | -3.5402 | 0.0046 | -151.2512645 | -35.28213917 |
| SSV (60) | -2.908112412 | 1.024215892 | -2.8394 | 0.0161 | -5.162396392 | -0.653828433 |
| SRT | -1.199194749 | 1.748489029 | -0.6858 | 0.5070 | -5.047593154 | 2.649203656 |
| Chlorine | 23.66434807 | 21.20627563 | 1.1159 | 0.2882 | -23.01034989 | 70.33904602 |
| Den | 11.04203289 | 4.580542987 | 2.4106 | 0.0346 | 0.960325752 | 21.12374003 |
| SL 2 | 26.86588711 | 10.98260897 | 2.4462 | 0.0325 | 2.693327743 | 51.03844647 |
| ISV2 | -5875.464716 | 4655.613973 | -1.2620 | 0.2330 | -16122.40198 | 4371.47255 |
| SSV2 | 0.006045204 | 0.002066251 | 2.9257 | 0.0138 | 0.001497416 | 0.010592993 |
| Dens2 | -0.161357261 | 0.06704094 | -2.4068 | 0.0348 | -0.308913374 | -0.013801148 |

Model 4

| StatTools | (Core Analysis Pack) | | | | | |
|-------------------------|---------------------------|-----------------------|--------------------------|--------------------------|--------------------|--------------------|
| Analysis: | Regression | | | | | |
| Performed By: | ksekiamah | | | | | |
| Summary | Multiple R | R-Square | Adjusted R-Square | StErr of Estimate | | |
| | 0.9539 | 0.9100 | 0.8124 | 30.64624546 | | |
| ANOVA Table | Degrees of Freedom | Sum of Squares | Mean of Squares | F-Ratio | p-Value | |
| Explained | 13 | 113895.5332 | 8761.194862 | 9.3284 | 0.0002 | |
| Unexplained | 12 | 11270.30833 | 939.1923608 | | | |
| Regression Table | Coefficient | Standard Error | t-Value | p-Value | Lower Limit | Upper Limit |
| Constant | 246.1924993 | 116.4862279 | 2.1135 | 0.0562 | -7.60918858 | 499.9941871 |
| SL | -73.80905738 | 63.40696287 | -1.1641 | 0.2670 | -211.9609616 | 64.34284682 |
| ORP | 0.073704712 | 0.084700745 | 0.8702 | 0.4013 | -0.110842357 | 0.258251781 |
| wat temp | 3.533060899 | 3.308764203 | 1.0678 | 0.3066 | -3.676116998 | 10.7422388 |
| sulfides | -0.159240269 | 0.187221913 | -0.8505 | 0.4117 | -0.567161776 | 0.248681237 |
| ISV | 428.819597 | 1191.674055 | 0.3598 | 0.7252 | -2167.615123 | 3025.254317 |
| F/M | -82.2214372 | 24.66298499 | -3.3338 | 0.0060 | -135.9574653 | -28.48540908 |
| SSV (60) | -2.535475626 | 0.978095112 | -2.5923 | 0.0236 | -4.666561805 | -0.404389447 |
| SRT | -0.816802509 | 1.732014489 | -0.4716 | 0.6457 | -4.5905379 | 2.956932881 |
| den | 9.021194421 | 4.250142147 | 2.1226 | 0.0553 | -0.239069816 | 18.28145866 |
| SL 2 | 19.73232033 | 9.021228083 | 2.1873 | 0.0492 | 0.076752844 | 39.38788782 |
| ISV2 | -3203.068709 | 4033.040717 | -0.7942 | 0.4425 | -11990.30957 | 5584.172148 |
| SSV2 | 0.005084608 | 0.001897499 | 2.6796 | 0.0201 | 0.000950312 | 0.009218904 |
| Dens2 | -0.130880662 | 0.061848335 | -2.1162 | 0.0559 | -0.265636607 | 0.003875283 |

