FATE AND DISTRIBUTION OF ATMOSPHERIC VOLATILE ORGANIC COMPOUNDS FROM WASTEWATER TREATMENT FACILITES

by

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We acknowledge and respect the Lək̓ʷəŋən (Songhees and Xʷsepsəm/Esquimalt) Peoples on whose territory the university stands, and the Lək̓ʷəŋən and W̱SÁNEĆ Peoples whose historical relationships with the land continue to this day.

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Abstract

Malodourous volatile organic compounds (VOCs) are found throughout the environment, from biogenic, geochemical and anthropogenic sources. A concerning anthropogenic source of malodours are wastewater treatment plants (WWTPs), where elevated levels of VOCs including several organosulfur compounds with low odour detection thresholds are produced and emitted. The ability to measure this class of malodourous compounds specifically, methanethiol (CH_3SH), dimethyl sulfide (CH_3SCH_3), and dimethyl disulfide (CH_3SSCH_3) by mobile mass spectrometry has enhanced our understanding of their fate and distribution in the environment surrounding wastewater treatment facilities. Organosulfur compounds can impact the environment including human health either through toxic effects, malodours, and/or as a source of sulfur dioxide (SO_2), thus lowering air quality.

This thesis summarizes the use of direct mass spectrometry in a purpose-built research vehicle to investigate odour control systems at three wastewater facilities on Vancouver Island both on-site in foul air collection ductwork and on-road in ambient air in the neighbouring community. The three WWTPs investigated varied in age, size, location, and odour control technology. VOCs were measured using proton-transfer time-of-flight mass spectrometry (PTR-TOF-MS) with concentrations of methanethiol (*m/z* 49.01), dimethyl sulfide (*m/z* 63.02), and dimethyl disulfide (*m/z* 94.99) assessed in real-time. Other VOCs known to contribute to the odour profile include oxygenated hydrocarbons (e.g., acetaldehyde, acetic acid, butanal) as well as monoterpenes were also monitored. Supplemental measurements taken with sorbent tubes on-site were evaluated with lab-based thermal desorption-gas chromatography-mass spectrometry, to assess the identity of compounds such as dimethyl sulfide and ethanethiol.

The distribution of atmospheric gases emitted from these facilities varied depending on the treatment methods employed as well as on the location, topography, and meteorology. On-site measurements were aimed at assessing the efficiency of odour control technologies and the on-road measurements provided insight into the spatiotemporal distributions of malodourous VOCs. Concentrations of reduced sulfur compounds in the collected foul air ranged from $10^2 – 10^4$ parts per billion by volume (ppb_v). The odour control systems included physical adsorption by activated carbon and biological treatments using biofilters and bioreactor systems. A chemical scrubber and a pilot scale UV advanced oxidation treatment process were also evaluated during this study. Efficiencies of odour control techniques are described, with methanethiol removal efficiency consistently being the greatest, with typical removal of 70-90% by odour control technologies. Using biological and physical treatments, dimethyl sulfide and dimethyl disulfide were found to be modestly removed, with removal efficiency of dimethyl sulfide at <40% and dimethyl disulfide removal efficiencies being low (<20%) to negligible. In some cases, we observed increases in dimethyl disulfide concentrations.

On-road measurements in the local communities around the WWTPs were also investigated for potential impacts from WWTPs. This includes mapping VOC concentrations over time and space, tracking plumes, and determining whether other sources of odours exist in the sample area. Typical ambient concentrations recorded at and within 2 km of WWTPs in the 0.2 -5 ppb$_v$ range for reduced sulfur compounds and 2 – 10 ppm$_v$ for methane. On-road concentrations for benzene, toluene, ethylbenzene, and xylenes (BTEX) associated with vehicle emissions were typically observed in the 0.5 – 5 ppb$_v$ range. Results from the drive portion of the campaign allowed for visualization of VOC distributions and produced neighbourhood scale information, including geospatial averages mapped at 50x50m, with detection of odourous VOCs within 1 km of WWTPs above odour thresholds under some conditions. Sources other than the WWTPs were also identified including pump stations, conveyance structures, and estuarine marine locations. This work illustrates the application of mobile real-time measurements to better understand the fate and distribution of VOCs in the community as well as characterize the effectiveness of mitigation strategies for malodourous compounds.

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List of Abbreviations

AC – Activated carbon

AOPs – Advanced oxidation processes

APCI-MS – Atmospheric pressure chemical ionization-Mass spectrometry

Aq – Aqueous

AQHI – Air quality health index

ATADs – Autothermal aerobic thermophilic digestion

BAF – Biological aerated filter

BTEX – Benzene, Toluene, Ethylbenzene, Xylene

BVOCs – Biogenic Volatile organic compounds

C – Degree Celsius

C/s – Celsius per second

CAPs – Criteria air pollutants

CFI – Canadian foundation for innovation

C_{in} – Concentration in

C_{out} – Concentration out

DL – Detection limit

DMDS – Dimethyl disulfide

DMS – Dimethyl sulfide

DMSO – Dimethyl sulfoxide

DMTS – Dimethyl trisulfide

DNA – Deoxyribonucleic acid

E/N – Electric field along drift axis/gas number density

FCPCC – French creek pollution control center

ft- Feet

g/hr – gram per hour

g/mol – Molecular weight, grams per mole

GC-MS – Gas chromatography-Mass spectrometry

GHG- Greenhouse gas

GIS – Global information systems

GNPCC – Greater Nanaimo pollution control center

GPS- Global positioning system

GWP – Global warming potential

Hh:mm- Hours:minutes

IDW- inverse distance weighting

IR – Infrared radiation

kg/year- kilogram per year

Km- kilometer

Km/h – Kilometer per hour

LOQ – Limit of quantitation

LPCI-MS – Low pressure chemical ionization-Mass spectrometry

m- meter

m/s – meter per second

m/z – mass-to-charge ratio

$M+H^+$ – Parent ion plus proton

m^3- Cubic meter

m^3/hr – cubic meter per hour

MBBR- Moving bed bioreactor

MeSH- Methanethiol

Min- Minute

mL – Milli-liter

mL/min – Milli-liter per minute

MMSL – Mobile Mass spectrometry lab

moles/yr – Moles per year

MS- Mass spectrometry

NOx – Nitrogen oxides

O_3 - Ozone

ODT- Odour detection threshold

OVOCs – Oxygenated Volatile organic compounds

PA – Proton affinity

PEEK- Poly-ether-ether-ketone

PFA- Perfluoro alkoxy

$PM_{2.5,10}$ – Particulate matter 2.5 – 2.5 microns or less

ppbv – Part-per-billion per volume

ppm – Part-per-million

pptr - Part-per-trillion

Psi – Pound per square inch

PTR-TOF-MS – Proton-transfer-time-of-flight-Mass spectrometry

RH – Relative humidity

RSC – Reduced sulfur compound

RT – Retention time

S# - Sample location #

SIFT-MS – Selective ion flow tube-Mass spectrometry

SS- Stainless steel

Stdev – Standard deviation

STP- Standard temperature and pressure

SVOCs – Semi-volatile organic compounds

Td- Townsend

TD-GC-MS – Thermal desorption-gas chromatography-mass spectrometry

ug/m$_3$- Microgram per cubic meter

UK – United Kingdom

USA- United states of America

UV – Ultraviolet

VDC- Volts direct current

VOCs – Volatile organic compounds

WBST – Wet bio-scrubber tower

WWTP(s) – Wastewater treatment plant(s)

WWTP1,2,3 – Wastewater treatment plants 1, 2 or 3

Chapter 1: Introduction and background information

Real-time monitoring of volatile organic pollutants is essential for identifying the variables that contribute to air pollution, assessing the effectiveness of current pollution control systems, and devising efficient management plans. The ability to monitor processes in real time enables the researchers and operators to collaborate on developing operational parameters for the systems to best manage the output of pollutants to the atmosphere. During operations, wastewater treatment systems are dynamic, and many factors contribute to the output of gaseous pollutants, such as the total flow through the systems, the processing times, ambient temperature, stormwater input, and overall health of the wastewater systems. The condition of the media, dosing of reagents, maintenance, and the condition of odour abatement technologies all play a role in the performance of these systems. Sampling done at one discrete time or infrequently does not allow for proper optimization of dynamic systems, as many processes are cycled during operations, fans, filling, draining, and backwashes occur which may influence the output of gaseous pollutants. If these processes are not characterized, they may lead to improper assumptions on operational performance and gaseous outputs. Also, to assess the contributions to air pollution regarding the fate and distribution of the pollutants, real time monitoring of volatile organic compounds (VOCs) surrounding the facility and in the neighbouring community is essential, as the mixture of VOCs released do not all behave similarly, and may undergo transformation, distributing at different rates and distances. Real time VOC monitoring allows for the assessment of the fate, distribution, and impacts to local air quality in a dynamic system influenced by meteorological conditions and industrial emissions.

1.1 Air pollution

Air pollution arises from the competition between emission, advection, and photochemical processes in the atmosphere, which determine the movement, chemical transformation, and concentration of contaminating pollutants.[1–3] Contributions to air pollution can come from primary sources, which can either be point or diffuse. Some point sources include emissions from industry such as, oil refineries, wastewater treatment facilities and goods manufacturing plants. Point sources may provide a route for treatment of the air pollutants before release to the atmosphere as their output is generally from an exhaust stack which can accommodate an air treatment technology, although this is not implemented in all cases. Another primary source can arise from dynamic sources such as vehicle exhaust from combustion engines, including boats, planes, cars, trucks and buses, which disperse pollutants while moving.[4,5] Secondary sources of air pollution can arise from chemical transformation of pollutants in the atmosphere or come from diffuse sources which are challenging to capture and treat before release to the atmosphere. For example, chemical transformations involving air and heat, typically from air passing thru or over hot engines can contribute to NO_x

production.[6] Some diffuse sources arise from volatilization of chemicals from infrastructure or personal use items such as asphalt, paints, plastics, cosmetics and from tailings ponds.[7] Another class of air pollutants are the greenhouse gases (GHGs), carbon dioxide and methane, which have effects on the planets warming. Addressing the emissions and ambient concentrations of GHGs is important in dealing with climate change. The dynamic nature of air pollution is induced from primary and secondary sources, which can emit a range of chemicals and particulate matter that can impact health and the environment.

1.2 Criteria air pollutants (CAPs)

In Canada, a class of air pollutants is referred to as the criteria air pollutants or CAPs, including ozone (O_3), fine particulate matter ($PM_{2.5}$ and PM_{10}) and nitrogen oxides (NO_x). The air quality health index (AQHI) was introduced in Canada to create an easy-to-understand air quality rating for the public.[8–10] The CAPs which inform the air quality index (AQHI) are ground-level ozone, $PM_{2.5}$ and PM_{10}, and nitrogen dioxide (Equation 1).[11,12] In some cases, carbon monoxide and sulfur dioxide are added to the index for certain regions.[11] The measurement of CAPs is done using standardized equipment and is cost effective, which has in part driven the use of these metrics for reporting air quality. Also, the health effects associated by the CAPs drive the need for adequate reporting. The ability to continuously measure and relay criteria air pollutants (NO_2, O_3, $PM_{2.5}$) has led to their widespread monitoring and usage for air quality indices which are used as proxies in some jurisdictions.[13,14] There are dedicated air quality monitoring stations operated by both provincial and federal government agencies which are located at fixed locations around the country. The measurements of CAPs are then relayed to the public at a national, provincial, and in some cases, a regional scale. The equipment used at government agencies are standardized and quality assured, using standalone monitors for ozone, PM and NO_x. This instrumentation when used in non-government applications are referred to as government equivalent sensors, which meet the requirements of standards set by the government monitoring regulations and are not to be confused with low-cost air quality sensors. The recent development of low-cost air quality sensors have been used to monitor air quality (particularly $PM_{2.5}$), which can act as early warning signals and increase spatial heterogeneity at the neighbourhood scale, although these devices are not the government equivalent sensors used in government reporting.[15,16] There are some cases of air pollution that do not conform to the description captured by the AQHI, such as volatile organic compounds which affect human and environmental health which are not routinely measured but should not be overlooked.

$$(1)\quad Air\ quality\ health\ index\ (AQHI) = 10/(10.4 * \left(100 * \left(e^{(0.000871*NO_{2a})}\right) - 1 + e^{(0.000537*O_{3a})} - 1 + e^{(0.000487*PM_{2.5a})} - 1\right))$$

$$NO_2, O_3, PM_{2.5} = Trailing\ 3hr\ average\ concentrations$$

1.3 Volatile organic compounds

Volatile organic compounds (VOCs) are organic molecules that can vaporize at typical ambient temperatures and pressures.[17,18] They can be categorized according to their boiling points, with substances with lower boiling points demonstrating greater volatility.[19,20] A VOC is a type of organic compound that has a boiling point of 250°C or lower when evaluated at 101.3 kPa.[2,19,21] As the level of volatility rises, the probability of a chemical being released into the atmosphere also increases. Measuring highly volatile organic compounds is challenging, as they are predominantly present in the atmosphere, typically as trace gases, found in parts-per-trillion to parts-per-billion (pptr_v-ppb_v) rather than solids or trapped on surfaces.[2,19,21] The least volatile chemicals in the atmosphere account for a smaller fraction of the atmospheric components, as the majority are found in solid or liquid form or on surfaces such as particles, structural materials, and are generally referred to as semi-volatile organic compounds (SVOCs).[7]

The fate and distribution of VOCs in the atmosphere are impacted by a variety of variables, from proximity to point source locations, such as industry, diffuse sources such as marine aerosols, biogenic emissions and vehicle exhaust.[2,14,22] Other variables such as meteorological conditions, including temperature, windspeed, direction and irradiance influence fate and distribution.[2,11,14,22,23] Atmospheric lifetimes of VOCs can vary widely, involving their reactivity with atmospheric oxidants determining the fate and distribution of these compounds, impacting their ability to affect public health.[1,2,11] VOCs are difficult to measure, occur at trace levels and in complex mixtures which require sophisticated technology to track and report on.[21,24,25] Contributions to air pollution arising from VOC inputs are not trivial and should be considered.

The atmosphere is inherently oxidizing as it contains high levels of Oxygen (21%), and some trace oxidants such as ozone, hydroxyl radicals and hydrogen peroxide. The oxidizing effect of the atmosphere tends to transform VOCs when dispersed in the atmosphere. Since many VOCs are found in lower oxidation states, such as organosulfur compounds like methanethiol at oxidation states of -II, will oxidize and become more polar and less volatile, transforming VOCs into semi-volatile compounds (SVOCs).

1.4 Semi-volatile organic compounds (SVOCs)

Semi-volatile organic compounds (SVOCs) are not as abundant in the gas phase at lower temperatures due to their lower volatility than VOCs, and are comprised of many organic compounds which can have detrimental effects on health and the environment, such as poly aromatic hydrocarbons and organochlorine pesticides.[26] SVOCs have many sources, such as industrial additives and personal care products, and are defined as having vapour pressures between 10^{-2} and 10^{-8} kPa at 25°C.[7] Some SVOCs are generated from VOCs once they are dispersed into the atmosphere, where transformation into more polar and less volatile forms can take place. These reactions can also form secondary organic aerosols (SOAs), which is the case for sulfur containing compounds.[27] These SOAs contribute to the particulate matter in the atmosphere and can contribute to poor human health.[28] The chemical interactions in the atmosphere, including sunlight-induced photochemical reactions, transform organic compounds and nitrogen oxides into photochemical oxidants, particularly ozone, which can exacerbate pollution episodes.[23,29] The reactions involving ozone and nitrogen oxides drive the generation of photochemical smog (NO_2) and can have detrimental effects on respiratory health. [14,23]

1.5 Odourous Organosulfur Compounds

Organosulfur compounds are typically odourous volatile gases when in the smaller thiol form which contain at least one carbon bound to a sulfur. They are found in a variety of conformations such as the simple methanethiol (MeSH) with a methyl-group attached to a sulfur, dimethyl sulfide (DMS), ethanethiol, including two carbons and the more complex dimethyl disulfide, which is containing two sulfurs and two methyl groups bound by a sulfur-sulfur bond. The thiol groups are akin to alcohols although they are more acidic, less soluble in water and have lower boiling points.[30] One of the differences from alcohols is their ability to oxidize into sulphonic acids, adopting two oxygens rather than the formation of a ketone.[30] In some cases, dimethyl trisulfide can be detected in gas samples along with other forms of thiols (Appendix D). These compounds are notorious for their odours and their low odour detection thresholds in the ppb_v range (Table 1). Reduced sulfur compounds arise in nature from decomposition of amino acids such as methionine and cysteine and have other biogenic sources, ocean spray and on the ocean shorefront from decomposing seaweed (Equation 2).[27,31] Dimethyl sulfide and methanethiol have been linked to a common precursor metabolite dimethyl sulfoniopropionate (DMSP) also found in the marine environment which undergoes bacterial transformation to either DMS or MeSH.[31] Because they have such low odour detection thresholds, methanethiol and other mercaptans have been added to natural gas in many cases to aid in the detection of natural gas leaks.[32]

(2) General enzymatic process of amino acid decomposition:

$$HS - CH_2 - (R) + H_2O \rightarrow_{desulphydrase}^{Cysteine} \rightarrow CH_3CO - COOH + HS^{-}_{(aq)} + NH_4^{+}{}_{(aq)}$$

$$-(R) = H_2N - CH - COOH$$

Dimethyl sulfide (DMS) is released as an reduction product from sulfate reducing organisms and is a critical player in the global sulfur cycle.[27] These sulfur containing gases are found at appreciable concentrations at wastewater treatment plants, agricultural feedlots, marine phytoplankton, and composting facilities among other places.[33] Other anthropogenic sources can be from burning diesel fuel and other hydrocarbon fuels containing sulfur compounds.[4,34] Sampling methanethiol (MeSH) and dimethyl disulfide (DMDS) can be a challenging process for offline techniques like GC-MS, as they can be mis represented by transformation and degradation during storage, transport and analysis. For example methanethiol can readily oxidize to DMDS and cause issues with adequate reporting for these compounds.[35] In the presence of activated carbon and oxygen, reactions of thiols to disulfides has been characterized in the literature (Equation 3).[36] Their ability to cause nuisance odours has driven the need to have adequate odour abatement techniques to combat their release into the atmosphere from point sources and limit the transportation to nearby communities. They have reaction pathways linked to dimethyl sulfoxide (DMSO), and sulfur dioxide (SO_2) which are the higher oxidation products from methanethiol, DMS and DMDS.[30] The contribution to SO_2 from methanethiol and DMS has recently been assessed showing >90% of methanethiol transforming to SO_2, while DMS contributes an estimated 40-80%, which further suggests that proper analysis of these emissions is valuable information to assess the global SO_2 budget.[31] The final oxidation state of sulfur in organosulfur VOCs (i.e. methanethiol) is +VI in gaseous SO_3 which reacts with water to yield H_2SO_4 , contributing to acid rain and cloud condensation nuclei in the form of sulfate aerosols (i.e. ammonium sulfate).[31] Therefore, understanding the fate and distribution of organosulfur compounds such as the thiols is not only important for controlling nuisance odour, but also as a potential contributor to SO_2 and H_2SO_4 production.

(3) General reaction of mercaptans to disulfides:

$$2(CH_3-(CH_2)_n-SH)\xrightarrow{Air+Activated\ carbon} CH_3-(CH)_2-S-S-(CH_2)_n-CH_3$$

1.6 The sulfur cycle in the environment

The sulfur cycle is a complex mechanism of transformation, uptake and deposition of sulfur species around the globe.[27] The importance of sulfur species regarding atmospheric chemistry is for its contribution to cloud condensation nuclei. Contributions of sulphate to the atmosphere in the form of SO_2, form aerosols and induce cloud formation. Another aspect of Sulphur emission is for the contribution to sulfuric acid production and in turn a driver for low pH in clouds and creation of acid rain.[27]

The sulfur cycle finds itself in each compartment of the earth's environment from the atmosphere to the aquatic environments and in soils and rocks. In aquatic and terrestrial environments, it is a micronutrient for microbial growth, is found as trace impurities in rocks and can be transformed by biogenic processes. Of the biogenic processes driven by microbes, there are a range of sulphate-reducing bacteria that can transform sulphate species to lower oxidation states to form sulfides, such as hydrogen sulfide and dimethyl sulfide. There are sulfide oxidizing bacteria which can metabolize sulfides into sulphates, these processes take place in the aquatic and terrestrial environments depending on the reducing potential of the environment. Sulfur is a component of some amino acids and plays a critical role in biology, in formation of proteins and in metabolic processes. There are geochemical processes including deposition of sulphates into the aquatic environment from leaching processes and particle distribution into the atmosphere from dust and sea-spray. Also, in-soluble sulfates are deposited into the terrestrial environment.

As sulfur is cycled through the environment it encompasses oxidation states from -II to +VI, from sulfides to sulphates, playing numerous roles. In the context of malodours, these compounds are generally in the -II or -I oxidation states, giving rise to odour causing molecules of methanethiol, dimethyl sulfide and dimethyl disulfide. In the context of wastewater treatment, sulfur is concentrated in waste and generally ends up for a period of time in a highly reducing state during transit, decomposition, or treatment, where it forms hydrogen sulfide and methanethiol among other reduced sulfur compounds, causing nuisance odours. Knowing the sulfur cycle is key information for understanding the transformation and removal of odourous sulfides from waste gases. Many treatment methods are based on either biological or chemical oxidation processes, transforming species into non-odourous sulphate species.

1.7 Wastewater treatment

Wastewater treatment technologies are used to remove a portion of pollutants and toxins from wastewater before it is released into the environment or reused. These technologies target different contaminants and can be categorized based on their goals. Common methods include preliminary treatment like screening, primary sedimentation treatment, secondary oxidative treatment and tertiary treatment such as advanced biological treatment, chemical precipitation, filtration, disinfection, and ozonation.[20,37–39] The choice of technology depends on a number of factors including the volume of wastewater, cost, and available space. Basic treatment methods involve settling ponds with aeration for oxidation and bioremediation.[20,37,39] The main goal of wastewater treatment is to reduce biochemical oxygen demand, total suspended solids, and Coliforms before discharge.[19,37,39–42] The secondary goal is to reduce the nutrients such as nitrogen and phosphorous to the environment, to combat algal blooms and eutrophication. Treatment technologies use heat, agitation, aeration, mechanical separation, and chemicals to expedite the process and enhance removal of harmful components.[41,42] Overall, wastewater treatment technologies play a crucial role in protecting the environment and public health by ensuring that wastewater is treated effectively before being released.

Wastewater treatment can be defined in a broad sense by treatment steps from preliminary to tertiary. Preliminary treatment uses screens or grates to separate large particles and debris from wastewater. Primary treatment uses sedimentation tanks or clarifiers to settle suspended solids and separate organic materials, fats, solids and oils from the water. Secondary treatments can use activated sludge, trickling filters, and revolving biological contactors.[41] Secondary and tertiary treatment frequently use advanced biological treatment processes like membrane bioreactors and sequencing batch reactors to remove nutrients and trace pollutants.[19,41] Chemical precipitation and filtration remove dissolved contaminants and phosphorus from wastewater, while disinfection can be done using UV radiation and ozone gas to disinfect and oxidize organic and inorganic contaminants.[42]

Advanced treatment and resource recovery involve nutrient removal to prevent eutrophication, and resource recovery through anaerobic digestion, thermal hydrolysis, and nutrient recovery technologies. These methods can generate biogas, biosolids for soil amendment, recover heat from processes and water for irrigation or industrial use.[19,42]

1.8 Wastewater treatment VOCs and air pollution

Urban wastewater treatment releases pollutants such as greenhouse gases and volatile organic compounds, which have negative effects on human health through respiratory stress and malodours, as well as contributing to global warming.[19,43] Understanding the fate and distribution of trace gases released from treatment processes is critical for implementing effective regulations, policies, and odour control technologies.[20,40] Mobile measurements conducted in real-time can offer policymakers crucial data to formulate efficacious remedies. Municipal wastewater treatment plants are tasked with the purification of urban and industrial wastewater to eliminate contaminants and generate water that complies with environmental laws.[20,37] Nevertheless, they produce air pollution through the release of greenhouse gases, bio-aerosols, and volatile organic compounds, including unpleasant-smelling organosulfur compounds.[20,40,44] The emissions originate from many steps in the treatment process, including the raw sewage influent itself and the primary treatment, for example screening and sedimentation.[19,40,44] In addition, centrifugation during the processing of biosolids and anerobic digestion also contribute to emissions.[19,41] The primary factor affecting the air quality in the immediate area is the emission of volatile organic compounds, which result in disagreeable odours and toxicity, adding to atmospheric pollution.[2]

Urban wastewater treatment plants (WWTPs) release a significant quantity of volatile organic compounds; therefore, several treatment techniques are frequently used to minimize the emission of noxious gases, which are typically referred to as foul air at WWTPs. Generally, treatment is done with either a physical or chemical process. The treatment methods encompass activated carbon adsorption, sophisticated oxidation processes, as well as chemical and biological treatment.[39,41] Activated carbon utilizes porous carbon materials to absorb and eliminate volatile organic pollutants from gases emitted during wastewater treatment. Advanced oxidation techniques employ potent oxidants like ozone or hydrogen peroxide to decompose noxious molecules.[39] Biological treatment employs microorganisms to break down volatile organic chemicals found in wastewater through biodegradation. Adopting these treatment techniques can substantially decrease the release of noxious gases from wastewater treatment plants and enhance the air quality in the surrounding area.[19,20,39] Some treatment methods may have unintended consequences, allowing for transformation of chemical species, may be unreactive for certain species and produce and release chemicals downstream of treatment. [40,44] Also, if not properly maintained these systems can become sources of pollution. When in the close proximity to treatment facilities it may negatively impact an individuals' well-being, exposing them to unpleasant organosulfur chemicals that lead to odour complaints.[19,40,44] Wastewater treatment generally entails the elimination of hazardous hydrogen sulfide and the removal of organosulfur compounds, such as methanethiol and dimethyl sulfide, but to a lesser degree for the organosulfur compounds.[37,40,43,44]

Past research has examined and identified volatile organic compounds in wastewater, with a specific focus on understanding the mixture of gases released.[20,21,44] There are reports looking at total VOCs and total reduced sulfur compounds from WWTPs, and only few studies have reported individual organosulfur compound concentrations.[45] WWTPs generate a wide range of VOCs, although not all are toxic or produce unpleasant odours in the community. Typically, there has been more research on highly toxic substances like hydrogen sulfide due to the significant impact on health.[46] However, a smaller category of organosulfur compounds, which cause odour issues and affect mental well-being, have not been thoroughly studied in terms of their behavior and spread from wastewater treatment plants and associated infrastructure. This thesis will focus on the fate and dispersion of key odourants released from WWTPs, such as methanethiol (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS).

The trace gases emitted from wastewater treatment are generally in the parts-per-billion (ppb_v) range. Some gases including methane and hydrogen sulfide (H_2S) can be found in parts-per-million (ppm_v) ranges. Hydrogen sulfide is known to be acutely toxic and has strict regulations associated with it, therefore it is closely monitored by wastewater operators. The less regulated organosulfur compounds, methanethiol, DMS, and DMDS are found in the ppb_v range and require specialized techniques to properly measure their concentrations.[20,40,44] Generally, gases in the ppb_v range would not be as much of a concern, although the organosulfur compounds MeSH, DMS, and DMDS are in a group of chemicals which humans are very sensitive to, and have very low odour detection thresholds, in the ppb_v range (Table 1).[44,47] Having such a low odour detection threshold means that even at ppb_v levels of emissions they can still cause odour complaints in the nearby communities. The Henry's Law solubility constants which determine the amount of gas partitioning into an aqueous solution is an important factor to consider during the wastewater treatment and odour control process (Table 1). The concentrations found on-site at WWTPs generally follow a trend of highest concentrations of H_2S>MeSH>DMS>DMDS pre-treatment and post treatment can follow similar ranges but with H_2S being greatly reduced to below the regulatory limits. [20,40,43,44] Methanethiol, DMS and DMDS follow similar trends, although in some odour control systems we can see a different trend with DMS or DMDS at higher concentration levels post-treatment, either through transformation or treatment non-compatibility.[44] It is important for operators, engineers, and managers of these processes to understand the fate and distribution of these volatile odourous gases.

