Estimation of Volatilization Rate of Volatile Organic Compounds from Wastewater

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A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science in Engineering.

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DECLARATION

I declare that this research report is my own unaided work. It is being submitted for the degree of Master of Science in Engineering at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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Seitlotli Mamonyamane Ntlatleng

_________________ day of ____________________ year ____________________

DEDICATION

To my mother, Lisa and my late father, Marumo Ntlatleng

ABSTRACT

Air pollution became a major concern in South Africa in the late 1980's and regulatory requirements for the chemical process industries to reduce hazardous emissions have increased ever since. Volatile organic compounds (VOCs) contribute significantly to the formation of ozone and photochemical oxidants and their associated impact on human health has become a major issue worldwide. Volatilisation is a significant process in determining the fate of organic compounds in the environment.

In this study, volatilisation rate of VOCs (specifically benzene, toluene, ethylbenzene, and xylene) from a wastewater collection basin, also called the oily sewer basin (OSB) was measured using a flux chamber method and the VOCs were characterised. Theoretical models that can be used to estimate volatilisation rate were also studied. Meteorological data was collected to evaluate the effect of temperature, humidity and wind speed on volatilisation rate.

This study showed that toluene and ethylbenzene have the highest volatilisation rate compared to benzene and o-xylene. It was found that system conditions and physico-chemical properties of a compound have a significant effect on volatilisation. It was also identified that the measured concentrations of VOCs escaping from the OSB do comply with Occupational Health and Safety Act and Regulations 85 of 1993 standards. It was recommended that surfactants be used to inhibit volatilisation of VOCs.

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CHAPTER 1: INTRODUCTION

Tropospheric air pollution has been a problem from the 13th century. Air pollution problems from then until the mid-20th century were primarily associated with sulphur dioxide and soot particles (Finlayson-Pitts and Pitts, 1997). According to Finlayson-Pitts and Pitts (1997), it was after the observations of the impacts of photochemical air pollution in Los Angeles in the 1940's that high concentrations of ozone and photochemical oxidants became a major concern worldwide. In South Africa, air pollution became a problem in the late 1980's as a result of concerns expressed over high emissions from industries in the highveld (Chiloane, 2004). Atasoy et al. (2004) state that the uncontrolled emissions of volatile organic compounds (VOCs) occurring today are increasingly subject to legislative controls because of their serious implications on human health and are precursors in the production of tropospheric ozone (Lee et al., 2002). It is for this reason that VOCs emissions must be monitored and controlled.

Many wastewater treatment plants are concerned about the emission of VOCs which are harmful to employees and residents living near the plant (Lee et al., 2004). According to Lee et al. (2004) and Chao et al. (2005a), for VOCs in bodies of water, volatilization seems to be the most likely pathway for the VOCs to take in the environment. It is important to understand the volatilisation process, in order to be able to predict and estimate mass flux of VOCs over a body of water. It is also important to understand the relationship between volatilization rate of VOCs and the system parameters in order to design a system/process to capture and destroy them before they escape into the atmosphere.

The wastewater disposal site under study is called the Oily Sewer Basin (OSB) and it serves the surrounding chemical industries. The OSB is fed by all the process drains on the site. The wastewater is from the processes themselves, washing process equipment, leaks (valves, vessels, pipe sections etc.) and accidental spills that are washed down the drains. As the process conditions over the plant fluctuate so does the composition of the contaminated water that is received by the OSB. It is therefore complex to estimate the exact composition of the wastewater and the vapour that volatilises from the OSB, but it has been shown to contain acetone, benzene, toluene, ethylbenzene and xylene (BTEX) components, C6-C12 alkanes and other BTEX derivates.

All the wastewater and storm-water from the plants that may be contaminated with VOCs is collected via a drainage system to the OSB, where the material separates into aqueous and organic layers. The organic layer is skimmed with scrapers to remove the tarry, viscous substance that accumulates on the surface. The aqueous layer is treated in a bioreactor to destroy the organic molecules dissolved in the water. While the liquid is separating into the two layers, the organic surface layer is exposed to the atmosphere and VOCs evaporate, forming fugitive emissions.

The VOCs emission flux from the wastewater can be measured using a flux chamber but mass transfer models are preferred in estimating this flux (Bunyakan et al., 2006). Existing mass transfer models are based on volatilisation of solutes from pure water instead of industrial wastewater and they only look at the effect of wind speed and liquid temperature (Bunyakan et al., 2006). Therefore, it is necessary to look at other factors that affect volatilisation rate such as, solubility, depth of the basin and presence of surfactants.

The main purpose of this research is to estimate the level of volatilisation rate for a range of individual VOCs (particularly benzene, toluene, ethylbenzene and xylene). In addition, this research aims to develop a model to estimate/predict the VOCs flux from the OSB using mechanistic modelling and taking diurnal variations into account. Mechanistic modelling uses theoretical principles and equations to model a process or system.

The primary objectives of this research are to:

- characterise the vapours volatilising from the OSB
- analyse and discuss the effects of wind speed and depth of the collection basin on the volatilization rate
- compare government standards with the measured emissions
- evaluate existing models
- compare direct measurements of VOCs from the oily sewer basin with model estimates

The novelty of this work lies not in finding a model to estimate volatilisation rate but also in providing an understanding of the theoretical explanations of the effect of system parameters such as surface turbulence, basin dimensions and surfactants on the VOC flux over the water body. This will to enable future work to use add-on pollution control technologies to capture, recover and/or destroy VOCs.

The remainder of this research report consists of four chapters. Chapter 2 is the literature review, which gives further justification for this research by discussing in detail the impact of VOCs on the environment and human health. It also provides an understanding of the volatilisation process as well as a comparison of the different models that are used to predict volatilisation rate. Chapter 3 discusses the method employed in this study, a detailed site description and the sampling and analysis method. The raw data collected and the VOC flux predicted by the model, are presented and discussed in chapter 4. Chapter 5 gives the summary of important findings, conclusions and recommendations.

CHAPTER 2: LITERATURE REVIEW

2.1 Characterization of Wastewater

Some of the chemical wastewater is produced from the Fischer-Tröpsh process; therefore to characterize the wastewater the process must be understood. This will give an indication of what could be in the wastewater under study.

There is insufficient information on the reaction mechanism of Fischer-Tröpsch Synthesis to predict the hydrocarbon products under different reaction conditions (Ngwenya, 2003). It is thought that the reaction occurs via a polymerization mechanism where carbon-carbon bonds are formed from carbon derived from the reaction of carbon monoxide with hydrogen using a metal catalyst surface. The chemistry of Fischer-Tröpsch is described by the following equations:

$$(2n+1)H_2 + nCO \longrightarrow C_nH_{2n+2} + nH_2O \qquad (1)$$

$$2nH_2 + nCO \longrightarrow C_nH_{2n} + H_2O \qquad (2)$$

$$2nH_2 + nCO \longrightarrow C_nH_{2n}OH + (n-1)H_2O \qquad (3)$$

Undesired side reactions such as the water gas shift reaction and the Boudouard reaction, which results in carbon deposition on the catalyst, also occur:

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad (4)$$

$$2CO \longrightarrow C + CO_2 \qquad (5)$$

The Fischer-Tröpsch reaction is described as non-selective and its product slate varies considerably with catalyst, reaction conditions and process design. The products mainly consist of paraffins, olefins, variable amounts of alcohols, aldehydes, acids, esters and aromatic compounds (Ngwenya, 2003). All these compounds may be in the wastewater but volatilisation of all the compounds cannot be studied. According to Chao et al. (2005a), to avoid the influence of the molecular shape on molecular diffusion, chemicals with the same physico-chemical properties must be considered. Thus aromatic hydrocarbons (BTEX compounds) were chosen for this research because of the availability of thermodynamic properties data in literature.

2.2 Volatile Organic Compounds

The term volatile organic compound (VOC) refers to the entire set of the vapour phase atmospheric organics excluding carbon monoxide and carbon dioxide (Seinfield and Pandis, 1998). Atasoy et al. (2004) define VOCs, including aromatic hydrocarbons, as vapour phase atmospheric organics with a vapour pressure greater than 1mmHg. The VOCs may come from both biogenic and anthropogenic sources. Anthropogenic sources include wastewater treatment plants (WWTPs) (Atasoy et al., 2004 and Bunyakan et al., 2006), vehicle emissions and fuel production and consumption (Seinfeld and Pandis, 1998). Toxic effects of VOCs arising from WWTPs have significant adverse consequences, not only on public health but also on the wastewater plant workers within the industrial setting (Atasoy et al., 2004).

Volatile organic compounds are central to atmospheric chemistry from the urban to the global scale. According to Finlayson-Pitts and Pitts (1997), the chemistry involving VOCs and nitrogen oxides (NO_x) is complex, and it results not only in the formation of ozone but a variety of additional oxidizing species. A number of VOCs undergo complex photochemical reactions to form smog. The smog formed contains a range of secondary air pollutants which are mostly oxidants (Atasoy et al., 2004).

According to Finlayson-Pitts and Pitts (1997), ozone is primarily formed by photolysis of nitrogen oxide, it then dissociates in the presence sunlight to form an electronically excited oxygen atom which reacts with water vapour to form a hydroxyl (OH) radical. The OH radical oxidises the organic compounds which in turn help to convert nitrogen oxide to nitrogen dioxide. Then the cycle starts again. A high concentration of ozone in the troposphere is associated with negative health impact and damage to vegetation (Zunckel et al., 2004 and Atasoy et al., 2004). Therefore VOCs must be regulated, controlled and monitored.

All VOCs are important because of their impact on human health and the environment but BTEX compounds are seen as the most harmful of these species in petrochemical industry. The BTEX compounds are important family of organo-pollutants which are components of gasoline and aviation fuels and are widely used in industrial processes. They are carcinogenic and neurotoxic and are classified as priority pollutants by the Environmental Protection Agency (EPA) (Yadav and Reddy, 1993). It has been shown that they can be degraded by aerobic and anaerobic bacteria. Their kinetic and thermodynamic properties are presented in Table 2.1.

Table 2.1: Physico-chemical properties of the BTEX compounds

Compounds	**Chemical Formula**	**Molecular Weight (g/mol)**	**H[a] (atm.m^3/gmol)**	**Vapour Pressure[b]**	**Boiling pt.[c] (K)**	**Molar volume[d] (m^3/mol)**
Benzene	C_6H_6	78.11	5.50×10^{-3}	0.125	353.2	0.096
Toluene	C_7H_8	92.14	6.68×10^{-3}	0.037	383.8	0.118
Ethylbenzene	C_8H_9	106.17	6.44×10^{-3}	0.013	409.3	0.141
o-Xylene	C_8H_{10}	106.17	5.27×10^{-3}	0.009	417.6	0.144

[a]Values were obtained from Atasoy et al. (2004) at 298 K, [b]values calculated from Antoine's equation (Antoine's constants found in Sinnot (1999)), [c]values obtained at 1 atm from Sinnot (1999),[d]values at normal boiling point obtained from Lee et al. (2004).

Benzene is a clear, colourless liquid with a sweet aromatic odour (Chiloane, 2004). According Hart and Schuetz (1966), benzene is the parent compound of all aromatic substances. Coal tar is said to be a significant source of benzene and large amounts of it are produced during petroleum refining by aromatization of alkanes (Hart and Schuetz, 1966). It is released when fossil fuels are burned, when gasoline evaporates and from wastewater (Chiloane, 2004, Chao et al., 2005a, Lee et al., 2004). According to Chiloane (2003), exposure to benzene over a period of 14 days has acute health effects, such as headache, dizziness and skin, eye and lung irritation; over a period longer than 365 days, the effects are chronic, and these include cancer, leukaemia, aplitic anaemia and reproductive problems in women.

Toluene is a clear, colourless liquid with a sweet benzene-like odour. It naturally occurs in crude-oil fuels and it is released during the process of making gasoline. It is a flammable liquid, its vapour is heavier than air and can decompose at high temperatures to form toxic gases. It is easily washed out by rain (Chiloane, 2004). According to Yoon and Park (2002), toluene is toxic to the liver, kidneys and central nervous system when it enters the body by skin contact and inhalation.

Ethylbenzene is a colourless liquid with a gasoline-like smell and molecular formula of C_8H_9. It is used in aviation and automotive fuels, in the manufacture of cellulose acetate and as a precursor to styrene. It may be released into the atmosphere from fugitive emissions from its use in gasoline, accidental spills and industrial use. Ethylbenzene is known to have acute and chronic health effects but no information is available in this regard. It is not classified as a carcinogen in humans by the EPA (Chiloane, 2004).

Xylene has three different isomers, meta-, ortho- and para-xylene. The combination of these forms is called xylenes. They occur naturally in petroleum and coal tar; and are used as solvents in the printing, gasoline, rubber and leather industries. Xylenes are not classified by the EPA as carcinogenic to human (Chiloane, 2004).They, like toluene, may be toxic to the liver, kidneys and central nervous system when they enter the body by skin contact and inhalation (Yoon and Park, 2002)..

The Occupational Health and Safety Act and Regulations 85 of 1993 for South Africa, has set occupational exposure limits for various chemicals including benzene, toluene, ethylbenzene and xylene in the workplace. The Occupational Exposure Limit – Control Limit (OEL-CL) like Threshold Limit Value (TLV) is defined as the maximum concentration of an airborne substance averaged over a reference period to which employees may be exposed by inhalation. The Occupational Exposure Limit – Recommended Limit (OEL-RL) is defined as the concentration of an airborne substance averaged over a reference period, at which, according to current knowledge, there is no evidence that it is likely to be injurious to employees.

The effects of hazardous chemicals on human health due to exposure differ depending on the nature of the substance and exposure period. Therefore, there are different categories of TLVs. The long-term exposure limit (8-hour time weighted average) is intended to control and restrict the total intake by inhalation over one or more working shifts. The short-term exposure limit (over 15 minutes) may be applied to substances where effects may be seen after brief exposure which has occurred once or repeatedly. The ceiling limit is the amount of chemical that should not be exceeded at any time

The OEL-RL short-term exposure limits for toluene, ethylbenzene and xylene are 560, 545 and 650 mg/m^3 respectively. The OEL-RL long-term exposure limit for toluene, ethylbenzene and xylene are 188, 435 and 435 mg/m^3 respectively. The OEL-CL long-term exposure for benzene is 16 mg/m^3. Benzene only has a long-term control limit.

2.3 Physico-Chemical Properties of the BTEX Compounds

Physico-chemical properties of chemical compounds give an indication of the rate at which a compound may volatilise. According to Mackay and Wolkoff (1973), compounds with high molecular weight and low vapour pressure usually evaporate slowly. Lee et al. (2004) and Chao et al. (2005 a) state that compounds with low Henry's law constants volatilise much more slowly than those with Henry's law constants. So, for example, benzene should evaporate more rapidly than toluene according to Mackay and Wolkoff (1973) and the data in Table 2.1 because benzene has a lower molecular weight and a higher vapour pressure; but according to Lee et al. (2004) and Chao et al. (2005a) toluene will volatilise faster than benzene because it has a higher H value. It can be seen that the general statements that Mackay and Wolkoff (1973) and Lee et al. (2004) and Chao et al. (2005a) may be contradictory. This will be further discussed in Chapter 4.

2.4 Volatilization Process

Volatilization is a significant process that determines the fate of many organic solutes in streams (Lee et al., 2003; Thomas, 1990). Volatilisation is the transport of chemicals from water bodies into the atmosphere (Smith et al., 1980). A good understanding of the evaporative transport of chemical compounds in water is necessary for better assessments of the environmental consequences of pollutants (Chiou et al., 1980). Knowledge of volatilization is necessary to determine the amount of chemicals that enter and leave the atmosphere and the change of pollutant concentrations in water bodies (Lee et al., 2004; Thomas, 1990).