Model 5

| StatTools (Core Analysis Pack) | | | | | | |
|---------------------------------------|---------------------------|-----------------------|--------------------------|--------------------------|--------------------|--------------------|
| Analysis: Regression | | | | | | |
| Performed By: ksekyamah | | | | | | |
| Summary | Multiple R | R-Square | Adjusted R-Square | StErr of Estimate | | |
| | 0.9530 | 0.9083 | 0.8236 | 29.71555269 | | |
| ANOVA Table | Degrees of Freedom | Sum of Squares | Mean of Squares | F-Ratio | p-Value | |
| Explained | 12 | 113686.6586 | 9473.888217 | 10.7290 | < 0.0001 | |
| Unexplained | 13 | 11479.18293 | 883.0140717 | | | |
| Regression Table | Coefficient | Standard Error | t-Value | p-Value | Lower Limit | Upper Limit |
| Constant | 255.2892486 | 111.3892903 | 2.2919 | 0.0392 | 14.64731718 | 495.93118 |
| SL | -72.0347355 | 61.37303131 | -1.1737 | 0.2616 | -204.6231087 | 60.55363769 |
| ORP | 0.061951974 | 0.078493041 | 0.7893 | 0.4441 | -0.107621933 | 0.23152588 |
| wat temp | 3.0860389 | 3.073807469 | 1.0040 | 0.3337 | -3.554518411 | 9.726596212 |
| Sulfides | -0.163800036 | 0.181293939 | -0.9035 | 0.3827 | -0.555461781 | 0.227861708 |
| ISV | 201.4064213 | 1056.651334 | 0.1906 | 0.8518 | -2081.350002 | 2484.162844 |
| F/M | -75.95949656 | 20.15221022 | -3.7693 | 0.0023 | -119.4956999 | -32.42329324 |
| SSV (60) | -2.498900834 | 0.945405284 | -2.6432 | 0.0203 | -4.541324777 | -0.45647689 |
| Den | 9.27932605 | 4.086750851 | 2.2706 | 0.0408 | 0.450437605 | 18.10821449 |
| SL 2 | 19.0965506 | 8.649037689 | 2.2079 | 0.0458 | 0.411440664 | 37.78166053 |
| ISV2 | -2454.489931 | 3594.932096 | -0.6828 | 0.5067 | -10220.86855 | 5311.888691 |
| SSV2 | 0.005006386 | 0.001832831 | 2.7315 | 0.0171 | 0.001046794 | 0.008965978 |
| Dens2 | -0.134312733 | 0.059553448 | -2.2553 | 0.0420 | -0.262970135 | -0.005655332 |

Model 6

| StatTools (Core Analysis Pack) | | | | | | |
|--------------------------------|---------------------------|-----------------------|--------------------------|--------------------------|--------------------|--------------------|
| Analysis: Regression | | | | | | |
| Performed By: ksekyiamah | | | | | | |
| Summary | Multiple R | R-Square | Adjusted R-Square | StErr of Estimate | | |
| | 0.9529 | 0.9080 | 0.8358 | 28.67460817 | | |
| ANOVA Table | Degrees of Freedom | Sum of Squares | Mean of Squares | F-Ratio | p-Value | |
| Explained | 11 | 113654.5774 | 10332.23431 | 12.5661 | < 0.0001 | |
| Unexplained | 14 | 11511.26415 | 822.2331535 | | | |
| Regression Table | Coefficient | Standard Error | t-Value | p-Value | Lower Limit | Upper Limit |
| Constant | 259.4614442 | 105.3915334 | 2.4619 | 0.0274 | 33.41908623 | 485.5038021 |
| SL | -68.87802107 | 57.02614393 | -1.2078 | 0.2471 | -191.1869354 | 53.4308933 |
| ORP | 0.058694053 | 0.073925831 | 0.7940 | 0.4405 | -0.099861085 | 0.217249191 |
| wat temp | 2.763645278 | 2.476699237 | 1.1159 | 0.2833 | -2.548346275 | 8.075636831 |
| sulfides | -0.143523501 | 0.141660699 | -1.0131 | 0.3282 | -0.447355483 | 0.16030848 |
| F/M | -75.00573507 | 18.83728054 | -3.9818 | 0.0014 | -115.4076836 | -34.60378652 |
| SSV (60) | -2.375348683 | 0.66409867 | -3.5768 | 0.0030 | -3.799698669 | -0.950998696 |
| den | 9.0831085 | 3.816428866 | 2.3800 | 0.0321 | 0.897682672 | 17.26853433 |
| SL 2 | 18.40594636 | 7.578456874 | 2.4287 | 0.0292 | 2.151772941 | 34.66011978 |
| ISV2 | -1782.033642 | 666.5306312 | -2.6736 | 0.0182 | -3211.599667 | -352.4676171 |
| SSV2 | 0.004740735 | 0.001148623 | 4.1273 | 0.0010 | 0.002277183 | 0.007204287 |
| Dens2 | -0.130972748 | 0.054923354 | -2.3846 | 0.0318 | -0.248771625 | -0.01317387 |