Table 1: Common wastewater VOCs Odour detection thresholds and Henrys law solubility constants, including reduced sulfur compounds. All values calculated at STP.

Compound	Odour Detection Threshold (ppb_v^{STP})[47]	Common smell associated[47, 48]	Henrys law Solubility constant[49] H_s^{cp} ($mol/(m^3Pa)$)
Hydrogen sulfide	0.50	Eggy sulfide	$1.0x10^{-3}$
Dimethyl sulfide	0.39	Vegetable sulfide	$5.3x10^{-3}$
Ethanethiol	0.01	Earthy, sulfidy	$2.8x10^{-3}$
Benzyl sulfide	2.0	Sulfidy	1.9
Methanethiol	0.02	Sulfidy, pungent	$3.8x10^{-3}$
Dimethyl disulfide	0.02	Rotton cabbage, sulfidy	$5.8x10^{-3}$
Acetaldehyde	0.11	Green sweet	$1.3x10^{-1}$
Acetic acid	1000	Sour	$4.0x10^{1}$
Acetone	19000	Chemical sweet, pungent	$2.7x10^{-1}$
Phenol	44.1	Medicinal	$1.8x10^{1}$
Toluene	2000	Floral, pungent, solventy	$1.6x10^{-3}$

There are several challenges and impacts which can be considered when studying wastewater treatment. This thesis will focus on the organosulfur compounds methanethiol, dimethyl sulfide and dimethyl disulfide, their remediation during treatment, odour control, and their emissions into the community, focusing on the fate and distribution of these compounds. Removal of reduced sulfur compounds from foul air involves some combination of biological, chemical, or physical transformation. When released to the atmosphere, these compounds will ultimately be oxidized and contribute to the global sulfur cycle.

Greenhouse gases such as carbon dioxide and methane can be released from WWTPs in conjunction with the myriad of VOCs. During treatment processes carbon dioxide (CO_2) and methane (CH_4) are lost to the atmosphere. In some cases, CH_4 is produced during digestion and collected as a valuable energy source and used on-site. The term greenhouse gas is referring their capacity to absorb outgoing infrared radiation (IR) and thus trap heat in the near-surface atmosphere. This contributes to the warming of the near-surface global temperature. Not all greenhouse gases have the same effect on global warming, and a metric to compare the potency of greenhouse gases has been developed called global warming potential (GWP) which is a measure of heat trapping capacity of a GHG relative to 1 kg of CO_2 over a specified time horizon. The GWP potential depends on the wavelength and intensity of IR absorption as well as its atmospheric lifetime. CH_4 has a GWP of 86, over a 25-year time horizon.[27] Methane has recently become a topic in the fight against climate change as reducing methane emissions will result in a greater reduction in temperatures than carbon dioxide in less time.[50] The emissions of GHGs from wastewater treatment is an under reported metric and is crucial in understanding the contributions of wastewater treatment to global GHG budgets.[51]

1.9 Odour Mitigation Strategies Used to Treat Foul Air

There are a number of treatment processes that are employed to reduce or eliminate malodourous compounds. These can be broadly characterized as relying on physical, chemical, and/or biological processes. Physical odour control involves adsorption onto a high surface area media with strong affinity for VOCs. Chemical treatment generally employs some form of oxidation which transforms reduced sulfur compounds into less odourous compounds. Biological treatments rely on bacterial metabolism to transform compounds, typically oxidizing VOCs into less odourous compounds. The WWTPs described in this chapter and evaluated in chapter 3, employed some combination of these odour control technologies to minimize the output of toxic or odourous gases.

The decrease in VOC load from pre-treatment to post-treatment will be discussed in chapter 3, regarding the removal efficiency of specific VOCs, methanethiol, dimethyl sulfide and dimethyl disulfide. The metric for removal will be discussed in terms of removal described by Equation 4. This may be referred to as the percentage of decrease or the percentage which was removed by the treatment process.

$$\text{(4)} \qquad \%\ \text{Removal Efficiency} = (C_{in} - C_{out})/(C_{in})\ x\ 100$$

1.9.1 Wet scrubber towers

Wet scrubber towers are a popular and effective technology for odour remediation in wastewater treatment plants. They operate on the principle of absorption, where odourous gases are dissolved or entrapped in a liquid scrubbing solution. The gas stream passes through a scrubbing solution, transferring odour-causing compounds from the gas phase to the liquid phase. These towers are particularly effective at removing water-soluble and absorbable odour compounds like hydrogen sulfide and ammonia. They offer high removal efficiency, versatility, and low operating costs. They are sometimes combined with biological treatment using an inert substrate which hosts microbial communities capable of biologically oxidizing the trapped pollutants, sometimes referred to as biological trickling filters.[52] A biological trickling filter is run as a first step before the media scrubber at the primary treatment odour control at WWTP3 discussed in chapter 3. Proper maintenance and monitoring are also crucial to prevent fouling, scaling, or corrosion of scrubber components.[1,17,39] A general design of the wet scrubber tower is shown in Figure 1, where scrubbing solution is circulated counter-current to the air flow. The air or gas stream is passed through the inert media where it encounters the scrubbing solution, certain VOCs will be removed from the gas stream before the gas stream is exhausted to the atmosphere or passed onto further treatment methods. This form of odour remediation is employed at WWTP1 to treat the foul air coming from their auto thermophilic aerobic digestion (ATAD) wastewater treatment process and will be discussed later in the chapter and evaluated in chapter 3.

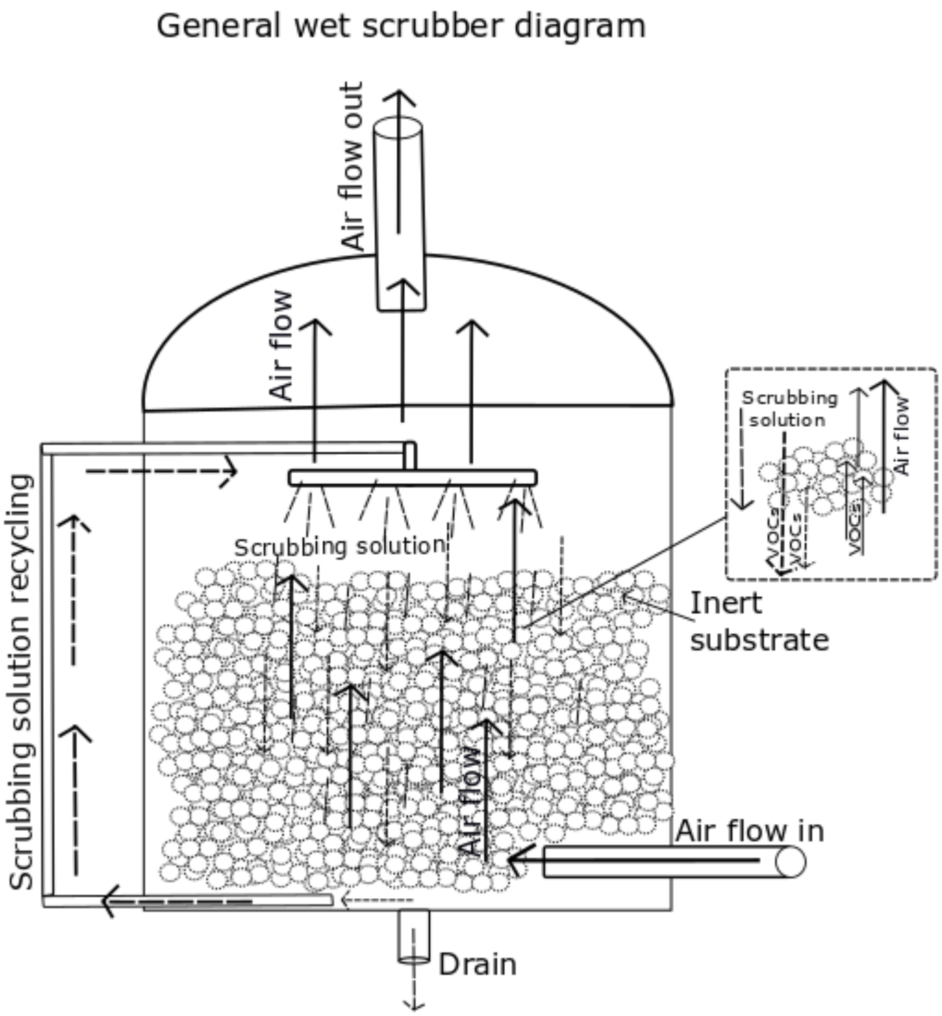

Figure 1: General diagram of a Wet-Scrubber

1.9.2 Chemical scrubbers

A common form of odour abatement technology used in wastewater treatment is the chemical scrubber, also referred to as chemical wet scrubber or chemical absorption scrubber. Chemical reactions with and absorption of odour-causing compounds in the gas stream are the basis for how these scrubber's work.[53] The chemical reagents used can react with particular odour compounds causing chemical transformation, which can deodourize and neutralize many nuisance VOCs. Depending on the target odourants, the scrubbing solution may differ; however, acidic odour compounds like hydrogen sulfide (H_2S) and organic acids are neutralized by alkaline substances such as sodium hydroxide ($NaOH$) or calcium hydroxide ($Ca(OH)_2$) (Equation 5).[1,39,44] The gases which are treated are injected into the system where they mix with a chemical reagent typically in an aqueous environment and can undergo these transformations, prior to the treated gas stream being exhausted from the system. This form of odour abatement is used after the wet-scrubber odour abatement technology at WWTP1 and provides an additional layer of treatment before the gases are emitted to the atmosphere (Chapter 3).

(5) Hydrogen sulfide reaction with sodium hydroxide:

$$H_2S + 2NaOH_{(aq)} \rightarrow Na_2S + 2H_2O$$

1.9.3 Advanced oxidation – UV – Ozone process

Advanced oxidation processes (AOPs) are an attractive method for odour abatement because of their high efficiency in breaking down compounds that cause odours. For example, UV and ozone-based AOPs have began to emerge as common solutions for odour abatement in many industrial settings, such as wastewater treatment. A simplified diagram of an AOP is shown below (Figure 2). The process of advanced oxidation using UV irradiation can work in two ways either through direct photolysis of the VOC or to produce oxygen derived oxidation agents such as ozone and hydroxyl radicals, by breaking down oxygen into atomic oxygen which rapidly converts to ozone in the presence of oxygen and in the presence of water will also produce hydroxyl radicals (equations 9-12).

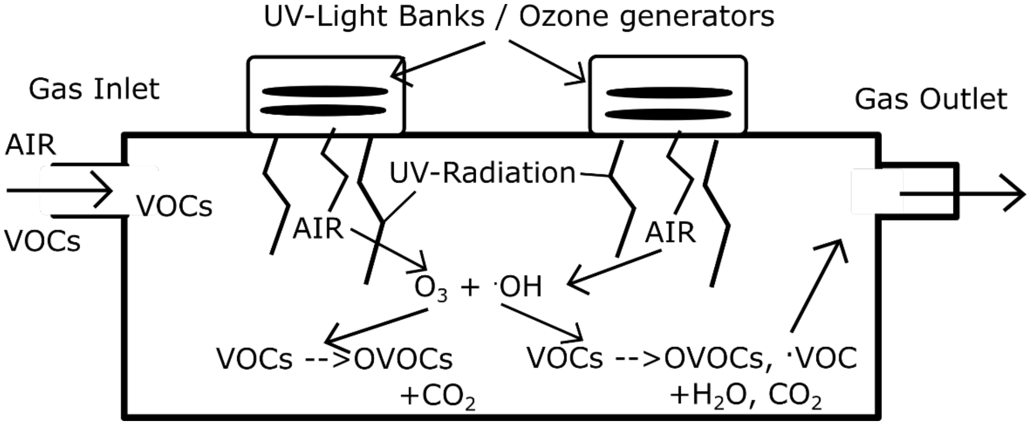

Figure 2: General diagram of AOPs using UV-radiation and Ozone

The ozone can directly react with VOCs in several pathways. For example, the reaction with an alkene will undergo ozonolysis, resulting in oxidative cleavage of the carbon-carbon bond. Although, ozone reactions in an indirect manner through hydroxyl radical production is a typical pathway for transforming VOCs in a gas stream as well (Equations 6-12). Wastewater gases contain a variety of organic and inorganic odourants that react easily with ozone (O_3) and hydroxyl radicals (•OH) (Equation 10-12). UV and ozone-based AOPs have several benefits for odour abatement in wastewater treatment plants, such as rapid reaction kinetics and high efficiency in breaking down a variety of odourants. Furthermore, AOPs can be easily adaptable to particular odour profiles and treatment goals, and it can be seamlessly integrated into currently operating odour control systems. To maximize odour removal effectiveness and save operating expenses, however, attention must be paid to ozone dosage, contact time, and reaction conditions.[1,17,19,20,39,53] An AOP utilizing UV-light banks and ozone production was piloted at WWTP1 to test its ability to eliminate odours from part of the wastewater treatment process and will be discussed in chapter 3.

(6) Oxygen photolysis (l < 240 nm): $O_2 + \text{hv} \rightarrow 2O^{\cdot}$

(7) Ozone formation reaction: $O^{\cdot} + O_2 \rightarrow O_3$

(8) Ozone photolysis (l < 320 nm): $O_3 + hv \rightarrow O_2 + O^{\cdot 1D}$

(9) Hydroxyl radical formation: $O^{\cdot 1D} + H_2O + hv \rightarrow 2OH^{\cdot}$

(10) Hydrogen abstraction: $OH^{\cdot} + VOC \rightarrow R^{\cdot} + H_2O$

(11) Oxygen addition: $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$

(12) Oxygen abstraction and subsequent oxidation reactions:

$$RO_2^{\cdot} \rightarrow RO^{\cdot} \rightarrow RCHO \rightarrow CO_2$$

1.9.4 Biofilters and Bioreactor systems – biological process

Biofilter systems pass gaseous odourants through a densely packed material, such as bark, peat, or compost, where microorganisms exist in a biofilm. The filter material absorbs pollutants, while the biofilm decomposes them, utilizing biological oxidation of the substances.[52] A typical form of sulfur oxidation is from chemoautotrophic bacteria like *thiobacillus thiooxidans* which metabolizes sulfides to sulfates (Equation 13).[27]

(13) General sulphide oxidation mechanism:

$$HS^{-}_{(aq)} + 2O_2 + H_2O \rightarrow SO_4^{-2}{}_{(aq)} + H_3O^{+}$$

During operation, the gas stream is passed through a chemically inert carrier material that is inhabited by microorganisms and a liquid medium of water or final effluent is circulated over the bed, either constantly or periodically.[1,39] A general design of a biofilter is given in Figure 3, the gas stream is piped into the substrate where it becomes in contact with microorganisms which can metabolize certain VOCs before the gas stream is released into the atmosphere. These systems are generally accompanied by a sprinkler system to keep the system hydrated and create a favorable environment for bacterial growth. These systems are generally low maintenance and inexpensive to operate but do require a large footprint. The structure of the filter bed does need to remain well packed and may need to be refreshed after a certain period. Another consideration when using biological treatment methods is the exposure of the filter bed to compounds which may inhibit or irradicate the biological growth causing poor performance. This type of abatement technology is used at WWTP1 to treat the air which comes from their solids de-wetting room, where solids collected during treatment are centrifuged to reduce water content, releasing odourous gases in the process (Chapter 3).

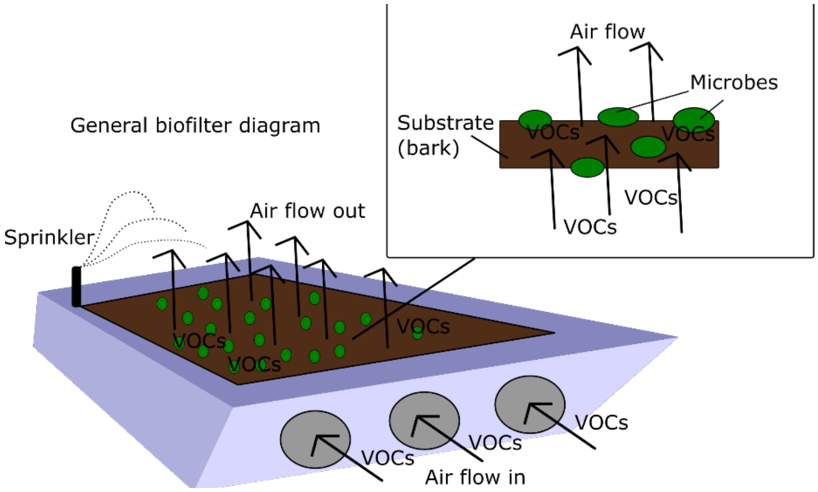

Figure 3: General diagram of a Biofilter bed

Bioreactor systems, on the other hand, involve the cultivation of specific microbial cultures in a controlled environment to degrade odour compounds in wastewater. Unlike biofilters, which rely on naturally occurring microbial communities, bioreactors are engineered systems designed to optimize microbial degradation processes. Bioreactors offer a controlled environment with precise conditions for microbial strain growth and activity. They can be used for microbial cultivation and targeting specific odour compounds from wastewater. Some bioreactor systems also use special substrates or packing materials that promote trapping or chemical conversion of odourous gases. Bioreactors can operate in continuous flow mode, allowing constant treatment of odourant-containing gas streams. They can achieve high odour removal efficiency and maintain the growth environment using sensors and monitoring systems. They also offer flexibility for process optimization, adapting to changing wastewater characteristics and odour profiles.[1,39,41,54,55] These systems require little maintenance or intervention after they are operating, with the exception of poisoning of the bacterial community by toxic compounds which may enter the system. A simple diagram of a bioreactor design is shown below (Figure 4). This form of odour abatement is utilized at WWTP2 to treat their gas streams coming from the wastewater treatment processes throughout the plant (Chapter 3).

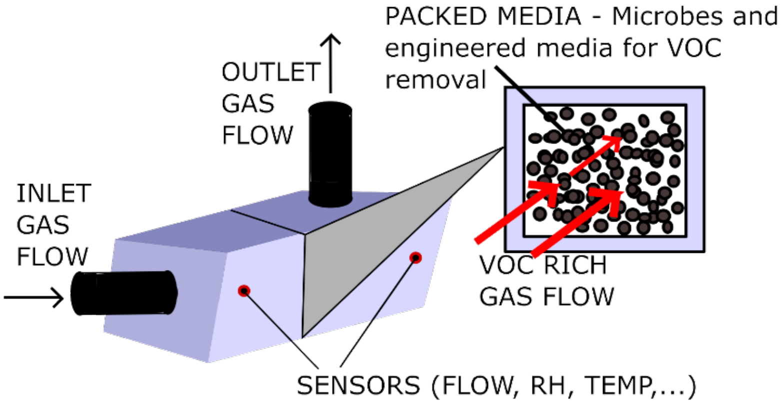

Figure 4: General diagram of a Bioreactor-biofilter

1.9.5 Media scrubbers - Activated carbon– physical / hybrid process

Activated carbon (AC), is a popular choice for odour abatement in wastewater treatment facilities due to its exceptional adsorption properties. The activated term refers to the process of heating the carbon causing fissures and creating more micropores and enhancing the total surface area of the carbon. Furthermore, the oxidation of the activated carbon will increase the carbon-oxygen bonds configuring the structure to provide a distribution of basic and acidic groups on the AC to provide a well-rounded ability to trap VOCs.[56] The main process involved in retaining substances is due to the microporous nature and will trap gases onto the surface where they can be retained in a semi-liquid state, condensing onto the substrate and held close to the carbon by van der Waals forces.[57] Conventional activated carbon adsorption uses porous carbon materials to capture and retain odour-causing compounds in wastewater gases, however, AC can also be functionalized to enhance the surface properties of AC to improve its adsorption capacity and/or accelerate catalytic decomposition of specific odour compounds. This can be achieved through chemical modification or physical blending with other materials.[1,39] These systems intercept wastewater gas emissions and pass them through beds of activated carbon or modified activated carbon. The treated gas is then discharged into the atmosphere or subjected to further treatment processes. A general carbon scrubber workflow is shown below, where the gas stream to be treated enters the carbon bed and travels through the media where it can be adsorbed to the carbon and thus removed from the gas stream before the gas exits the scrubber, leading to minimized VOC output, post-treatment (Figure 5). Additionally, considerations for using activated carbon for scrubbing VOCs is the lifetime of the sorbent, as it becomes ineffective and loses its trapping efficiency over time and will need to be replenished. Periodic sampling of the sorbent can be done to assess the nature of the sorbent quality, also monitoring the VOCs coming out of the scrubber's gas stream can be a useful tool to track the effectiveness of the sorbent. Monitoring the VOCs in the scrubbed air can be used to check for breakthrough and incompatibility of certain VOCs to be trapped as well. This form of odour abatement is implemented at WWTP2 at two sites throughout the wastewater treatment process and is the main odour abatement method used at WWTP3 (Chapter 3). This form of scrubber is referred to as a media scrubber by industry.

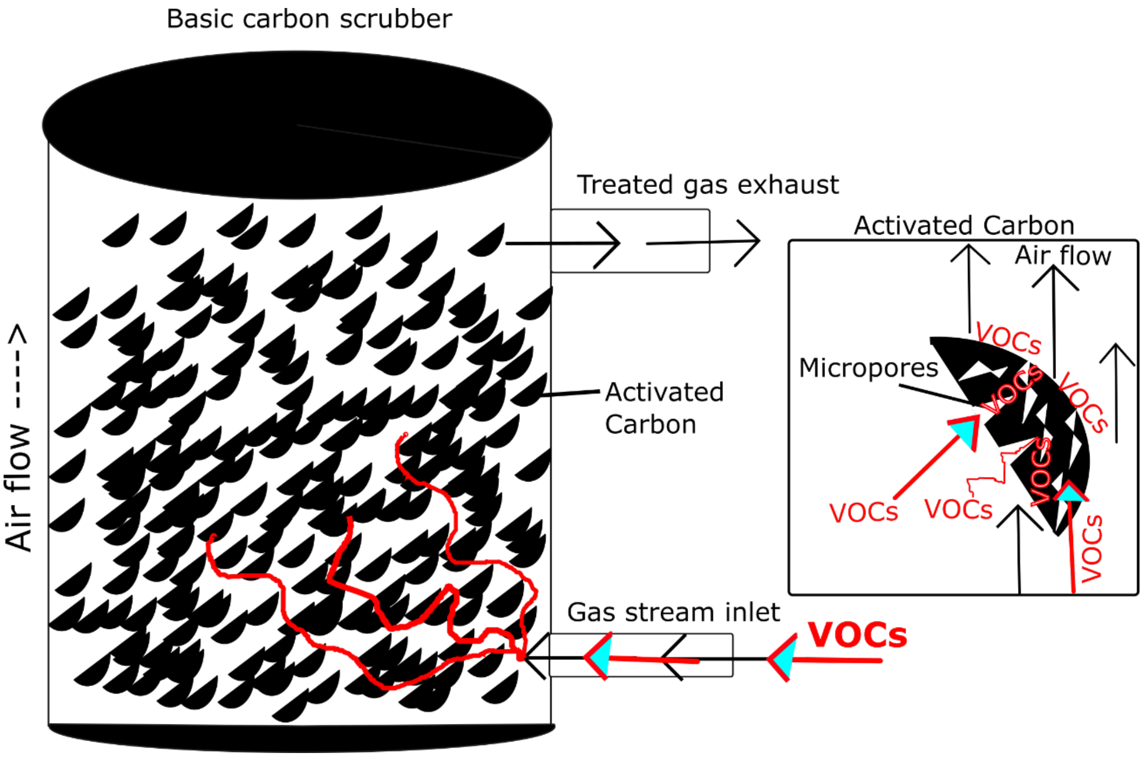

Figure 5: General representation of an activated carbon scrubber system

1.10 Techniques for measuring gases at wastewater treatment plants.

Gas-phase analytical techniques for determining the VOCs in the foul air at wastewater treatment facilities are usually done by offline GC-MS measurements.[20,21,40,44] These types of measurements require special techniques to evaluate gases off-site, which introduces challenges and misinterpretations of chemical speciation, as some compounds are reactive and will undergo chemical transformation before they can be measured by this technique.[1,2,18,19,21,40,44] For example, the use of specialized silico-lined containers for collection of reactive organosulfur compounds are needed to lower the risk of chemical transformation from oxidation during transportation.[35] In some cases, reduced sulfur compounds are all oxidized before measurement and a non-direct measurement is taken and reported for the total concentration of these gases. Gas-chromatography-Mass spectrometry has its advantages as it allows for separation of gases before measurement by the MS, which can aid in deconvoluting complex mixtures of gases, but faces the aforementioned challenges of transporting the gases and having a time-delay between collection and detection which can impact the measurement.[19,21,40] At most wastewater treatment facilities, chemical/colorimetric methods of detection are used, such as draeger tubes™, or standalone detectors for gases such as hydrogen sulfide. These methods give information on one or a mixture of gases, but do not allow for exclusive detection of multiple gases at one time. Also, annual or semi-annual measurements may be taken with more sophisticated techniques such as GC-MS, but these are not done on a frequent basis, do not capture temporal or spatial trends of VOCs, and can be costly.

1.11 Real-time monitoring

VOCs can be monitored in real time using a range of techniques, from specialized mobile laboratories to inexpensive stationary sensors.[16,22,24,58,59]

Figure 6: Picture of Smell Van from UBC engineering department

Static real-time monitoring stations, which are frequently used by government institutions to report AQHI values to the public, are one way to accomplish this. They can produce data at a minute to hourly scale. To provide reports on the temporal trends of atmospheric gases in particular regions, real-time stationary monitoring is a useful first step in compiling a greater variety of data.[11,29] Many studies have utilized Proton-transfer-reaction Mass spectrometry to better measure in real time to monitor VOCs from a range of hosts, such as emissions of biological VOCs from Fungi.[60] Cheap sensors have recently entered the field and are able to provide medium quality/order of magnitude measurements in more locations, providing a more detailed understanding of the spatial changes in air quality than is possible with a single permanent monitoring station.[15,58,59] A mobile lab in a van or an airplane, for example, might make measurements while traveling, and in recent years, mobile laboratories have become more common (Figure 6).[14,16,22,23] This has made it possible to conduct measurements over ground or in remote areas. Though these techniques are often more costly and less used than fixed monitoring stations, innovative real-time monitoring has been carried out more frequently by vehicles (buses, cruise ships), pedestrians, satellites, and cyclists due to the increased availability of low-cost sensors.[14–16,22,24,61] Taking measurements while moving is not an easy task, and it might be particularly difficult depending on the equipment being used. While these methods provide valuable information about the relationship between the spatiotemporal distributions of gases and their many unknown sources, they also provide a clearer understanding of what is happening between the stationary monitoring sites and what is happening on the ground.