The fugitive VOC emissions from WWTPs seem to occur mainly through the following mechanisms (Atasoy, 2004):

- diffusive volatilisation, which is driven by the concentration differences between the air and the aqueous phase

- convective stripping via agitation
- evaporation which is driven by a temperature difference between the air and the aqueous phase
- simultaneous impacts of the above mechanisms

Atasoy et al. (2004) define volatilisation as a quiescent or wind driven loss of VOCs. According to Mackay et al. (1979), the volatilisation process consists of diffusion of solutes from the bulk of the water to the interface, followed by transfer across the interface and finally diffusion from the interface to the bulk of the air phase. This transfer of chemicals from the water to the atmosphere depends on the chemical and physical properties of the pollutant, the presence of other pollutants and their physical properties, wastewater velocity, depth, turbulence of the water body and the atmosphere above it. Other factors that affect volatilization include solubility, molecular weight, and vapour pressure of the chemical, Henry's law constant (H) and the nature of the air-water interface through which it passes (Lee et al., 2004; Thomas, 1990).

Volatilisation is not only a mass transfer process but it can be explained using thermodynamics. According to Gianniou and Antonopoulos (2007) and Lufu (1999), an evaporation process depends on the availability of thermal energy and the vapour pressure deficit between the evaporating surface and the overlying air, which in turn depends on meteorological factors such as temperature, relative humidity and wind speed and direction. Lufu (1999) states that for evaporation to occur, there must be a continuous supply of heat to meet the latent heat requirement, the partial pressure in the atmosphere must be lower than the vapour pressure of the surface of the evaporating body. The factors that affect volatilisation and the methods used to estimate volatilization rate are discussed in depth in the remainder of this chapter.

2.5 Factors Affecting Volatilization

The factors that affect the volatilization process change rapidly and over a wide range in the natural environment. This complicates the task of providing data for modelling. The processes are often nonlinearly interdependent and do not behave in a simple, deterministic way (Thomas, 1990). For example, according to Smith et al. (1980), chemical compounds of low molecular weight and high vapour pressure have shown to volatilise rapidly, however, some high-molecular-weight, low solubility compounds may volatilise at an appreciable rate because they have a high activity coefficient in aqueous solution. Thus it is important to understand the relationship between emission rate of VOCs and the system parameters that affect the emission.

The volatilisation rate may be increased by mixing and thermal energy and inhibited by dissolved chemicals. Three fundamental solute parameters, Henry's law constant (H), molecular weight (M) and molar volume at the normal boiling point (V_b) are used to correlate volatilisation rate (Lee et al., 2004). According to Thomas (1990), the volatilisation process depends, in addition to the thermodynamic or physical properties of a chemical listed above, diffusivity coefficient and the presence of modifying materials such as adsorbents, organic films, electrolytes and emulsions. Furthermore, volatilisation is affected by the chemical and physical properties of the water body and atmospheric conditions.

2.5.1 Physical and chemical properties of the solute

Solubility

Solubility in water is one of the parameters that affects the fate and transport of organic chemicals in the environment. The extent of solubility affects the transport pathways of chemicals from water bodies such as volatilisation and deposition from the atmosphere by rain.

Solubility of a chemical in water may be defined as the maximum amount of the chemical that will dissolve in pure water at a specific temperature. According Lyman (1990), no organic compound is completely insoluble in water; they are all soluble to some extent.

Solubility in water is a function of temperature, and most organic compounds become more soluble as temperature increases. Benzene is an example of a compound whose solubility increases with increasing temperature. There are some chemicals however, whose solubility may either decrease at higher temperatures depending on the nature of the chemical and the temperature range involved (Lyman, 1990).

The presence of dissolved salts and organic matter has an effect on solubility. The presence of dissolved salts may lead to moderate decreases in solubility (referred to as salting out) whilst organic matter may increase the solubility of many organic chemicals in water. The solubility of aromatic hydrocarbons however, is not affected by the presence of organic matter. Surfactants can also increase the solubility by forming organic droplets into which the solute partitions (Lyman, 1990).

Henry's law constant (H)

According to Thomas (1990), Lee et al. (2004) and Chao et al. (2005a) the value of H gives an indication of processes that control the rate of volatilisation. H can be calculated in different ways and its units differ according to the way it is measured and calculated. For example:

$$H = {}^{C_g}\!/_{C_L} \qquad \text{(dimensionless)} \qquad (6)$$

$$H = {}^{P_{vp}}\!/_{S} \qquad (\text{atm.m}^3/\text{mol}) \qquad (7)$$

$$H = {}^{P_{vp}}\!\!\diagup_{C_L} \qquad \text{(atm.m}^3\text{/g)} \qquad (8)$$

where P_{vp} is the vapour pressure of the solute at a specific temperature and S is the solubility of that solute at the same temperature, C_g and C_L are concentrations of the gas and liquid phase respectively. For the purpose of this report, several definitions of H have been used.

According to Thomas (1990), values of H in the following ranges give an indication of what will happen to a chemical compound in a water body:

If H is less than 3×10^{-7} atm.m^3/mol, the compound is less volatile than water and its concentration increases as the water evaporates.
In the range of $10^{-7} < H < 10^{-5}$ atm.m^3/mol, the compound volatilises slowly at the rate that depends on the value of H. The gas phase resistance is dominant over that of the liquid by a factor of at least ten. The rate is controlled by slow molecular diffusion into the atmosphere.
When H is below 2×10^{-3} atm.m^3/mol, the compound tends to be quite soluble in the liquid and volatilisation is controlled by gas phase resistance.
When H ranges between 10^{-5} and 10^{-3} atm.m^3/mol, both the liquid and the gas phase resistance are significant. Volatilisation of compounds in this range is less rapid.
Where H is higher than 10^{-3} atm.m^3/mol, the liquid phase resistance dominates by a factor of at least ten. The transfer is liquid phase controlled.

Most of the hydrocarbons are hydrophobic and have relatively high values of H, the resistance lies in the liquid phase. If the atmospheric concentration is negligible, the transfer coefficient is independent of the value of H (Thomas, 1990). According to Paasivirta et al. (1999) and Thomas (1990) the H is dependent on temperature via the temperature dependence of solubility and vapour pressure. Seinfeld and Pandis (1998), state that Henry's law can only be used for dilute solutions.

Vapour pressure

It is important to have a reliable method of estimating the vapour pressure of organic materials in order to predict the behaviour and fate of chemicals that are introduced into the environment. In turn, vapour pressure may be used to estimate the rate of evaporation of chemicals (Grain, 1990).

In order to estimate vapour pressure using the Clausius-Clapeyron equation (9) at a desired temperature, the following information is required: critical temperature, critical pressure, and heat of vaporisation (ΔH_v) at some reference temperature

$$\frac{d \ln P_{vp}}{dT} = \frac{\Delta H_v}{\Delta Z R T^2} \tag{9}$$

where R is the gas constant, T is the temperature and ΔZ is the compressibility factor

Another method of estimating vapour pressure with good accuracy is Antoine's equation (10) which is applicable over the pressure range of 760 mmHg to 10^{-3} mmHg. According to Grain (1990), none of the equations can estimate pressures below 10 mmHg without a 10 % deviation from experimental data.

$$\ln P_{vp} = A - \frac{B}{T - C} \tag{10}$$

Effect of surfactants, organic mass and dissolved solutes

Surfactants are surface active agents which can reduce volatilisation rate even with good mixing (Smith et al., 1980). The effect of surfactants on volatilisation is related to the ability of surfactants to form micelles and can be understood from the concept of solubility and phase partitioning. Surfactant molecules exist as monomers, when dissolved in water below a certain concentration. The surfactant molecules conglomerate to form micelles, when the concentration in the water is above the critical micelle concentration. The surfactant micelles provide a microscopic organic environment into which solutes may partition. This property promotes an apparent aqueous solubility of relatively water-insoluble solutes. A solubility enhancement for a solute will decrease its depletion rate in the liquid phase by volatilisation (Lee et al., 2004).

According to Lee et al. (2004), the inhibition effect of surfactants on volatilisation depends on the concentration, molecular size, structure and polarity of the surfactant. It is also stated that, surfactants with a greater non-polar content may result in a greater solubility enhancement for a given organic solute and hence a greater reduction in the volatilisation rate.

According to Bunyakan et al. (2006), the presence of organic mass in the wastewater provides a barrier for mass transfer and reduces the degree of turbulence in the water due to an increase in viscosity, therefore reducing the volatilisation rate. In addition, suspended solids cause a reduction of volatilisation of VOCs from the wastewater. The mechanisms responsible for this decrease in volatilisation rate are: adsorption of VOCs onto the solid particles, the solid particles forming a barrier to mass transfer and suppression of liquid turbulence.

Properties of the water body

The transfer of a chemical involves several sequential steps depending on the type of the water body involved. Each of the stages has a characteristic rate, diffusion velocity or resistance, and the slowest stage is the rate controlling step of the overall volatilisation rate.

For a stratified water body, the stages may be (Thomas, 1990):

- release from the sediments
- diffusion through the hypolimnion
- diffusion through the thermocline
- diffusion through the epilimnion to just below the surface
- diffusion through the stagnant surface liquid film
- transfer across the air-water interface
- diffusion through the atmospheric film to the bulk of the atmosphere

The transfer of the chemical through these layers is only possible by bulk movement or molecular diffusion. In a well mixed water body, the resistance lies in the gas and liquid phase interfacial layers and a concentration gradient develops in the surface layers (Thomas, 1990).

According to Bunyakan et al. (2006), volatilisation of VOCs from wastewater due to surface wind speed may depend on water depth. At a given wind speed, volatilisation rate is inversely proportional to water depth. This is because at high water depth, the degree of turbulence due to the surface wind is lower than that at the lower depth.

2.5.2 Meteorological effects

Atmospheric conditions, particularly wind speed and stability are rate controlling factors. According to Thomas (1990), volatilization is relatively insensitive to atmospheric temperature, since the principal effect of temperature is on the vapour pressure. Atmospheric temperature affects the class of chemicals whose volatilization is controlled by processes that occur in the vapour phase (for example, compounds with a low H value). Liquid temperature affects volatilisation directly through its effect on H, and indirectly through its effect on vapour pressure. It also affects the liquid mass transfer coefficient through its effect on diffusivity (Thomas, 1990). Paasivirta et al. (1999), state that the effect of temperature on the volatilisation can be seen through the effect of seasonal and diurnal variation on emission rate. This is further discussed at in Chapter 4, when diurnal variation effect on the measured emission rate is looked at.

Wind modifies surface hydrodynamics and depending on the wind speed, ripples may form and thus increase the transfer of chemicals into the atmosphere. This effect of wind on volatilisation rate is due to the increased surface area for evaporation. According to Gholson et al. (1991), surface wind velocity and surface temperature control liquid turbulence and diffusion. The volatilisation process is also a function of humidity. When the air is humid, the evaporation rate of water decreases, consequently reducing the volatilisation rate of the organic compounds present in the wastewater.

2.6 Method Selection

This section presents the different methods that can be used to estimate volatilisation rate. This includes direct measurement of emission rate and theoretical models that can be used to predict volatilisation rate.

2.6.1 Direct estimation method - flux chamber method

The flux chamber method is an enclosure method used for direct measurement of volatile organic emissions from quiescent liquid surfaces. As can be seen from Figure 2.1, it works by enclosing a representative area of the source surface, and then a controlled flow of pure inert sweep gas is added to the chamber. Organic vapours escaping from the water surface enter the headspace of the chamber and are mixed with the sweep air, and then released through the chamber exit (Cheng and Chou, 2003; Gholson et al., 1991; Tillman and Smith, 2004).

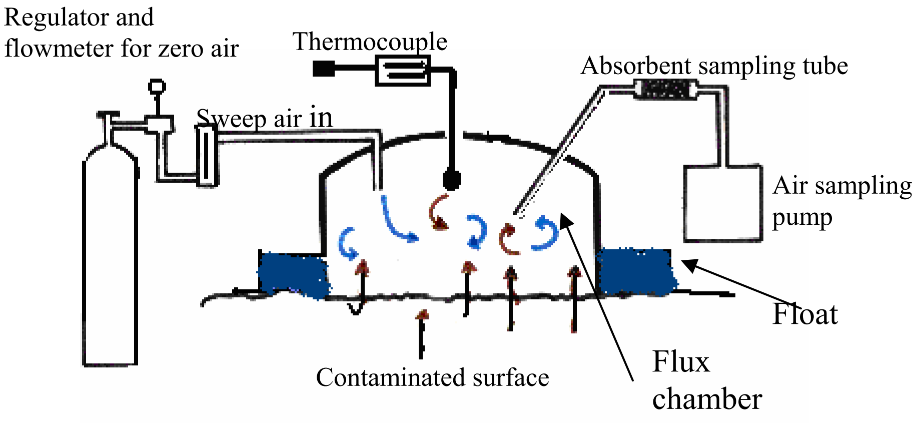

Figure 2.1: A schematic representation of the flux chamber method (Adapted from http://www.leederconsulting.com/images/flux_chamber_air.gif)

The concentrations of the emitted compounds are measured from the absorbent sampling tube. The emission rate is given by (Gholson et al., 1991):

$$E_i = {}^{C_i f}\!\big/_{A} \qquad (11)$$

where f is the sweep flow rate (l/min), A is the surface area enclosed (m^2), C_i is the concentration of the emitted gas (mg/l) and E_i is the emission rate (mg/ m^2.min)

According to Gholson et al. (1991), for this method to measure the true emission rate, the chamber gas sampled must be well mixed and the chamber must not disturb the surface in a way that might alter the natural emission rate. Placing the chamber on a liquid surface can affect the surface wind velocity and temperature to some extent, but, since the turbulent motion of the surface is as a result of a large scale process, the effect of the chamber is regarded as minimal. Chamber insertion depth may affect the diffusion and mixing of compounds at the surface and should be kept at minimum.

Chamber sweep flowrate and inlet height could affect the surface and vapour phase concentrations inside the chamber. In order to prevent a build-up of volatile organics in the chamber, the sweep flow must be optimised. If the sweep flowrate is too low, the vapour-phase concentration of organics will reach a point where gas phase resistance will control the emission process. Therefore, a high sweep flowrate is needed to maintain a good concentration gradient across the liquid-gas interface. This is similar to the natural environment; air turbulences and mixing prevent the gas phase concentrations from reaching significant levels. It is recommended that sweep flowrates above 2*l*/min be used to prevent concentration build-up in the chamber which adversely affect both precision and accuracy. (Gholson et al., 1991)

The chamber might cause a reduction in surface temperature and a decrease in the rate of evaporation by attenuation of solar radiation. Conversely, the greenhouse effect could cause an increase in surface temperature.

2.6.2 Mackay and Wolkoff method

Mackay and Wolkoff (1973) analysed the volatilization of chemicals from water bodies on the basis of thermodynamic equilibrium considerations (Thomas, 1990). The ratio of contaminant to water in the vapour phase is generally greater than the ratio in the liquid phase, thus it can be said that evaporation causes a decrease in concentration of contaminant in the liquid phase. If the actual water evaporation rate is available, then the aqueous contaminant concentration can be expressed as a function of time (see Equation 12). The rate of volatilisation of a contaminant is then calculated from the rate of evaporation of water and the ratio of the contaminant to water in the vapour.