Model 7

| StatTools (Core Analysis Pack) | | | | | | |
|---------------------------------------|---------------------------|-----------------------|--------------------------|--------------------------|--------------------|--------------------|
| Analysis: Regression | | | | | | |
| Performed By: ksekyamah | | | | | | |
| Summary | Multiple R | R-Square | Adjusted R-Square | StErr of Estimate | | |
| | 0.9507 | 0.9039 | 0.8398 | 28.31910491 | | |
| ANOVA Table | Degrees of Freedom | Sum of Squares | Mean of Squares | F-Ratio | p-Value | |
| Explained | 10 | 113136.266 | 11313.6266 | 14.1073 | < 0.0001 | |
| Unexplained | 15 | 12029.57554 | 801.971703 | | | |
| Regression Table | Coefficient | Standard Error | t-Value | p-Value | Lower Limit | Upper Limit |
| Constant | 287.5623742 | 98.0399957 | 2.9331 | 0.0103 | 78.59506993 | 496.5296785 |
| SL | -66.53553719 | 56.2437159 | -1.1830 | 0.2552 | -186.4161799 | 53.34510549 |
| wat temp | 1.562742064 | 1.936865752 | 0.8068 | 0.4324 | -2.565589563 | 5.691073691 |
| sulfides | -0.169120316 | 0.136233156 | -1.2414 | 0.2335 | -0.459494415 | 0.121253783 |
| F/M | -77.97459507 | 18.23351844 | -4.2764 | 0.0007 | -116.8384197 | -39.11077047 |
| SSV (60) | -2.350383212 | 0.655129671 | -3.5877 | 0.0027 | -3.746759051 | -0.954007372 |
| den | 8.975262002 | 3.766725305 | 2.3828 | 0.0308 | 0.946677062 | 17.00384694 |
| SL 2 | 17.48390166 | 7.396100465 | 2.3639 | 0.0320 | 1.719486688 | 33.24831664 |
| ISV2 | -1861.429518 | 650.816394 | -2.8601 | 0.0119 | -3248.611825 | -474.2472109 |
| SSV2 | 0.004598464 | 0.001120494 | 4.1040 | 0.0009 | 0.002210188 | 0.00698674 |
| Dens2 | -0.127058071 | 0.05402341 | -2.3519 | 0.0328 | -0.242206244 | -0.011909898 |

Model 8

| StatTools (Core Analysis Pack) | | | | | | |
|---------------------------------------|---------------------------|-----------------------|--------------------------|--------------------------|--------------------|--------------------|
| Analysis: Regression | | | | | | |
| Performed By: ksekyiamah | | | | | | |
| Summary | Multiple R | R-Square | Adjusted R-Square | StErr of Estimate | | |
| | 0.9485 | 0.8997 | 0.8433 | 28.00853955 | | |
| ANOVA Table | Degrees of Freedom | Sum of Squares | Mean of Squares | F-Ratio | p-Value | |
| Explained | 9 | 112614.1889 | 12512.68766 | 15.9503 | < 0.0001 | |
| Unexplained | 16 | 12551.6526 | 784.4782877 | | | |
| Regression Table | Coefficient | Standard Error | t-Value | p-Value | Lower Limit | Upper Limit |
| Constant | 295.4978426 | 96.47567435 | 3.0629 | 0.0074 | 90.97854929 | 500.0171359 |
| SL | -49.89120971 | 51.75016638 | -0.9641 | 0.3494 | -159.5966617 | 59.81424224 |
| sulfides | -0.135310186 | 0.128206723 | -1.0554 | 0.3069 | -0.407096299 | 0.136475926 |
| F/M | -79.07267666 | 17.98325315 | -4.3970 | 0.0005 | -117.1954703 | -40.949883 |
| SSV (60) | -2.371440881 | 0.647430737 | -3.6628 | 0.0021 | -3.74393273 | -0.998949031 |
| den | 9.032464775 | 3.724757039 | 2.4250 | 0.0275 | 1.13633259 | 16.92859696 |
| SL 2 | 15.13091818 | 6.722338301 | 2.2508 | 0.0388 | 0.880197593 | 29.38163877 |
| ISV2 | -1939.834984 | 636.4633898 | -3.0478 | 0.0077 | -3289.077096 | -590.5928708 |
| SSV2 | 0.004574641 | 0.001107821 | 4.1294 | 0.0008 | 0.002226166 | 0.006923116 |
| Dens2 | -0.12674495 | 0.053429576 | -2.3722 | 0.0306 | -0.240010592 | -0.013479308 |