1.12 Recent mobile mass spectrometry studies

Mobile mass spectrometry is a growing field of interest as it allows for in-situ measurement for a range of VOCs in the environment. Taking the laboratory to the field gives researchers a better understanding of the complex nature of environmental fate and distribution. Also, mass spectrometry is a very sensitive and selective technique which is versatile and advancing in ways of sample introduction, ionization and deployment techniques. Some recent work, within the last 6 years, using mobile mass spectrometry includes work published in 2018 by Rishabh *et al*, which used mobile deployment of an aerosol-mass spectrometer to study the submicron particulate in a city over a 20-day period, looking at emissions of organic aerosols, defining their spatiotemporal distributions in the city.[62] Another study using a mobile laboratory, by Wagner *et al*, implemented a selected ion flow tube mass spectrometer (SIFT-MS) to characterize VOCs in the city of York, in the UK during 2020.[63] This study was able to produce maps of vehicular emissions in the city and create a profile of spatiotemporal distributions of VOCs utilizing mobile deployments, taking on-road measurements.[63] A review of mobile applications of time-of-flight mass spectrometers published in 2022 by Hutterli *et al*, provides a great range of applications of mobile mass spectrometry, for fence line monitoring, indoor air quality assessment, and even airborne deployments.[64] Also published in 2020 was work done by Richards *et al*. described in a PhD dissertation, using mobile PTR-TOF-MS data collected with the mobile mass spectrometry lab for chemometric analysis to discriminate and apportion VOCs measured from a moving vehicle.[65] A multi-year study published in 2018 by Healy *et al*, utilized mobile APCI-MS and LPCI-MS to measure emissions from a chemical waste disposal facility, producing a vast amount of data regarding spatial and temporal variations of VOCs taken in the field.[66] A recent study published in 2021 by Popp *et al*, used mobile mass spectrometry deployments to study hydrology and biogeochemical processes in groundwater, providing new insights for analyzing dissolved gases in a real world setting.[67] The recent advancements in mobile deployments using mass spectrometry has opened up a new paradigm in sampling, allowing in-situ examinations of processes taking place in the environment.

1.13 Study rationale

Using real-time monitoring with a mobile mass spectrometry lab (MMSL) on-site and in the community helps with complementary information to accompany already established gas monitoring regime's at WWTPs, which include mostly aqueous measurements of VOCs, but with some measurement of gaseous VOCs such as Hydrogen sulfide. Hydrogen sulfide is produced in similar conditions to the malodourous organosulfur compounds such as methanethiol, dimethyl sulfide (DMS) and dimethyl disulfide (DMDS). The organosulfur compounds are generally less characterized throughout WWTPs as regulatory limits have been set for the aqueous portion of treatment in-part with regulation set on toxic hydrogen sulfide gas. Although, the organosulfur compounds cause nuisance odour complaints and can impact the quality of life in the neighbouring communities and furthermore add to air pollution. The accompanying measurements from the MMSL also enable us take inventories on the less characterized VOCs and GHGs, watch dynamic changes with treatment methods, including temporal and seasonal changes. Typically, mass balance equations have been used in wastewater facilities to estimate VOC concentrations in the air using dissolved VOC concentrations, which may not give accurate results.[20] With long term monitoring over a year cycle, we can discern diurnal and seasonal traits as well as the spatiotemporal distribution of the VOCs from the WWTPs in the local communities. The use of GIS software in combination with the rich data set from the MMSL has allowed for geospatial analysis of VOC emissions in the study areas. This work provides better data for operators, managers and policy makers that deal with wastewater and the impacts on the environment and community.

1.14 Study sites background information.

Three wastewater treatment plants were evaluated in this study over the period 2021-2024. The on-site foul air ductwork was measured for over a year at each site, with a thorough investigation surrounding their odour abatement technologies. The three sites varied in date of commissioning, land area use, capacities of water treated, and technologies used for wastewater treatment and odour control. One similar trait is all wastewater plants in the study were located close to the ocean (<3km) and located on Vancouver Island.

The French Creek Pollution Control Center (FCPCC) located in Parksville, B.C. will be referred to as WWTP1. It was commissioned in 1977, upgraded in 1997 and currently undergoing further upgrades (2024/25). It serves a population of approximately 29,000 people, is built on 9 acres of land and treats about 3.8 billion liters of water a year. The odour control operations at WWTP1 include wet scrubber towers, a chemical scrubber and a basic biofilter to control odour outputs to the local community and environment. During the sampling campaign a new odour treatment pilot study was conducted using UV advanced oxidation in place of the biofilter. WWTP1 is currently in the process of updating the plants technologies, and the data collected during this sampling campaign was used in part to inform planning strategies. Historically the WWTP has generated malodours which have been detected off-site and been reported to the management and operator staff which has led to further investigation of VOCs on and off-site at this WWTP, which was initiated in 2019. This preliminary work was completed in 2021 and described in Davidsons's Thesis.[68] The work described here was conducted after some modifications were made at this facility and includes a systematic evaluation of new and existing odour control systems, and the use of new sorbent tube sampling followed by lab-based TD-GC-MS analysis to assist with molecular identification. The sampling locations and study site are described further in Chapter 3.

The Greater Nanaimo Pollution Control Center (GNPCC) is located on Hammond Bay Rd in Nanaimo, B.C., will be referred to as WWTP2. It was commissioned in 1970 and upgraded in 2009 and again in 2020 to include advanced secondary treatment and foul air capture. Is situated on 15 acres of land, serves a population of over 104,000 people and treats approximately 11 billion liters of water a year. This site captures and uses the biogas produced on-site to operate the wastewater plant, flares off excess biogas and can supply the grid with excess power produced via biogas burning. The odour treatment onsite consists of module and modified activated carbon scrubbers and a main odour treatment system consisting of two large biofiltration/bioreactor units to reduce odour release to the nearby community. An overview of the study site and sampling locations are found in Chapter 3.

The wastewater treatment plant at McLoughlin point (Esquimalt, B.C.) will be referred to as WWTP3 and was recently commissioned in 2021 on three acres of land. It serves a population of over 350,000 people, treating 36 billion liters of water a year. This site has employed several advanced techniques to treat the wastewater and was engineered to collect and treat foul air to reduce odour emissions throughout the facility. The odour control technology uses activated carbon scrubber towers to remove odourous compounds through a physical sorption process. Also, a modified activated carbon scrubber at the secondary water treatment odour control. The sampling locations and an overview of the site are further discussed in Chapter 3. On such a small footprint the plant operates on a vertical design rather than the more land intensive horizontal design used at WWTPs 1 and 2.

1.15 Thesis organization

Chapter 2 discusses the experimental methodology; including the instrumentation and calibrations used for the work done in this thesis. Chapter 3 discusses the on-site odour abatement technologies at WWTPs 1-3, in regard to their efficacy for removal of reduced sulfur compounds such as methanethiol, dimethyl sulfide, dimethyl disulfide, and other VOCs. The concentrations of VOCs and their variability from emission stacks will be discussed and evaluated and a look at a potent GHG methane will also be considered. The use of TD-GC-MS to complement PTR-TOF-MS measurements will also be discussed and further described in Appendix D. Some small bench scale experiments are discussed in the chapter and presented in Appendix C. Furthermore, a comparison of physical, chemical, and biological treatment methods employed at the three WWTPs is presented.

Chapter 4 discusses the spatial distribution of VOCs generated from wastewater treatment and other potential sources. Community maps including the ground level VOC concentrations recorded will be presented and discussed. Additional single day maps are presented in Appendix B. Furthermore, the potential association of WWTP gases with odour complaints in local communities will be addressed.

Chapter 5 will include a summary of the findings from on-site sampling discussed in chapter 3. A summary of the work discussed in chapter 4 from the on-road measurements will be presented. This chapter includes suggestions for future work in this field of research.

Chapter 2: Experimental methodology

2.1 Mobile Mass spectrometry laboratory

A state-of-the-art mobile mass spectrometry laboratory (MMSL) was implemented in the work from this thesis. It was used to examine three wastewater treatment facilities, measuring gases on-site in real-time during treatment and in the foul air systems that gather and lower the emission of foul air. In addition, measurements were taken while driving to assess the spread of volatile organic compounds (VOCs) emitted by the treatment facilities and to assess other sources in the neighboring area. The MMSL contains rack mounted government equivalent sensors for GHGs (CH_4, CO_2, H_2O), Nitrous oxides (NO_x) and Ozone (O_3), as well as a ruggedized Proton-transfer-time-of-flight mass spectrometer which can analyze VOCs directly from the air if their proton affinity is higher than that of water.[24] All measurements are concurrently recorded with a high precision GPS and vehicle mounted weather station. The purpose and focus of these analyses are to enhance our understanding of the sources and chemical transformations of these volatile organic compounds (VOCs) within the local community and on-site at the WWTPs.

Alterations were made to the sampling inlet in 2022, when a new inlet and manifold were installed, thus creating a shared pathway for ambient gases to travel to the on-board sensors. The installation of the new stainless-steel inlet protruded out from the roof of the MMSL and was coupled in the interior of the van to a glass manifold where all the gas analyzers were plumbed in to sample the outside ambient atmosphere. The addition was characterized for the dead-time and any concentration loss during transit through the new materials, as this replaced individual PFA lines which were plumbed through the van and fed each sensor. Furthermore, the design of the new manifold was taken into consideration to improve the flow pathway and volume of gas through the inlet to adequately sample while moving in the vehicle and limit any losses or bias in measurements.

The Mobile Mass Spectrometry Lab (MMSL) is intended to analyze air contaminants at the regional or community scale, with the ability to sample at point sources or while moving (Figure 7). With support from a Canadian Foundation for Innovation grant (CFI Grant #32238), development got underway in 2016 and was first built by Ph.D. candidate Larissa Richards and post-doctoral fellow Nick Davey. Among the group's initial initiatives were monitoring volatile organic compounds (VOCs)

Figure 7: Photo of Mobile Mass Spec Lab, taken on-site at WWTP3.

at coffee roasteries and breweries [69], also analyzing BVOCs from blueberry bushes in-situ at farmland in Abbotsford. The MMSL was utilized for MSc student Jon Davidson's thesis research starting in 2018, where he made improvements in method creation and data processing methodologies.[68] There is a thorough breakdown of the instrumentation and mobile lab setup found in Davidson J's thesis while a briefer description is given in this thesis.[68] The MMSL wasn't fully research-ready for on-road data collecting until these first major mobile deployments in 2018. I served as Davidson J's undergraduate research assistant, and our contributions to the technique centered on determining the best course of action for background collecting and calibrations, as well as managing the MMSL, while Davidson made major headway for most of the data processing tools utilized in this thesis. This thesis expands on and includes one of the same regions as his thesis work, which was among the first deployments at a wastewater treatment plant on Vancouver Island.[68] The layout and methodology for sampling using the MMSL is further discussed in Chapter 2.

PTR-TOF-MS uses a flow-drift tube to influence the gaseous hydronium ions' (H_3O^+) chemical ionization of gas-phase analytes. The electrons are ejected from a hollow cathode discharge and collide with water vapours to produce high-purity H_3O^+ by a process akin to chemical ionization. After that, H_3O^+ is injected into a drift tube and combined with sample air. Analytes' proton affinity (PA) with respect to water (691 kJ mol^{-1}) determines the process of proton-transfer (Equation 14). This technique is useful for measuring many VOCs in the atmosphere as it allows for real-time measurements, with duty cycles as low as 1 second, this is achievable since no chromatography is done.

The general proton-transfer reaction follows:

$$H_3O^+ + R \rightarrow RH^+ + H_2O \tag{14}$$

Analytes with a PA higher than water can become protonated. The fact that the two main atmospheric gases N_2 and O_2 do not ionize is one benefit of this technique. Also, when analyzing data most ions are measured as their $[M+H]^+$ form which is convenient as it is their molar mass plus 1 mass unit (M+1) given from the proton addition.

The PTR-ToF-MS uses a time-of-flight as the mass spectrometer. The principle of time-of-flight MS analysis involves a packet of ionized air entering into the high vacuum (10^{-7} mbar) of the time-of-flight region. The ion packet is pulsed with an equal amount of kinetic energy given to all the ions and they are propelled in the high vacuum region where they distribute by differing velocities in the flight path and hit the detector in order of lowest mass to highest mass. This technique cannot distinguish between structural isomers as seen in the sample mass spectrum in Figure 8, where dimethyl sulfide and ethanethiol would show up at the same mass-to-charge. The time-of-flight mass analyzer is used because of its applicability for fast duty cycles giving full scan mass spectra and is much faster than a quadruple mass analyzer. In addition, it does not lose sensitivity in a full scan operation in contrast to quadruple mass analyzers.

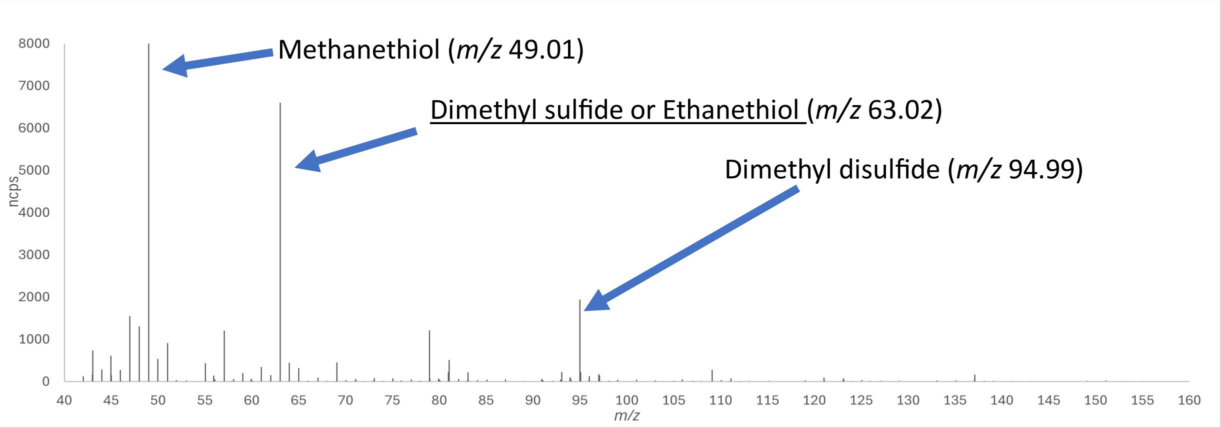

Figure 8: Sample mass spectrum from the PTR-ToF-MS taken at WWTP1, showing elevated levels of three reduced sulfur compounds, measurements are taken without chromatography and cannot distinguish between structural isomers. An example of isomers are underlined on the spectrum.

The PTR-ToF-MS used hydronium ions (H_3O^+) as reagent ions and a sample integration time of 1 second. Every *m/z* from 21-330 was observed. Mass calibration was achieved using the proprietary software (ioniTOF) using the detection time of three known peaks, *m/z* 21.02 ($H_3{}^{18}O^+$), 29.99 (NO^+), and 59.04 ($C_3H_7OH^+$). Mass calibration happened every 15 seconds. Fast sampling frequencies allowed for the best geographical and temporal resolution. Throughout all of sampling, the instrument resolution was approximately 1,500 ± 200 *m/z*/Δ*m/z* for full width at half mass of *m/z* 59.04. Drift tube pressure and voltage were constant at 2.2 mbar and 600 V, respectively. The reduced electric field intensity (E/N) employed during all of sampling was 130 ± 1 Td. The ToF pressure throughout the trip varied between 6 (± 1.8) × 10^{-7} mbar. The PTR-ToF-MS sample intake flowrate was sometimes changed, although it was typically fixed at 500 mL min^{-1}. Three gas analyzers for Greenhouse gases (Los Gatos, FGGA-24r), NOx (Thermo, 42i), and O_3 (Thermo, 49i) are installed in the MMSL to accompany the mass spectral data collected. A photo of the instrumentation is shown in Figure 9. Also, in Figure 9 the outside of the MMSL including the Stainless-steel sample inlet mounted off the top of the vehicle is shown. The on-site sampling in the ductwork discussed in chapter 3 was done by directly attaching our instruments inlet to PFA tubing which was brought to the sampling location where it would have the sample pulled to the MMSL, generally assisted by an external pump which was teed off on the inlet side of the pump and pulled into the instruments by their respective on-board pumps. This configuration allowed for fast flows through the sample line to decrease dead times in the tubing and to overcome the fan system in the ductwork.

The experimental design for the sampling of ambient atmospheric gases discussed in chapter 4, was similar to the on-site ductwork sampling using the same technology and settings previously described above. The only modification done during the drive sampling was that all the instruments were plumbed to the vehicle's inlet manifold which is mounted off the front top of the vehicle to pull in the air sample while moving and evenly distribute the air sample to each of the instruments. While driving, slow speeds <50 Km/h were typical and where onsite and near point sources, drive speeds were reduced as much as possible in the range of 15km/h. At some locations we had parked and turned the engine off to collect more sample points at discrete locations, including onsite at the WWTP, near the pumpstations, and at points of interest which were given to us by the wastewater plant staff to enhance the capture of possible nuisance odours. The drive routes remained consistent, although some days construction and road work had influenced minor changes in the drive routes. All samples were accompanied by precise GPS measurements which allowed for mapping of the gas samples over space. Measurements of VOCs were done by mass spectrometry except methane, which was measured by the GHG analyzer.

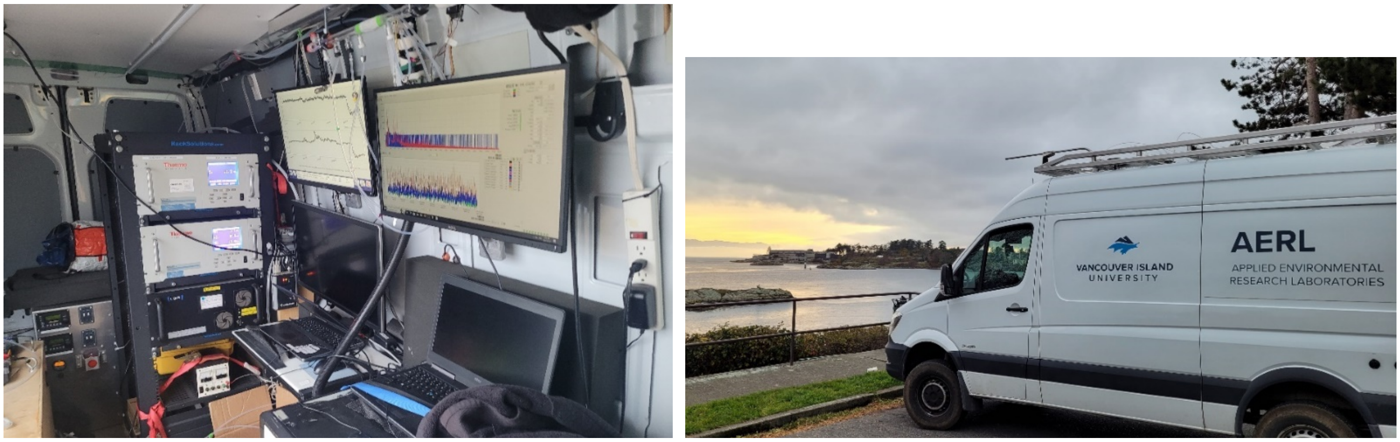

Figure 9: (Left) Photo of inside Mobile Mass Spec Lab, showing instrumentation. (Right) Photo of Mobile Mass Spec Lab taken in Esquimalt during community drive sampling.

2.3 Instrument Calibrations

The analytes measured by PTR-TOF-MS were calibrated directly utilizing a DynaCal 320 calibration gas generator from VICI Metronics (Washington, USA), together with VOC-containing permeation tubes from KIN-TEK Analytical (Texas, USA). The concentration range was limited by the emission rate of the permeation tube and the flow rate of dilution air from the DynaCal. Calibrations were conducted using a 1-second integration time. Calibrations were primarily conducted by connecting the DynaCal to the PTR-TOF-MS heated PEEK tubing, through a 1uM SS filter. However, following modifications to the sampling inlet, calibration was extended to the whole sample inlet to detect any possible wall losses resulting from the new configuration. After sampling the new inlet configuration, there was negligible wall loss detected, and a shorter transit time from inlet to sensors from 15 seconds to 5 seconds was achieved.

Routine calibrations were done throughout the sampling campaigns to track any loss of sensitivity throughout the campaign. During the sampling campaign if sensitivity changed by more than 20% an adjustment in the calibration output was made.

Typical calibration curves are shown in Figure 10, illustrating the linearity and sensitivity of signal to concentration for Methanethiol, Dimethyl sulfide (DMS), Dimethyl disulfide and Ethyl benzene. These calibrations were obtained June of 2023. Limits of detection were estimated using Equation 15.[70] Raw data is shown from a DMS calibration made in duplicate to illustrate calibration data collection and variability (Figure 11).

Further investigation of calibrations for the PTR-TOF-MS were conducted to address possible influence from humidity on sensitivity for the three compounds. Methanethiol has a proton affinity <100 kj/mol higher than that of water (Appendix C). The proton affinity is critical in the mechanism of ionization using the PTR-TOF-MS. This experimentation found that methanethiol sensitivity was significantly reduced up to by 40% under very high humidity conditions (>99% RH) typically only encountered during sampling of concentrated gas streams, data is plotted in Appendix C. During ductwork sampling, H_2O concentrations were measured by the on-board GHG analyzer at the inlet/outlet of the treatment process and were comparable. This suggests that while absolute concentrations could be affected, the treatment efficiency could still be monitored with some confidence.

Annual calibrations were done at CD NOVA (Burnaby, BC) and Ministry of Environment (Nanaimo, BC) for the 42i NOx analyzer and 49i O_3 analyzer. This accompanied regular assessment of zero concentrations and monitoring the performance of the units with monthly span checks.

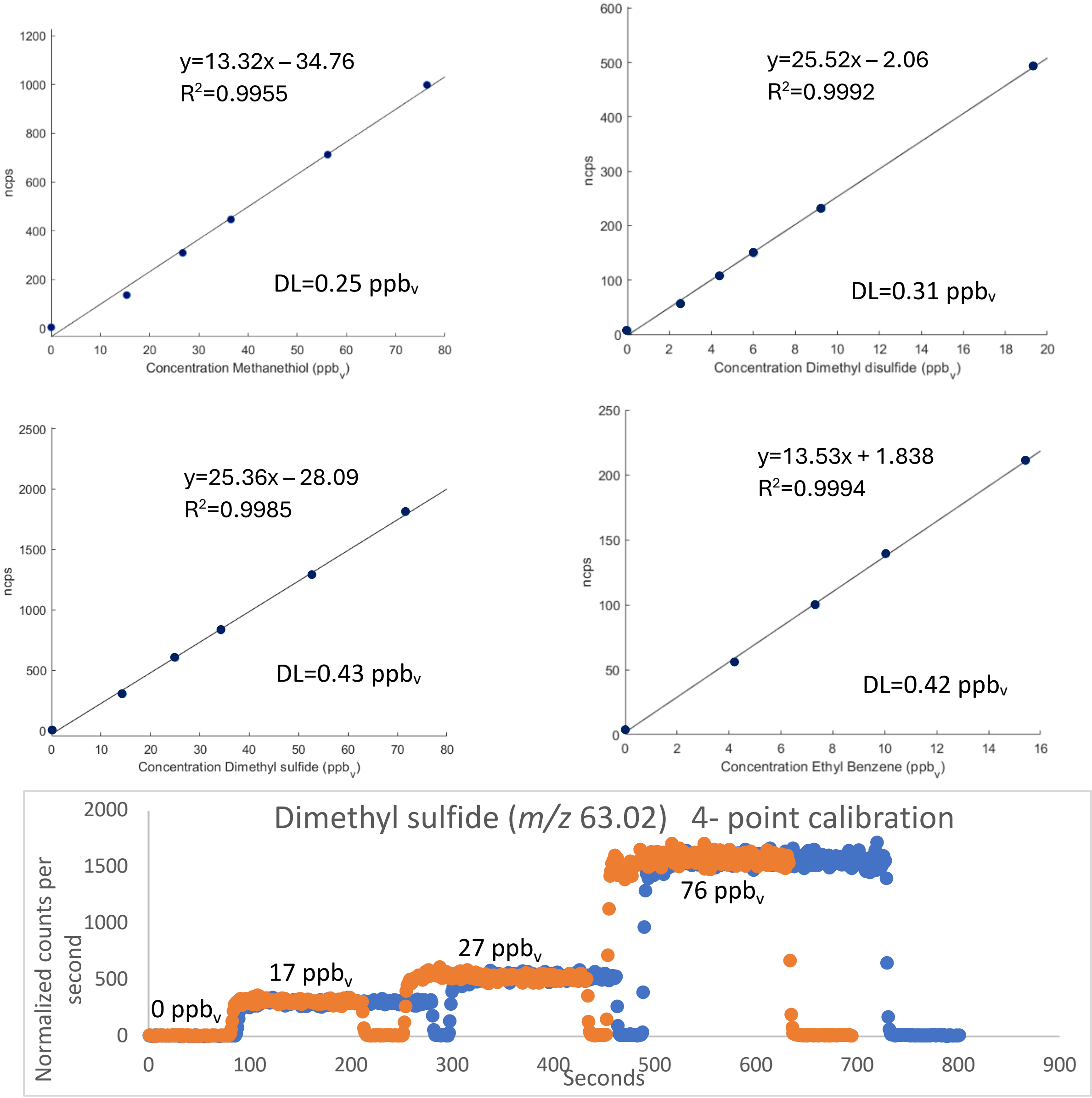

Figure 10: (Top) Calibration slopes from PTR-TOF-MS calibrations using the DynaCal, of Methanethiol, dimethyl sulfide, dimethyl disulfide and ethylbenzene. Done during 2023 at the start of the sampling campaigns. DLs were determined by Eq 5. 1-sec integration time. (Bottom) Timeseries of 4-point calibration of Dimethyl sulfide (m/z 63.02), done in duplicate. Normalized signal counts on y-axis and concentrations are labelled at peaks. Orange and Blue traces are individual runs done separately on the same day. 1 second integration time.

(15) $$DL_{a,ppb} = 3\ x\ (\frac{s_{a,zero}}{Slope_a})$$

2.4 Thermal desorption-gas chromatography-mass spectrometry

Sorbent tubes come with a variety of sorbents, designed to trap classes of VOCs from a gas stream, which can be introduced in a dynamic or static manner (Figure 11). This allows collection of gas samples in the field, which can be taken back to the lab for analysis. Tailored Sorbent tubes are available to trap specific types of VOCs which may be polar, non-polar or oxygen sensitive/readily oxidizable. Each tube has a capacity and a preference for VOC trapping efficiency, so selection can be a major consideration in sample design and application. In this study we used Sulfacarb sorbent tubes (Markes International), designed to suppress oxidation of reduced sulfur compounds, and were chosen because we were interested in this class of compounds (Figure 11). In addition, we also used Tenex TA (Markes International) sorbent tubes to collect a wider variety of VOCs.

Figure 11: (Left) Photo of Sorbent tubes in package from Markes International. (Mid) Photo of sorbent tube deployed at WWTP collecting ambient air around primary treatment. (Right) Photo of sorbent tube deployed into ductwork.

Sorbent tubes were collected on-site and, in the community, to supplement the direct measurements from the MMSL (Figure 11 and 12). The gas samples were collected using small handheld pumps to flow gas through the tubes at a known rate and for a specified time (Pocket pump Touch). After collection, tubes were sealed, kept cold in a cooler and were bagged and labelled and analyzed in a timely manner by TD-GC-MS. The TD-GC-MS analysis gave the ability to separate our gas samples using chromatography which was not done during direct measurement using the PTR-TOF-MS on board the MMSL as seen in Figure 8. These measurements were used for confirmation of gas speciation and as supplemental information to our work done with the MMSL.

Figure 12: Photo of deployment at fence line of WWTP3 using sorbent tubes for collection of air samples, seen mounted on tripod.

A Thermal desorption unit (TD100-xr, Markes International) was connected to a GC-MS (Polaris Q, ThermoFinnigan, TraceGC Ultra 2000ThermoQuest) with an ion-trap, which is more sensitive compared to a single quadrupole instrument. The thermal desorption unit allowed for sample introduction to the GC-MS from the sorbent tubes (Figure 13). The programs used were tailored to evaluate reduced sulfur compounds by separating common isomers which were unresolvable with the PTR-TOF-MS, and to validate our measurements taken on-site (Appendix C).

Figure 13: (Left) Photo of TD-GC-MS setup, TD100xr coupled to TraceGC and PolarisQ. (Right) Thermal desorption unit, TD100xr, loaded with sorbent tubes.