Mackay and Wolkoff (1973) model can be expressed as:

$$\ln\left(\frac{C_{i0}}{C_i}\right) = {EP_{is}M_i 10^6 t} \Big/ {18GP_w C_{is}} \tag{12}$$

where:

C_i is concentration of compound i at time t

C_{io} is the initial concentration of i *in water*

C_{is} is the concentration of i at the interface

E is amount of water that evaporates from solution per day

P_{is} is vapour pressure of pure liquid i

M_i is the molecular weight of i and 18 is the molecular weight of water

t is time

G is the amount of water in the basin (g)

P_w is partial vapour pressure of water

In order to develop this model, the following assumptions were made (Mackay and Wolkoff, 1973):

- The contaminant concentration used is that which is truly in solution, that is, there are no colloidal, suspended, ionic, complexed or absorbed forms of the contaminant.
- The vapour formed is in equilibrium with the liquid at the interface
- Mixing is sufficiently rapid that the concentration at the interface is equal to that of the bulk of the water
- The water evaporation rate is negligibly affected by the presence of the contaminant

This model represents situations where the compounds evaporate from the upper layers without a concentration gradient appearing. These are situations where perfect mixing and equilibration of the liquid phase occurs. This situation might not be approached in practice, where the evaporation rate may be reduced by the delay in transferring the contaminant from the bulk of the liquid to the depleted interfacial area.

2.6.3 Liss and Slater method

The Liss and Slater method uses a two film theory model. It is a classic theory describing organic solute evaporating from a liquid surface. It is a generally accepted method for calculating volatilisation rates of organic solutes from water (Mackay and Yeun, 1983).

According to Chao et al. (2005a) and Thomas (1990), this model assumes that there is a transient layer through which chemicals pass by molecular diffusion, to form the interface between the liquid and gas film. Molecular diffusion, as well as mass transfer coefficients, depends on layer geometry and composition and it is affected by environmental conditions. This is because environmental conditions affect thickness, diffusivity, resistance, and geometry of the layer. The liquid and gas film transfer resistances of a chemical are related to its respective mass transfer coefficients. Figure 2.2 gives a schematic description of the two-film theory, for which the mass flux of volatilisation can be expressed as (Chao et al., 2005a):

$$Q = k_L\left(C_L - C_L^*\right) = k_g\left(C_G^* - C_G\right) \tag{13}$$

where Q is volatilization mass flux, k_L is the liquid-phase transfer coefficient; k_g is the gas-phase transfer coefficient, C_L and C_L^* the concentration of the bulk liquid and liquid side of the interface respectively. C_G and C_G^* are the concentration in the bulk air and f the interface of the gas side, respectively. Figure 2.2 explains the volatilisation process as a three step process, diffusion of a solute from the bulk of the water to the interface, followed by transfer across the interface and then diffusion from the interface into the bulk of the air (Mackay et al., 1979).

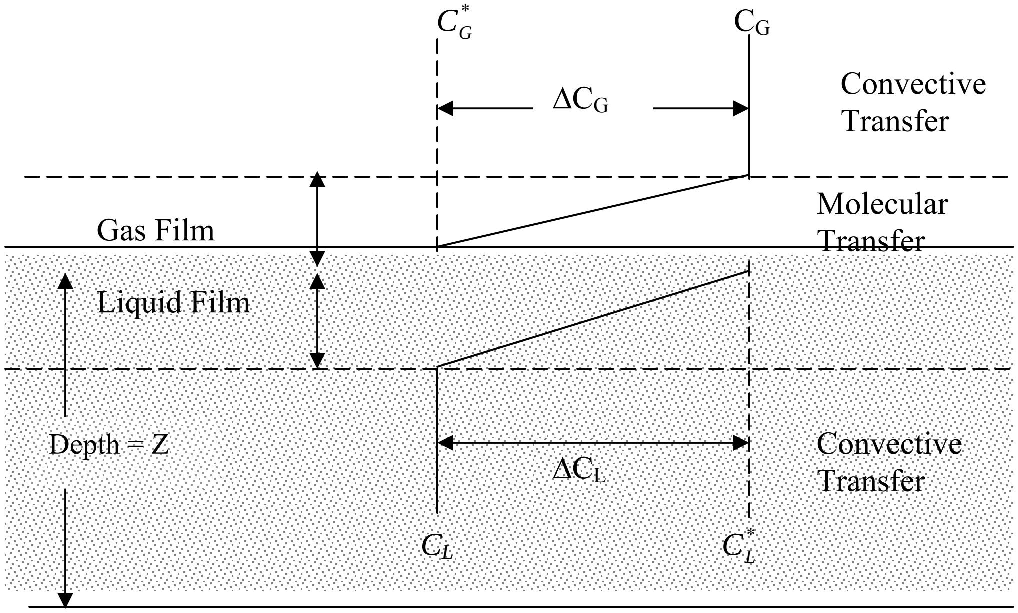

Figure 2.2: Two-layer model of gas-liquid interface (adapted from Thomas (1990))

This model is based on the following assumptions (Thomas, 1990):

- The main body is well mixed and has a thin surface layer which has a concentration gradient. Therefore diffusion is not the rate limiting step.
- The air above the surface is well mixed.
- At the interface between these two layers there is a concentration discontinuity and the ratio of concentrations across the interface (air to water) is assumed to be given by Henry's Law.
- Molecules diffuse through the layers at a rate dependent on the phase exchange coefficient, rather than vaporizing directly from solution along with the water vapour.

According to Chao et al. (2005a), if the solute dissolved in water and that in the air reach thermodynamic equilibrium quickly at the interface, then C_L^* in equation (13) can be replaced by C_G^*/H. Since C_G^* is close to zero in the open space then Q can be written as:

$$Q = K_{OL}\left(C_L - C_G^*\right) \cong K_{OL} C_L \tag{14}$$

Mackay et al. (1979) state that, in calculating the volatilisation rate, the liquid and gas phase resistance must be summed and often the resistance in one phase dominates. In terms of this study liquid phase resistance dominates because BTEX compounds are highly volatile.

$$1/K_{OL} = 1/k_L + 1/H'k_g \qquad (15)$$

where H' = dimensionless Henry's law constant, K_{OL} = overall mass transfer coefficient

$1/K_{OL}$, $1/k_L$ *and* $1/H'k_g$ refer to the total volatilisation resistance, the liquid film resistance and gas film resistance, respectively.

The liquid mass transfer coefficient of highly volatile compounds (high H solutes) is essentially equal to the overall mass transfer coefficient ($k_L = K_{OL}$) and the major resistance to mass transfer lies in the liquid phase. The opposite applies to low H solutes, where the major resistance to mass transfer lies in the gas phase. The values of k_G and k_L cannot be calculated because C_G^* and C_L^* cannot be measured. Therefore, the Southworth (1979) equations for estimating phase exchange coefficients, k_G and k_L, can be used to compute the overall liquid-phase mass transfer coefficient. These coefficients are empirical in that they are not readily derived using basic physical principles but equations were modelled from laboratory data (Thomas, 1990).

According to Chao et al. (2005b) for two-film theory, the general expression for K_{OL} is:

$$K_{OL} = \left[\frac{1}{k_L} + \frac{1}{H'k_G}\right]^{-1} \qquad \text{(cm/hr)} \qquad (16)$$

For the gas-phase transfer coefficient, Southworth's equation is (Thomas, 1990):

$$k_G = 1137.5(V_{wind} + V_{curr})\sqrt{18/M} \qquad \text{(cm/hr)} \qquad (17)$$

where:

V_{curr} is the velocity of the wastewater into the basin (m/s), V_{wind} is the velocity of the wind over the basin (m/s) and M is the molar mass of the volatilising compound (g/mol).

The equation derived for the liquid phase exchange coefficient depends on the wind speed. For $V_{wind} < 1.9$ m/s:

$$k_L = 23.51\left(\frac{V_{curr}^{0.969}}{Z^{0.673}}\right)\sqrt{32/M} \qquad \text{(cm/hr)} \qquad (18)$$

where Z is the depth of the basin in meters.

For $1.9 < V_{wind} < 5$ m/s:

$$k_L = 23.51\left(\frac{V_{curr}^{0.969}}{Z^{0.673}}\right)\sqrt{32/M} \times e^{0.526(V_{wind}-1.9)} \qquad \text{(cm/hr)} \qquad (19)$$

Cohen et al. (1978) defined three regions for k_L:

When $V_{wind} < 3$ m/s, the water surface is relatively calm, flow is aerodynamically smooth, k_L values are typically 1-3 cm/hr and appear to be strongly influenced by mixing originating from within the water body, this wind speed does not have a significant effect on the value of k_L and volatilisation rate is dominantly affected by underlying hydrodynamics that are site specific.

For the range 3 < V_{wind} < 10 m/s, k_L may increase from 3.5 to 30 cm/hr, this increase can be attributed to the onset of ripples and an increase in surface roughness. Above 6m/s wave growth is appreciably higher which increases the rate of mass transfer of solutes from the water body. When V_{wind} > 10 m/s, waves may begin to break, k_L as well as the mass transfer rate will increase due to increased surface area, spray, bubble entrainment and disintegration of wave crests. At this wind speed k_L may reach 70 cm/hr.

2.6.4 Kinetic theory method

This method is based on a chemical mass balance. According to Atasoy et al. (2004), the simplest method of estimating an emission rate, through combining a variety of measured and empirical or theoretical data, is the use of a mass balance. It relies on knowing the wastewater flowrate and influent and effluent aqueous phase pollutant concentrations accurately. The mass of any compound that cannot be accounted for in the effluent, is assumed to be volatilised. Since volatilization of organic compounds from water is regarded as a first order reaction (Chao et al., 2005a; Lee et al., 2004 and Chao et al., 2005b) then:

$$V \, {dC_L}/{dt} = -K_{OL} A(C_L - C_i) \qquad (20)$$

where:

$$K_{OL} = \left[1/k_L + 1/Hk_g \right]^{-1} \qquad (m/s) \qquad (21)$$

$H = MP_i / (RTC_i)$ dimensionless Henry's constant, k_L is the liquid phase exchange coefficient and k_g is gas phase exchange coefficient.

Integrating equation (20) results in:

$$C_L = C_0 e^{-kt} \tag{22}$$

$$k = B \times \exp\left(-E/_{RT}\right) \tag{23}$$

where:
t is the reaction time
C_0 is the initial concentration of a compound *in* water
C_L *is* concentration of a compound at time *t*
k is the volatilisation rate constant and can be expressed as a function of activation energy (Lee et al., 2004).

2.6.5 Chio and Freed method

This method is based on the gas dynamic and thermodynamic considerations involving the mean free path of molecules and the vapour pressure of the chemical taking the effect of air and sub-water turbulences into consideration. A Langmuir type equation is used to describe and observe rates of volatilization from both single-component and multi-component systems. (Thomas, 1990)

This approach uses the modified Knudsen diffusion theory (Chao et al., 2005a; Lee et al., 2004; Chiou et al., 1980). It employs the partial pressure difference between the interface (P_i) and the bulk air (P_b) as the thermodynamic driving force for evaporation and assumes that the two sides of the air-water interface, the concentration C_i and the partial pressure P_i are in constant equilibrium (Chiou et al., 1980). According to Chao et al. (2005a), the volatilization rate is determined by the product of the partial pressure difference and a tuning factor which is specific for particular conditions.

$$Q = \frac{V}{A}\frac{dC_L}{dt} = \beta\left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}}\left(P_i - P_b\right) \tag{24}$$

where β is evaporation coefficient which depends on atmospheric pressure and air turbulence and is dimensionless.

The bulk air partial pressure, P_b can be dropped for all organic compounds evaporating into the ambient air since the existing vapour densities are negligible. Vapour density is the concentration of a chemical in the air (Lee et al. 2004). This is referred to as infinite dilution or infinite ventilation and can be applied to volatilisation at open surfaces. Then substitute

$$P_i = \left(\frac{C_i}{C_L}\right)P = \alpha P \tag{25}$$

where P is partial pressure corresponding to the bulk aqueous concentration C_L at temperature, T , assuming that the solutes are dilute.

$$Q = \alpha\beta\left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} P = \alpha\beta H\left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} C_L \tag{26}$$

Using Henry's law where $P_{vp} = HC_L$

According to Chiou et al. (1980), this model represents the effect of liquid mixing and air turbulence on evaporative loss of solutes by α and β terms. At ambient conditions, β has a value of less than 1 and depends on the extent of turbulence which affects the movement of the vapours from the interface to the bulk air phase. The coefficient β can be determined from measured values of Q and α, on the other hand, depends on system conditions. If the relative loss of the solute is less than or comparable to that of water then α should be equal to 1 for all conditions. As sub-water mixing increases, the value of α increases and so does the volatilisation rate for high H solutes.

2.7 Comparison of the Methods

Volatilisation is controlled by various environmental, physical and chemical processes and this makes it very complex to model. Thomas (1990) explains why there are inadequacies in the modelling equations. Firstly, the gas and liquid phase transfer coefficients are not known with certainty for diverse environmental conditions and a wide range of chemicals. Secondly, environmental and hydrodynamic factors that affect the movement of chemicals in water and their transfer into the atmosphere are complex to quantify. These factors include wind speed, stratification, content of sediments and the presence of surfactants. The values of these factors vary with time and are non-linearly interdependent. This causes a problem in using time-averaged values and reduces the validity of the models.

The overall mass transfer coefficient, which is dependent on the gas and liquid phase exchange coefficients, is complex to predict both in laboratory studies and under environmental conditions (Smith et al., 1980). The mass transfer coefficients have only been verified for a few chemicals in the laboratory experiments using stirrer and fans to simulate environmental conditions. It is extremely difficult to quantify the error in calculated values of volatilisation rate constants due to the complexity of performing in-situ volatilisation experiments. According to Thomas (1990), the values of volatilisation rate obtained from the models are generally higher by a factor of ten or smaller by a factor of three, compared to that for actual environmental situation.

Comparing the methods discussed, it can be said that the Liss and Slater method with Southworth's equations is a recommended method. This model incorporates the effect of the resistance of liquid and gas film, vapour pressure, solubility and temperature represented by the H value, while Southworth's equations incorporates the effects of water depth, velocity of the water and wind speed, and molecular weight on volatilisation. According to Thomas (1990), the Liss and Slater method is a more realistic approach than Mackay and Wolkoff method.

CHAPTER 3: METHODOLOGY

3.1 Sampling Site

The investigated site is situated in the northernmost corner of the Free State Province of South Africa, on the southern banks of the Vaal River, and forms part of the Vaal Triangle. This area lies at an altitude of about 1500 meters above sea level (http://www.places.co.za/html/sasolburg.html). The sampling site is marked by a red spot on the map as seen on Figure 3.1.