Model 9

| StatTools (Core Analysis Pack) | | | | | | | |
|---------------------------------------|--|---------------------------|-----------------------|--------------------------|--------------------------|--------------------|--------------------|
| Analysis: Regression | | | | | | | |
| Performed By: ksekylamah | | | | | | | |
| Summary | | Multiple R | R-Square | Adjusted R-Square | StErr of Estimate | | |
| | | 0.9455 | 0.8939 | 0.8440 | 27.95035882 | | |
| ANOVA Table | | Degrees of Freedom | Sum of Squares | Mean of Squares | F-Ratio | p-Value | |
| Explained | | 8 | 111885.058 | 13985.63226 | 17.9022 | < 0.0001 | |
| Unexplained | | 17 | 13280.78349 | 781.2225582 | | | |
| Regression Table | | Coefficient | Standard Error | t-Value | p-Value | Lower Limit | Upper Limit |
| Constant | | 227.605958 | 65.80512539 | 3.4588 | 0.0030 | 88.76927936 | 366.4426367 |
| Sulfides | | -0.146816501 | 0.127384824 | -1.1525 | 0.2650 | -0.415574988 | 0.121941985 |
| F/M | | -76.60059155 | 17.76252866 | -4.3125 | 0.0005 | -114.0762512 | -39.12493187 |
| SSV (60) | | -2.558744536 | 0.616309867 | -4.1517 | 0.0007 | -3.859044695 | -1.258444377 |
| Den | | 8.953298779 | 3.7161164 | 2.4093 | 0.0276 | 1.112978508 | 16.79361905 |
| SL 2 | | 8.779995657 | 1.336581867 | 6.5690 | < 0.0001 | 5.960054412 | 11.5999369 |
| ISV2 | | -2038.65226 | 626.8508411 | -3.2522 | 0.0047 | -3361.191929 | -716.1125905 |
| SSV2 | | 0.004835544 | 0.001072026 | 4.5107 | 0.0003 | 0.002573767 | 0.007097321 |
| Dens2 | | -0.118965312 | 0.052706976 | -2.2571 | 0.0375 | -0.230167311 | -0.007763313 |

Model 10

| StatTools (Core Analysis Pack) | | | | | | |
|---------------------------------------|---------------------------|-----------------------|--------------------------|--------------------------|--------------------|--------------------|
| Analysis: Regression | | | | | | |
| Performed By: ksekyiamah | | | | | | |
| Summary | Multiple R | R-Square | Adjusted R-Square | StErr of Estimate | | |
| | 0.9411 | 0.8856 | 0.8411 | 28.2041416 | | |
| ANOVA Table | Degrees of Freedom | Sum of Squares | Mean of Squares | F-Ratio | p-Value | |
| Explained | 7 | 110847.3167 | 15835.33095 | 19.9068 | < 0.0001 | |
| Unexplained | 18 | 14318.52486 | 795.4736036 | | | |
| Regression Table | Coefficient | Standard Error | t-Value | p-Value | Lower Limit | Upper Limit |
| Constant | 169.4179188 | 42.59001426 | 3.9779 | 0.0009 | 79.93961916 | 258.8962185 |
| F/M | -66.56293935 | 15.62146779 | -4.2610 | 0.0005 | -99.38242534 | -33.74345337 |
| SSV (60) | -2.182154019 | 0.527309557 | -4.1383 | 0.0006 | -3.289990289 | -1.074317749 |
| den | 7.938941699 | 3.643174747 | 2.1791 | 0.0429 | 0.284915577 | 15.59296782 |
| SL 2 | 8.335702901 | 1.291405005 | 6.4548 | < 0.0001 | 5.622561663 | 11.04884414 |
| ISV2 | -1685.169327 | 551.6614007 | -3.0547 | 0.0068 | -2844.166922 | -526.171731 |
| SSV2 | 0.004310136 | 0.00097908 | 4.4022 | 0.0003 | 0.002253166 | 0.006367107 |
| Dens2 | -0.107043764 | 0.052151302 | -2.0526 | 0.0549 | -0.216609585 | 0.002522056 |