2.5 Data analysis

Data collected from instruments onboard the MMSL including the Greenhouse gas (Los Gatos, FGGA-24r), NO_x (Thermo, 42i), and O_3 (Thermo, 49i) analyzers were interfaced in real-time to in-house developed software (Underway) for data compilation and visualization. This software also integrates data from the GPS and weather station on-board the MMSL, into a common file and with a common timestamp. This data is saved to a .csv file and further used in our in-house developed data analysis code, written in MATLAB®. The PTR-ToF-MS (Ionicon, PTR1000) data is collected with vendor supplied software (IoniTOF) and saved to the hard drive, then analyzed in vendor software, PTR-MS Viewer 3 (IONICON Analytik GmbH, Austria). The vendor software (PTR-MS Viewer 3) includes post-processing, additional mass calibrations, and a peak list tool to export specific peaks of choice. Furthermore, data is saved to .csv files for input into the data analysis script. Once data is ready for the data analysis script, it will take the data files from all on-board instruments, mass spectrometer, standalone gas analyzers, GPS, weather station and fuses them into one spreadsheet where date and times are synchronized from each unit and calibrations are applied to our mass spectrometry data where applicable. The data analysis script further writes .SHP files for importing into GIS software for map creation when analyzing data collected during a drive. The data is then ready for figure creation, which are created in MATLAB®, data is extracted from MATLAB® and data tables and mass spectra are created using Excel (Microsoft®). The data generated from the sorbent tube deployments, analyzed by TD-GC-MS, were processed using the Xcalibur® software suite (Thermo Scientific™, San Jose, USA).

Chapter 3: On-site VOC Measurements at WWTPs

All fieldwork described in this chapter was led by Trevor Michalchuk, including instrument calibrations, data workup, visualization, and interpretation. Assistance was provided by Lily Eggert (Undergraduate) and Erik Krogh (Supervisor). Additional site logistics was provided by plant operators and staff.

3.1 Introduction and Background

The control of and the release of VOCs and malodourous compounds is an important feature of WWTP design and operations. This is especially true when these facilities are located near residential communities where the emissions can impact the quality of life of residents. As such, it is important to measure VOCs in the ambient air at the WWTP sites (fenceline monitoring) as well as inside the foul air collection/treatment systems to address the following questions with a particular interest on the malodourous reduced sulfur compounds.

1) Which VOCs are present and at what concentrations?
2) How does the composition and concentration of target VOCs change in response to different engineered treatment systems?

To answer these questions and provide actionable information to on-site operators, the Mobile Mass Spectrometry Laboratory (MMSL) was deployed at three wastewater treatment plants on Vancouver Island to measure the volatile organic compounds produced during wastewater treatment processes, including before and after various odour control technologies. This was accomplished with the methodology discussed in Chapter 2. There are a number of VOCs associated with wastewater treatment which we can measure with the PTR-ToF-MS shown in Table 2. Broadly, these include three VOC classes including hydrocarbons (e.g., isoprene, benzene, toluene, ethylbenzene/xylenes, and monoterpenes), oxygenated hydrocarbons (e.g., acetaldehyde, acetone, acetic acid), and reduced sulfur compounds (e.g., methanethiol, dimethyl sulfide, and dimethyl disulfide). Each site contained several technologies for odour control management, based on physical, chemical and/or biological processes, such as activated carbon scrubbing towers, wet-scrubbers, bioreactors, and advanced oxidation processes. Each of these treatment processes aims to trap or transform gaseous compounds to less hazardous or odourous forms, through adsorption, absorption and chemical or biological transformation.

In this section an overview of the investigation of odour controls is undertaken at three WWTPs, addressing the effectiveness for removal of malodourous compounds, focused on methanethiol (*m/z* 49.01), dimethyl sulfide (*m/z* 63.02) and dimethyl disulfide (*m/z* 94.99). A more comprehensive evaluation of this data is available in Appendix D.

Assessment of individual duct sampling days is found in Appendix A. Also, during some on-site visits evaluation of treatment processes was done by sampling headspace VOCs during treatment cycles, which uncovered when, where and which processes were producing odourous gases in the treatment system (Appendix A). In addition to real-time measurements with the MMSL, time integrated samples were collected on sorbent tubes for subsequent lab-based analysis by thermal-desorption gas chromatography mass spectrometry (TD-GC-MS) (Appendix D). Further characterization of select chemical transformations were carried out in a laboratory setting under controlled conditions to characterize factors that influence the reaction (Appendix C). This section will be discussed in terms of each wastewater treatment plant, the corresponding odour treatment methods and their effectiveness for removal of methanethiol, dimethyl sulfide and dimethyl disulfide. The data will be displayed in the order following the naming conventions WWTP1, WWTP2 and WWTP3.

Table 2: Typical WWTP VOCs monitored by PTR-ToF-MS, including formulae, mass-to-charge and potential interferents.

m/z	Potential Formula	Potential Compound	Potential Interferents
41.039	$(C_3H_4)H^+$	Propyne	Propandiene
45.025	$(C_2H_4O)H^+$	Acetaldehyde	Ethylene oxide
47.041	$(C_2H_6O)H^+$	Ethanol	Formic acid
49.010	$\mathbf{(CH_4S)H^+}$	**Methanethiol**	Fluoroethane
55.047	$(C_4H_6)H^+$	Butadiene isomers	Butyne isomers; Alkyl fragments
57.069	$(C_4H_8)H^+$	Butadiene isomers	Butyne isomers; Alkyl fragments
58.065	$(C_3H_7N)H^+$	Propenamine	Propanimine
59.048	$(C_3H_6O)H^+$	Acetone	Propanal
61.028	$(C_2H_4O_2)H^+$	Acetic Acid	
63.022	$\mathbf{(C_2H_6S)H^+}$	**Dimethyl sulfide**	Ethanethiol
63.022	$\mathbf{(C_2H_6S)H^+}$	**Ethanethiol**	Dimethylsulfide
67.054	$(C_5H_6)H^+$	Cyclopentadiene	
69.069	$(C_5H_8)H^+$	Isoprene	Pentadiene isomers
71.086	$(C_5H_{10})H^+$	Pentene	Butanoic acid /Alcohol fragments
73.060	$(C_4H_8O)H^+$	Butanal	Butanone; Butenol
75.041	$(C_2H_2O_3)H^+$	Glyoxylic acid	
77.060	$(C_3H_8O_2)H^+$	Propanediol	Propanethiol/alkyl fragments
79.057	$(C_6H_6)H^+$	Benzene	Ethylbenzene/Xylene fragment
81.069	$(C_6H_8)H^+$	Terpene fragments	Hexenal/Hexenol fragments
83.049	$(C_6H_{10})H^+$	Cyclohexene	Hexadiene
89.055	$(C_4H_8O_2)H^+$	Butanoic Acid	Dioxane isomers; Acetoin
93.070	$(C_7H_8)H^+$	Toluene	p-Cymene fragment; Chloroacetone
94.998	$\mathbf{(C_2H_6S_2)H^+}$	**Dimethyl disulfide**	
97.028	$(C_5H_4O_2)H^+$	Furfural(s)	Ethylfuran
105.070	$(C_8H_8)H^+$	Styrene	pentanediol
107.086	$(C_8H_{10})H^+$	Ethylbenzene	Xylene isomers; Terpene fragment
109.065	$(C_7H_8O)H^+$	Methylphenol(s)	Anisole
115.097	$(C_7H_{14}O)H^+$	Heptanal	
121.102	$(C_9H_{12})H^+$	Propylbenzene	Trimethylbenzene/ Ethyltoluene isomers
123.080	$(C_8H_{10}O)H^+$	Phenylethanol	Methylanisole
137.132	$(C_{10}H_{16})H^+$	Monoterpenes (α-pinene)	p-Cumenol; Methylbenzoic acid isomers

3.2 Sample site background, data and results:

Background information about the layout and sample locations from each wastewater treatment plant is described, followed by a section including the data and results from the on-site sampling.

The data shown below are in boxplot form to display the distribution of the measured concentrations of all of observations. Typical measurements are taken at 1 Hz and include a minimum of 300 observations. The median value is indicated as horizontal red line inside the box. The size of the box represents the 25-75th percentile in the data. Roughly 95% of data within the whiskers and outliers are shown with crosses. The data presented is an overview of the results from each of the odour control systems analyzed. Individual sample days including all sample points and additional analytes are presented in Appendix A. In addition, an intensive breakdown of inter-sample day comparisons of individual odour controls is found in Appendix D.

3.2.1 French Creek Pollution Control Centre - WWTP1

The water treatment technologies at WWTP1 include use of autothermal thermophilic aerobic digestion (ATADs), sedimentation ponds and bio trickling filters. This site does not currently capture and use any of its biogas.

WWTP1 employs a combination of odour remediation technologies (Figure 14). The odour control streams at WWTP1 are divided into three sections (Figure 14) utilizing a wet bio-scrubber and chemical scrubber combination for the foul air associated with the digestors, a stand-alone ‘in-ground’ biofilter for the foul air generated from the biosolids de-watering process, and a trickling filter room for treating the headworks and raw sewage intake foul air. The focus of this discussion will be on the wet-bio scrubbers, chemical scrubber and biofilter odour control technologies and a short evaluation of a pilot scale AOP odour control unit. The MMSL was operated on-site by sampling air from designated locations for real-time analysis of VOCs. Supporting instrumentation measured CAPs (O_3, NO_x) and GHGs (CO_2, CH_4, H_2O). A total of nine sampling trips at WWTP1 were conducted over the duration of this study corresponding to a total sampling time of 25 hours including over 90,000 observations. Six on-site evaluations of the ductwork were completed, and an additional 3 days of evaluation were done for the odour control pilot project. The dates, times, and activity are detailed in Appendix A.

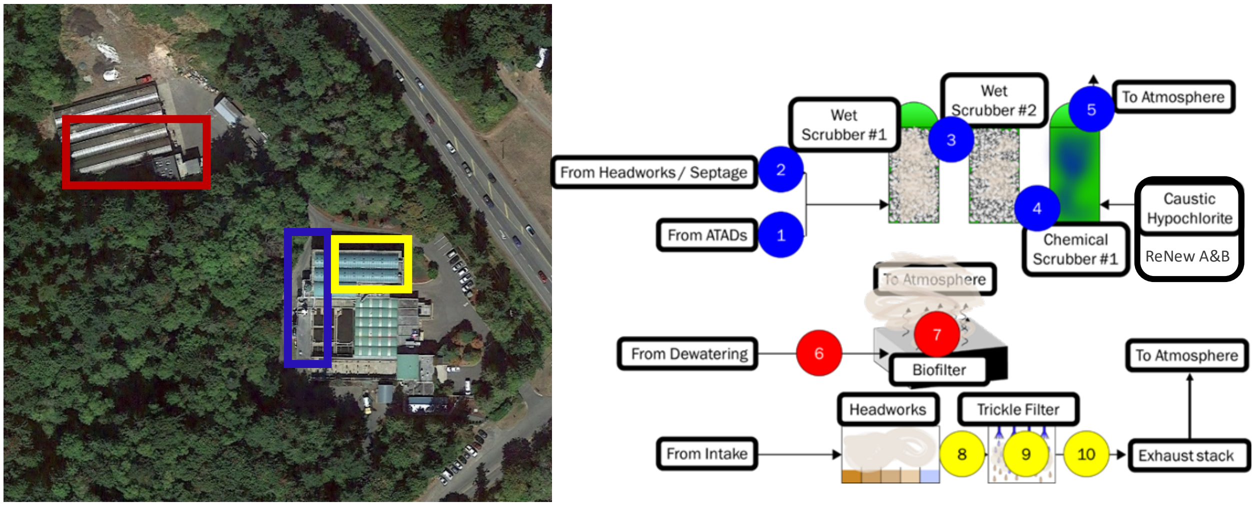

Figure 14: (Left) Aerial photograph of WWTP1 site showing main WWTP in the center and the storage bays and biofilter in the top left corner. Right) Diagram of Sample points onsite WWTP1, general flow of air is shown, Figure adapted from Davidson J (2021). The three odour streams are denoted by the blue, red and yellow colours on the diagram along with the sample location numbers and coloured boxes on the aerial photograph.

The wet-bio scrubber towers (WBST) are used as the first line of odour control after autothermal thermophilic aerobic digestion (ATAD) of the wastewater, which is the main source of odour at this facility containing high levels of malodourous compounds. The VOC measurements were taken at the foul air outtake from the ATADs at sample point S1 before any treatment, after the first treatment tower WBST1 sampled at S3, and after the second treatment tower WBST2 sampled at S4. The gas stream is then passed through a chemical scrubber and sampled at S5 (Figure 15).

Figure 15:(Left) Photo of the covered ATADs, (Middle) ATAD foul air sample location S1, (Right) Photo of WBSTs and Chemical scrubber at WWTP1.

The scrubbing solution changed part-way through the study in December 2022 from Caustic soda (NaOCl) to ReNew A & B™ (CHEM-AQUA, Ontario). These solutions are used to help the neutralization and oxidation of VOCs before release into the atmosphere. The scrubbing solution ReNew A & B contains a proprietary blend of alcohols, ethers and coco betaine to help eliminate odours and was in use after Dec 2022. This odour control technology was offline one of the days during the campaign as it was undergoing maintenance.

Foul air exhausted from the biosolids de-watering room was passed through a simple biofilter consisting of woodchips and shells which are kept hydrated to give a substrate for oxidizing bacteria (Figure 16). This area of the plant is noticeably odourous during de-watering operations. This process is not continuous and runs intermittently as a batch process. Fans draw out the foul air and pass it through the filter when centrifuges are in operation. Some days while sampling, operations were not running, so no adequate comparison could be made. In some cases, the pre-biofilter was sampled while the exhaust fan was running, but once the sampling lines were changed to post-biofilter the fans stopped and this data was not used in evaluations of removal efficiencies. One consideration for evaluation of this system is the incoming air is measured in ductwork, while the output is measured at the interface of the biofilter and the atmosphere and will have some dilution of the gases through the high surface area of the biofilter.

Figure 16: (Left) Photo of ductwork exhausting the de-watering room and sample point S6. (Right) Photo of biofilter and sample location S7 at WWTP1.

During the sampling campaign at this facility pilot evaluation study was conducted using a proprietary advanced oxidation process (AOPs) technology (Figure 17). This odour control was achieved using multiple banks of UV-lights and modified activated carbon filters, producing powerful oxidants ozone and hydroxyl radicals. The combination of the techniques allowed for VOCs to be trapped and transformed by the filters and oxidants. During the study VOCs were monitored pre-treatment and post treatment and included measurement of ozone post-treatment (Appendix A). The measurements taken were also compared to the biofilter concentrations pre- and post-treatment, as this technology would replace the existing biofilter.

Figure 17: Photo of temporary demonstration advanced oxidation unit for odour control to treat exhaust air from de-watering process at WWTP1. Air was sampled at the inlet on the left of unit and outlet at the right (May/June 2022).

3.2.2 Evaluation of odour control systems at French Creek Pollution Control Centre (WWTP1).

ATAD Foul Air Treatment

The treatment of foul air from the auto-thermal aerobic digestors at WWTP1 was effective at reducing the malodourous VOC load. The untreated foul air stream at S1 had highly elevated levels of reduced sulfur compounds throughout the sampling campaign for methanethiol (mean=3790 ppb$_v$, %RSD=47), dimethyl sulfide (mean=2300 ppb$_v$, %RSD=160) and dimethyl disulfide (mean=300 ppb$_v$, %RSD=55) (Table 3). The large relative standard deviation (RSD) across six sampling days indicates the large variability, especially for dimethylsulfide. The ATADs concentration ranges are not out of the ordinary for wastewater treatment plants evaluated by other researchers, with typical maximum concentrations of methanethiol observed at two locations in Ontario ranging from 6000-10,000 ppb$_v$ in the ATADs foul air stream.[71] Previous observations at this facility had lower median values of DMS at 400 ppb$_v$ compared to the median of 1290 ppb$_v$ in this study, and similar median values for DMDS both at 300 ppb$_v$ in ATAD foul air (Table 3).[68]

Table 3: ATAD foul air median concentrations for MeSH, DMS and DMDS at WWTP1.

ATAD Foul air (S1) median concentrations (ppb$_v$)						
Sample site	Aug/22 (day 1)	Mar/23 (day 2)	May/23 (day 3)	Sept/23 (day 4)	Nov/23 (day 5)	Feb/24 (day 6)
Methanethiol	3420	3260	3185	2025	7290	3565
Dimethyl sulfide	70	9735	1300	635	1305	730
Dimethyl disulfide	50	445	525	190	290	355

The most concerning exhaust point is from the output of the treated ATAD foul airstream by wet bio scrubber towers and the chemical scrubber (S5) which has 10x the output as the other exhaust locations onsite. The post-treatment concentrations from each sample location exhausted to the atmosphere (S5, S7, S10) showed an average of 1500 ppb$_v$ methanethiol from (S5) wet bio scrubber towers and chemical scrubber treatment, an average of 150 ppb$_v$ from the biofilter treatment (S7), and the trickling filter wastewater treatment room air exhaust (S10) at 100 ppb$_v$ of methanethiol, very close to the previous observations which had a median of 150 ppb$_v$ in the trickling filter room (Figure 18).[68] The concentrations recorded are all much higher than odour detection thresholds (Figure 18).

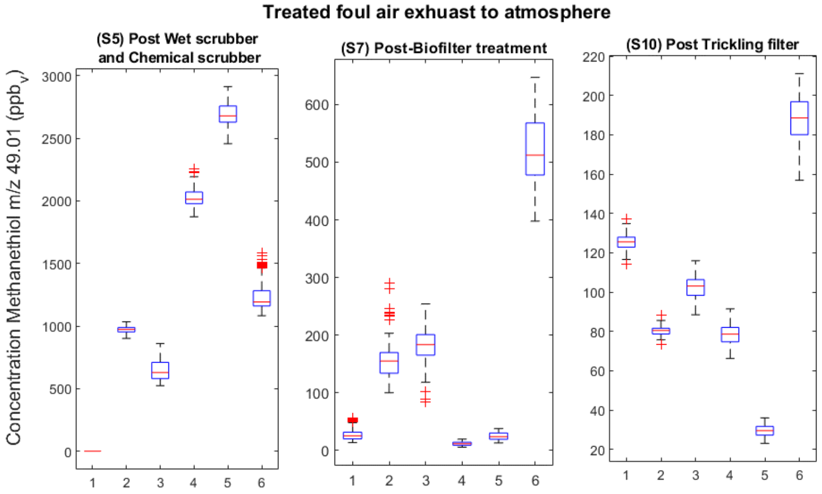

Figure 18: Methanethiol concentrations from exhaust points at WWTP1, post-chemical scrubber, post-biofilter treatment and post trickling filter room treatment. Sampling days 1-5, 1-August 2022, 2-March 2023, 3- May 2023, 4-Sept 2023,5- November 2023, 6- February 2024. Boxplots from days 1, 4 and 5 from post biofilter did not have the exhaust fan running and sample day 5 did not have chemical scrubber in operation. Y-axis is scaled differently for each sample location.

Wet bio scrubber's odour control

The three main reduced sulfur compounds were treated by the odour control systems with higher efficiencies for methanethiol compared to DMS and DMDS. The overall removal efficiencies for both wet bio-scrubber towers in tandem ranged from 27-80% for methanethiol and 20-96% for DMS with the exception of Aug 2022 sampling which indicated a significant increase. These findings indicate that the wet bio scrubber towers when operated together, are lowering the concentrations of methanethiol and DMS from S1 to S4 over the sampling campaign, although if only one tower is used inconsistent removal occurs (Table 4). The removal efficiencies of WBSTs for reduced sulfur compounds are similar to other studies done using wet bio scrubbers, which find at best 70% removal efficiency of methanethiol and lower efficiencies for DMS and DMDS.[72] The DMDS removal efficiency was quite variable from both WBSTs as half the days sampled (Mar 2023, May 2023, Sept 2023) removal efficiency was seen from 17-71%, and sample days 1, 5 and 6 (Aug 2022, Nov 2023, Feb 2024) the removal efficiencies were poor ranging from negligible removal efficiency of <5% to increased concentrations from S1 to S4 of 79-190% (Table 4). During sampling day 5, additional measurements were collected on sorbent tubes and analyzed using TD-GC-MS, which yielded similar results to the PTR-MS, and confirmed most of the signal at *m/z* 63.02 was from dimethyl sulfide and not ethanethiol (Appendix D). This suggests that DMDS removal is not consistent throughout the campaign and the WBSTs can become a source in some instances. The concentrations of the dominant VOCs methanethiol, DMS and DMDS post WBSTs treatment were found to be variable across the sampling campaign and had mean values of 1800 ppbv (%RSD=63), 550 ppbv (%RSD=70), 260 ppbv (%RSD=60) (Appendix D). The concentrations post treatment generally follows a trend of concentrations MeSH>DMS>DMDS, similar to the input concentrations trends seen (Table 3). The concentrations post treatment (S4) was similar to observations at this site in 2019/20, with median concentrations of methanethiol, dimethyl sulfide and dimethyl disulfide within 10-25% of previous values. [68]

Table 4: Percent removal of MeSH, DMS and DMDS from WBSTs at WWTP1.

% Removal from WBSTs odour control						
S1→S4	Aug/22 (day 1)	Mar/23 (day 2)	May/23 (day 3)	Sept/23 (day 4)	Nov/23 (day 5)	Feb/24 (day 6)
Methanethiol	55	27	80	45	48	62
Dimethyl sulfide	-140	96	26	58	20	40
Dimethyl disulfide	-190	71	52	17	-79	0

Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. % removals within +/-5% are reported as 0.

The WBSTs did not appear to independently lower the concentrations of MeSH, DMS, and DMDS on each sampling day. It was found that on half of the sampling days either WBST1 or WBST2 would have a negative removal efficiency, thus increasing concentrations of the gases at one of the WBSTs. This may have occurred from fouling of the unit, or improper operational parameters, such as an imbalance of gas flow to water flow through the tower. For example, sample days 1 and 2 showed a negative removal efficiency at WBST1, which was brought to the attention of the operators of the WWTP, so adjustments could be made. The water flow rates were adjusted at WBST1 for sample day 3, which lead to improved operations for removal of MeSH from negative removal efficiencies (>-25%) to 60% removal (Table 5). DMDS removal also improved from -60% to 30% after these adjustments were implemented (Appendix D).

Table 5: Percent removal of methanethiol from WBSTs from all sample days at WWTP1.

Median concentrations and removal efficacy for methanethiol						
Sample site	Aug/22 (day 1)	Mar/23 (day 2)	May/23 (day 3)	Sept/23 (day 4)	Nov/23 (day 5)	Feb/24 (day 6)
S1 (ppb_v)	3420	3264	3188	2027	7292	3563
S3 (ppb_v)	3828	4087	1198	2294	2653	1012
S1→S3 (%)	-12	-25	62	-13	64	72
S4 (ppb_v)	1534	2381	629	1115	3828	1348
S3→S4 (%)	60	42	47	51	-44	-33

Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. % removals within +/-5% are reported as 0.

Chemical scrubber odour control

Concentration ranges for the input to the chemical scrubber (S4) were from 500-3750 ppb_v methanethiol, which encompasses a large range which the chemical scrubbers must work (mean=1800 ppb_v, %RSD=60) (Appendix D). The median concentration from the chemical scrubbers (post-treatment, S5) of methanethiol, DMS and DMDS was 1230, 600, 340 ppb_v, respectively (Appendix D). These concentrations were higher compared to the previous sampling done in 2019-2020, with medians of MeSH, DMS and DMDS at 250, 400, 200 ppb_v, respectively.[68] The treatment by the chemical scrubbers showed a similar trend in effectiveness for all three compounds, where 3/5 days sampled showed positive removal efficiency for all compounds ranging from 21-99% removal (Table 6). The first sampling day in Aug 2022, the chemical scrubber was run using a caustic solution rather than ReNew A & B used in the latter sample days, which showed >80% removal efficiency for all three compounds. During the sampling period where ReNew A & B were used, removal efficiencies were <60% across all three compounds, suggesting this is a less effective scrubbing solution to remove these three compounds (Table 6).

Table 6: Percent removal of MeSH, DMS and DMDS from the chemical scrubber at WWTP1.

% Removal from Chemical scrubber odour control						
S4→S5	Aug/22 (day 1)*	Mar/23 (day 2)	May/23 (day 3)	Sept/23 (day 4)	Nov/23 (day 5)	Feb/24 (day 6)
Methanethiol	99	59	N/A	-81	30	11
Dimethyl sulfide	99	45	N/A	-137	21	0
Dimethyl disulfide	80	21	N/A	-122	28	0

*Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. N/A indicates chemical scrubber was non-operational that day. % removals within +/-5% are reported as 0. *-Caustic scrubbing solution was used*

WBSTs and Chemical scrubber odour controls

When the chemical scrubber and WBSTs are used in conjunction for odour control they generally work more effectively at reducing the concentration of methanethiol, dimethyl sulfide and dimethyl disulfide, than if used individually. Although, these systems are not consistent in their ability to remove DMDS and may be a source of DMDS during some treatment operational conditions. The one exception to the improvement of odour control when used in tandem, was when the chemical scrubber had become a source of DMDS on day 4, which lead to the operational staff making changes to the dosing of the chemical scrubber, leading to improved removal on the subsequent sampling days (Table 7). Thus, indicating that operational parameters play a key role in the efficacy of the odour controls, and monitoring input and output concentrations can inform when operational modifications are necessary to improve odour control efficacy.

Table 7: Sample day summary of removal efficiencies from WBSTs and chemical scrubber odour controls in tandem at WWTP1.

Removal efficacy (%) from WBSTs and chemical scrubber odour control in tandem						
S1→S5	Aug/22 (day 1)	Mar/23 (day 2)	May/23 (day 3)	Sept/23 (day 4)	Nov/23 (day 5)	Feb/24 (day 6)
Methanethiol	100	70	80	0	63	67
Dimethyl sulfide	97	98	26	0	37	38
Dimethyl disulfide	42	77	52	-85	-30	-7

Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. % removals within +/-5% are reported as 0.

Estimation of emissions rates from ATAD Foul Air Treatment exhaust from WBSTs and Chemical scrubber odour control (S5).

An average of 1500 ppb$_v$ of methanethiol was observed at sample point S5 over the sampling campaign which exhausts to the atmosphere. At STP this corresponds to a concentration of ~3000 µg/m^3. Combining this with an estimated average exhaust flow of 3050 m^3/hr, this yields an is a flux of 9.0 g/hr of methanethiol or 79 kg annually using Equation 16 below. Similarly, the annual flux for dimethyl sulfide and dimethyl disulfide are estimated to be 41 and 35 kg. Using these estimates, we calculate the annual flux of total reduced organosulfur from this facility to be ~ 3000 moles S (Table 8). These emission factors contribute to under reported inventories and can be employed in dispersion and chemical fate models.

(16) Emission rate (@ STP) = Concentration x flow rate =

$$\frac{Kg}{year} = \left(\frac{ppb_v * MW}{24.45}\right) * \left(\frac{m^3}{hr}\right) * \left(\frac{1kg}{1x10^9ug}\right) * \left(8760\frac{hours}{year}\right)$$

Table 8: Estimated flux rates from exhaust from S5 for methanethiol, dimethyl sulfide and dimethyl disulfide at WWTP1.

Compound	Average concentration (ppb_v)	Molecular weight (g/mol)	Average flux (kg/hr)	Yearly emissions (kg/year)	Total moles/yr
Methanethiol	1500	48.1	0.0090	79	1600
Dimethyl sulfide	600	62.1	0.0047	41	660
Dimethyl disulfide	340	94.2	0.0040	35	370
Total Sulfur from MeSH, DMS and DMDS	---------------	32.1	--------------	96	3000

Biosolids Foul Air Treatment

Biofilter bed odour control

Foul air from the de-watering process was passed through a biofilter. On days where the exhaust fans were operating normally, the average removal efficiency for methanethiol was 70%, although on one occasion (May 2023) it appeared to act as a source with a removal efficiency of -20% (Table 9). The removal efficiency for DMS was typically less at 40-50% and 10% for DMDS, indicating that on most days these systems can reduce malodourous VOCs (Table 9). However, efficacy appears to be highly variable, and these systems can become a source of these compounds emphasizing the need to manage and rejuvenate this biofilter media.