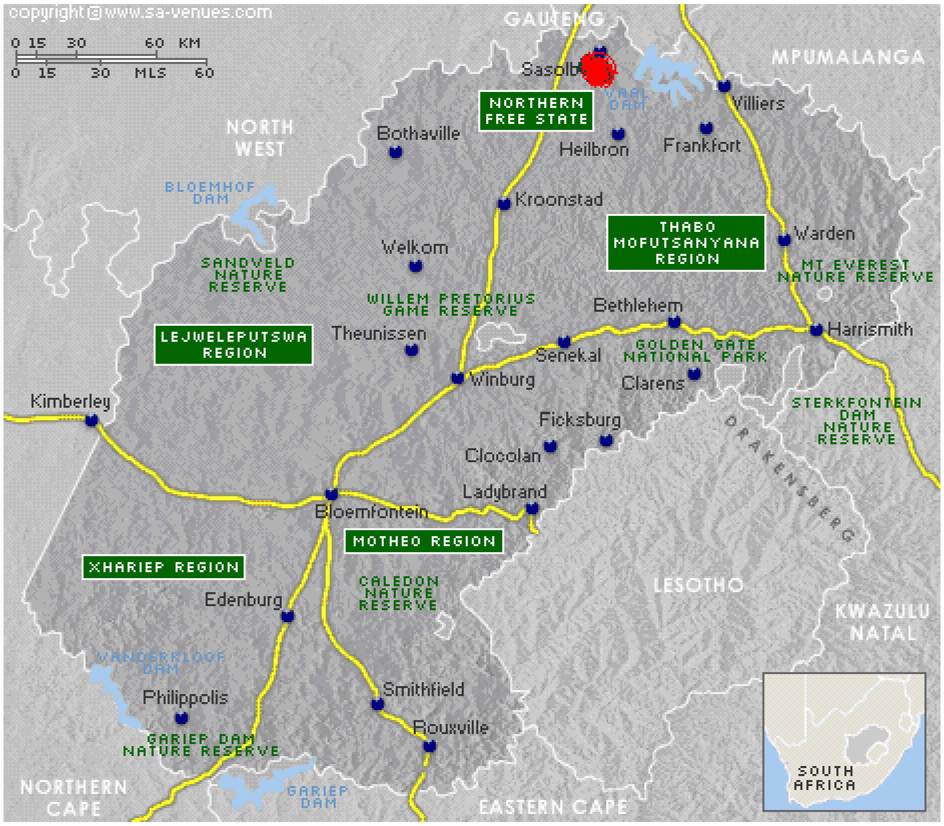

Figure 3.1: The map of the Free State Province

(Adapted from http://www.sa-venues.com/maps/freestate_relief.htm)

The wastewater disposal site, called the Oily Sewer Basin (OSB) serves the surrounding synthetic fuel industries. All wastewater and storm water from the plants that may be contaminated with VOCs are collected via a drainage system to the OSB, where the material separates into aqueous and organic layers. The organic layer is skimmed with scrapers to remove the tarry, viscous substance that accumulates in the basins. The aqueous layer is treated in a bioreactor to destroy the organic molecules dissolved in the water. While the liquid is separating into the two layers, the organic surface layer is exposed to the atmosphere and VOCs evaporate, forming a fugitive emission creating a health hazard in the surrounding work areas and in the local community.

The OSB basin is situated behind a slimes dam. It consists of two identical wastewater collection basins of 3.5 m deep, 110 m long and 12 m wide. The wastewater flows into the OSB of 10.11 mega litres per day. The type of wastewater entering the basin contains storm water and contaminated water from all over the plant, since process conditions over the plant fluctuates so does the composition of the contaminated water that is received by the OSB. In addition, the sand from the slimes dam is blown into the basin by strong winds. It is therefore complex to estimate the exact composition of the vapour that volatilises from these plants.

The following compounds were studied to estimate the volatilization rate of VOCs: Benzene, Toluene, Ethylbenzene, and o-Xylene. These compounds form part of the products and by-products in synthetic fuel processing.

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3.2 Sample Preparation

3.2.1 Gas phase sample collection

The gas phase sample was collected using a floating flux chamber with an internal diameter of 35cm. The flux chamber was placed at the middle of the basin. Organic vapours escaping from the water surface enter the headspace of the flux chamber and are immediately mixed with sweep air. Zero air was used as sweep air and at a sweep rate of 5 *l*/min. Air from inside the chamber passes through two carbon molecular sieve adsorbent traps (Tenax TA and Carbograph 1TD) in series. The first trap removes all VOCs from the air stream, with the second trap acting as a check for ion breakthrough of the first trap. After 10 minutes sampling period, the traps were removed and analyzed using a GC with a flame ionization detector. Three day-time and two night-time gas samples were collected.

3.2.2 Liquid phase sample collection

Prior to sampling, three liquid samples were taken from three different points along the length of the basin, at 20 m, 42 m and 62 m. A qualitative analysis was done on the samples in order to understand the dynamics of the basin and to design the analytical method for other samples to be taken.

Three day-time and two night-time liquid samples were collected from the middle of the basin at the beginning of each sampling period. The solid surface layer was skimmed off before the samples were taken. The liquid samples (Figure 3.2) were stored in pre-washed glass bottles and transported to the laboratory where they were stored at 4˚C.

These samples form three different layers after settling. The top layer is an organic layer containing suspended solids, the middle layer is a watery layer and the bottom layer contained heavier solids. The different layers (as shown in Figure 3.3) were separated by decanting the top layer and centrifuging the bottom layer. The temperature of both the gas and liquid phase were measured, during sampling, as well as meteorological parameters such as wind direction and speed, humidity and the incident solar radiation.

Figure 3.2: Liquid sample immediately after sampling

Figure 3.3: The three layers of the liquid sample prior to decanting

3.3 Sample Processing and Analysis

The detailed analysis of gas and liquid samples was done by the company to whom the OSB belongs, to determine the concentration of the different compounds present in the wastewater.

The bottom layer of each of the three samples was divided into two portions, one to be used for wet analysis and one for dry analysis. The dry sample was dried in an oven at 40 °C and analysed with Perkin Elmer FT-IR (Fourier Transform Infra Red) spectrometer on the Universal ART sampling accessory. The wet sample was also analysed using the FT IR spectrophotometer.

The watery layer of each sample was analyzed using a gas chromatograph equipped with a flame ionisation detector (GC-FID) and a gas chromatograph connected to a mass spectrometer (GC MS). The GC used was AGILENT FFAP (Model 19091F-105) with a 50m capillary column with an inside diameter of 200 μm and thickness of 0.3 μm. Hydrogen was used as a carrier gas at a flow velocity of 35cm/s. The GC was operated at an injection temperature and volume of 220 °C and 1μL respectively, a detector temperature of 240 °C and an oven of 60 °C. This method did not give a clear resolution for BTEX compounds. An external standard of Benzene (± 10 ppm) and toluene (± 10 ppm) was used to analyse for organic components in the GC-FID. It showed that benzene and toluene were below 10 ppm. Finally head space analysis was performed on a sample and again proved that non-acidic components are below the detection limit. Thus organic compounds present in the wastewater could not be quantified. High Performance Liquid Chromatography (HPLC) was used to quantify organic acids in the water. A GC-MS was used to quantify and qualify certain organic species in the gas sample.

3.4 Measurement of Volatilisation Rate

3.4.1 Direct measurement

Direct measurements of volatilisation rate of VOCs were done using the flux chamber method as described in the literature review. A float was fixed to the flux chamber (as in figure 2.1) in order to reduce liquid surface disturbances that might result from chamber insertion in the wastewater. Prior to placing the floating flux chamber, the suspended solids were scraped off. The sweep flowrate was kept at 5 *l*/min, since literature shows that a sweep flow of more than 2 *l*/min is needed to maintain a good concentration gradient across the liquid-gas interface. The gas exit flowrate and the sampling period were kept at 0.1 *l*/min and10 minutes respectively. To validate the results, two samples were taken consecutively for each sampling time. Equation (10) was then used to calculate the volatilisation rate.

3.4.2 Estimation of volatilisation rate by modelling

The Liss and Slater model based on the two film model was found to be the best model to use, to estimate mass flux of VOCs from the OSB. Mass transfer coefficients were calculated using Southworth's equation. Since the composition of BTEX compounds in the liquid phase of the OSB can not be quantified, it was assumed that thermodynamic equilibrium exists between the gas and liquid phase in order to estimate the liquid composition. Making this assumption allowed Henry's law and Raoult's law to be used to calculate the liquid phase concentration of the BTEX compounds.

According to Treybal (1980), Raoult's law relates the vapour pressure of components to the composition in solution. It assumes ideal behaviour, that is, the physical properties of the components are similar. Assuming ideality means that (Treybal, 1980):

- molecules of component in the solution must be similar in size, structure and chemical nature
- average intermolecular forces in the solution remain unchanged on mixing the components
- the volume of the solution changes linearly with composition
- there is no absorption or transformation of heat when mixing
- the total vapour pressure of the solution varies linearly with composition

The total vapour pressure (P_{total}) above the solution is equal to the sum of vapour pressures of the components.

$$P_{total} = P_A + P_B + ...P_n \tag{27}$$

$$P^* = P_{vap} x \tag{28}$$

where P^* is the partial pressure, P_{vap} is the vapour pressure and x is concentration in solution.

Henry’s law on the other hand depends on temperature, pressure and concentration (Treybal 1980). According to Seinfeld and Pandis (1998), Henry’s law is only applicable to dilute solutions. If the solution is not sufficiently dilute, the concentration of the solute relative to its partial pressure in equilibrium deviates from ideality. Equations 6 and 7 in the literature can be used to express the equilibrium between the gaseous and dissolved solutes by Henry’s law constant. A sensitivity analysis on this model was done using varying wind speeds and water depth in the basin. The results of this sensitivity analysis are presented in the next chapter.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Observed Characteristics of the OSB

On the sampling days, from the 17th of April to 19th of April 2007, the OSB was covered completely by suspended solids, waxes, oils, soil and plant material. The wind speed ranged between 1.4 to 5.2 m/s. On the 22nd of November 2007, another visit to the OSB was made. The wind was very strong at a speed of 9.2 m/s, carrying with it sand from a nearby slimes dam. The top solid layer had been moved by the wind to the end of the basin. The oily layer on the surface moved at lower velocity compared to the water layer beneath it. Pieces of wax could be seen floating on the surface. There were drops and bubbles forming in the water at different points along the basin. These bubbles and drops would rise to the surface and burst.

4.2 Meteorological Data

The atmospheric temperature, relative humidity and wind speed were measured using a hand held psychrometer, whilst solar radiation data was provided by the local power station. The values of these parameters are presented in Table 4.1. The value of the solar radiation in the table is an estimate, since solar radiation changes with movement of the earth and therefore with time. Evidence of this can be seen in ambient temperature data which changes every ten minutes, except for readings taken in the early morning. The correct values of solar radiation could not be interpolated from the given data (see Appendix A). It was raining from around 10:00 in the morning on the 18th of April 2007 until midnight. This can be seen by the high relative humidity on sample 5, 6, 7 and 8. Only day and night samples could be taken because of the unavailability of instruments at the company to analyse the gas samples.

Table 4.1: Meteorological conditions during sampling

Sample no.	Date and Time of day	Ambient Temperature(ºC)	Relative Humidity (%)	Wind Speed (m/s)	Solar Radiation (Watts/m^2)
1	17 April (Day) 17/04/07 14h20	27.8	46.4	5.2	606.13
2	17 April(Day) 17/04/07 14h31	25	46.4	5.2	606.13
3	17 April(night) 18/04/07 01h15	16.3	73	1.4	0.00
4	17 April(night) 18/04/07 01h27	16.2	73	1.4	0.00
5	18 April(day) 18/04/07 13h51	15.6	91.2	3.4	147.76
6	18 April(day) 18/04/07 14h02	17.2	91.2	3.4	147.76
7	18 April(night) 19/04/07 00h55	16	83.3	3.1	0.00
8	18 April(night) 19/04/07 01h06	15.9	83.3	3.1	0.00

Table 4.2 shows the observed flux chamber temperature changes for measurements done on the 17th, 18th and 19th of April 2007(see Appendix B for all system and meteorological conditions). It can be seen that the chamber temperature increased by 2 to 3 ºC for each consecutive sample except for sample 2. This could be due to the large difference in temperature between the liquid and the gas phase, creating a temperature gradient. This could also be to greenhouse effect as explained in literature. There was no noticeable temperature change for sample 2 because the temperature difference between atmosphere and the wastewater was smaller. However, the temperature increases do not explain the changes in emission rate of toluene for each consecutive sample, since one would expect

the emission rate to increase as the temperature increases. In all cases the toluene emission rate is lower in the second, consecutive sample. This anomaly will be explained later in the report. The emission rates for other organic compounds not discussed in the report are included in Appendix C.

Table 4.2: Observed flux chamber temperature changes

Sample	Chamber T (˚C)	Ambient T (˚C)	Emission rate of toluene(g/hr.m^2)	Liquid T (˚C)
1	32	27.8	4.5	36
2	32	25	2.9	
3	24	16.3	1.8	32
4	27	16.2	1.1	
5	23	15.6	2.2	32
6	25	17.2	1.1	
7	23	16	2.2	35
8	26	15.9	1.4	

4.2.1 Comparison of observed night- and day-time BTEX volatilisation rates

Table 4.3 shows the effect of diurnal variation on volatilisation rates of the BTEX compounds from the OSB. It can be seen from the values of emission rate on the 17th (day) and 17th (night) of April that there is a decrease in volatilisation rate at night when compared to that during the day, except for benzene. The high volatilisation rate value during the day could be because of the high temperature. There is no noticeable change in volatilisation rate for 18th (day) and 18th (night) except for benzene. This can be attributed to the high relative humidity and the overcast sky on 18th during the day. The behaviour of benzene is inexplicable at this point.

It can be seen that toluene has the greatest volatilisation rate followed by ethylbenzene. This shows that the Henry's law constant is a better indicator of the rate of volatilisation than vapour pressure, as discussed in physico-chemical properties section in the literature review. Thus the statement of Lee et al. (2004) and Chao et al. (2005a) statement that the compound with the lowest H value will evaporate at a slowest is true.

Table 4.3: Average values of emission rates of BTEX compounds

	Measured BTEX volatilisation rates (g.hr^{-1}.surface^{-1})			
Date	17 April day	17 April night	18 April Day	18 April night
Benzene	0.2	0.3	0.8	0.4
Toluene	3.7	1.45	1.65	1.8
Ethylbenzene	2.05	0.85	0.8	0.8
o-Xylene	0.600	0.4	0.45	0.45

4.2.2 Comparison of the measured BTEX concentration to national OHS guidelines

The BTEX gas samples were measured over a period of ten minutes each; these concentrations give an indication of concentration to which a person working at the OSB will be exposed in a period of ten minutes. The ten minutes sampling period used in order to compare results (as in table 4.2). The Occupational Health and Safety (OHS) Act and Regulations 85 of 1993 for South Africa, gives a guideline concentration for toluene, ethylbenzene and xylenes for exposure periods of 15 minutes and for a period of 8 hours. The BTEX concentrations and the OHS guideline values for 15 minutes are given in Table 4.4 except for benzene which is given for long period of exposure.

Table 4.4: Comparison of measured BTEX concentrations to OHS guideline

	Measured BTEX concentrations(mg/m^3)				OHS-Guideline (mg/m^3)
Date	17 April Day	17 April night	18 April Day	19 April night	
benzene	0.043	0.064	0.171	0.086	16
Toluene	0.791	0.310	0.353	0.385	560.00
Ethylbenzene	0.438	0.182	0.171	0.171	545.00
o-Xylene	0.128	0.086	0.096	0.096	650.00

The BTEX concentrations were calculated using equation 11 and measured emission rates divided by total surface area. Rearranging equation 11:

$$C_i = E_i A / f$$

It can be seen that all the compounds comply with the standards for all the sampling days, while ethylbenzene and toluene are higher in concentration than the rest.

4.3 Qualitative Results for the Liquid Sample (bottom and top layer)

The results presented here are interpretations made from the FT-IR spectrometry graphs (shown in Appendix D and E). The bottom and top layer of all the liquid samples had the same properties which can be interpreted as follows:

4.3.1 Wet sample

The wet samples were analysed and found to contain aliphatic hydrocarbons and water. Absorption in the following characteristic bands was detected: 2957 cm^{-1} corresponding to –CH, 2919 and 1463 cm^{-1} corresponding to $–CH_2$ and 2850 and 1377 cm^{-1} to $–CH_3$ stretching vibrations. The samples contained water, as indicated by the broad absorption band at 3341 cm^{-1} (due to the -OH stretching vibration) and at 2139 cm^{-1} and 1637 cm^{-1} which makes the interpretation of the other compounds very complex.
The absorption at 719 cm^{-1} is indicative of the – $(CH_2)_n$ where n=4 or n>4.