Model 11

| StatTools (Core Analysis Pack) | | | | | | | |
|---------------------------------------|---------------------------|-----------------------|--------------------------|--------------------------|--------------------|--------------------|--------------|
| Analysis: Regression | | | | | | | |
| Performed By: ksekyamah | | | | | | | |
| Summary | Multiple R | R-Square | Adjusted R-Square | StErr of Estimate | | | |
| | 0.9267 | 0.8588 | 0.8142 | 30.49578283 | | | |
| ANOVA Table | Degrees of Freedom | Sum of Squares | Mean of Squares | F-Ratio | p-Value | | |
| | Explained | 6 | 107495.9789 | 17915.99648 | 19.2647 | < 0.0001 | |
| | Unexplained | 19 | 17669.86264 | 929.9927706 | | | |
| Regression Table | Coefficient | Standard Error | t-Value | p-Value | Lower Limit | Upper Limit | |
| | Constant | 183.9171905 | 45.41270227 | 4.0499 | 0.0007 | 88.86731229 | 278.9670688 |
| | F/M | -62.14847419 | 16.72989586 | -3.7148 | 0.0015 | -97.16454866 | -27.13239972 |
| | SSV (60) | -1.447050378 | 0.418475773 | -3.4579 | 0.0026 | -2.322930237 | -0.571170518 |
| | den | 0.649352529 | 0.878319585 | 0.7393 | 0.4688 | -1.188991491 | 2.487696548 |
| | SL 2 | 6.708086699 | 1.102096648 | 6.0867 | < 0.0001 | 4.401371906 | 9.014801493 |
| | ISV2 | -1119.405099 | 516.6912964 | -2.1665 | 0.0432 | -2200.852411 | -37.95778654 |
| | SSV2 | 0.003208522 | 0.000885405 | 3.6238 | 0.0018 | 0.001355348 | 0.005061696 |

Model 12

| StatTools | | (Core Analysis Pack) | | | | |
|-------------------------|---------------------------|-----------------------|--------------------------|--------------------------|--------------------|--------------------|
| Analysis: | | Regression | | | | |
| Performed By: | | ksekyiamah | | | | |
| Summary | Multiple R | R-Square | Adjusted R-Square | StErr of Estimate | | |
| | 0.9245 | 0.8548 | 0.8185 | 30.14811824 | | |
| ANOVA Table | Degrees of Freedom | Sum of Squares | Mean of Squares | F-Ratio | p-Value | |
| Explained | 5 | 106987.6609 | 21397.53217 | 23.5420 | < 0.0001 | |
| Unexplained | 20 | 18178.18067 | 908.9090333 | | | |
| Regression Table | Coefficient | Standard Error | t-Value | p-Value | Lower Limit | Upper Limit |
| Constant | 178.5524867 | 44.31814887 | 4.0289 | 0.0007 | 86.10644816 | 270.9985253 |
| F/M | -58.43836837 | 15.77756258 | -3.7039 | 0.0014 | -91.3497872 | -25.52694954 |
| SSV (60) | -1.349096705 | 0.392422475 | -3.4379 | 0.0026 | -2.167675644 | -0.530517765 |
| SL 2 | 6.882654762 | 1.064232539 | 6.4672 | < 0.0001 | 4.662704587 | 9.102604938 |
| ISV2 | -1013.339867 | 490.7157533 | -2.0650 | 0.0521 | -2036.954991 | 10.27525738 |
| SSV2 | 0.0031492 | 0.000871709 | 3.6127 | 0.0017 | 0.001330846 | 0.004967554 |