Table 9: Sample day summary of removal efficiencies from biofilter odour control at WWTP1.

Removal efficacy (%) from biofilter odour control						
S6→S7	Aug/22 (day 1)	Mar/23 (day 2)	May/23 (day 3)	Sept/23 (day 4)	Nov/23 (day 5)	Feb/24 (day 6)
Methanethiol	**N/A**	59	-20	**N/A**	**N/A**	80
Dimethyl sulfide	**N/A**	45	-130	**N/A**	**N/A**	43
Dimethyl disulfide	**N/A**	21	-350	**N/A**	**N/A**	0

Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. N/A indicates treatment was non-operational that day. % removals within +/-5% are reported as 0.

Pilot study of AOP odour control

During several weeks in May/June 2023 a demonstration trial of an advanced oxidations process treatment system was used to treat the foul air that goes to the biofilter bed. All three reduced sulfur compounds showed excellent removal efficiency of >99%

(Table 10). This method of odour control does use an energy intensive process with operational maintenance and running costs which may hinder the widespread adoption at this facility. Although, the short duration study may have unknown challenges with use beyond the characterized period. In addition to the VOC measurements, ozone concentrations were measured after treatment, which indicated this method of treatment can release unreacted ozone, which should be considered with the operations of this method (Appendix A). Notwithstanding the limitations of this study and potential impacts of ground level ozone emissions, the data suggests this method of odour control was the most effective for removal of these compounds compared to the other odour controls on-site. However, it may be a good choice for intermittent point source treatments such as the de-watering process here.

Table 10: Sample day summary of removal efficiencies from AOP pilot study at WWTP1.

% Removal efficacy (%) from AOP odour control				
Pilot AOP	May 24, 2023	May 25, 2023	May 29, 2023	June 12, 2023
Methanethiol	99.9	99.9	99.9	99.8
Dimethyl sulfide	99.8	99.5	99.8	94.7
Dimethyl disulfide	99.3	98.6	99.1	99.6

Summary WWTP1

The information from this sampling campaign was able to further inform the operations team at WWTP1 on how the odour control systems were working and gave them the insight needed to make changes in their treatment systems operations. Some changes included adjusting water circulation flows and replacing media in the WBST, evaluating chemical agents and dosing in the chemical scrubbers, scheduled cleaning accumulated sludge in the odour controls systems, and performance testing new technology during a demonstration trial.

Further upgrades to the foul air treatment systems will improve the removal of malodours from the exhaust stream and potentially improve the on and off-site air quality. This study encompasses over 25 hours of on-site evaluation of treatment systems. The comparison to the earlier observations in 2019/20 is for reference only. During the intervening time there have been several alternations to onsite operations and the area has experienced ~5-6% growth with the total influent flow increasing from $3.6\text{x}10^6$ m^3 to $3.8\text{x}10^6$ m^3 from 2020 to 2023.[68,73]

3.2.3 Greater Nanaimo Pollution Control Center - WWTP2

The water treatment technology at WWTP2 was upgraded in 2020 to include secondary treatment. The odour control technologies at WWTP2 are relatively passive and are generally 'green' processes. It has an extensive foul air collection system and a large capacity bioreactor treatment system. This facility also employs two stand-alone modular carbon scrubber odour control technologies to treat foul air from the primary screening and biosolids de-watering buildings (Figure 19). This site captures and stores biogas from their anerobic digestion processes and uses this on-site to periodically run power generators. The remainder is flared (Figure 20).

Figure 19: Photo of modular carbon scrubber used to treat foul air for biosolid de-watering process at WWTP2.

Figure 20: (Left) Photo of biogas storage ball. (Right) Photo of flare onsite WWTP2.

On-site ductwork measurements taken with the MMSL before and after treatment processes and modular odour control technologies. The on-site sampling days and times are recorded in Appendix A. The layout of the facility and sampling locations are shown in Figure 21. Photos of the upgraded secondary treatment and clarifier is shown in Figure 22. Individual sample days are presented as supplemental information in Appendix A and include all sample sites from WWTP2.

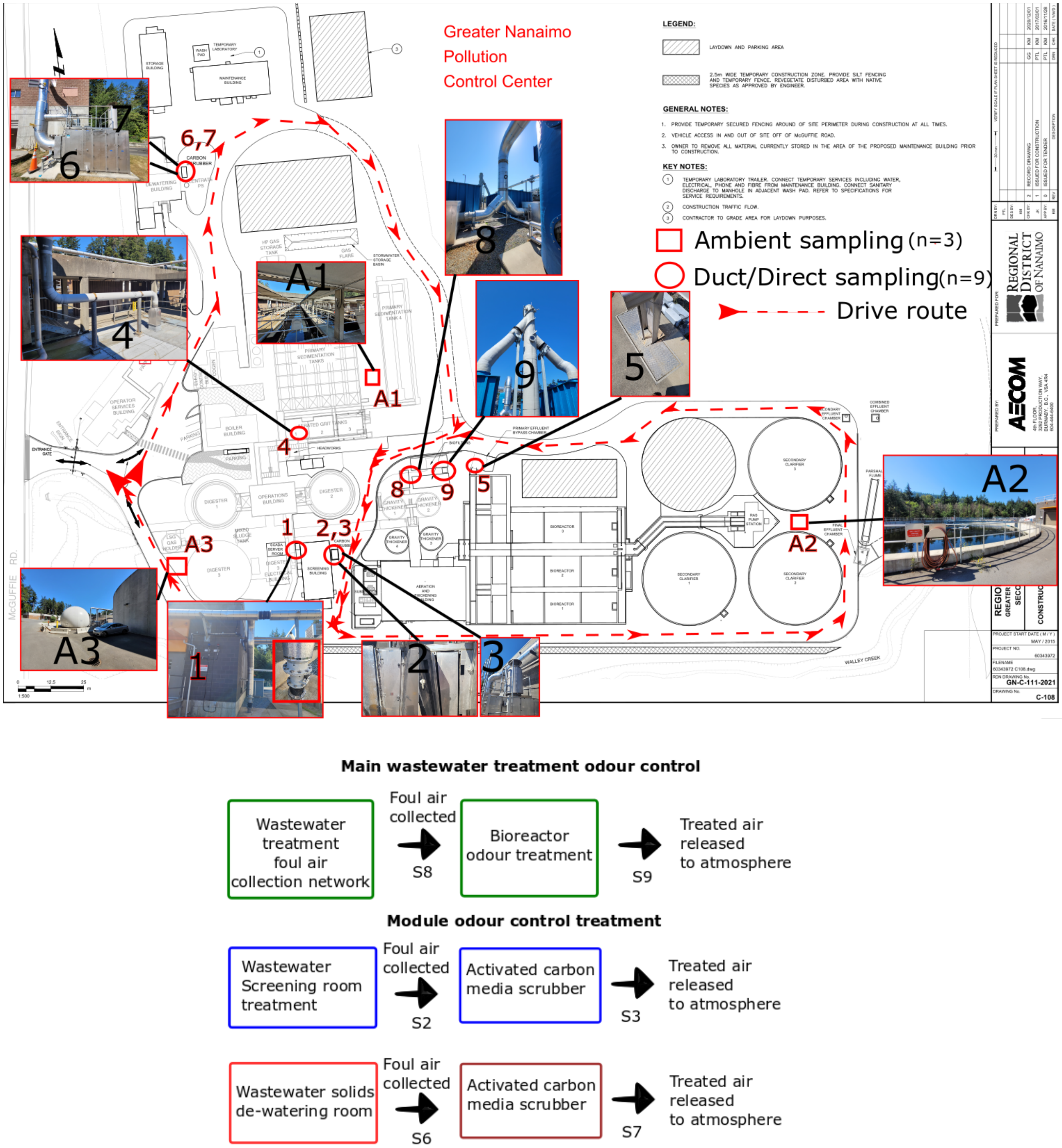

Figure 21: Overview of WWTP2 site and sampling locations.

Figure 22: (Left) Photo of secondary water treatment system aeration tanks. (Right) Photo of clarifiers at last step before water discharge to environment.

The main odour control technology at WWTP2 consists of two large modular bioreactors which immediately follow a large wet scrubber/rain tower. The bioreactors are run in parallel and share a common exhaust tower which releases air ~50 ft above the ground. Samples were taken between wet scrubber and bioreactors at sampling point S8 as well as at top of the combined exhaust tower at sampling point S9 (Figure 23).

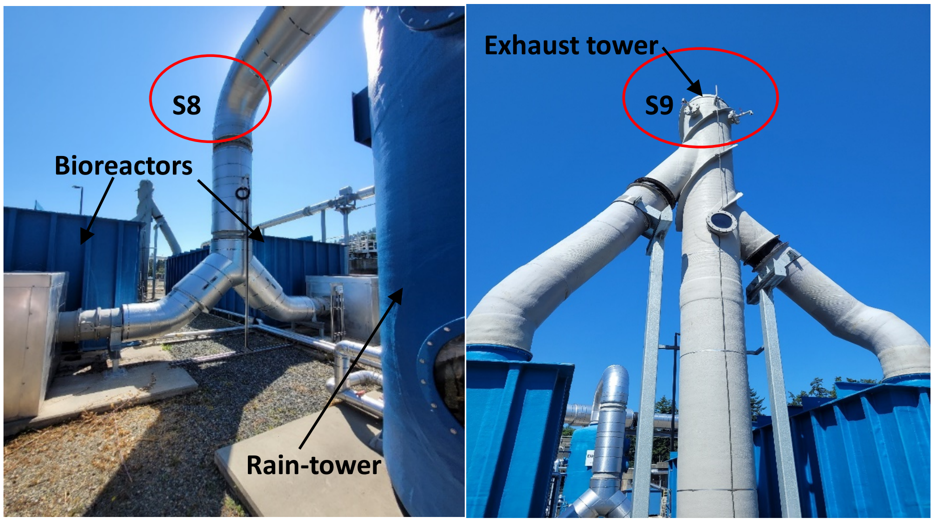

Figure 23: (Left) Photos of bioreactor odour controls, rain tower and sample locations S8. (Right) Photo of final exhaust stack and sampling location S9 at WWTP2.

3.2.4 Evaluation of odour control systems at Greater Nanaimo Pollution Control center (WWTP2)

Main Digestor and Wastewater Foul Air Treatment

Bioreactor odour control

The foul air collection network pre-treatment (S8) was evaluated across eight on-site sampling days. The concentrations and day-to-day variability are illustrated in Figure 24. The mean concentrations of methanethiol, dimethyl sulfide and dimethyl disulfide in this foul air stream were 130 ppb_v (%RSD=70), 90 ppb_v (%RSD=95), 6 ppb_v (%RSD=70), respectively. This are significantly lower than those observed from the digestors at WWTP1. The bioreactor system eliminated a large portion of malodourous methanethiol from the foul air stream, typically removing 80%.

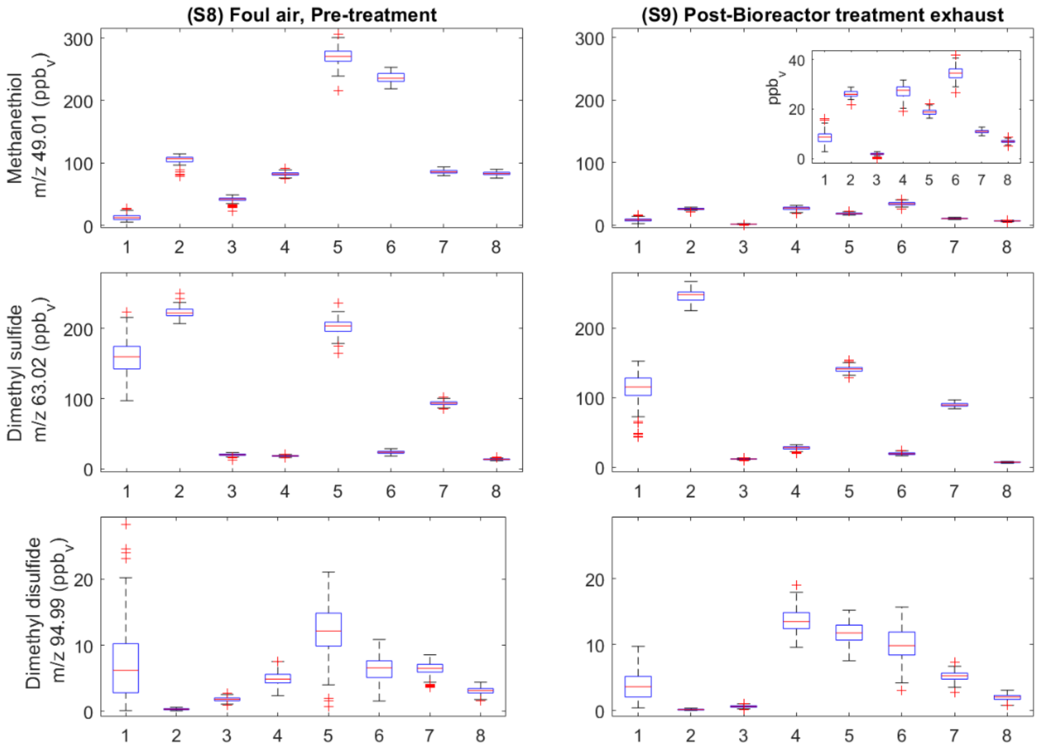

Figure 24: Boxplot summaries from main odour control bioreactors at WWTP2. sample days,1-August 2022,2-Nov 2022,3-Jan 2023, 4-April 2023,5-June 2023,6-Sept 2023,7-Nov 2023,8-Feb 2024 at WWTP2.

Removal efficiency for DMS was more modest and inconsistent with an average of 30% removal. The average removal efficiency for DMDS was 40% on six of the eight sample days but showed modest increases on two days (Table 11).

Table 11: Percent removal from biofilter odour control for MeSH, DMS and DMDS at WWTP2.

% Removal from Bioreactor odour control								
S8→S9	Aug/22 (day 1)	Nov/22 (day 2)	Jan/23 (day 3)	Apr/23 (day 4)	Jun/23 (day 5)	Sep/23 (day 6)	Nov/23 (day 7)	Feb/24 (day 8)
Methanethiol	30	76	95	86	93	86	87	92
Dimethyl sulfide	28	-12	40	-56	31	17	0	46
Dimethyl disulfide	42	67	75	-17	0	-67	23	34

-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. % removals within +/-5% are reported as 0.

This variability in effectiveness may originate from the biological nature of the treatment system and physical properties of the gases. The ambient temperature can greatly influence the nature of wastewater treatment and bioreactor efficiency, with hotter temperatures allowing for faster microbial respiration, but also for increased volatility of the VOCs. Also, the amount of wastewater being treated at the WWTP can influence variability in the system. A thorough breakdown of the odour control capabilities, including full scan mass spectra and an inter-day analysis of odour control systems is found in Appendix D.

Estimation of emission rates from bioreactor odour control exhaust at WWTP2.

The average flow rate at the exhaust stack is 18,650 m^3/hr. Average fluxes are in Table 12 and were calculated from averages from the entire sampling campaign using Equation 16. The total yearly flux of the three reduced sulfur compounds, reported in terms of sulfur is 17.7 kg/year from WWTP2.

Table 12: Estimated flux of methanethiol, dimethyl sulfide and dimethyl disulfide from exhaust stack (S9) at STP at WWTP2.

Compound	Average Conc. (ppb_v)	Molecular weight (g/mol)	Conc. At STP ($\mu g/m^3$)	Average flux (kg/hr)	Yearly flux (kg/year)	Yearly moles (mole/year)
Methanethiol	20.1	48.1	39.6	0.00038	6.5	130
Dimethyl sulfide	50.2	62.1	127.6	0.0024	21	340
Dimethyl disulfide	6.2	94.2	23.9	0.00044	3.9	40
Total sulfur (from MeSH, DMS and DMDS)	--------------	32.1	----------	-----------	18	550

This WWTP study consisted of over 17 hours of on-site evaluation including over 61,000 observations. The data from this study indicates that consistent removal of methanethiol is seen by both the activated carbon scrubbers and bioreactor at >80% removal efficiency, while inconsistent DMS and DMDS were removed by either of the systems. All three reduced sulfur compounds are released above their odour detection thresholds but are not excessively high, <20 ppb$_v$, and will be diluted by the atmosphere after release. Using a biological treatment system can reduce costs associated with replenishing sorbents and high energy consumption from advanced controls like photo-oxidation.

Primary screening room and Biosolids processing exhaust

Module carbon scrubber odour control

The inputs to the small module carbon scrubbers sampled at sampling points S2 ad S6 were generally below 30 ppb$_v$ for methanethiol, dimethyl sulfide and dimethyl disulfide including one scrubber (S6) which had very low input concentrations across all compounds <5 ppb$_v$ throughout the sampling campaign (Figure 25, Appendix D). These carbon scrubbers were quite effective in reducing the concentrations of malodourous sulfur compounds well below 2 ppb$_v$ with MeSH, DMS, and DMDS often recorded at instrument detection limits in the exhaust air (Figure 25, Appendix D).

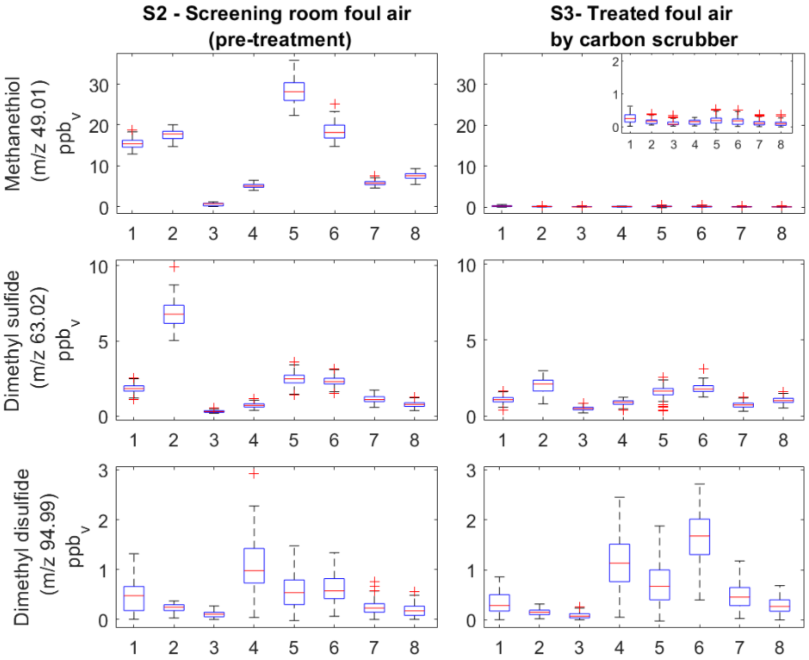

Figure 25: Boxplot summaries for methanethiol, dimethyl sulfide and dimethyl disulfide concentrations from S2 and S3, module carbon scrubber treatment at WWTP2. Sample days,1-August 2022,2-Nov 2022,3-Jan 2023, 4-April 2023,5-June 2023,6-Sept 2023,7-Nov 2023,8-Feb 2024.

The removal of methanethiol by the activated carbon scrubbers was 80-95% removal efficiency (Table 13), which is similar to findings in the literature, the less effective removal of DMS and DMDS are also found at other activated carbon scrubbing technologies described in 2016 by Shammay *et al.*[74] The removal of DMS and DMDS by the activated carbon scrubbers was negligible with some indication of removal on a portion of the days, although with such low concentrations at the input and post-treatment (<5 ppb_v), it is hard to judge the removal efficiencies of these systems (Table 13). The module charcoal scrubbers were not removing all the DMS or DMDS from the gas stream, indicating these systems do not work for total removal of DMS or DMDS even at low concentrations, but are generally effective for MeSH removal. On Sept 2023, Nov 2023 and Feb 2024 production of DMDS was observed at S3, suggesting that activated carbon may lead to the production of DMDS via partial oxidation of MeSH to DMDS under some conditions.

Table 13: Summary of removal efficiencies from module carbon scrubbers S3 and S7 at WWTP2.

Removal efficacy (%) from modular carbon scrubbers								
S2→3 (%)	Aug/22 (day 1)	Nov/22 (day 2)	Jan/23 (day 3)	Apr/23 (day 4)	Jun/23 (day 5)	Sep/23 (day 6)	Nov/23 (day 7)	Feb/24 (day 8)
Methane-thiol	98	99	86	100	100	99	98	99
Dimethyl sulfide	50	71	-67	0	33	40	50	-38
Dimethyl disulfide	50	38	0	0	0	-200	-150	-50
S6→7 (%)	Aug/22 (day 1)	Nov/22 (day 2)	Jan/23 (day 3)	Apr/23 (day 4)	Jun/23 (day 5)	Sep/23 (day 6)	Nov/23 (day 7)	Feb/24 (day 8)
Methane-thiol	55	99	83	100	0	0	0	0
Dimethyl sulfide	13	41	67	100	0	0	0	0
Dimethyl disulfide	-15	57	96	50	0	-50	50	0

-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. S2-S3 is Module carbon scrubber 1 and S6-S7 is Module scrubber 2.

3.2.5 McLoughlin Point Wastewater Treatment Plant - WWTP3

This modern facility commissioned in 2022 (Figure 26) entrains all foul air for treatment and the reduction of ambient air odour emissions. The wastewater technologies broadly include primary, secondary and tertiary treatment before release to the environment. These technologies include sedimentation (primary), biological aerated filters (secondary), moving bed bioreactors (secondary) and disk filtration (tertiary). The odour control technology used at WWTP3 are media scrubber towers, where activated carbon and modified activated carbon is used to trap and eliminate malodours from the foul air streams. VOCs at this site were evaluated pre and post odour control systems focusing on the primary and secondary wastewater treatment odour control technologies (Figure 27). Additional data from individual sample days including the tertiary treatment VOCs and odour controls is found in Appendix A. This study includes over 43 hours of onsite evaluation including >154,000 observations. Including, some dynamic headspace sampling of processes done to further investigate treatment processes and their potential contributions to malodours. The sample locations are displayed on an aerial photograph of the WWTP in Figure 27. The MMSL was brought on-site to take real-time measurements and sorbent tubes were collected and analyzed in the lab to confirm measurements taken on-site. A summary of sample times and dates are found in Appendix A.

Figure 26: Site photo of WWTP3.

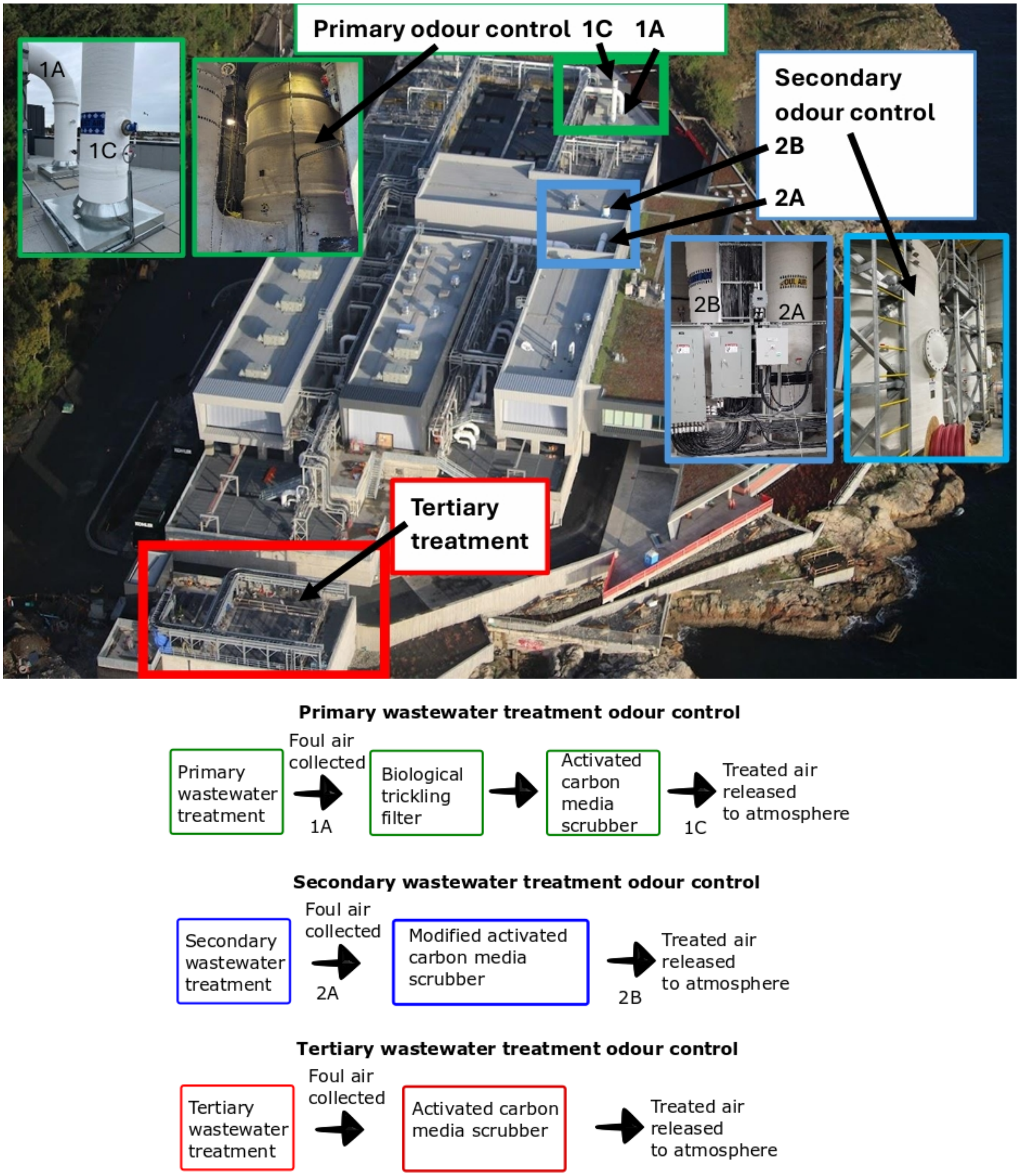

Figure 27: Sample locations at WWTP3, showing ductwork, scrubbers and exhaust locations.

There are several large capacity media scrubbers (activated carbon) used for odour control on-site at WWTP3. Foul air from the primary treatment process, is collected and passed through a biological trickling filter containing media beds of active microbes. Dissolvable gases are removed as foul air passes counter current to the water. After treatment by the biological trickling filter the gas stream runs into the activated carbon (Sulfasorb-XL, Azzuro, AZ, USA) scrubber tower to remove additional VOCs (Figure 28). The odour control associated with primary treatment will be referred to as activated carbon scrubbers in the following section. A separate series of scrubbers are used for the foul air associated with secondary treatment (Figure 27). This odour control does not include an upstream biological trickling filter and employs a modified activated carbon (CPS-12, Trane) which is blended with oxidizers to help oxidize the VOCs in the gas stream. During the campaign the secondary odour control media was replaced with fresh substrate in July 2022. This site also employes three smaller modular carbon scrubbers to help eliminate odours during headspace equilibration in holding tanks and foul air associated with tertiary treatment. WWTP3 transports biosolids to another location through underground conveyances and does not de-water or handle biosolids on-site.