4.3.2 Dry sample

The dry samples were analysed and found to be aliphatic hydrocarbons containing alcohol, ester, silica, carboxylic acid and carboxylic acid salt.
Table 4.5 shows characteristic absorptions bands detected in the dry sample.

Table 4.5: FT-IR adsorption bands interpretation for a dry sample

Group type	Absorption band (cm^{-1})
–CH	2955
$–CH_2$	2916
$–CH_3$	2848
$–(CH_2)_n$	719
-OH of an alcohol / carboxylic acid	3298
C-O of an alcohol/ Si-O of a silica	1027
C=O of the carboxylic acid	1736
C-O of the carboxylic acid salt	1544
C-O of the carboxylic acid/ester	1163
C=O stretching vibration of an ester	1736

4.4 Qualitative and Quantitative Results for the Liquid Sample (watery layer)

The non-acidic components present in the sample could not be quantified using the available GC-FID, because of the low levels present. External standards of benzene (+/- 10 ppm) and toluene (+/- 10 ppm) were prepared, to show that the benzene and the toluene content of the samples were below 10ppm. Even a headspace analysis was preformed on the samples and again this proved that the concentrations of the non-acidic components were below the detection limit. The following table presents the concentration data for the carboxylic acids that could be detected. Samples 1, 2 and 3 are the samples collected along the length of the basin and they show a gradual increase in the acetic acid concentration. It can be seen that formic acid was present in each phase for most samples. This can be attributed to biodegradation of organic matter in the wastewater.

Table 4.6: Carboxylic acids detected in the wastewater

Date Time	Sample name	Formic acid (ppm)	Acetic acid (ppm)	Butric acid (ppm)
16/04/2007 14h30 sample 1	water layer	28	-	-
	bottom layer	7	-	-
	top layer	16	9	-
16/04/2007 14h30 sample 2	water layer	59	-	-
	bottom layer	155	-	7
	top layer	-	11	-
16/04/2007 14h30 sample 3	water layer	27	-	-
	bottom layer	55	23	13
	top layer	10	16	-
17/04/2007 14h30	water layer	36	-	-
	bottom layer	-	-	13
	top layer	20	-	-
18/04/2007 01h30	water layer	75	2651	-
	bottom layer	-	-	7
	top layer	-	-	6
18/04/2007 14h15	water layer	31	-	-
	bottom layer	11	-	-
	top layer	-	<5	11
19/04/2007 01h30	water layer	30	-	-
	bottom layer	15	6	-
	top layer	7	-	-

4.5 Comparison of the Model's Prediction to the Measured Volatilisation Rate

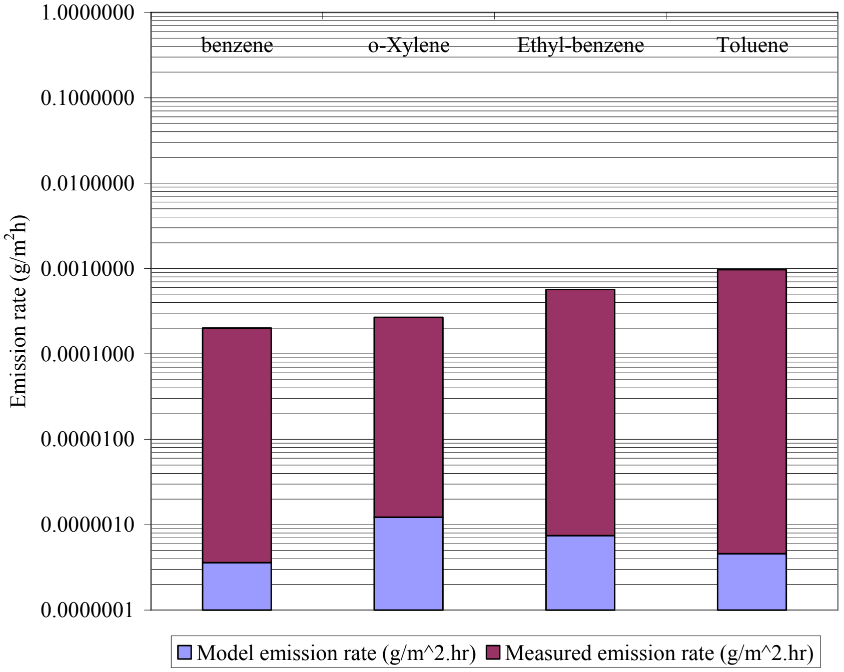

Figure 4.1: Comparison between the predicted and the measured volatilisation rate

Table 4.7: Comparison between model's and measured data

Model emission rate (g/m^2.hr)	Measured emission rate (g/m^2.hr)
0.00000036	0.000200
0.00000122	0.000267
0.00000074	0.000567
0.00000046	0.000967

Figure 4.1 is a log scale plotted using data from table 4.7. Figure 4.1 shows how badly the Liss and Slater model predicts volatilisation rate under environmental conditions. The model gives very low values of volatilisation rate and therefore the values do not appear

on the graph. The measured data is for the 17th of April 2007 day sample. The poor prediction is because of unavailable input data (BTEX composition of the liquid sample). Henry’s and Rauolt's law were used to calculate the liquid phase concentration. This method is incorrect because it is based on invalid assumptions. Henry’s and Rauolt's law assume ideal behaviour and the real system is far from ideal. The values of H used at the actual temperature are not available in literature; therefore, to improvise H values at liquid temperature of 298 K were used. This contributed significantly to the model’s underestimation of volatilisation rate. The effect of temperature on volatilisation can therefore not be discussed. (Refer to Appendix F for the model’ prediction calculation)

The model would be more applicable to a well mixed system because in a well mixed water body the resistance lies in the gas and liquid phase interfacial layers and a concentration gradient develops in the surface layers (as in figure 2.2). In reality, from the observations made on the OSB, the water body seems to be stratified rather than well mixed. Therefore, volatilisation from the OSB might be affected by diffusion through other layers and their different temperatures. The high values of the measured data could have resulted from this effect.

4.6 Sensitivity Analysis of the Selected Model

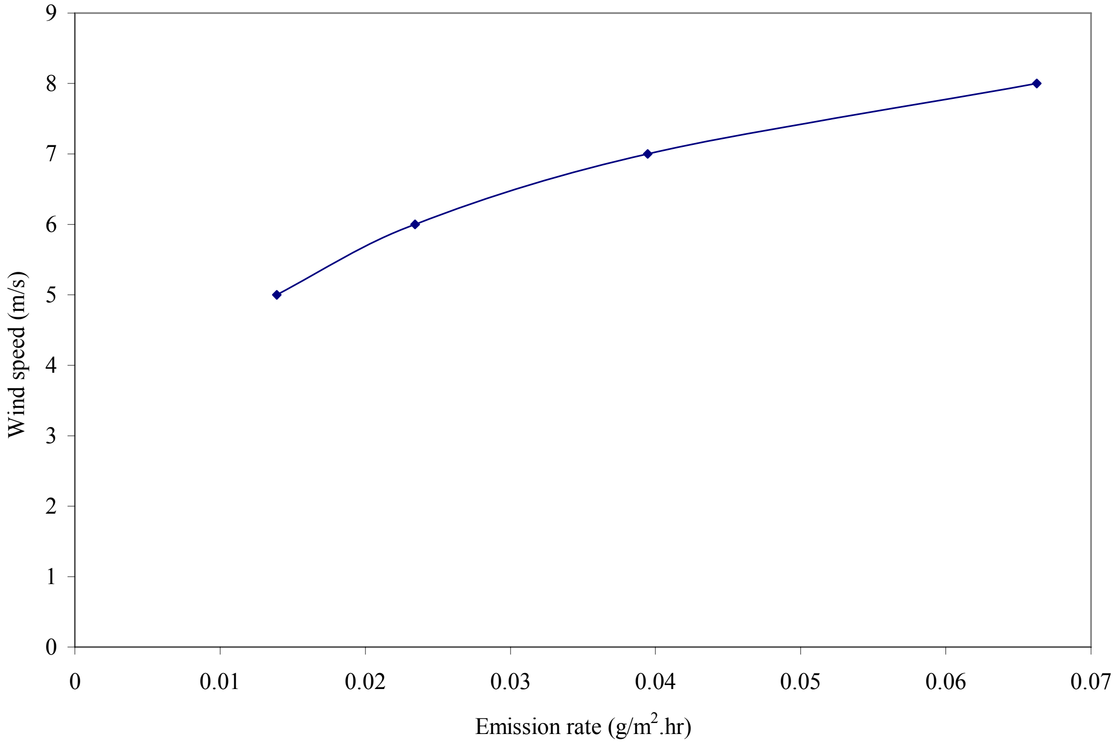

Figure 4.2: The model's sensitivity to changes in wind speed

Figure 4.2 shows how the selected model behaves when wind speed is varied at a constant water depth of 1m. It can be seen that computed volatilisation rate increases with increasing wind speed, as expected. It is discussed in literature that, when wind speed increases, mass transfer of solutes from the water body increases because of an increase in surface area. This can also be proven by measured data. Figure 4.3 shows how the measured emission rate of toluene increases with increasing wind speed. The depth of the OSB was constant at 3.5m. This graph was drawn using the data collected during the different sampling days. As discussed in the literature review, wind speed does not affect measurements inside the chamber but affects surface hydrodynamics which in turn affects volatilisation rate.

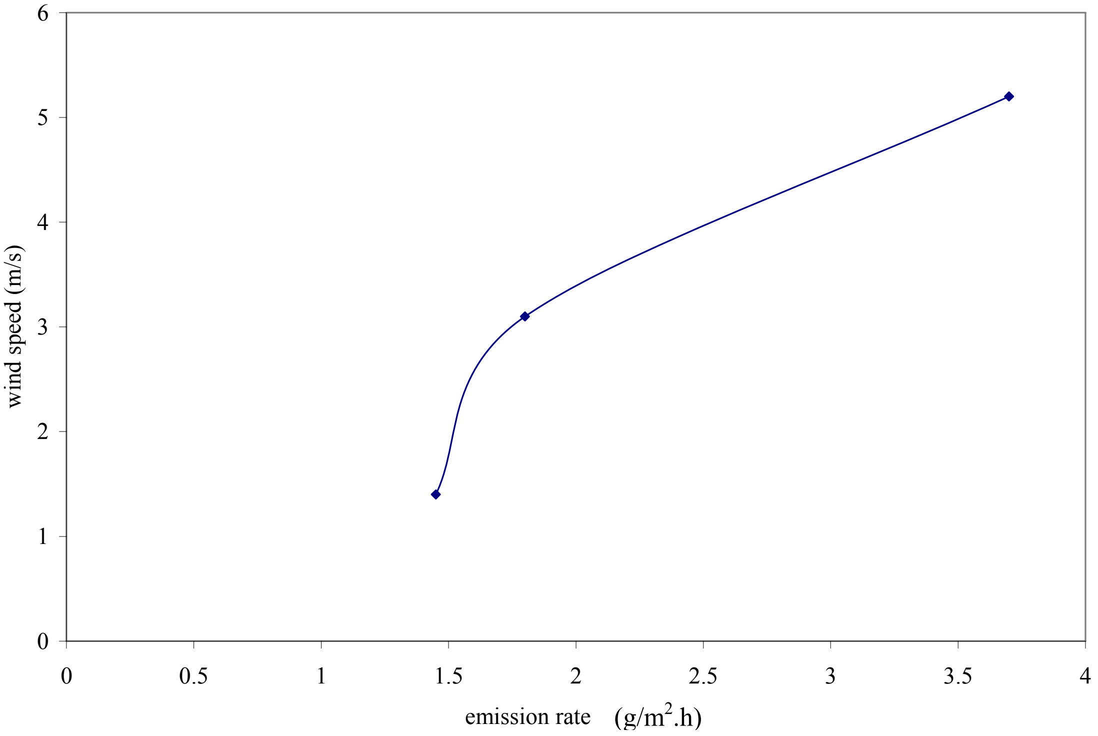

Figure 4.3: The change of measured emission rate with wind speed

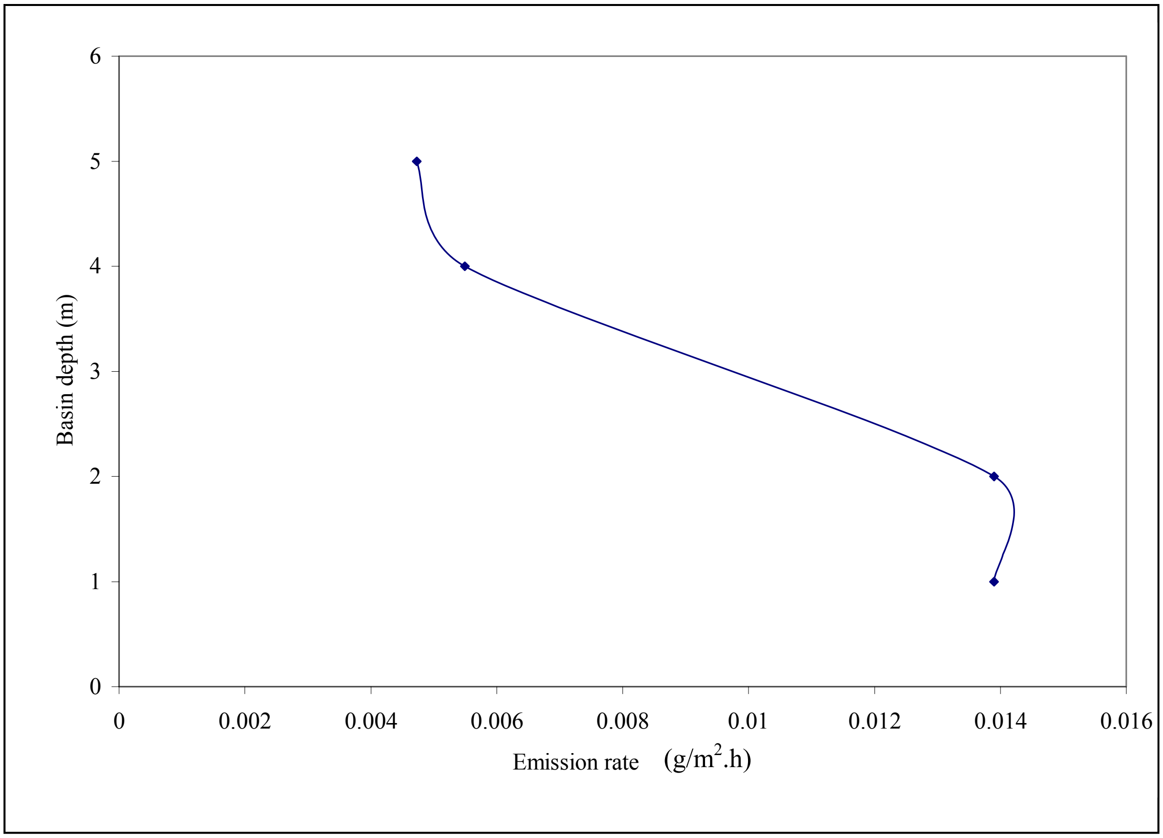

Figure 4.4: The model's sensitivity to changing water depth

It can be seen in Figure 4.4 that, the model predicts an increase in emission rate with a decrease in water body depth at the constant wind speed of 5.2 m/s. This is an expected behaviour because by decreasing water depth the velocity of wastewater is increased, which creates turbulence in the water body. Turbulence has a mixing effect, which increases the rate of volatilisation. It can be also seen that there is a limit to how low the water level in the basin can be; below 1m the model predicts a decrease in volatilisation rate.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

The vapours volatilising from the OSB were characterised. It was found that the BTEX compounds together with styrene, 4-ethyltoluene, 1,3,5-trimethylbenzene and 1,3,4-trimethylbenzene were escaping from the OSB into the atmosphere. The BTEX compounds in the wastewater could not be quantified using the GC-FID, but FT-IR could detect the aliphatic hydrocarbons, carboxylic acids and silica.