Model 13

| StatTools (Core Analysis Pack) | | | | | | |
|---------------------------------------|---------------------------|-----------------------|--------------------------|--------------------------|--------------------|--------------------|
| Analysis: Regression | | | | | | |
| Performed By: ksekyiamah | | | | | | |
| Summary | Multiple R | R-Square | Adjusted R-Square | StErr of Estimate | | |
| | 0.9076 | 0.8238 | 0.7902 | 32.40668937 | | |
| ANOVA Table | Degrees of Freedom | Sum of Squares | Mean of Squares | F-Ratio | p-Value | |
| Explained | 4 | 103111.7777 | 25777.94443 | 24.5459 | < 0.0001 | |
| Unexplained | 21 | 22054.06383 | 1050.193516 | | | |
| Regression Table | Coefficient | Standard Error | t-Value | p-Value | Lower Limit | Upper Limit |
| Constant | 149.8568233 | 45.23593073 | 3.3128 | 0.0033 | 55.78355546 | 243.9300911 |
| F/M | -51.31625258 | 16.54938913 | -3.1008 | 0.0054 | -85.73259133 | -16.89991383 |
| SSV (60) | -1.428204298 | 0.419806407 | -3.4021 | 0.0027 | -2.301239514 | -0.555169083 |
| SL 2 | 6.830570484 | 1.143639081 | 5.9727 | < 0.0001 | 4.452242818 | 9.208898151 |
| SSV2 | 0.003577324 | 0.000910127 | 3.9306 | 0.0008 | 0.00168461 | 0.005470037 |

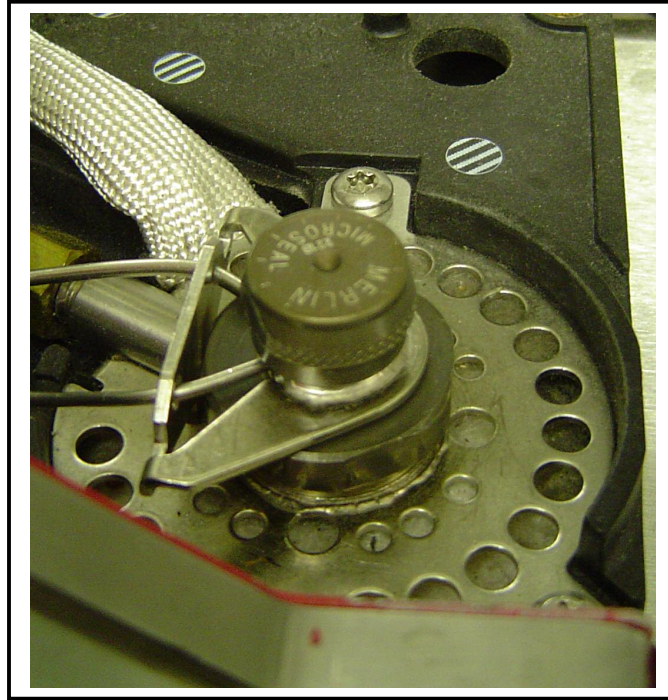
APPENDIX IV



Appendix IV - 1: An Aerial view of the DC WASA blue plains AWWTP



Appendix IV - 2: Designed flux chamber with stack for the secondary aeration tank