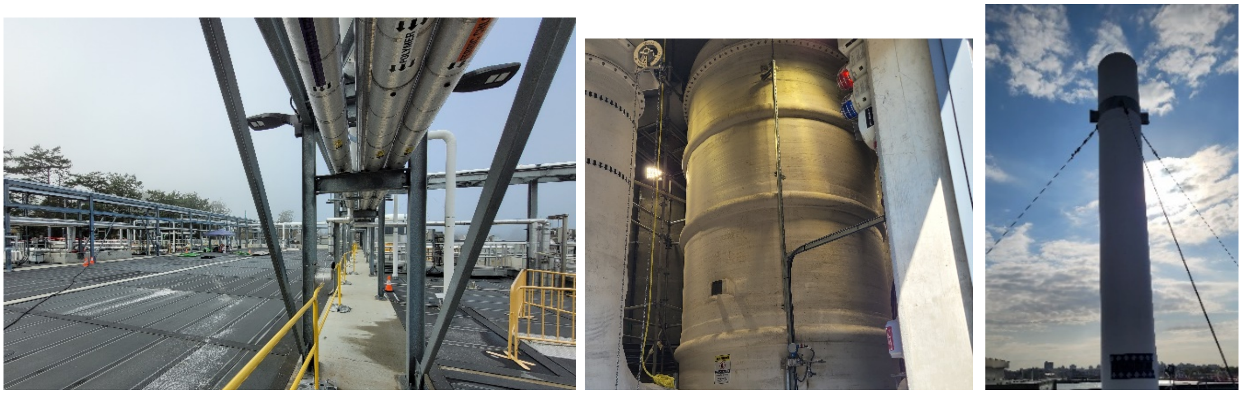

Figure 28: Photos from WWTP3, (left) primary treatment settling ponds, (middle) odour control activated carbon scrubber tower, and (right) exhaust tower.

3.2.6 Evaluation of odour control systems at McLoughlin Point Wastewater treatment plant (WWTP3)

Activated carbon media scrubbers

The input concentrations to the activated carbon media scrubbers were variable across the sampling campaign for both scrubber systems, with mean concentrations of methanethiol to the primary and secondary treatment odour control at 520 ppb$_v$ (%RSD=70) and 350 ppb$_v$ (%RSD=80), respectively (Figure 29, Appendix D). For DMS and DMDS inputs to the media scrubbers were found to be generally low <100 ppb$_v$ across the sampling campaign (Figure 29, Appendix D). These foul air concentrations fall in between those observed at WWTP1 and 2.

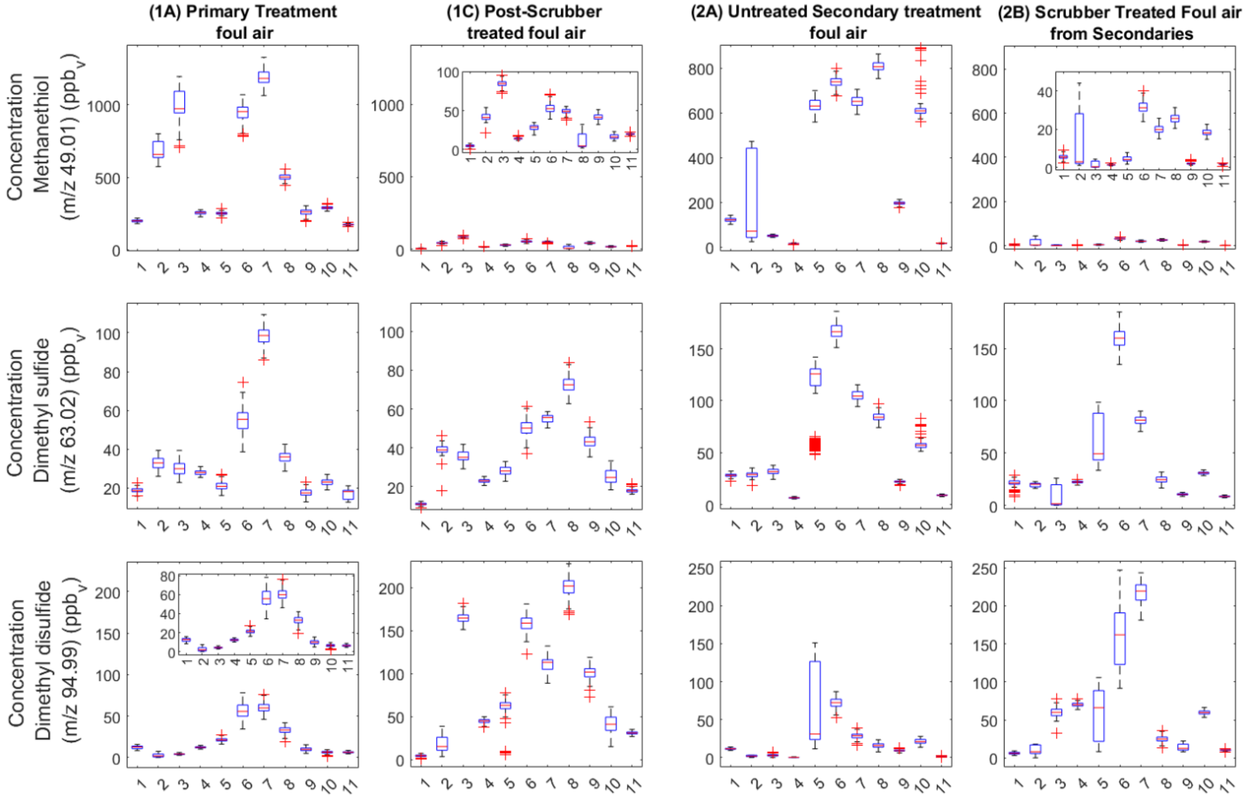

Figure 29: Boxplot summaries from odour controls at WWTP3, showing concentrations pre and post treatment by carbon scrubbers. 1-April 2022, 2-November 24, 2023, 3-November 25, 2023, 4-February 2023, 5-April 2023, 6-May 2023, 7-July 2023, 8-August 2023, 9-October 2023, 10-November 2023, 11-February 2024.

The odour control systems at WWTP3 work very well for methanethiol removal. Even with a highly variable input of methanethiol to the scrubbers, the removal efficiencies were found to be quite high. Both activated carbon scrubber towers sampled post-treatment at sampling points 1C and 2B were observed to significantly lower the concentration of methanethiol with removal efficiencies typically greater than 90%

(Table 14). These findings are similar to the activated carbon scrubber from WWTP2 and also from previous studies done showing removal efficiencies >90% for methanethiol by these systems.[74]

Table 14: Summary of percent removal of methanethiol from media scrubber towers 1C and 2B at WWTP3.

Removal efficacy (%) of methanethiol from activated carbon media scrubber odour controls											
MeSH	21-Apr, 2022 (day 1)	24-Nov, 2022 (day 2)	25-Nov, 2022 (day 3)	10-Feb, 2023 (day 4)	12-Apr, 2023 (day 5)	30-May, 2023 (day 6)	27-Jul, 2023 (day 7)	22-Aug, 2023 (day 8)	19-Oct, 2023 (day 9)	10-Nov, 2023 (day 10)	22-Feb, 2024 (day 11)
1A→1C	98	94	92	94	89	94	96	98	84	94	88
2A→2B	96	95	97	91	99	95	97	97	99	97	90

1A-1C is primary treatment media scrubber, 2A-2B is secondary treatment media scrubber.

Modest amounts of dimethyl sulfide (DMS) were removed on half of the sampling days at >20% removal efficiency from activated carbon scrubber used to treat foul air from the primary treatment process with half of the sampling days showing a modest increase (-20% removal efficiency), indicating an inconsistent ability to remove DMS (Table 15). This may originate from the condition of the sorbent bed which does not use a blended modified activated carbon like the secondary foul air scrubber tower sampled at 2A and 2B. The DMS removal from the modified activated carbon scrubber was better than that from the unmodified activated carbon but still relatively modest with an average removal efficiency of 35%. There was only one day when secondary foul air scrubber appeared to act as a source of DMS (Table 15). These findings are corroborated by the findings by Shammay *et al*, describing poor removal efficiencies for DMS by activated carbon, with removal efficiencies recorded at best 40%.[74] The evidence from this study shows the modest efficacy of these modified carbon systems for DMS removal, although they are somewhat better than the non-modified activated carbon scrubber towers.

Table 15: Summary of removal efficiencies of DMS from Media scrubbers 1C and 2B at WWTP3.

% Removal of DMS from activated carbon media scrubber odour controls											
DMS	21-Apr, 2022 (day 1)	24-Nov, 2022 (day 2)	25-Nov, 2022 (day 3)	10-Feb, 2023 (day 4)	12-Apr, 2023 (day 5)	30-May, 2023 (day 6)	27-Jul, 2023 (day 7)	22-Aug, 2023 (day 8)	19-Oct, 2023 (day 9)	10-Nov, 2023 (day 10)	22-Feb, 2024 (day 11)
1A→1C	40	-18	-18	18	-32	16	44	0	-148	-8	0
2A→2B	25	32	72	-240	43	6	23	56	52	46	0

Axes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. % removals within +/-5% are reported as 0. 1A-1C is primary treatment media scrubber, 2A-2B is secondary treatment media scrubber.

The dimethyl disulfide removal efficiency for scrubber tower at 1C and 2B averaged -300%, indicating these systems do not work well for removal of DMDS and in fact, were more likely to be a source (Table 16). During the sorption process it has been observed that the incomplete oxidation of methanethiol to dimethyl disulfide may occur leading to elevated quantities of DMDS relative to the incoming foul air.[56] This phenomenon may be a proxy for the quality and lifespan of the sorbents in the scrubbing towers and was further investigated (Figure 30). In addition, headspace measurements were made from spent sorbents obtained from the media scrubbers at WWTP3 and found high concentrations of DMDS, up to fifty-times higher compared to MeSH (Appendix C). This suggests transformation is occurring on the sorbent media as methanethiol input to the scrubbers are generally twenty-five times higher then the DMDS inputs (Appendix C).

Table 16: Summary of removal efficiencies of DMDS from Media scrubbers 1C and 2B at WWTP 3.

% Removal of DMDS from activated carbon media scrubber odour controls											
DMDS	21-Apr, 2022 (day 1)	24-Nov, 2022 (day 2)	25-Nov, 2022 (day 3)	10-Feb, 2023 (day 4)	12-Apr, 2023 (day 5)	30-May, 2023 (day 6)	27-Jul, 2023 (day 7)	22-Aug, 2023 (day 8)	19-Oct, 2023 (day 9)	10-Nov, 2023 (day 10)	22-Feb, 2024 (day 11)
1A→1C	64	-610	-1000	-266	-180	-628	-86	-507	-919	-534	-400
2A→2B	-31	-381	-1000	-1000	9	47	-666	-87	-64	-181	-629

-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. % removals within +/-5% are reported as 0. *Negative removal efficiency is capped at -1000%. 1A-1C is primary treatment media scrubber, 2A-2B is secondary treatment media scrubber.*

Investigation of methanethiol conversion to dimethyl disulfide

A bench scale flow through experiment was done to confirm that conversion of methanethiol to dimethyl disulfide was possible under the conditions found in the odour control system at WWTP3. The experimental setup and further details are found in Appendix C. During this experiment temperature and humidity were investigated for their effect on the production of DMDS on new activated carbon sorbents provided by operators at WWTP3. This was tested with only the addition of methanethiol to the system. The production of DMDS was observed after the sorbent tube was substantially loaded with methanethiol under humid conditions (>70% RH) and breakthrough was occurring (t=20 min) (Figure 30). Following the observation of DMDS production, the sorbent flow tube was heated (50°C) and a dramatic production of DMDS occurred at t=45 min, while the concentration of methanethiol diminished below detection limits (Figure 30). This confirmed the transformation of MeSH to DMDS can occur on these sorbents in humid conditions, consistent with observations from stack testing reported here. During the experiment the humidity was decreased to <50% RH to observe the effect of humidity on this transformation and was found that MeSH was observed above detection limits and DMDS concentrations dropped below detection limits (t=72 min), and when heat was applied under these conditions a much less dramatic transformation occurred with some production of DMDS but a less sharp decline of MeSH at t=78 min (Figure 30). This indicated that humidity and temperature play a key role in the transformation of MeSH to DMDS. With these observations, we believe this process is responsible for the increased concentrations of DMDS post treatment observed during the on-site odour control evaluations. The results from the bench scale experiments are consistent with literature findings where MeSH was converted to DMDS on the sorbents (Figure 30).[36]

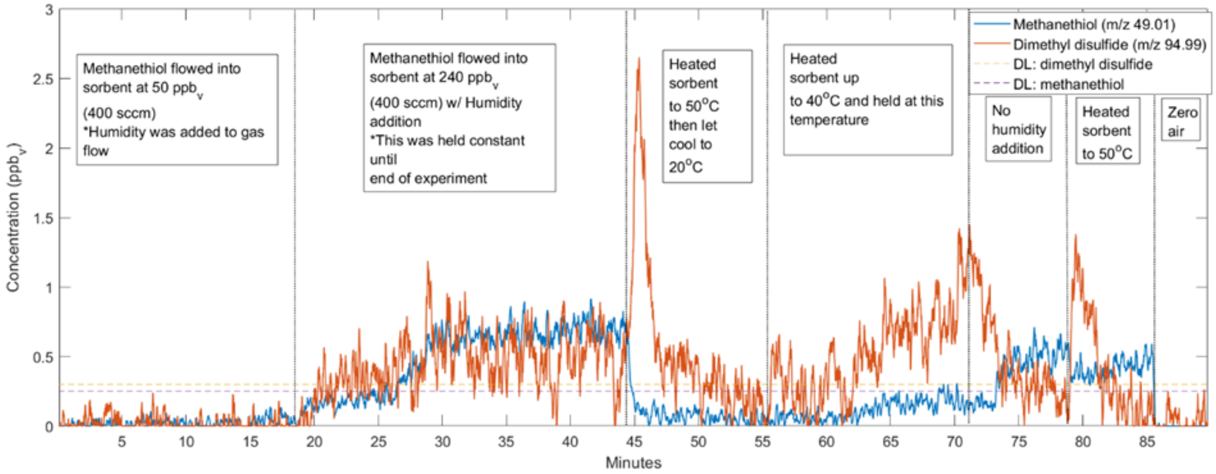

Figure 30: Timeseries from experimental data investigating the production of DMDS from MeSH on sorbents obtained from WWTP3.

Estimation of organosulfur emission rates from secondary treatment odour control exhaust

The estimated flux of reduced sulfur compounds from secondary treatment odour controls was calculated (Equation 16). This was done using the design flow rate for the system of 30850 m^3/hr and average concentrations over the sampling campaign (Table 17). The average estimated yearly flux of the three compounds reported as sulfur, is 60 kg/year. Similarly, the estimated flux from the primary treatment scrubbers was 55 kg/year of sulfur (Appendix D).

Table 17: Estimated flux from the secondary odour controls for methanethiol, dimethyl sulfide and dimethyl disulfide from WWTP3.

Compound	Average Conc. (ppb$_v$)	Molecular weight (g/mol)	Conc. At STP (µg/m^3)	Average flux (kg/hr)	Yearly flux (kg/year)	Yearly moles (mole/year)
Methanethiol	10	48.1	19.7	0.00060	5.3	110
Dimethyl sulfide	40	62.1	101.6	0.0031	27	440
Dimethyl disulfide	60	94.2	231.2	0.0071	62	660
Total sulfur (from MeSH, DMS and DMDS)	--------------	32.1	----------	-----------	60.9	1900

The efficacy of activated carbon scrubbing is depending on the VOC which it encounters and does not have the same efficiencies across all compounds which also may hamper its effectiveness in total malodourous control. The data agrees similarly with the activated carbon scrubbers found at other WWTPs like WWTP2 which has poor efficiency in removing DMS and DMDS but works well for removing methanethiol. With this information operators and engineers were informed on the efficiencies of the odour abatement technology to aid in decisions on how to manage these systems or plan for modifications/upgrades.

3.2.7 Methane emissions from WWTPs

Additional measurements collected included the concentration of methane in the exhaust stacks at each of the WWTPs. The odour control technology generally does not eliminate any methane during the process. It was observed that the inlet and outlet concentrations were very close in concentration and the focus of this section is to provide output concentrations (post-treatment) which are released to the atmosphere. Table 18 shows concentrations of methane recorded at each of the exhaust points from all three WWTPs. The concentrations of methane were highest at WWTP1, where a median concentration of 1400 ppm$_v$ was recorded at S5, while other points onsite were generally less than 40 ppm$_v$. It is worth noting that the GHG analyzer employed has a linear dynamic range up to 1000 ppm$_v$, and any concentrations above that threshold should be considered semi-quantitative. At WWTP1 they do not capture or flare biogases as is done at WWTP2. The biosolids at WWTP3 are handled and processed off-site at a separate facility which produces biogas. WWTP2 has the lowest concentration at < 50 ppm$_v$ of methane at all the exhaust locations, while WWTP3 has a modest concentration of methane of 100 ppm$_v$ in its exhaust stacks (Table 18). Furthermore, methane is an important GHG with a global warming potential some 86-fold greater than carbon dioxide on a 20-year time horizon.[50] It is commonly under reported from municipal wastewater facilities.[51] Thus, we calculated estimated annual flux data (Equation 16) to contribute to global methane inventories from wastewater treatment plants (Table 18). These annual fluxes of methane, when scaled to amount of wastewater treated are 6.6 tonne/year/10^9L for WWTP1, 0.32 tonne/year/10^9L for WWTP2 and 0.91 tonne/year/10^9L for WWTP3. Considering the amount of wastewater treated at WWTP3 it has a relatively low output of methane per billion liters treated compared to that of WWTP1, although they have a similar total annual flux of methane.

Table 18: Median methane concentrations and estimated annual flux at known exhaust points at WWTPs 1-3.

	Sample Location (Exhaust points*)	Median methane Concentration (ppm)	Estimated annual flux of methane (tonne/year)
WWTP1	S5 (Post-wet + chemical scrubber)	1440	25.2
WWTP1	S7 (Post-biofilter)	40	n/a
WWTP1	S10 (Post bio-trickling filter)	8	n/a
WWTP2	S3 (Post-activated carbon scrubber)	5	n/a
WWTP2	S5 (Post-primary sedimentation treatment)	48	n/a
WWTP2	S7 (Post-activated carbon scrubber)	5	n/a
WWTP2	S9 (Post-bioreactor)	33	3.5
WWTP3	1C (Post-activated carbon scrubber)	100	9.8
WWTP3	2B (Post-modified activated carbon scrubber)	130	23.1

**Exhaust points refer to locations which vent to the atmosphere. Annual fluxes were reported where flow rates could be obtained.*

3.3 Conclusions

The data from the on-site ductwork sampling at the WWTPs has identified many VOCs at elevated concentrations. They range in concentrations depending on where they originate in the treatment stream, and how well they are removed by odour control systems and operational conditions (Table 19). The odours contributed by WWTPs are dominated by the organosulfur compounds such as MeSH, DMS and DMDS. In addition, several oxygenated VOCs (OVOCs) also contribute to malodours, such as acetaldehyde and acetic acid. In general, higher concentrations of reduced sulfur compounds, oxygenated VOCs and hydrocarbons were found in the untreated foul air streams at the WWTPs, with the exception being DMDS which was observed to be increasing under some circumstances. The ranges of exhaust (post-treatment) concentrations from the three WWTPs studied are summarized in Table 19. Interestingly, the dominant reduced sulfur compound in the exhaust air from WWTP1 was MeSH followed by DMS and then DMDS, whereas at WWTP2 we observe that DMS was the dominant reduced sulfur compound being exhausted followed by MeSH and then DMDS. At WWTP3 the composition of exhaust air changes again with the concentration of DMDS being greater than DMS which is greater than but similar to MeSH.

Table 19: Summary of 25-75 percentile concentration ranges for calibrated VOCs from the WWTPs post-foul air treatments.

m/z	**Potential Formula**	**Potential Compound**	**Conc. WWTP1 exhaust, S5,S7,S10 (ppb$_v$)**	**Conc. WWTP2 exhaust, S3,S5,S7,S9 (ppb$_v$)**	**Conc. WWTP3 exhaust, 1C,2B (ppb$_v$)**
45.025	$(C_2H_4O)H^+$	Acetaldehyde	2-860	3-70	2-10
49.010	$(CH_4S)H^+$	Methanethiol	25-2500	1.5-40	6-155
59.048	$(C_3H_6O)H^+$	Acetone	3-250	2-60	3-45
61.028	$(C_2H_4O_2)H^+$	Acetic Acid	2-12	1-7	7-10
63.022	$(C_2H_6S)H^+$	Dimethyl sulfide	2-1000	8-250	7-180
69.069	$(C_5H_8)H^+$	Isoprene	1-40	2-14	7-48
79.057	$(C_6H_6)H^+$	Benzene	0-1	0-2	1-5
93.070	$(C_7H_8)H^+$	Toluene	0-22	0-14	6-34
94.998	$(C_2H_6S_2)H^+$	Dimethyl disulfide	20-400	0.5-40	8-340
107.086	$(C_8H_{10})H^+$	Ethylbenzene/xylenes	0-3.5	0-2	1-11
137.132	$(C_{10}H_{16})H^+$	Monoterpenes (α-pinene)	2-66	1-100	2-45

*Exhaust refers to the outlet concentrations at the odour control technology post-treatment. 25-75 percentile range calculated from sample points listed above.

The total odour contributions from methanethiol, dimethyl sulfide and dimethyl disulfide are summarized in Table 20, where odour potency of the combination of RSCs is calculated scaled to their respective odour thresholds (Equation 18). Methanethiol and DMDS have the same odour thresholds while DMS has an ODT 19.5 times higher than MeSH and DMDS. While the order of the mean concentrations differs between the sites, it is found that WWTP1 and 2 have similar contributors to the total odour, with MeSH being the dominant odourous compound (Table 20). At WWTP3 the dominant odourous compound is DMDS which is also the greatest contributor to their total sulfur flux. Furthermore, this shows that the most dramatic influences on odour are attributed to methanethiol and dimethyl disulfide, so focusing on the treatment of these compounds would be most valuable in regard to odour control.

Table 20: Global mean concentration and relative contribution to total odour profile for reduced sulfur compounds at main exhaust points.

	Rank order of mean concentrations	Total odour potency of RSCs	% Total Odour		
			MeSH	DMS	DMDS
WWTP1 (S5)	MeSH > DMS > DMDS	36480	80	2	18
WWTP2 (S9)	DMS > MeSH > DMDS	557	70	9	21
WWTP3 (1C,2B)	DMDS > DMS>MeSH	2180	22	6	76

**ODTs are listed in Table 1. Mean values used are the same as the values used in the annual flux calculations. ODT$_{(highest)}$ is DMS, for the three compounds listed.*

$$(18) \qquad Total\ RSC\ odour\ potency = a_{MeSH}[MeSH] + a_{DMS}[DMS] + a_{DMDS}[DMDS]$$

$$a_{RSC} = \frac{ODT_{highest}}{ODT_{RSC}}$$

$$ODT_{highest} = ODT_{DMS} \qquad ODT_{RSC} = ODT_{MeSH}, ODT_{DMS}, ODT_{DMDS}$$

At all three WWTPs it was found that the post-treatment concentrations of hydrocarbons were quite similar, with total hydrocarbons ranging throughout the treated sample locations from 3-140 ppb$_v$ (Table 19). The highest to lowest concentration of total oxygenated VOCs found on-site post-treatment was at WWTP1>WWTP2>WWTP3 (Table 19). This could be attributed to the high pre-treatment concentrations of OVOCs at WWTP1 >2000ppb$_v$, while WWTP2 and 3 had much lower concentrations <100 ppb_v. Also, the biological treatment at WWTP2 may in some cases generate OVOCs during the treatment process, where as WWTP3 utilizes activated carbon which can remove a portion of these compounds before their release. The total organosulfur compounds found post-treatment was found in ranking order of WWTP1>WWTP3>WWTP2, where WWTP1 also has the highest concentration of these compounds pre-treatment >2500 ppb_v, <1000 ppb_v at WWTP3 and WWTP2 had <130 ppb_v (Table 19). The effectiveness of the treatment methods contributes to the total output of these VOCs although the total input of these concentrations also should be considered as the loading to the treatment systems also follows the same trend as the treated exhaust concentrations.

It was observed that operational conditions play a major role in the performance of odour control systems, from the condition of sorbent media, flow rates in wet scrubbers, fouling of systems with sludge, quality of biofilter media and dosing of chemical agents. The operations at wastewater treatment plants are inherently dynamic and involve frequent upkeep and management to keep treatment systems in working order. Interpreting the data collected at working WWTPs can be challenging as many factors can influence observed concentrations. These factors include the amount of wastewater coming into the plant, maintenance schedules, hardware failures, installations and changes to operations of wastewater treatment systems, not to mention factors such as diurnal and seasonal variability in influent composition.

In this discussion we focused on three of the dominant malodourous gaseous VOCs measured, methanethiol, dimethyl sulfide and dimethyl disulfide. Of the three organosulfur compounds, methanethiol was typically the best removed by all the treatment processes on the order of 80% or better removal from the inlet concentrations (Table 21). This may be due to the similarity of methanethiol and hydrogen sulfide, as many systems are engineered around regulations associated with this toxic gas. Although H_2S concentrations were not monitored in this study, operators routinely measure these to remain within the allowable limits of concentration of worker safety. An interesting observation after treatment, was the production of dimethyl disulfide in some treatment systems, most dramatically observed in the activated carbon scrubbers and the wet scrubber systems. The biofilters, bioreactors, and chemical scrubbers were not observed to act as a significant source of dimethyl disulfide although their removal efficiency was generally less than 20% (Table 21). All of the operational WWTP odour treatment systems showed modest removal efficiency for DMS ranging from 0 - 40% (Table 21). The wet scrubbers and the biofilter systems generally showed better removal efficiency for DMS compared to the activated carbon scrubber towers.

During this study it was observed that advanced oxidation treatment was very promising, with a high removal efficiency greater than 98% for all three reduced sulfur compounds measured. This short duration pilot study also noted elevated ozone in the exhaust gases which may need to be investigated further.

Furthermore, emissions from the three WWTPs were evaluated at the main odour controls for the three reduced sulfur compounds investigated and was estimated a total yearly emission as sulfur from the three compounds combined was 97 kg/year at WWTP1 and 18 kg/year from WWTP2 and 115 kg/year from WWTP3. Interestingly the WWTPs all had a different major contributor to the sulfur flux, WWTP1 had the majority of sulfur contributed by methanethiol, WWTP2's major contributor was dimethyl sulfide and WWTP3's majority of sulfur was from dimethyl disulfide. When normalized to approximate annual wastewater influent treated the annual flux of sulfur per billion litres treated is 25.5 kg/year/10^9 L at WWTP1, 1.6 kg/year/10^9 L at WWTP2 and 3.19 kg/year/10^9 L at WWTP3. In this perspective WWTP1 has the highest output of sulfur contributed from MeSH, DMS and DMDS during the treatment of wastewater, while WWTP2 and WWTP3 output much less sulfur, with a 10-fold difference from WWTP1. Although, WWTP2 and WWTP3 include new and upgraded wastewater treatment technologies compared to WWTP1 which is currently undergoing updates to the wastewater systems.

Concentrations of a potent greenhouse gas, methane were also recorded and used to estimate the annual fluxes ranging from 3-25 tonnes/year at the main exhaust points for the three WWTPs examined here. Scaling these by amount of wastewater treated yields a similar output of methane per 10^9L for WWTP2 and WWTP3, while WWTP1 had 6 times greater output than WWTP2 and 3.

This work has outlined and characterized VOC concentrations over time and treatment processes. This data was used by engineering service departments to better control the release of three malodours organosulfur compounds (methanethiol, dimethyl sulfide, dimethyl disulfide) and resulted in significant improvements in performance of the odour control systems and operations of three WWTPs. At each of the exhaust points the concentrations of the malodourous compounds were found above their odour thresholds and although treated with an odour control technology were not entirely removed from the exhaust gas stream. While dispersion in the atmosphere will result in significant dilution, it is possible that under some atmospheric conditions malodours resulting from WWTP operations may be reported in the nearby vicinity. The focus of the next chapter is on monitoring these compounds in a moving vehicle to provide neighborhood scale spatial distributions.

Table 21: Average removal efficiencies of methanethiol, dimethyl sulfide and dimethyl disulfide from odour control technologies at WWTP1, 2, 3.