The mass flux over the OSB for a broad range of VOCs has been estimated using the flux chamber method and by a mass transfer model. The accuracy of values predicted by the model selected to estimate the rate of volatilisation is dependent on the availability of data and resources. This mass transfer model was based on the two-film theory and the gas and liquid phase mass transfer coefficients equations used, took account of the effect of wind speed, water depth, wastewater flowrate and the molecular weight of the compounds evaporating. The influence of wind speed and water depth on the selected model was investigated by means of sensitivity analysis. It was found that the model predicts an increase in volatilisation rate with increasing wind speed at a given water depth. It was also found that the model predicts an increase in volatilisation rate with decreasing water depth. This proves that the model is sensitive to changes in water depth and wind velocity.

Main findings of this research are summarised as follows:

- VOCs volatilising from the OSB contain higher concentrations of toluene and ethylbenzene
- The selected model could not give accurate estimation of VOC flux over the OSB because of the dynamic nature of the OSB.
- The extent to which the model predictions deviate from actual emission rate varies according the meteorological conditions and the physicochemical properties of organic compounds being examined.

- Direct measurements using the flux chamber method is the preferable to mass transfer models and recommended in this study contrary to what Bunyakan et al. (2006) suggested.
- The measured VOC flux over the OSB does comply with the standards set by Occupational Health and Safety Act and Regulations 85 of 1993.
- Surfactants can be used to prevent volatilisation of VOCs. As discussed in the literature review, surfactants can have an inhibition effect on volatilisation rate.

For future research work on the oily sewer basin, it is recommended that a better analytical method be used to analyse the wastewater sample and another gas phase sample collection method that will not affect the surface conditions of the liquid surface. In the mean time the flux chamber method can be used as a first approximation to develop emission control strategies. The flux chamber can be used to measure the volatilisation rate of these compounds for the sole purpose of monitoring the changes in the vapour composition over the oily sewer basin and to make sure that standards are met. Complying with the environmental legislation and standards is important in order to avoid penalties and to keep the employees and the surrounding community safe.

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APPENDIX A: MEASURED SOLAR RADIATION

The incident solar radiation data given in Table A1 was provided by a power station in the vicinity of the sampling area.

Table A1: Incident solar radiation for the sampling days

Date/Time	Power station 2- Solar radiation(Watts/m^2)
17/04/2007 01:00:00	0
17/04/2007 02:00:00	0
17/04/2007 03:00:00	0
17/04/2007 04:00:00	0
17/04/2007 05:00:00	0
17/04/2007 06:00:00	0
17/04/2007 07:00:00	13.46
17/04/2007 08:00:00	131.45
17/04/2007 09:00:00	283.73
17/04/2007 10:00:00	293.1
17/04/2007 11:00:00	612.29
17/04/2007 12:00:00	557.16
17/04/2007 13:00:00	533.98
17/04/2007 14:00:00	606.13
17/04/2007 15:00:00	401.17
17/04/2007 16:00:00	204.81
17/04/2007 17:00:00	126.86
17/04/2007 18:00:00	50.35
17/04/2007 19:00:00	0
17/04/2007 20:00:00	0
17/04/2007 21:00:00	0
17/04/2007 22:00:00	0
17/04/2007 23:00:00	0
17/04/2007 24:00:00	0
18/04/2007 01:00:00	0
18/04/2007 02:00:00	0
18/04/2007 03:00:00	0
18/04/2007 04:00:00	0
18/04/2007 05:00:00	0
18/04/2007 06:00:00	0
18/04/2007 07:00:00	2.59
18/04/2007 08:00:00	4.23
18/04/2007 09:00:00	17.8
18/04/2007 10:00:00	37.94
18/04/2007 11:00:00	134.11
18/04/2007 12:00:00	62.82
18/04/2007 13:00:00	73.93
18/04/2007 14:00:00	147.76

18/04/2007 15:00:00	364.11
18/04/2007 16:00:00	291.6
18/04/2007 17:00:00	152.72
18/04/2007 18:00:00	21.18
18/04/2007 19:00:00	0.034
18/04/2007 20:00:00	0.196
18/04/2007 21:00:00	0
18/04/2007 22:00:00	0
18/04/2007 23:00:00	0
18/04/2007 24:00:00	0
19/04/2007 01:00:00	0
19/04/2007 02:00:00	0
19/04/2007 03:00:00	0
19/04/2007 04:00:00	0
19/04/2007 05:00:00	0
19/04/2007 06:00:00	0.002
19/04/2007 07:00:00	16.23
19/04/2007 08:00:00	196.13
19/04/2007 09:00:00	334.03
19/04/2007 10:00:00	484.84
19/04/2007 11:00:00	629.55
19/04/2007 12:00:00	624.48
19/04/2007 13:00:00	644.42
19/04/2007 14:00:00	799.53
19/04/2007 15:00:00	567.43
19/04/2007 16:00:00	437.27
19/04/2007 17:00:00	246.38
19/04/2007 18:00:00	50.01
19/04/2007 19:00:00	0.002
19/04/2007 20:00:00	0
19/04/2007 21:00:00	0
19/04/2007 22:00:00	0
19/04/2007 23:00:00	0
19/04/2007 24:00:00	0

APPENDIX B: Meteorological conditions and system conditions

Table B1: Gas phase sampling conditions on the 17th of April day-time

Meteorological Conditions:	
Temperature (C):	22.6 - 27.8
Wind speed (m/s):	5.2 - 5.2
Relative Humidity (%):	46.4 - 46.4

Sample	**Tube Number**	**Adsorbent**	**Sweep Rate (L/min)**	**Chamber T (˚C)**	**Ambient T (˚C)**	**Sample Start**	**Sample Stop**	**Sample Time (min)**	**Flow Rate (l/min)**	**Air Volume (L)**
1	S095598	Tenax TA	5	32	27.8	14:20	14:30	10	0.1	1
	S095522	Carbograph	5	32	27.8	14:20	14:30	10	0.1	1
2	S095593	Tenax TA	5	32	25	14:31	14:41	10	0.1	1
	S095530	Carbograph	5	32	25	14:31	14:41	10	0.1	1

The meteorological conditions apply for both the gas and liquid phase sample collection whilst the system parameters are for the flux chamber method

Table B2: Gas phase sampling conditions on the 17th of April night-time

Meteorological Conditions:	
Temperature (C):	16.2 - 16.3
Wind speed (m/s):	1.4 - 1.4
Relative Humidity (%):	73 -73

Sample	**Tube Number**	**Adsorbent**	**Sweep Rate (L/min)**	**Chamber T (˚C)**	**Ambient T (˚C)**	**Sample Start**	**Sample Stop**	**Sample Time (min)**	**Flow Rate (l/min)**	**Air Volume (L)**
3	S095599	Tenax TA	5	24	16.3	1:15	1:25	10	0.1	1
	S095525	Carbograph	5	24	16.3	1:15	1:25	10	0.1	1
4	S095594	Tenax TA	5	27	16.2	1:27	1:37	10	0.1	1
	S095521	Carbograph	5	27	16.2	1:27	1:37	10	0.1	1

The meteorological conditions apply for both the gas and liquid phase sample collection whilst the system parameters are for the flux chamber method

Table B3: Gas phase sampling conditions on the 18th of April day-time

Meteorological Conditions:	
Temperature (C):	15.6 - 17.2
Wind speed (m/s):	3.4 - 3.4
Relative Humidity (%):	91.2

Sample	**Tube Number**	**Adsorbent**	**Sweep Rate (L/min)**	**Chamber T (˚C)**	**Ambient T (˚C)**	**Sample Start**	**Sample Stop**	**Sample Time (min)**	**Flow Rate (l/min)**	**Air Volume (L)**
5	S095600	Tenax TA	5	23	15.6	13:51	14:01	10	0.1	1
	S095524	Carbograph	5	23	15.6	13:51	14:01	10	0.1	1
6	S095592	Tenax TA	5	25	17.2	14:02	14:12	10	0.1	1
	S095527	Carbograph	5	25	17.2	14:02	14:12	10	0.1	1

The meteorological conditions apply for both the gas and liquid phase sample collection whilst the system parameters are for the flux chamber method

Table B4: Gas phase sampling conditions on the 18th of April night-time

Meteorological Conditions:	
Temperature (C):	15.8 -16
Wind speed (m/s):	3.1 -3.1
Relative Humidity (%):	83.3

Sample	**Tube Number**	**Adsorbent**	**Sweep Rate (L/min)**	**Chamber T (˚C)**	**Ambient T (˚C)**	**Sample Start**	**Sample Stop**	**Sample Time (min)**	**Flow Rate (l/min)**	**Air Volume (L)**
7	S095595	Tenax TA	5	23	16	0:55	1:05	10	0.1	1
	S095528	Carbograph	5	23	16	0:55	1:05	10	0.1	1
8	S095591	Tenax TA	5	26	15.9	1:06	1:16	10	0.1	1
	S095523	Carbograph	5	26	15.9	1:06	1:16	10	0.1	1

The meteorological conditions apply for both the gas and liquid phase sample collection whilst the system parameters are for the flux chamber method

APPENDIX C: VOLATILISATION RATE FOR ALL ORGANIC COMPOUNDS PRESENT IN THE GAS PHASE

Table C1: Emission rates of BTEX compounds and its derivatives for 17 April day

Sample	Tube Number	Adsorbent	Sweep Rate (L/min)	Chamber T (˚C)	Ambient T (˚C)
1	S095598	Tenax TA	5	32	27.8
	S095522	Carbograph	5	32	27.8

		g/hr.surface
1	**Benzene**	0.2
2	**Toluene**	4.5
3	**Ethylbenzene**	2.3
4	**p-Xylene**	1.4
5	**m-Xylene**	1.4
6	**Styrene**	0
7	**o-Xylene**	1
8	**4-Ethyltoluene**	1.1
9	**1,3,5-Trimethylbenzene**	3.2
10	**1,2,4-Trimethylbenzene**	2

Sample	Tube Number	Adsorbent	Sweep Rate (L/min)	Chamber T (˚C)	Ambient T (˚C)
2	S095593	Tenax TA	5	32	25
	S095530	Carbograph	5	32	25

		g/hr.surface
1	**Benzene**	0.2
2	**Toluene**	2.9
3	**Ethylbenzene**	1.8
4	**p-Xylene**	1.7
5	**m-Xylene**	1.7
6	**Styrene**	0.3
7	**o-Xylene**	0.2
8	**4-Ethyltoluene**	0.7
9	**1,3,5-Trimethylbenzene**	2.7
10	**1,2,4-Trimethylbenzene**	1.6

Table C2: Emission rates of BTEX compounds and its derivatives for 17 April night

Sample	**Tube Number**	**Adsorbent**	**Sweep Rate (L/min)**	**Chamber T (˚C)**	**Ambient T (˚C)**
3	S095599	Tenax TA	5	24	16.3
	S095525	Carbograph	5	24	16.3

		g/hr.surface
1	**Benzene**	0.2
2	**Toluene**	1.8
3	**Ethylbenzene**	1
4	**p-Xylene**	0.7
5	**m-Xylene**	0.7
6	**Styrene**	0.2
7	**o-Xylene**	0.4
8	**4-Ethyltoluene**	0.5
9	**1,3,5-Trimethylbenzene**	1.5
10	**1,2,4-Trimethylbenzene**	0.7

Sample	Tube Number	Adsorbent	Sweep Rate (L/min)	Chamber T (˚C)	Ambient T (˚C)
4	S095594	Tenax TA	5	27	16.2
	S095521	Carbograph	5	27	16.2

		g/hr.surface
1	**Benzene**	0.4
2	**Toluene**	1.1
3	**Ethylbenzene**	0.7
4	**p-Xylene**	0.7
5	**m-Xylene**	0.7
6	**Styrene**	0.1
7	**o-Xylene**	0.4
8	**4-Ethyltoluene**	0.4
9	**1,3,5-Trimethylbenzene**	1.5
10	**1,2,4-Trimethylbenzene**	0.6

Table C3: Emission rates of BTEX compounds and its derivatives for 18 April day

Sample	Tube Number	Adsorbent	Sweep Rate (L/min)	Chamber T (˚C)	Ambient T (˚C)
5	S095600	Tenax TA	5	23	15.6
	S095524	Carbograph	5	23	15.6

		g/hr.surface
1	**Benzene**	0.7
2	**Toluene**	2.2
3	**Ethylbenzene**	1
4	**p-Xylene**	0.6
5	**m-Xylene**	0.6
6	**Styrene**	0.2
7	**o-Xylene**	0.5
8	**4-Ethyltoluene**	0.4
9	**1,3,5-Trimethylbenzene**	1.6
10	**1,2,4-Trimethylbenzene**	0.9

Sample	Tube Number	Adsorbent	Sweep Rate (L/min)	Chamber T (˚C)	Ambient T (˚C)
6	S095592	Tenax TA	5	25	17.2
	S095527	Carbograph	5	25	17.2

		g/hr.surface
1	**Benzene**	0.9
2	**Toluene**	1.1
3	**Ethylbenzene**	0.6
4	**p-Xylene**	0.5
5	**m-Xylene**	0.5
6	**Styrene**	0.1
7	**o-Xylene**	0.4
8	**4-Ethyltoluene**	0.2
9	**1,3,5-Trimethylbenzene**	1
10	**1,2,4-Trimethylbenzene**	0.7

Table C4: Emission rates of BTEX compounds and its derivatives for 18 April night

Sample	Tube Number	Adsorbent	Sweep Rate (L/min)	Chamber T (˚C)	Ambient T (˚C)
7	S095595	Tenax TA	5	23	16
	S095528	Carbograph	5	23	16

		g/hr.surface
1	**Benzene**	0.4
2	**Toluene**	2.2
3	**Ethylbenzene**	1
4	**p-Xylene**	0.8
5	**m-Xylene**	0.8
6	**Styrene**	0.2
7	**o-Xylene**	0.5
8	**4-Ethyltoluene**	0.6
9	**1,3,5-Trimethylbenzene**	1.8
10	**1,2,4-Trimethylbenzene**	1.1

Sample	Tube Number	Adsorbent	Sweep Rate (L/min)	Chamber T (˚C)	Ambient T (˚C)
8	S095591	Tenax TA	5	26	15.9
	S095523	Carbograph	5	26	15.9

		g/hr.surface
1	**Benzene**	0.4
2	**Toluene**	1.4
3	**Ethylbenzene**	0.6
4	**p-Xylene**	0.7
5	**m-Xylene**	0.7
6	**Styrene**	0.1
7	**o-Xylene**	0.4
8	**4-Ethyltoluene**	0.4
9	**1,3,5-Trimethylbenzene**	1.7
10	**1,2,4-Trimethylbenzene**	0.8