Appendix IV - 3: Merlin microseal for the GC-1

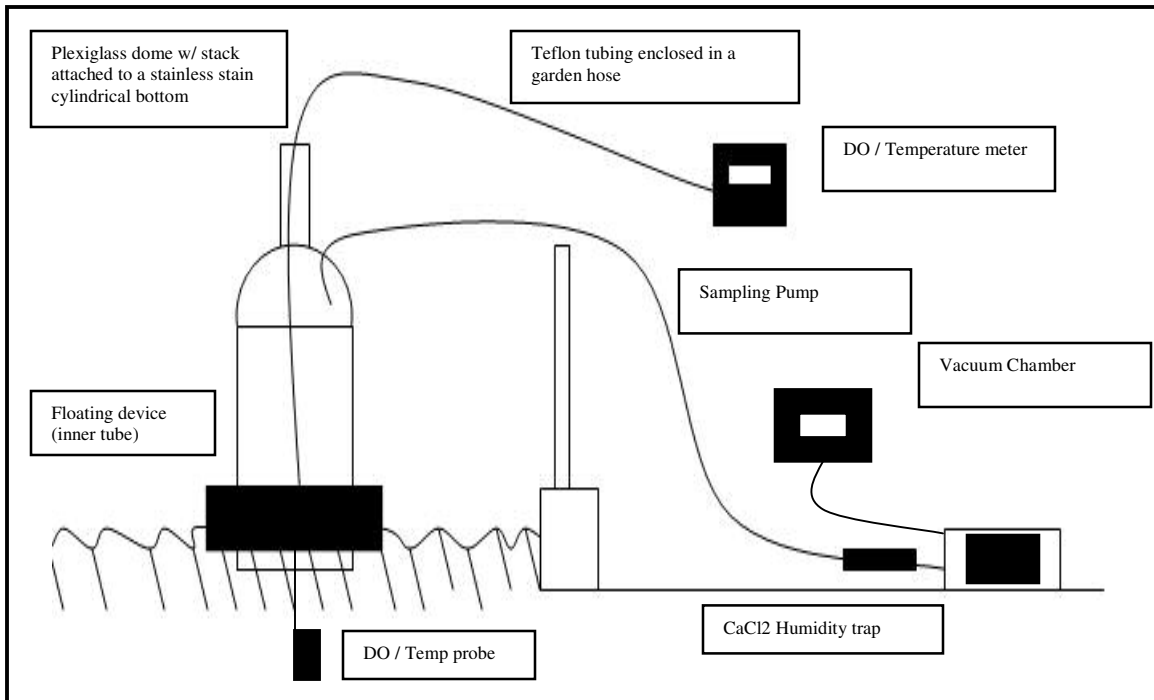




Appendix IV - 5: Exposure of SPME fibers in the Headspace method



Appendix IV - 6: Exposure of SPME fibers in the Tedlar bag method



Appendix IV -7: Schematic representation of the field sampling apparatus and set up



Appendix IV -8: Field sampling apparatus and set up

APPENDIX V

Table 1: Parameters used in statistical analysis.