%Decrease from odour control technologies (Average of removal efficiencies across all sample days)			
Odour control system	Methanethiol (CH_3SH)	Dimethyl sulfide (C_2H_6S)	Dimethyl disulfide ($C_2H_6S_2$)
WWTP1 – Wet scrubber 1 + 2	53%	17%	-22%
WWTP1 - Chemical scrubber	20%	0%	0%
WWTP1- Biofilter *	70%	38%	0%
WWTP2- Activated carbon scrubber 1 + 2	70%	23%	-8%
WWTP2- Bioreactor	81%	12%	20%
WWTP3- Activated carbon scrubber tower (primaries)	93%	-10%	-460%
WWTP3-Activated carbon/modified activated carbon scrubber (secondaries)	96%	11%	-360%

*Biofilter exhaust is measured on top of the filter bed and is open to ambient air, the pre-treatment concentrations are taken directly from ductwork and may influence the %removal as the air is diluted as it is passed through the filter bed.

-Negative % decrease indicates a higher concentration post-treatment and are highlighted in dark grey.

% removal efficiency of 0 +/-5% are reported as zeros.

-Negative removal efficiency is capped at -1000%, anything below this value will be shown as -1000%.

Chapter 4: Community Ambient Air Monitoring

All fieldwork was led by Trevor Michalchuk, including data collection, visualization, data analysis, data interpretation, and piloting the vehicle. Additional assistance was provided by Lily Eggert and Erik Krogh. Inverse distance weighted maps were generated with the assistance of Ben Odia (GIS student).

4.1 Introduction and Background

An integrated strategy, which incorporates both on-site and mobile VOC assessments, is a valuable tool for tackling odour complaints and mitigating the effects of VOC emissions. To comprehend and alleviate the effects of VOCs originating from wastewater treatment plants, a comprehensive evaluation of aspects such as emission sources, dispersion patterns, and neighborhood consequences is necessary. By employing tactics to reduce VOC emissions and manage odours, these facilities can enhance the safeguarding of public health and the environment, while also preserving community well-being.[75,76]

Mass spectrometry provides high sensitivity and specificity for identifying a diverse variety of VOCs with varying chemical compositions and quantities. This style of monitoring enables analysis of variations in emissions over time and space to assess daily patterns, yearly trends, and abrupt changes in air quality. Furthermore, it allows for adaptive sampling. If elevated concentrations are detected, we can focus in on that area in real time. Mobile mass spectrometry data can be integrated with additional environmental monitoring data, such as meteorological data and geographic information systems (GIS), to enable comprehensive examination and modeling of VOC dispersion.[75] This data fusion methodology provides a comprehensive evaluation of the spatial and temporal patterns of VOC emissions from wastewater treatment plants.

The main research questions related the community ambient air monitoring investigations are:

1) Can we detect any methanethiol, dimethyl sulfide or dimethyl disulfide in the ambient air around the wastewater treatment facilities?
2) At what distances from the wastewater treatment facilities can we measure the reduced sulfur compounds above their odour detection thresholds?
3) Are there other sources in the community of the three reduced sulfur compounds?

To answer these questions, the use of on-road mobile measurements using the MMSL was done in the community surrounding the three wastewater treatment facilities described in Chapter 1. In addition, to the facilities themselves, malodours can arise from associated infrastructure such vents in wastewater conveyances and pump stations. While wastewater treatment is known to contain elevated levels of reduced sulfur compounds and methane,[40,44,77] there are other sources of these compounds in a community for example, diesel exhaust may contain these compounds and natural gaspowered buses could also emit unburned methane.[4,34] Furthermore, a number of other bio- and anthropogenic sources can contribute to VOC loads in local airsheds including vehicular exhaust, composting facilities, and industry (e.g. pulp mills). For example, sulphate reducing bacteria and decomposition of seaweed has been found to cause release of reduced sulfur compounds. The atmospheric VOCs in a community can be a complex mixture of gases from multiple sources, therefore having on-road mass spectral measurements aids in the deconvolution and assessment of this mixture.

4.1.2 Data representation

The community drive data is represented in three ways, two using direct mapping of VOC concentrations. Interpolation mapping was done as the third form of visualization. The first method is using single day drives, which allows for the integration of local weather conditions such as wind speed and direction. These single day maps can provide insight and capture of gas plumes which may not be a daily occurrence and are usually highly dependent on wind speed and direction. The Single day maps are shown with a specific *m/z* plotted over space which has been converted to concentration of analyte, methanethiol, dimethyl sulfide and dimethyl disulfide. Also accompanying these analytes is methane as this gas is also emitted by the WWTP and was measured using a standalone GHG analyzer previously introduced in chapter 2. The mapping consists of a satellite image (google earth) with concentrations overlayed on the map, scaled to concentration by dot size and colour intensity with each dot being a discrete sampling point and accompanied by a wind-rose denoting the windspeed and direction during the sampling period. The maps were generated using .SHP files created using adapted Matlab® code originally written by Jon Davidson and then imported into QGIS for visualization. [78]

The second method of data representation is using a geospatial averaging method, which slices the map into imaginary 50m x 50m blocks, where any discrete sample which falls into the block will be compiled and used together for statistical analysis. This method allows for compilation of all drive data to look for patterns in the data, find the mean, standard deviation and maximum concentrations captured during the whole sampling campaign. Each block is scaled to analyte concentration by colour intensity and is subject to influence from all sampling days. This type of mapping can be tailored to any size block which is desired and was chosen at 50x50m blocks to capture more data points per block to average and analyze. These maps were made using code developed in Matlab® (adapted from Jon Davidson) and visualized using QGIS software (http://www.qgis.org).

The third form of representation is using total drive data in an interpolation algorithm, inverse distance weighting (IDW), which provides a distribution of concentrations over areas which were not sampled, informed by the collected data.[79] This form of interpolation uses the real data points collected to model unsampled locations based on concentration of the real data points and their distance to the modeled data points. Along with distance from the modeled data points to the real data points a power function is used in the model which is informed by a certain number of real data points which are close to the modeled data point or is given by an average calculated from the whole data set. The inverse distance from the real data points to the modeled data points is set to the power function and creates a model which simulates the concentrations being lower at farther distances from the real data points which inform the model. This form of interpolation was used to explore the possibility of using real-drive data to create geospatial models of concentrations in the study areas and is one of many forms of interpolation mapping. As with many forms of interpolation mapping, they require optimization to produce quality results, the IDW maps in this chapter are for example only and are not fully optimized and should not be taken as definitive. This form of mapping using a heat-map style visualization is a user-friendly format to explore for data presentation. These maps were generated with the assistance of Ben Odia in ArcGIS® using Python® scripts.

Elevation contour maps (generated by Ben Odia) from the community drive locations are presented at the beginning of the community drive sections to assess topography of the locations. Representative single day maps of methanethiol and dimethyl sulfide are shown in the following sections. In addition to the single day maps, geospatially averaged maps showing methanethiol, dimethyl sulfide, dimethyl disulfide and methane are presented. Furthermore, example interpolation maps using IDW are shown to explore an additional method of data visualization. On the IDW maps an overall average wind vector is shown from the compiled wind vectors during all the sampling days. Additional single day geospatial representations are included in Appendix B. The sampling dates and times from the community and on-site drives are summarized in Appendix B.

4.2 WWTP 1 – FCPCC Community and on-site Drives

Community drives took place from 2022-2024 in the surrounding location around WWTP1 (Figure 31). The sampling dates and times are summarized in Appendix B and include individual sample days mapping of VOCs. WWTP1 is adjacent to a small forest to the west and across the street from a marina to the northeast. It is in a residential area which includes many homes built close to the WWTP (<0.25-2 km). There is a small river and valley to the northwest of WWTP 1 which flows beside the WWTP property and drains into the ocean. The inland highway is located between the WWTP and the marina. The marina and the inland highway are sources of VOCs to the local area which may influence the air quality, these VOCs can be generated from vehicle exhaust including cars, trucks and boats. Marine and estuarine locations can be sources of reduced sulfur compounds from microbial activity and decomposition of vegetation and were included in the community drive route to characterize other possible sources of reduced sulfur compounds in the local area. The drive route encompasses all drivable directions around the WWTP within 2 km, as the air quality in the local area may be influenced by WWTP gases and has led to odour complaints from some of the residents in the area.

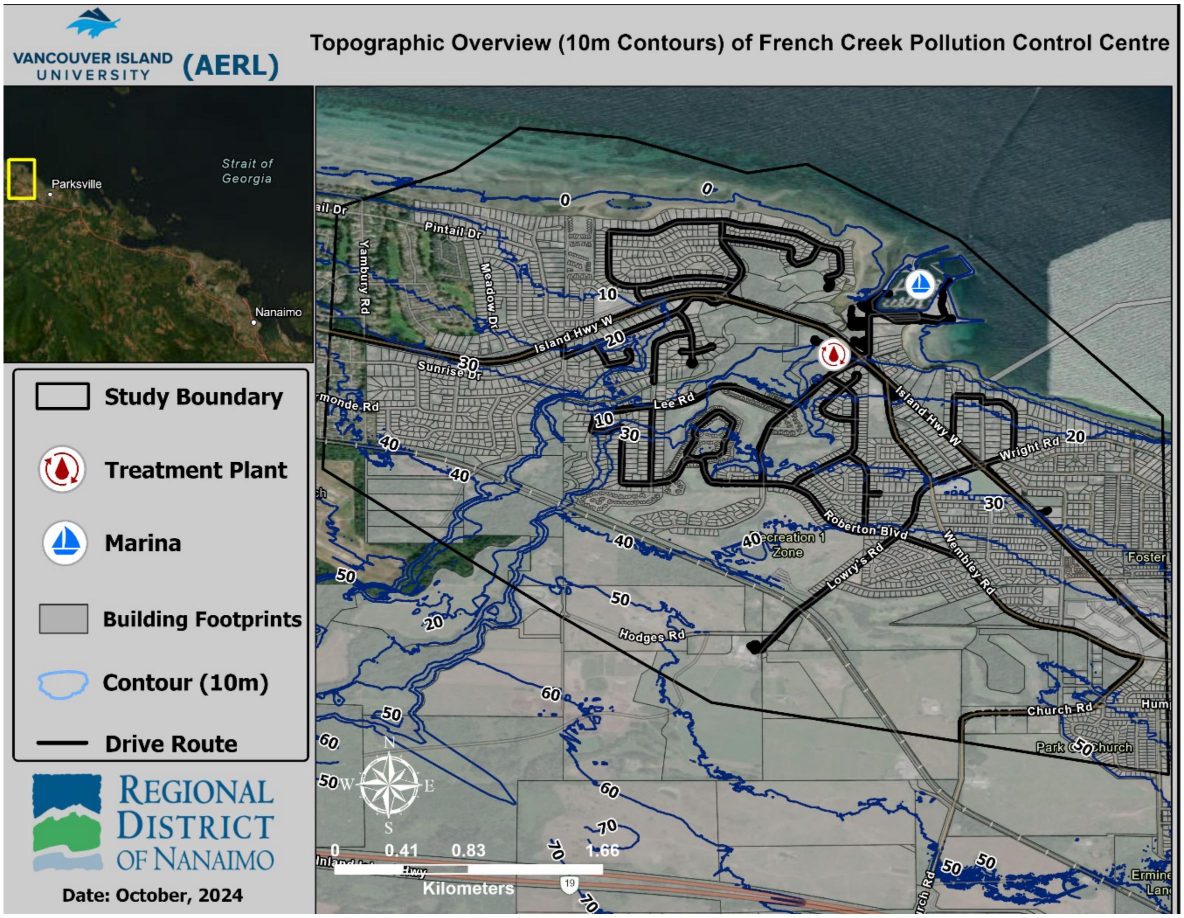

Figure 31: Contour map for FCPCC community drive area. Contours shown in meters (blue), WWTP1 (white circle) and typical drive route (black) are shown. Figure courtesy of Benjamin Ikhuoria Odia (Adv. Dip. GIS).

4.2.1 Single day mapping of WWTP1 community

An example map from a single day community drive (May 4, 2023) plotting methanethiol (MeSH) concentration over space is shown below (Figure 32). This day the windspeed was modest (<10 m/s) and wind direction was distributing MeSH downwind to the southeast and into the nearby community (Figure 32). Concentrations on-site were >5 ppb$_v$ and on the adjacent roadway were measured at concentrations ranging from 1-4 ppb$_v$. Further downwind up to 0.5 km away concentrations were detected in the range of 0.2-1.2 ppb$_v$ which is above the odour threshold for MeSH (ODT=0.02 ppb$_v$) and was a potential source of odour in the community. In addition to the methanethiol detected downwind of the WWTP, minor amounts were detected by the marina, which may be originating from biogenic sources or possibly from burning diesels fuels which are not sulfur free.

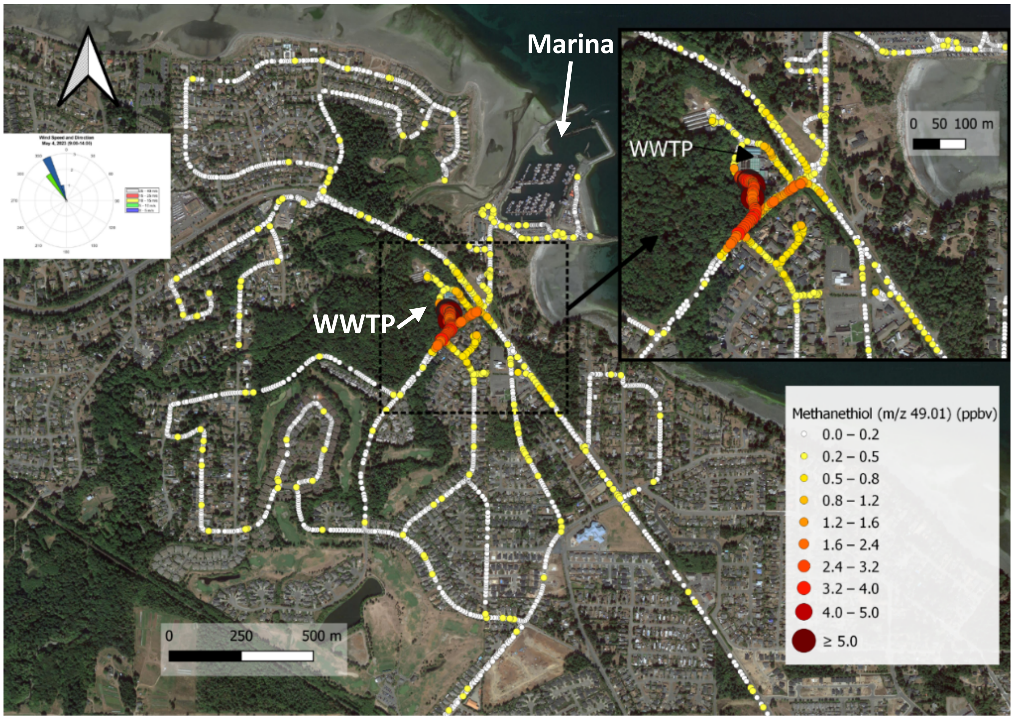

Figure 32: Satellite photograph of WWTP1 community, overlay contains concentrations measured of methanethiol over ground by MMSL. Windrose shows prevailing windspeed and direction during community sampling. May 4, 2023.

A single day map from November 6, 2023, showing concentrations of dimethyl sulfide is shown below in Figure 33. On this day concentrations of dimethyl sulfide (DMS) were >5 ppb$_v$ on-site at the WWTP. The wind was blowing to the west this day (<5 m/s) and elevated levels (0.5-1.2 ppb$_v$) of dimethyl sulfide (ODT=0.39 ppb$_v$) were detected in the community on the other side of the small forest (Figure 33). This day elevated levels of methanethiol were also detected in the same area (Appendix B). The concentrations of reduced sulfur compounds were low <2ppb$_v$ in the community, although they were above their odour detection threshold and were noticeable in the air down-wind of the WWTP and on-site. Also, minor amounts of dimethyl sulfide were detected on the roads close to the WWTP upwind. On this day minor amounts of dimethyl sulfide were detected near the marina and close to the beach, which may be originating from biogenic sources as they are upwind of the WWTP. This data illustrates the driving force that windspeed and direction play in distributing WWTP VOCs into a community, showing elevated levels of DMS up to 1 km from the WWTP.

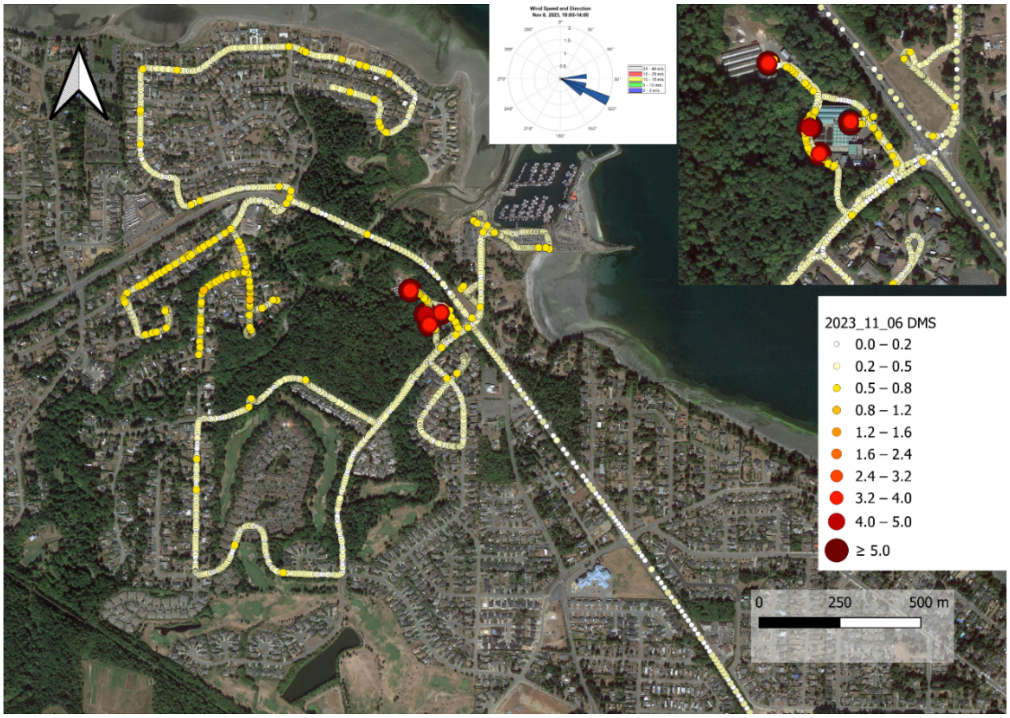

Figure 33: Satellite photograph of WWTP1 community, overlay contains concentrations measured of dimethyl sulfide over ground by MMSL. Windrose shows prevailing windspeed and direction during community sampling. Nov 6, 2023.

Not all drive days were influenced by the same wind speed and direction, although on other occasions VOC concentrations were found to also be above odour thresholds up to 1 km away from the WWTP. Therefore, the WWTP can have impacts on the local communities' air quality. Additional single day mapping is presented in the supplemental information Appendix B.

4.2.2 Geospatial Averaging Maps and Interpolation mapping using IDW for WWTP1

Geospatial averaged maps are shown below of methanethiol, dimethyl sulfide, dimethyl disulfide and methane (Figure 34). The maps consist of over 26 hours of data compiled over the whole sampling campaign and show the mean concentrations of each analyte in the given 50m x 50m block (>90,000 observations). The mean concentration shows the consistent nature of these analytes in a given space over the sampling campaign, dampening the effect of 'one-off' sampling days which have had a higher concentration in one area, and shows the greater likelihood of measuring the analyte in that area at any time. The main clustering of elevated concentrations of all analytes is found by the WWTP, which is expected. Although, other elevated concentrations have been found on the adjacent road south of the WWTP and to the west of the WWTP. Both elevated concentrations in those areas show probable influence on the air quality from the operations of the WWTP and may contribute to the generation of local odour complaints in those areas (Figure 34). Although Methane does not have a malodour associated with it, and has other possible sources, it is often emitted in higher quantities and in similar locations to the reduced sulfur compounds investigated in this study. Also, Methane is detected by instrumentation which may be more portable and less expensive than a mass spectrometer and still give vital information on the potential impacts from wastewater VOCs and could be used as a screening tool.

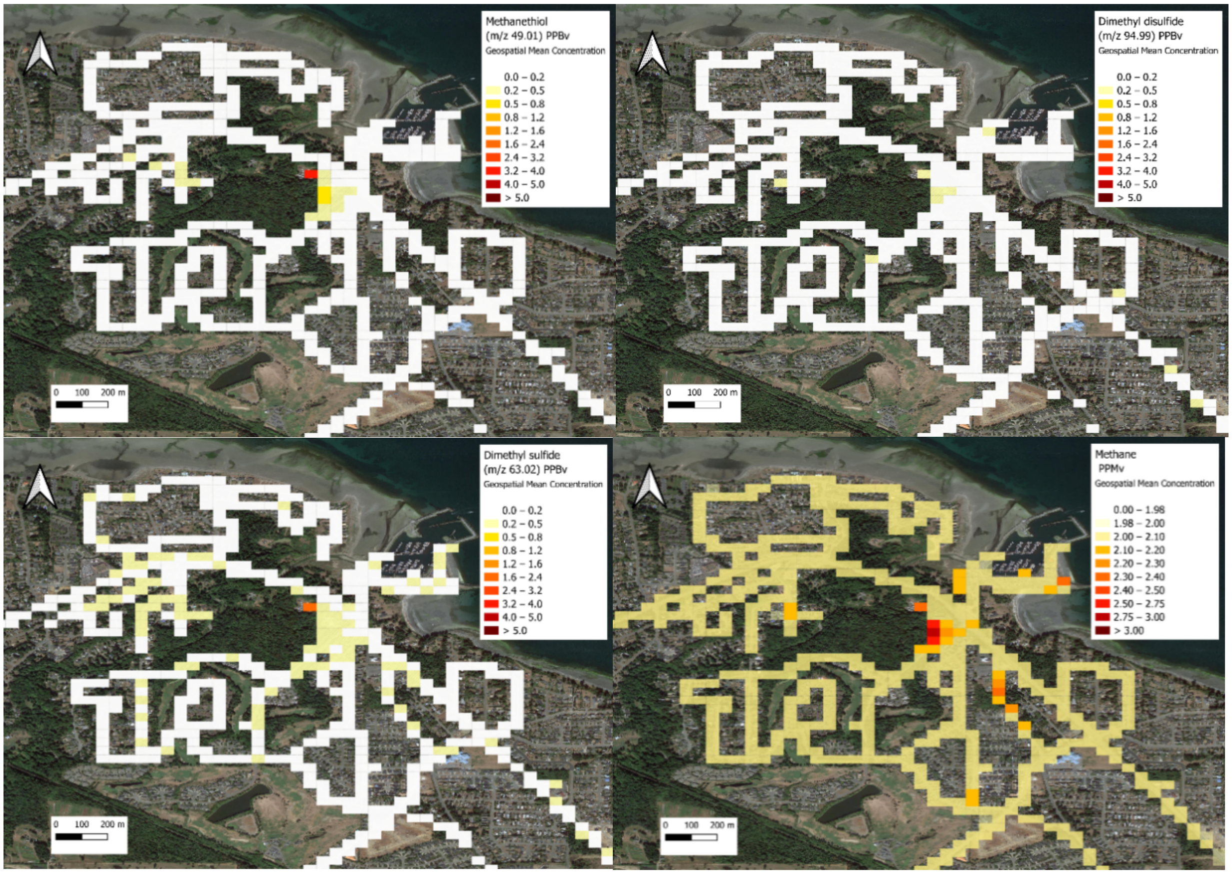

Figure 34: Geospatially averaged maps from WWTP1 community drive, showing concentration means of methanethiol, dimethyl sulfide, dimethyl disulfide and methane. All drive data from the campaign is compiled in these figures.

The IDW interpolation maps from WWTP1 show a hotspot for the reduced sulfur compounds and methane centralized at the WWTP (Figure 35). The intense red colour shows the elevated concentrations (>4 ppb_v) of the compounds on-site at WWTP1, while some minor elevated concentrations (>1 ppb_v) are seen surrounding the facility and to the west of the facility migrating into the close by neighborhood (Figure 35). There is a slight elevation in concentration captured near the southern edge of the map for dimethyl sulfide (>1.6 ppb_v) and methane (>4 ppm), where there is a local farm which has livestock and may be influencing the concentrations in that area (Figure 35). To note, this model has not been thoroughly optimized and is for example only. Yet, this form of mapping greatly reflects the geospatial averaging maps seen previously and provides a more user-friendly representation.

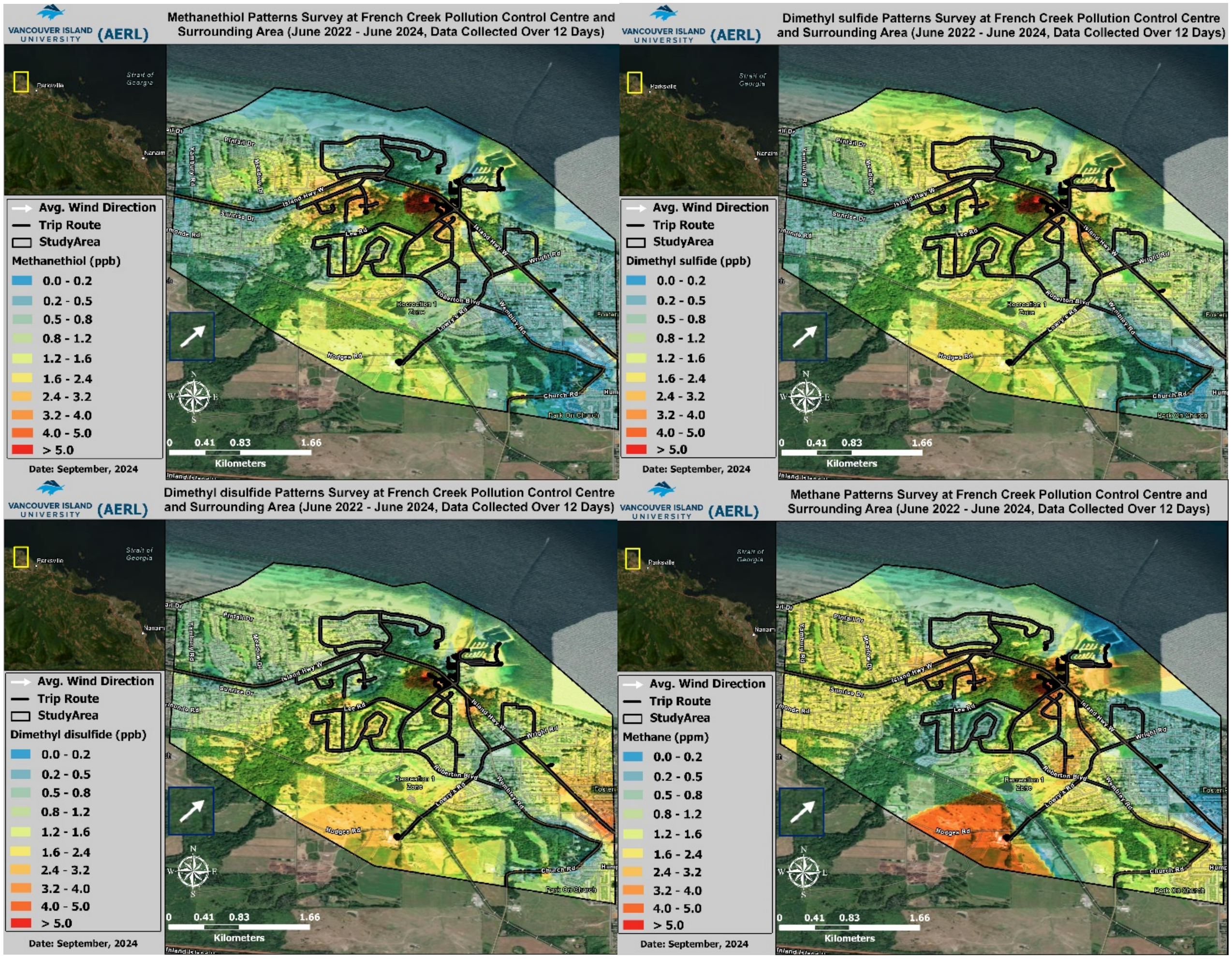

Figure 35: Community interpolation maps for methanethiol, dimethyl sulfide, dimethyl disulfide, and methane at WWTP1 using all drive data in IDW model. Figure courtesy of Benjamin Ikhuoria Odia (Adv. Dip. GIS).