APPENDIX D: FT-IR SPECTROMETRY GRAPHS FOR THE BOTTOM LAYER OF DRY SAMPLES

The following graphs are from FT-IR spectrometry results for dry samples

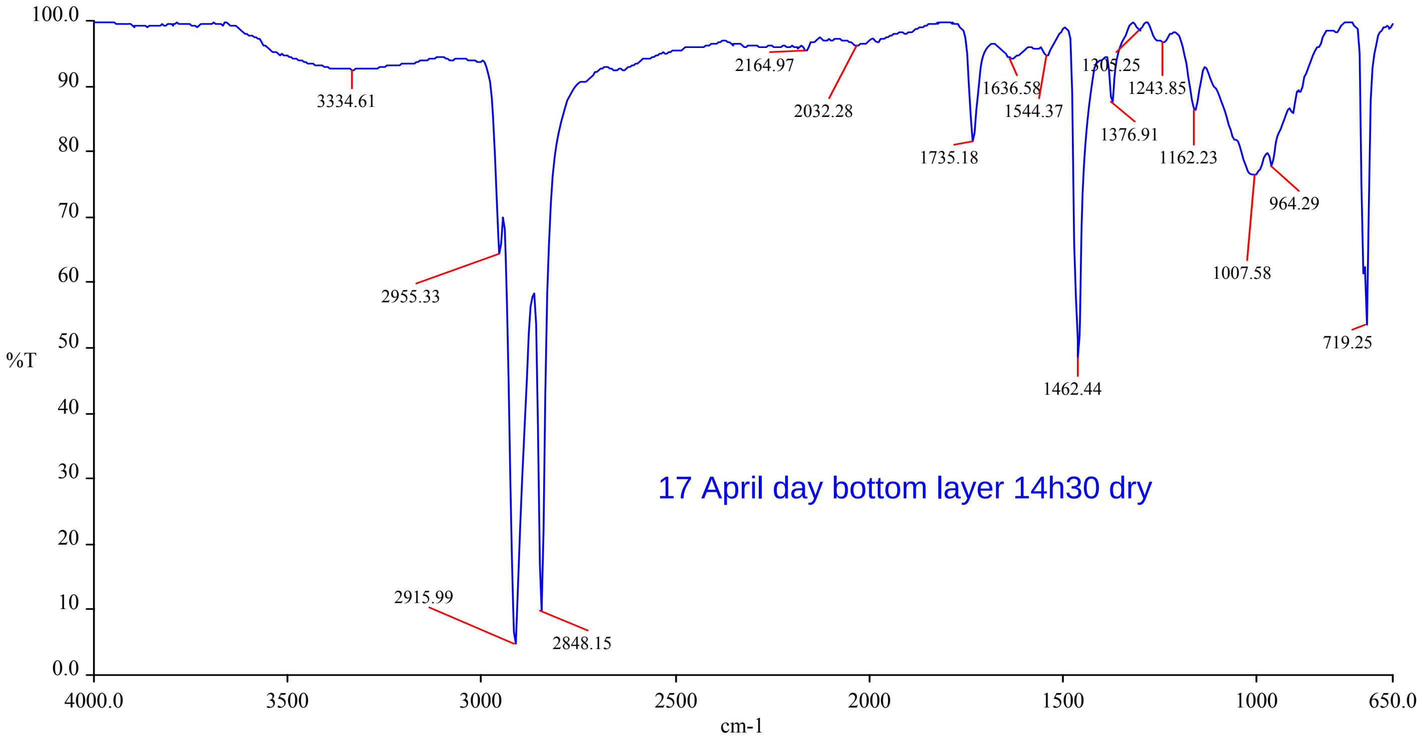

Figure D1: FT-IR adsorption bands for 17 April day dry sample

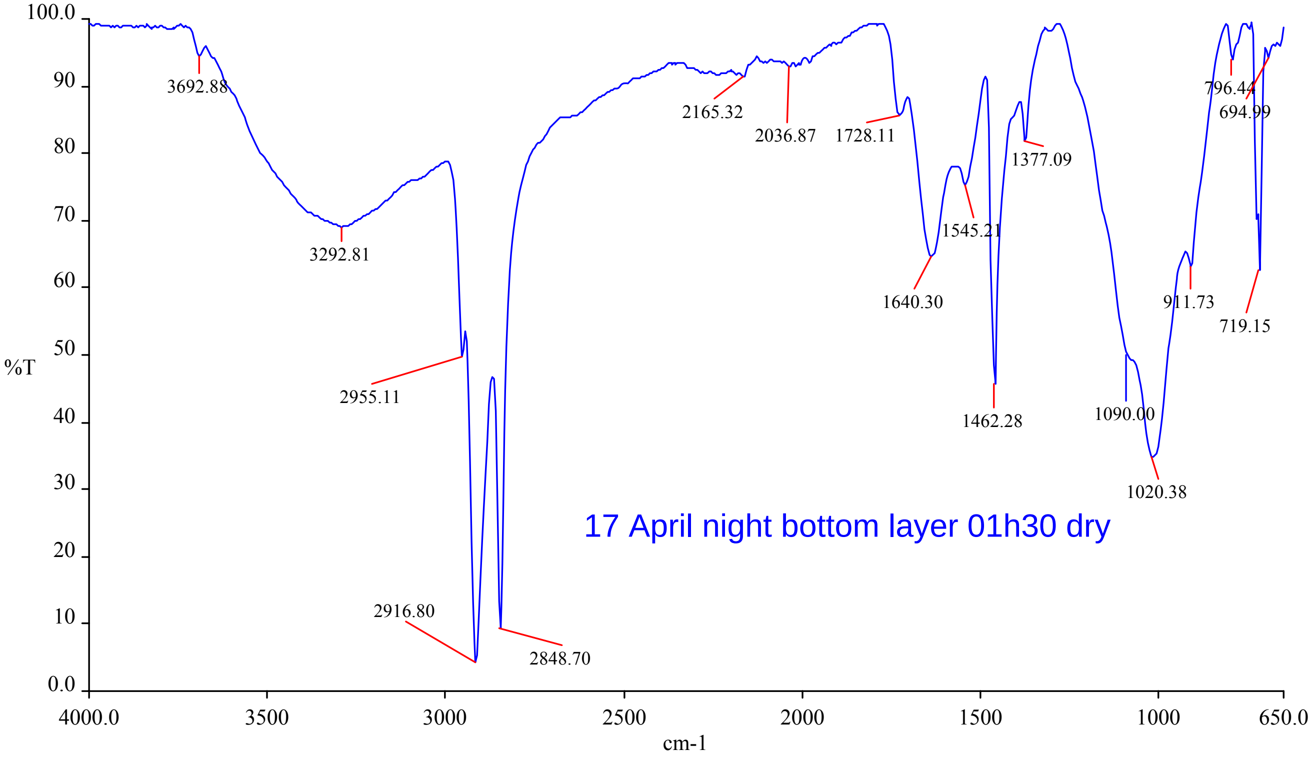

Figure D2: FT-IR adsorption bands for 17 April night dry sample

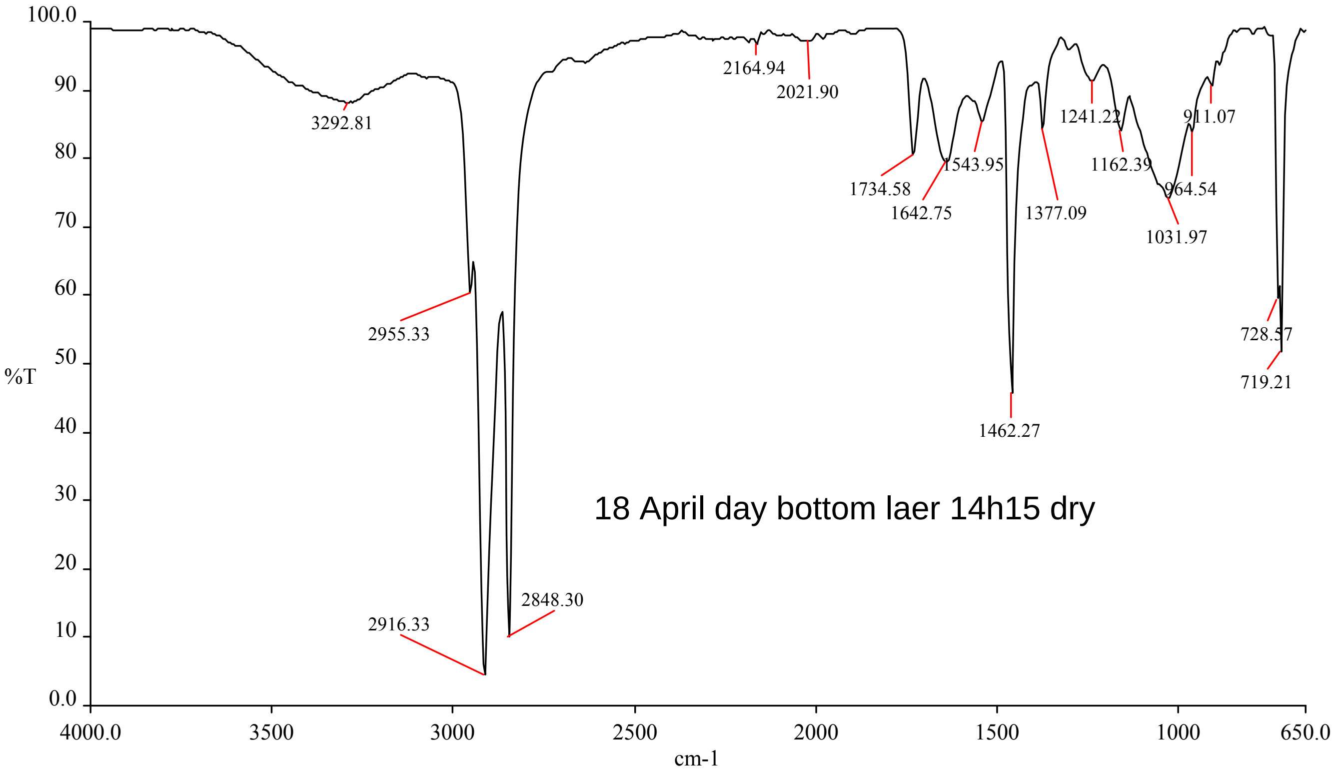

Figure D3: FT-IR adsorption bands for 18 April day dry sample

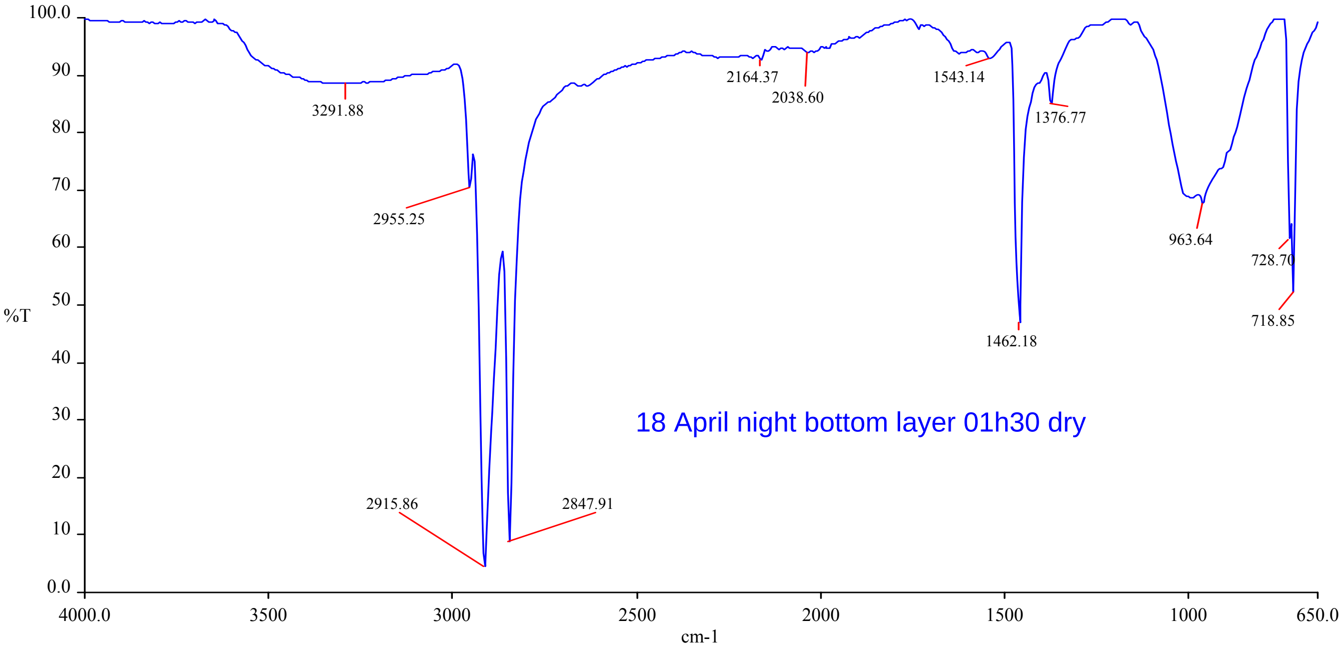

Figure D4: FT-IR adsorption bands for 18 April night dry sample

APPENDIX E: FT-IR SPECTROMETRY GRAPHS FOR THE BOTTOM LAYER OF WET SAMPLES

The following graphs are from FT-IR spectrometry results for wet samples

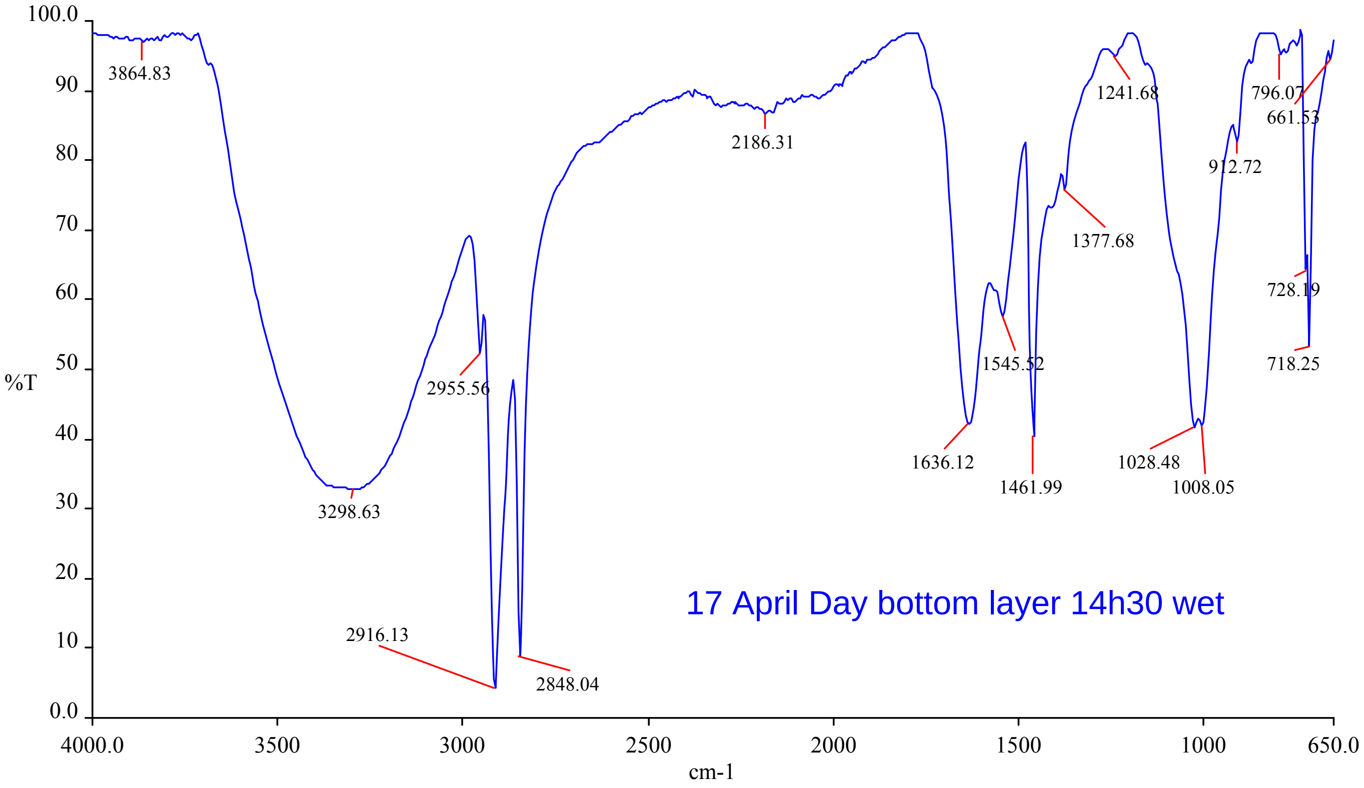

Figure E1: FT-IR adsorption bands for 17 April day wet sample

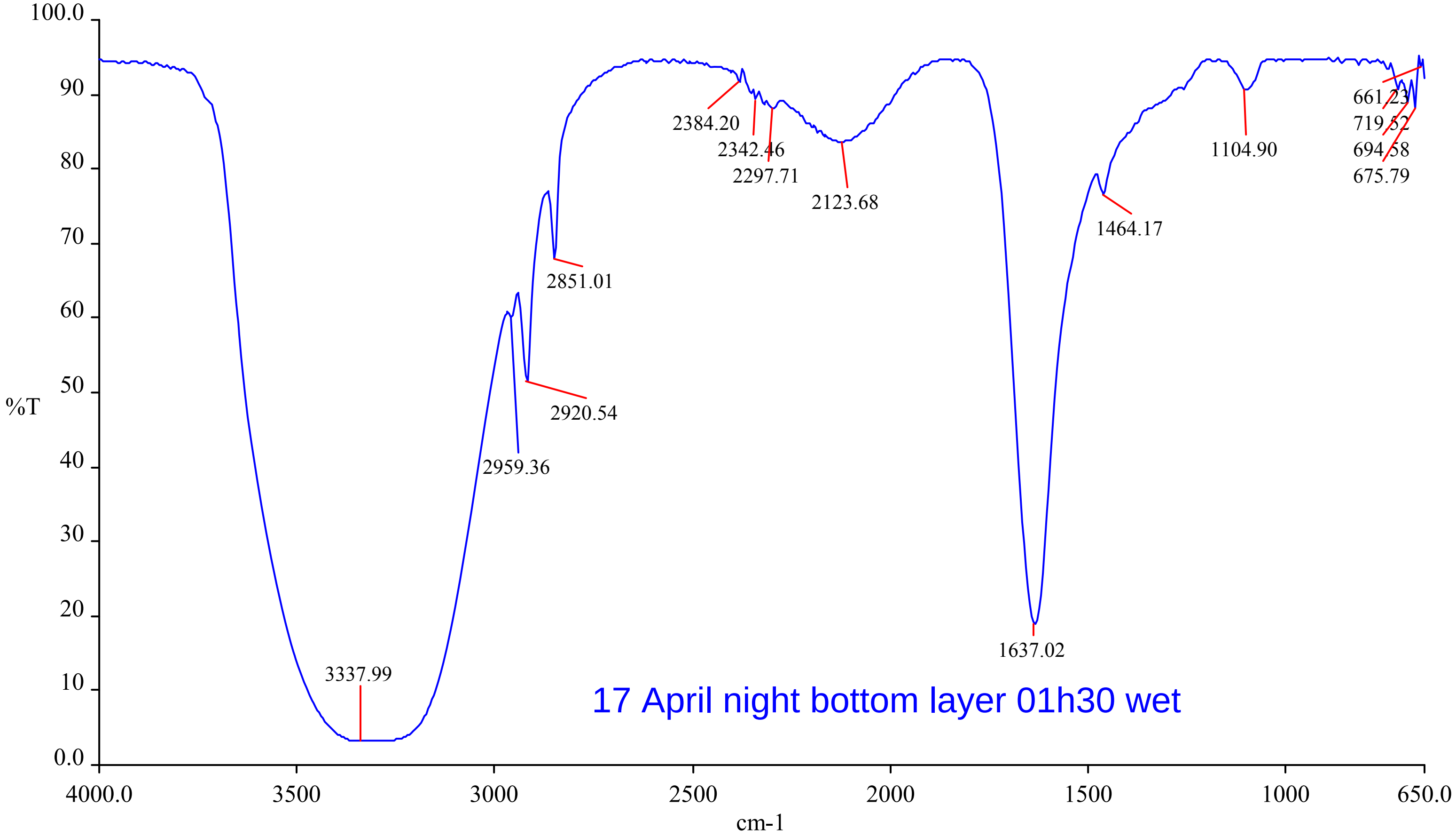

Figure E2: FT-IR adsorption bands for 17 April night wet sample

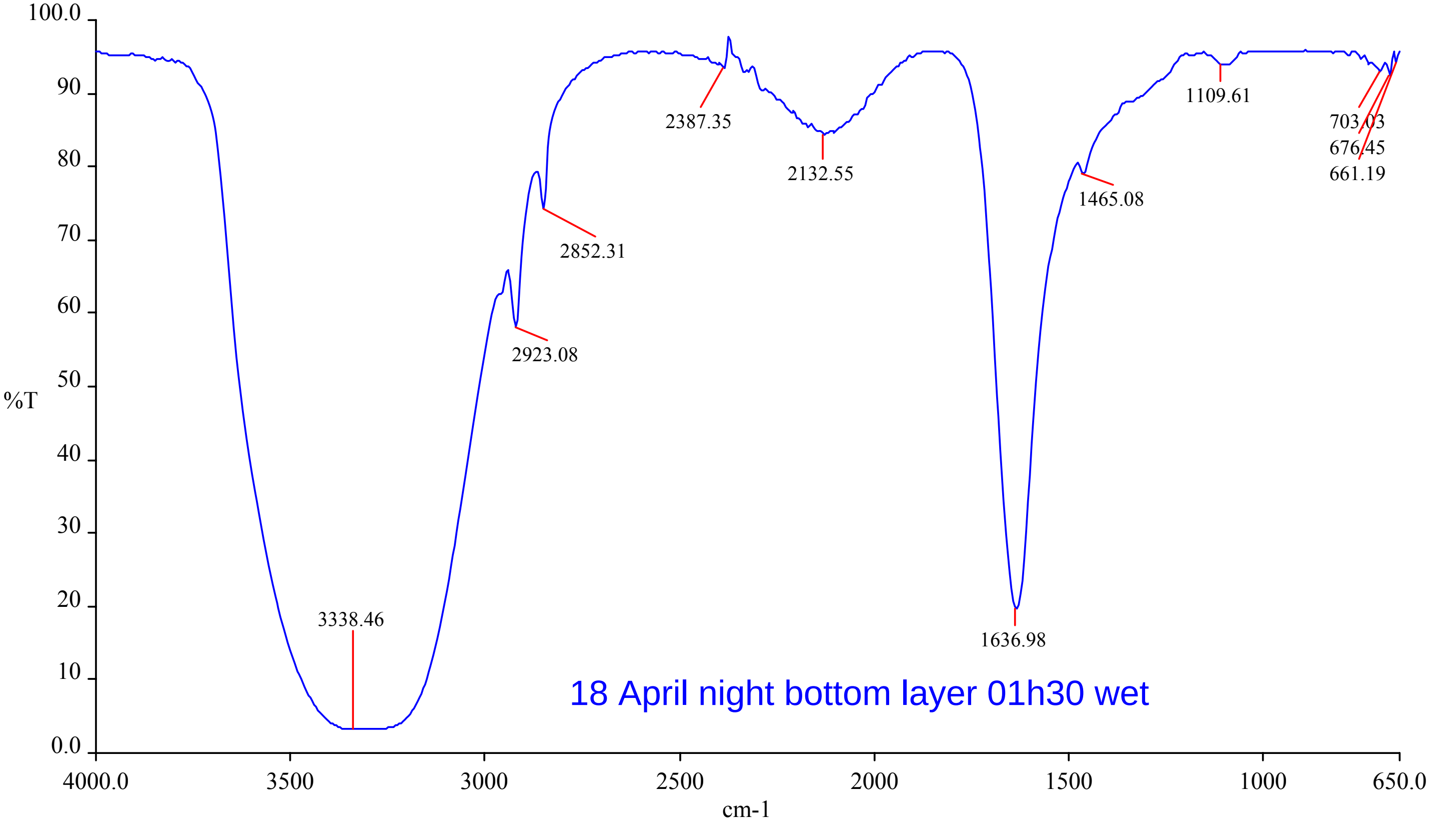

Figure E3: FT-IR adsorption bands for 18 April night wet sample

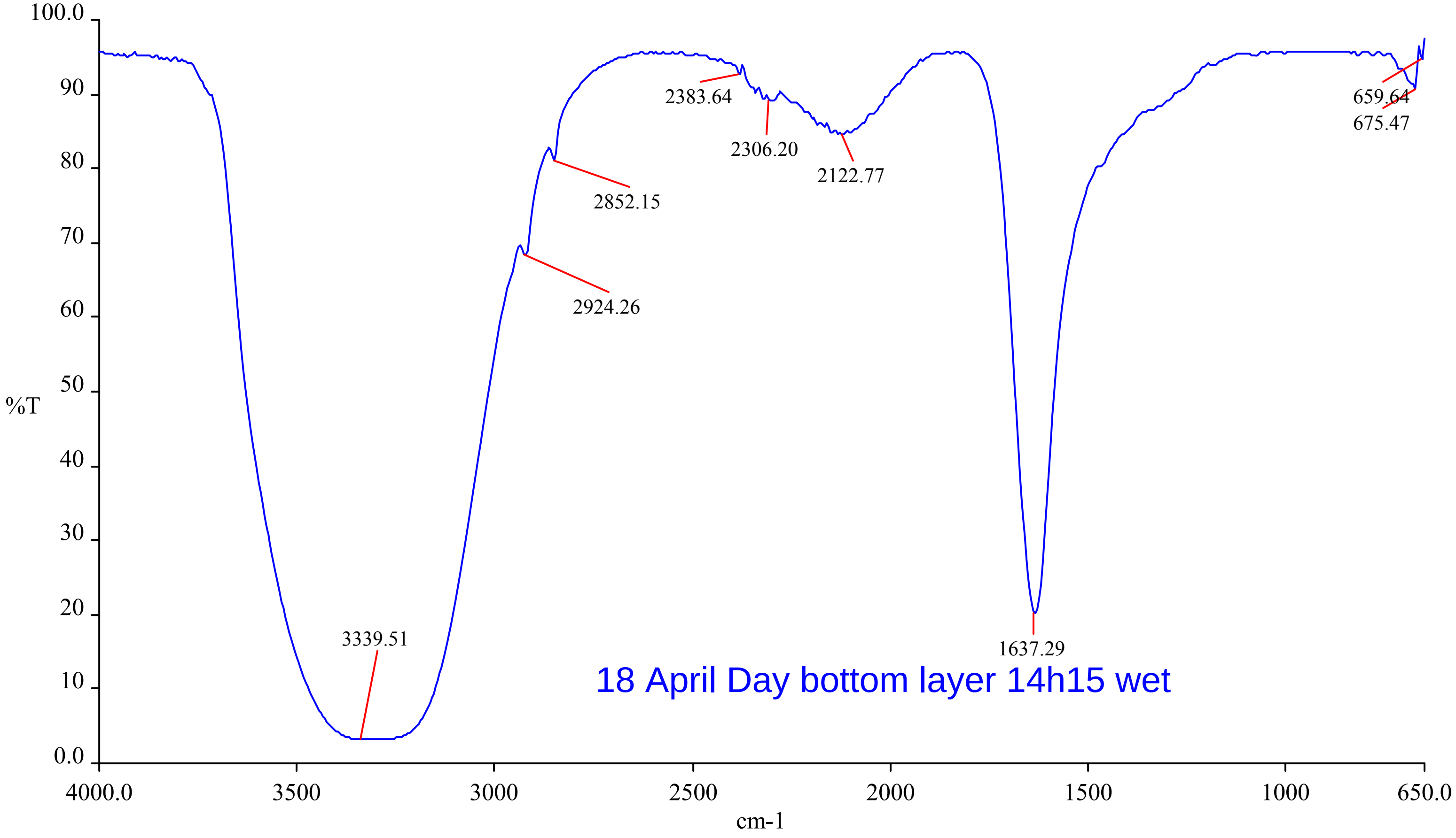

Figure E4: FT-IR adsorption bands for 18 April day wet sample

APPENDIX F: CALCULATIONS FOR MODEL ESTIMATION

Table F1: Calculations for liquid phase concentration using Henry's and Raoult's law

Compounds	A	B	C	P_{vap}(32)(atm)	g/hr.m^2	Henry's const(atm.m^3/gmol)	Henry's const(dimensionless)	Concentration (g/m^3)
benzene	15.9008	2788.51	-52.36	0.171	0.0002	0.0055	0.224806991	0.000285315
Toluene	16.0137	3096.52	-53.67	0.053	0.00096667	0.00668	0.273038309	0.001135423
Ethyl-benzene	16.0195	3272.47	-59.95	0.019	0.00056667	0.00644	0.26322855	0.000690398
o-Xylene	16.1156	3395.57	-59.46	0.013	0.00026667	0.00527	0.215405972	0.000397023
water	18.3036	3816.44	-46.13	0.047				
Liquid temp(K)	305.15	308.15	309.15					