| | Parameters | | | | | | | | | | | DMS | |
|-----------|------------|--------|----------|----------|------------|------|----------|-----------|------|----------|------|-----------|---------------|
| | Primary | | | | | | | Secondary | | | | Composite | Concentration |
| | SL | ORP | wat temp | sulfides | Spiked OUR | pH | sol iron | ISV | F/M | SSV (60) | SRT | den | 0.73* |
| 23-Feb-04 | 6.0 | -222.7 | 13.3 | 92.4 | 132.0 | 6.95 | 250 | 0.08 | 1.52 | 270 | 6.28 | 58.29 | 180 |
| 05-Mar-04 | 5.5 | -210.1 | 15.0 | 80.3 | 149.0 | 6.59 | 310 | 0.04 | 0.59 | 350 | 2.04 | 45.18 | 340 |
| 12-Mar-04 | 3.5 | -119.8 | 15.1 | 58.1 | 192.0 | 6.32 | 190 | 0.15 | 0.63 | 200 | 1.84 | 28.26 | 41 |
| 19-Mar-04 | 2.8 | 280.1 | 14.7 | 2.2 | 145.0 | 6.42 | 94 | 0.14 | 1.17 | 220 | 0.89 | 38.88 | 2.6 |
| 22-Mar-04 | 2.3 | 211.2 | 14.4 | 1.33 | 149.0 | 6.44 | 60 | 0.21 | 0.49 | 170 | 1.72 | 26.45 | 2.6 |
| 29-Mar-04 | 5.0 | -233.6 | 16.1 | 105.4 | 208.0 | 6.62 | 210 | 0.13 | 1.29 | 230 | 0.7 | 25.13 | 73 |
| 02-Apr-04 | 3.0 | -188.4 | 15.2 | 76.7 | 159.0 | 6.92 | 53 | 0.09 | 0.41 | 355 | 0.95 | 33.78 | 110 |
| 13-May-04 | 4.3 | -236.4 | 21.3 | 102.7 | 359.0 | 6.54 | 200 | 0.07 | 0.4 | 360 | 3.47 | 50.47 | 160 |
| 24-May-04 | 4.3 | -191.3 | 23.5 | 89 | 337.0 | 6.58 | 230 | 0.05 | 0.34 | 320 | 1.88 | 30.93 | 170 |
| 27-May-04 | 3.7 | -114.9 | 23.8 | 74.04 | 300.0 | 6.55 | 170 | 0.1 | 0.91 | 250 | 0.86 | 24.16 | 110 |
| 03-Jun-04 | 3.5 | -236.5 | 22.9 | 16.9 | 293.0 | 6.61 | 160 | 0.22 | 0.64 | 170 | 1.15 | 16.50 | 13 |
| 7-Jun-04 | 3.8 | -162.7 | 21.3 | 90.3 | 213.6 | 6.74 | 0.6 | 0.24 | 0.49 | 150 | 0.8 | 30.90 | 72 |
| 10-Jun-04 | 2.7 | -225.3 | 23.3 | 90.8 | 301.0 | 6.82 | 1.6 | 0.17 | 0.98 | 150 | 0.8 | 29.85 | 28 |
| 15-Jun-04 | 3.4 | -199.3 | 23.5 | 90.7 | 268.0 | 6.81 | 2.8 | 0.11 | 1.63 | 200 | 1.0 | 31.89 | 27 |
| 22-Jul-04 | 2.4 | -217.8 | 25.6 | 176.3 | 733.0 | 7.03 | 16.4 | 0.16 | 0.28 | 200 | 1.5 | 33.75 | 65 |
| 29-Jul-04 | 1.9 | -174.2 | 24.7 | 219.7 | 348.0 | 6.99 | 50.2 | 0.07 | 1.11 | 70 | 0.5 | 9.22 | 46 |
| 6-Aug-04 | 2.7 | -169.4 | 26.0 | 193.3 | 486.0 | 7.00 | 14.2 | 0.22 | 0.41 | 100 | 14.0 | 20.90 | 46 |
| 9-Aug-04 | 3.2 | -171.1 | 25.8 | 142.5 | 337.0 | 6.92 | 25.5 | 0.1 | 0.35 | 250 | 8.5 | 39.22 | 51 |
| 16-Aug-04 | 3.2 | -153.2 | 25.2 | 140.9 | 244.0 | 6.89 | 30.5 | 0.17 | 0.28 | 210 | 8.0 | 28.06 | 37 |
| 18-Aug-04 | 3.3 | -167.6 | 25.6 | 56.8 | 528.0 | 6.89 | 21.2 | 0.07 | 0.37 | 150 | 3.2 | 14.28 | 90 |
| 11-Oct-04 | 3.0 | -106.0 | 22.6 | 25.5 | 333.0 | 6.63 | 29.8 | 0.14 | 0.27 | 240 | 16.7 | 29.41 | 77 |
| 13-Oct-04 | 2.8 | -121.8 | 22.3 | 137.3 | 262.0 | 6.68 | 11.0 | 0.15 | 0.15 | 180 | 4.5 | 34.44 | 94 |
| 15-Oct-04 | 3.0 | -115.4 | 22.5 | 103.5 | 230.0 | 6.72 | 38.7 | 0.16 | 0.17 | 170 | 12.8 | 21.46 | 79 |
| 18-Oct-04 | 3.3 | -56.7 | 21.8 | 265.2 | 357.0 | 6.66 | 14.2 | 0.15 | 0.1 | 100 | 14.7 | 10.38 | 120 |
| 20-Oct-04 | 3.4 | -95.1 | 21.3 | 149.1 | 180.0 | 6.50 | 38.3 | 0.12 | 0.14 | 240 | 15.0 | 25.10 | 78 |
| 22-Oct-04 | 3.2 | -167.6 | 21.3 | 151.1 | 270.0 | 6.89 | 41.8 | 0.1 | 0.28 | 200 | 11.8 | 19.94 | 52 |

* Limit of quantification

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