ID of flux cham(m)	0.35							
enclosed area(m^2)	0.096211275							
sweep flow(m^3/hr)	0.3							
density of air(g/m^3)	1250							
Pt(atm)	1							Raoults law
sampling period								
	gas phase(g/m^3)	amount (g)	Molar mass(g/mol)	mole	Gas mole frac	mass frac(y)	*Pi(atm)*	liq mole fraction
benzene	6.41409E-05	6.41409E-08	78.114	8.2112E-10	1.9028E-08	5.13127E-08	1.90276E-08	1.10979E-07
Toluene	0.000310014	3.10014E-07	92.141	3.3646E-09	7.7966E-08	2.48011E-07	7.79663E-08	1.46423E-06
Ethyl-benzene	0.000181732	1.81732E-07	106.168	1.7117E-09	3.9666E-08	1.45386E-07	3.96659E-08	2.08065E-06
o-Xylene	8.55211E-05	8.55211E-08	106.168	8.0553E-10	1.8666E-08	6.84169E-08	1.86663E-08	1.42936E-06
air		1.25	28.966	0.04315404	0.99999984	0.999999487	0.999999845	

Table F2: Calculating the cross-sectional area of the basin

Basin dimensions (for one basin)	
Depth (m)	3.5
Width(m)	12
length(m)	110
Cross sectional Area of basin(m^2)	42

Table F3: Velocity of the wastewater into the basin

Wind speed (17 Apr)(m/s)	5.2
wastewater flowrate(Ml/day)	10.11
wastewater flowrate(m^3/s)	0.1170139
wastewater flowrate(m^3/s)(equal split)	0.05850695
velocity of wastewater(m/s)	0.016716271

Table F4: Calculating mass transfer coefficients and emission rate

	Molar mass(g/mol)	Henry's const(dimensionless)	Cl(g/m^3)	K_g (cm/hr)	K_L(cm/hr)	K_{OL}(cm/hr)	K_{OL}(m/hr)	Emission rate model(g/m^2.hr)	Emission rate Measured (g/m^2.hr)
benzene	78.114	0.224806991	0.000285315	2848.519	0.125626	0.125602	0.001256	0.00000036	0.000200
xylene	106.168	0.215405972	0.001135423	2443.356	0.107758	0.107735	0.001077	0.00000122	0.000267
Ethyl-benzene	106.168	0.26322855	0.000690398	2443.356	0.107758	0.107739	0.001077	0.00000074	0.000567
Toluene	92.141	0.273038309	0.000397023	2622.751	0.115669	0.115651	0.001157	0.00000046	0.000967