4.3 WWTP2 – GNPCC Community and on-site Drives

Community drives took place from 2022-2024 in the local community around WWTP2 (Figure 36). The sample dates and sampling times are summarized in Appendix B. WWTP2 is situated in a residential area, adjacent to a small forest to the north, and close to the ocean on the north and east sides (<0.5 km). A busy road is located near the fence line to the south of the WWTP and is a source of vehicular VOCs to the area, further to the south there are homes built on a large hill (>70 ft elevation). On the east side of the WWTP there is a school and on the west side there is a residential area with many homes. The drive route also passes by a pump station which delivers sewage to the WWTP and is on the northwest portion of the drive route near the ocean (Figure 36). The drive route encompasses drivable areas surrounding the WWTP and was chosen to investigate the likelihood of WWTP gases influencing the local air quality and generating odour complaints from the nearby residences.

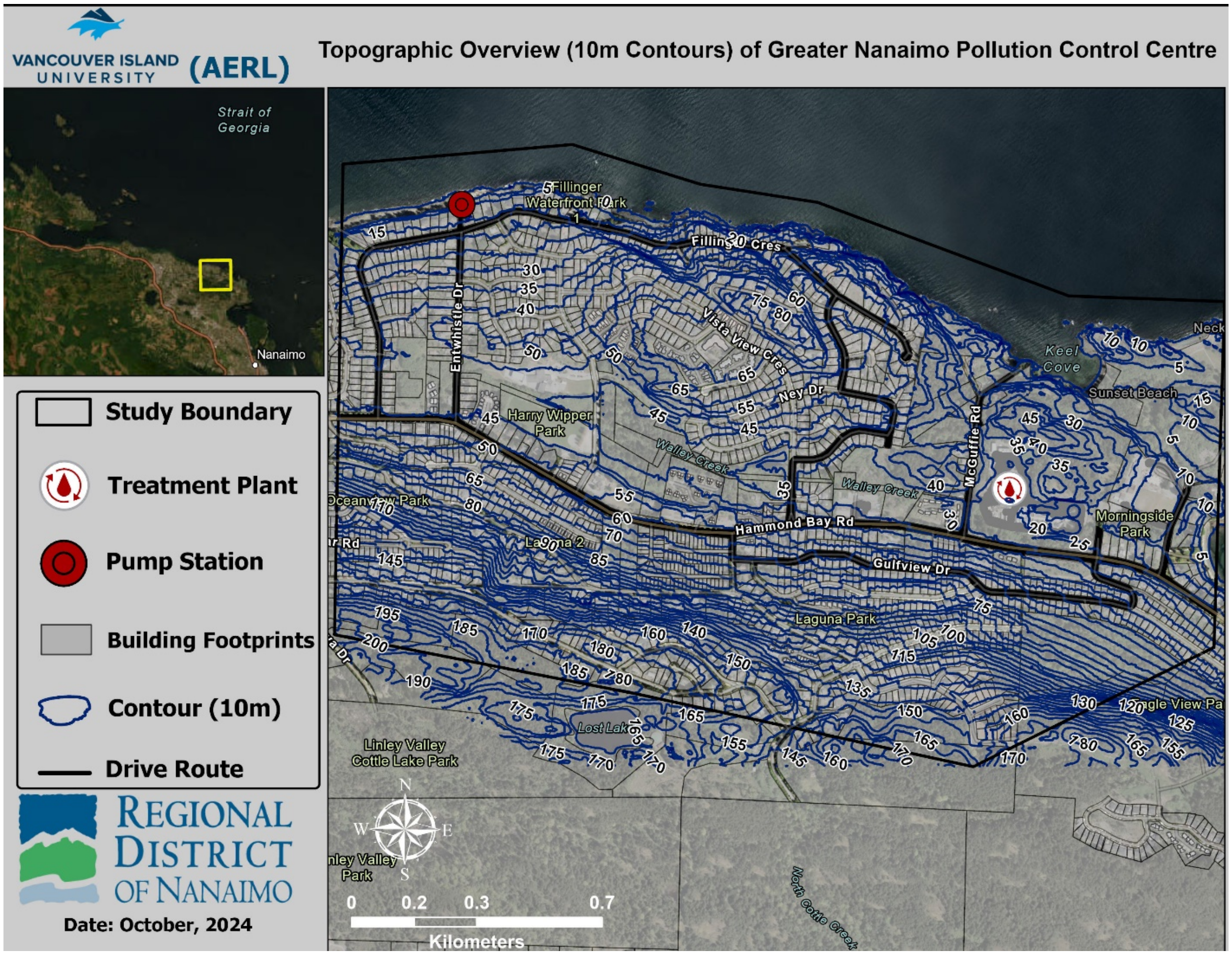

Figure 36: Contour map of WWTP2 community area labelled in meters(blue), Pumpstation marked on map (red circle), WWTP2 (white circle), typical community drive route (black). Figure courtesy of Benjamin Ikhuoria Odia (Adv. Dip. GIS).

4.3.1 Single day mapping at WWTP2 community

An example of the single day mapping from WWTP2 is shown below, concentrations of methanethiol (MeSH) are plotted as an overlay on the map (Figure 37). During this sampling day in June 2023, concentrations of MeSH are detected onsite clustered on the southern portion of the WWTP property and detected around the peripheries of the WWTP, in ranges of 0.2-1.8 ppb_v (Figure 37). Also, on this sampling day slightly elevated levels of MeSH (<0.8 ppb_v) were detected close to the pumpstation located on the northwest portion of the drive route and also found on the adjacent road to the WWTP and about 0.25 Km away to the west on a dead-end portion of the drive route at one of the parked sampling locations (Figure 37). The wind rose accompanying the map shows prevailing wind direction and speed (<0.5 m/s) during the sampling times and indicates possible intrusion of MeSH into the nearby community from the WWTP. Although concentrations were quite low in the community (>1ppb_v), they were detected above the odour threshold and could contribute to odours in the community.

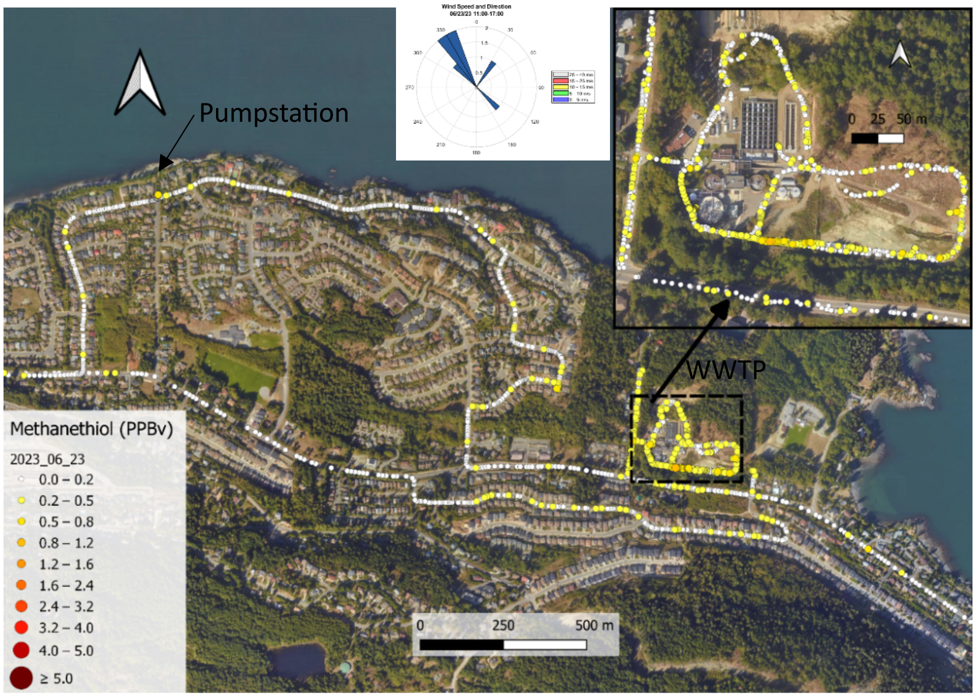

Figure 37: Single day community drive from WWTP2, showing concentration over ground measured by MMSL of methanethiol. Windrose shows prevailing windspeed and direction during sampling.

The accompanying single day map from June 23, 2023, for dimethyl sulfide is shown below (Figure 38). On this day dimethyl sulfide concentrations were elevated in some areas on-site >1.2 ppb_v. On the adjacent road to the west of the WWTP elevated concentrations of DMS (ODT=0.39 ppb_v) were also detected >1.2 ppb_v which are above odour detection thresholds and were detectable by olfactory assessment (Figure 38). Similarly to the methanethiol, the DMS was also detected near the pumpstation, and detected on the road at >0.8 ppb_v and in the cul-de-sac to the west of the WWTP about 0.25 km away (Figure 38). This information shows that the WWTP in some cases can be a source of odour to the near-by community, and that other sources of odours like the pumpstation could also play a role. Additional single day mapping is presented in the supplemental information appendix B.

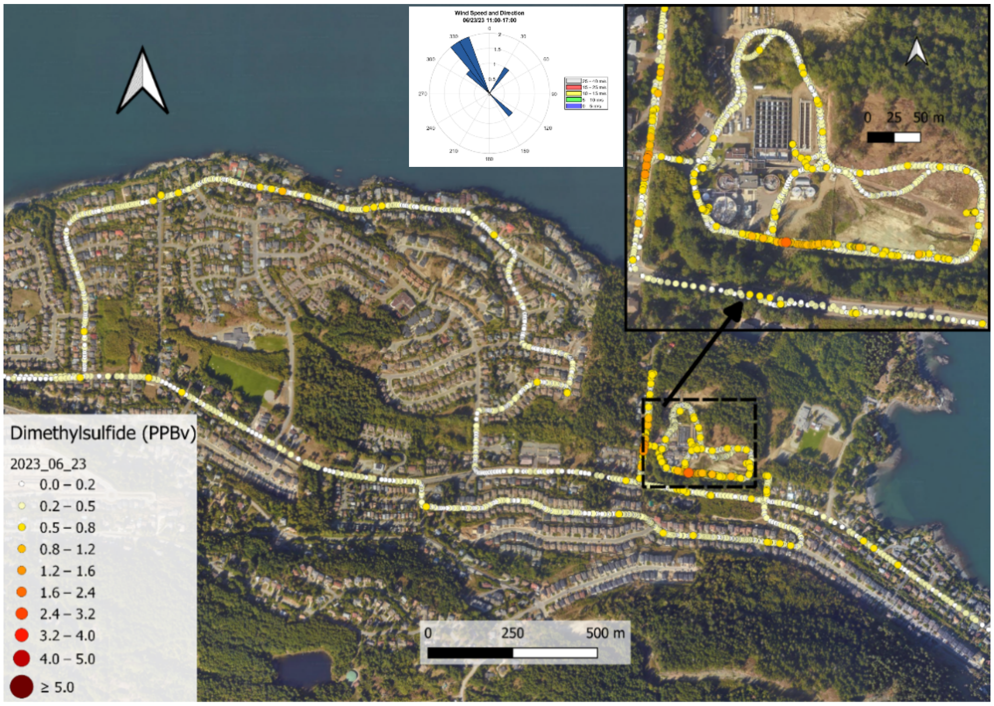

Figure 38: Single day community drive from WWTP2, showing concentration over ground measured by MMSL of dimethyl sulfide. Windrose shows prevailing windspeed and direction during sampling.

4.3.2 Geospatial Averaging Maps and Interpolation mapping using IDW for WWTP2

Maps showing the geospatially averaged concentrations from the whole campaign consisting of over 20 hours of data are illustrated below (>70,000 observations), including methanethiol, dimethyl sulfide, dimethyl disulfide and methane (Figure 39). The global mean from each 50m x 50m box is plotted, scaled to concentration by colour intensity. During the sampling campaign many weather events were observed, and single day excursions are dampened in this mapping style. The main clustering of elevated concentrations from all analytes shown are at the WWTP location, which is to be expected (Figure 39). The methanethiol concentrations from the whole campaign did not indicate any constant infiltration into the nearby community and were constrained to the WWTP site, indicating that when odours get into the community it is most likely that a certain meteorological condition is taking place and is not constant.

The concentrations of dimethyl sulfide on the other hand were detected at elevated levels (>0.5 ppb_v) when the global mean is considered during the sampling route, showing elevated levels near the road to the east of the WWTP and clustered around the adjacent road to the WWTP and at the Pumpstation (Figure 39). These findings for dimethyl sulfide could indicate that the WWTP is contributing to localized odours nearby the fence line of the WWTP and also originating from the pumpstation which can be distributed to the nearby community.

The dimethyl disulfide concentrations (>0.5 ppb_v) were mainly clustered around the WWTP and were observed in the nearby community >0.25 Km from the WWTP and could cause odour problems (Figure 39). Dimethyl disulfide also has other anthropogenic sources such as diesel exhaust and this may have influenced the elevated levels of DMDS (>0.5 ppb_v) seen in the southwest portion of the drive route as this location has lots of influence from traffic exhaust (Figure 39).

The methane levels were closely related to the methanethiol concentrations with most of the elevated signals (>2.1 ppm) detected on-site at the WWTP or close to the road and fence line adjacent to the WWTP and could serve as a potential proxy for methanethiol infiltration offsite (Figure 39).

The example interpolation by IDW method was done using the same data from the geospatial averaging (Figure 40). This form of mapping allows for interpolation of concentrations outside the range of the actual data points collected. This allows for another form of assessment for distribution of the wastewater gases in the local community. The higher concentrations (>1 ppb_v) of the reduced sulfur compounds were focused around the WWTP and the pumpstation (Figure 40) which greatly reflects the output from the geospatial averaging maps in Figure 39.

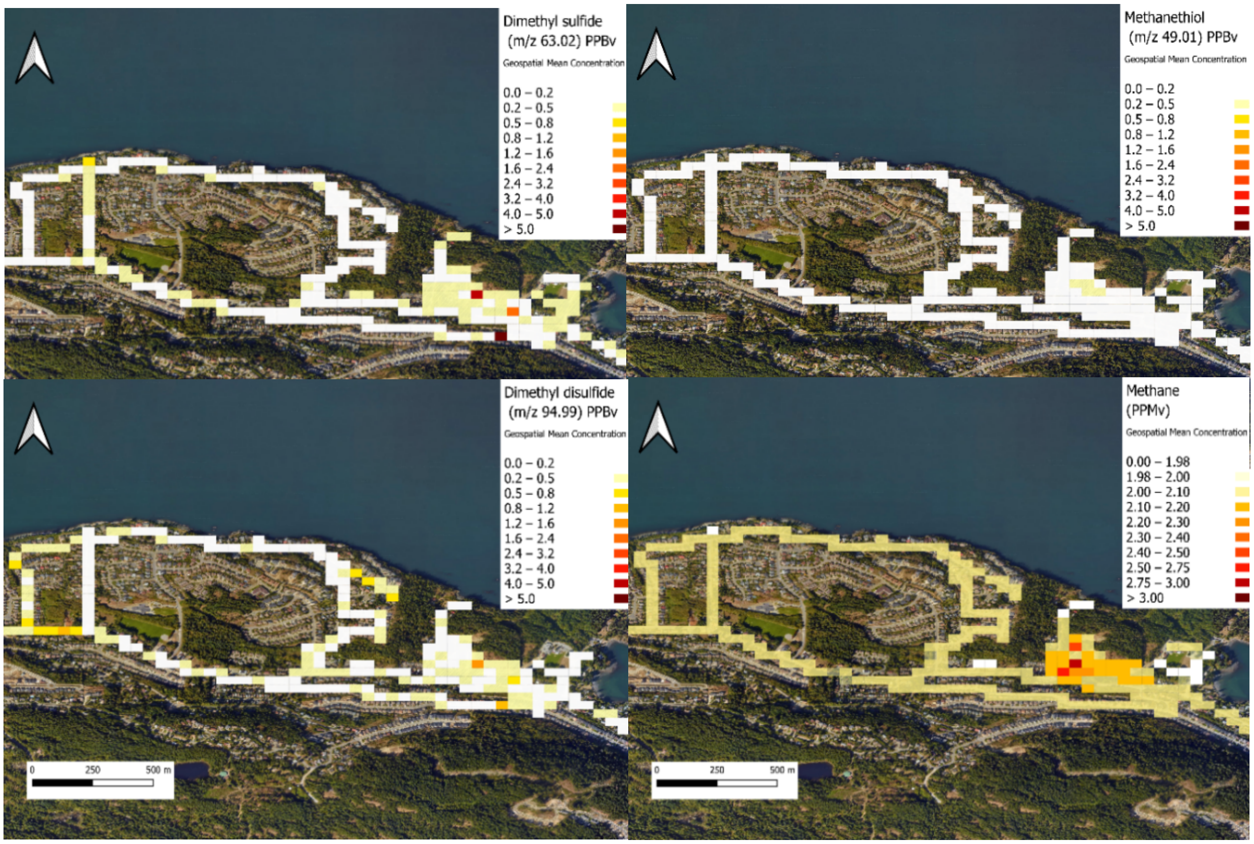

Figure 39:Geospatially averaged maps from WWTP2 community drive, showing concentration means of methanethiol, dimethyl sulfide, dimethyl disulfide and methane. All drive data from campaign is compiled in these figures.

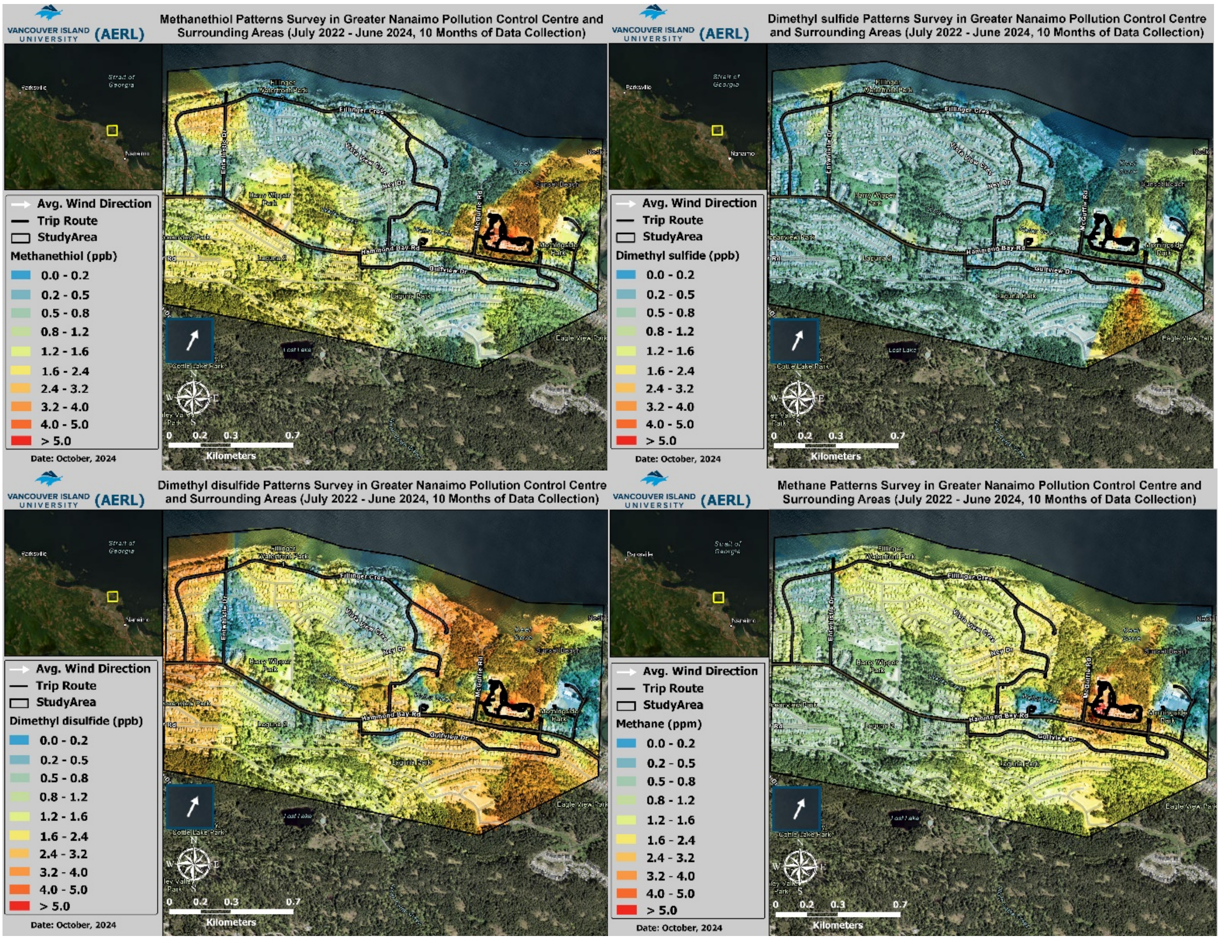

Figure 40: IDW interpolation maps for WWTP2, methanethiol, dimethyl sulfide, dimethyl disulfide, and methane. Figure courtesy of Benjamin Ikhuoria Odia (Adv. Dip. GIS).

4.4 WWTP3 - MPWWTP Community and on-site Drives

A total of 20 community drives were done in the community around WWTP3 and are summarized in Appendix B. These community drives were done to investigate the spatiotemporal distribution of methanethiol, dimethyl sulfide, dimethyl disulfide and methane. WWTP3 is located on a small peninsula extending into the bay area and close to small marinas, a sea-plane terminal and a cruise ship terminal. To the west of the WWTP there is a large pump station which feeds the WWTP and could be a possible source of VOCs (Figure 41). Many homes and apartments are located near the WWTP (>0.25km) and may be influenced by the WWTP emissions. The drive route extends >2 km from the WWTP on drivable roads and includes some near shore locations and passes by many residences and a small industrial area. This location is much more densely populated than WWTP1 or WWTP2 and has more vehicle traffic and businesses located on the drive route. There are two breweries located on the drive route one to the northwest in the small industrial area and one to the northeast and close to the ocean. There is a busy road located in the central part and far eastern portion of the drive route and is a likely source of VOCs as well as the near shore locations in some instances (Figure 46). The drive route also is co-located on roads which have conveyance lines extending to the WWTP and could be sources of VOCs. On some occasions additional sampling was done to investigate odours, including seaweed decomposition discussed below and manholes on conveyance lines of stormwater and sewage which is discussed in Appendix B. The drive route was chosen to best investigate possible infiltration of WWTP gases to the local community and to assess other sources of VOCs in the area.

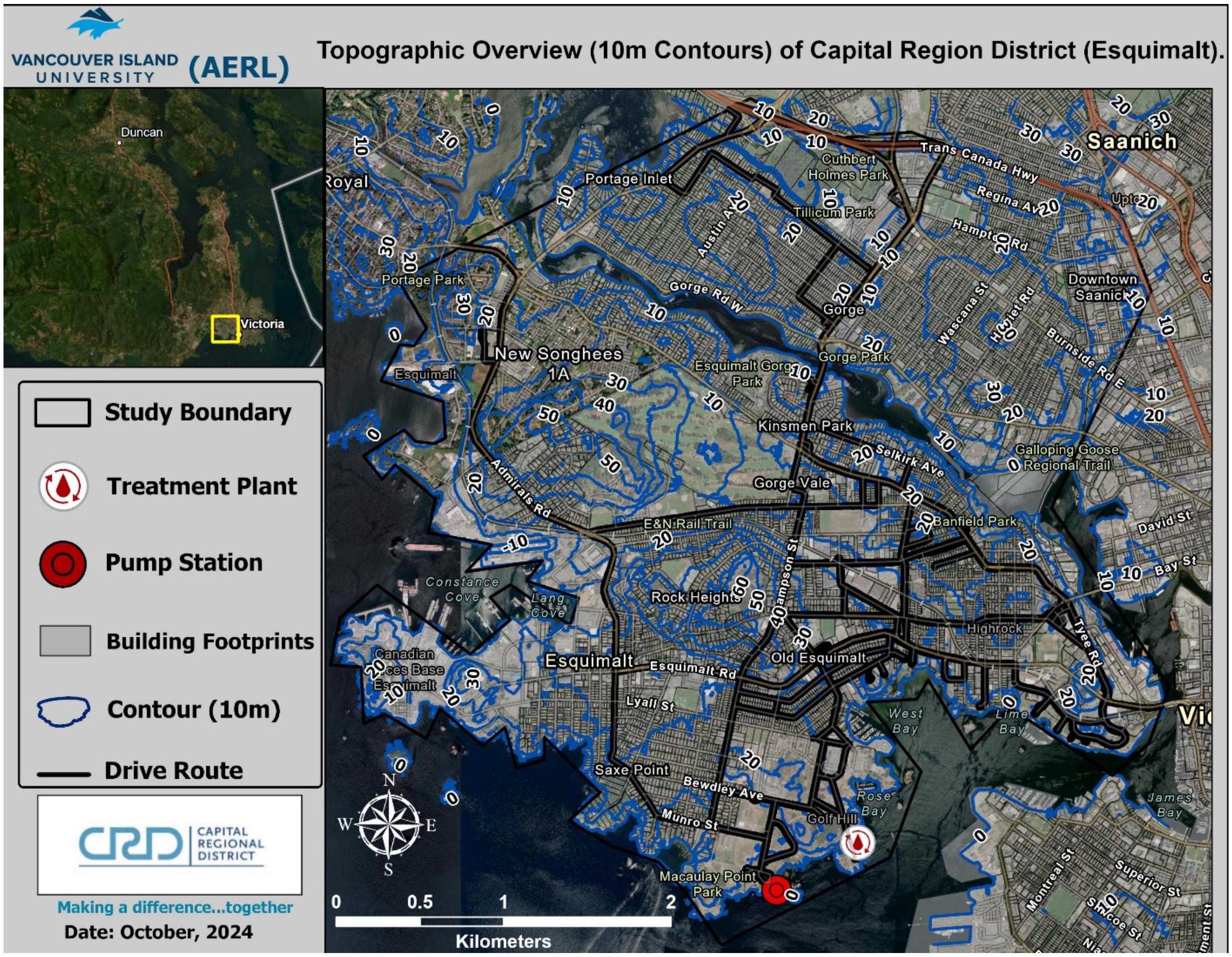

Figure 41: Contour map for WWTP3 area, WWTP3 (white circle), Pumpstation (red circle), typical community drive route (black), Contours are marked on map in meters. Figure courtesy of Benjamin Ikhuoria Odia (Adv. Dip. GIS).

4.4.1 Single day mapping from WWTP3 community

An example of a single day map showing concentrations of methanethiol (MeSH) from the May 30, 2023, community drive around WWTP3 is shown below (Figure 42). During the community drive a consistently elevated concentration of methanethiol (>0.2 ppb_v) was measured downwind of the WWTP (Figure 42). Most of the elevated concentrations (>0.5 ppb_v) of MeSH were found near the shore across the water up to 2 km from the WWTP was most likely caused from the wastewater treatment facilities VOCs infiltrating into the community (Figure 42). There were two other locations which had elevated methanethiol that day other than at the WWTP, which included the pumpstation in the southwest portion of the drive route, and on a central roadway which has conveyance lines and manholes from sewer and storm water present (Figure 42). This road was evaluated on the following day for sources of VOCs and discussed in Appendix B.

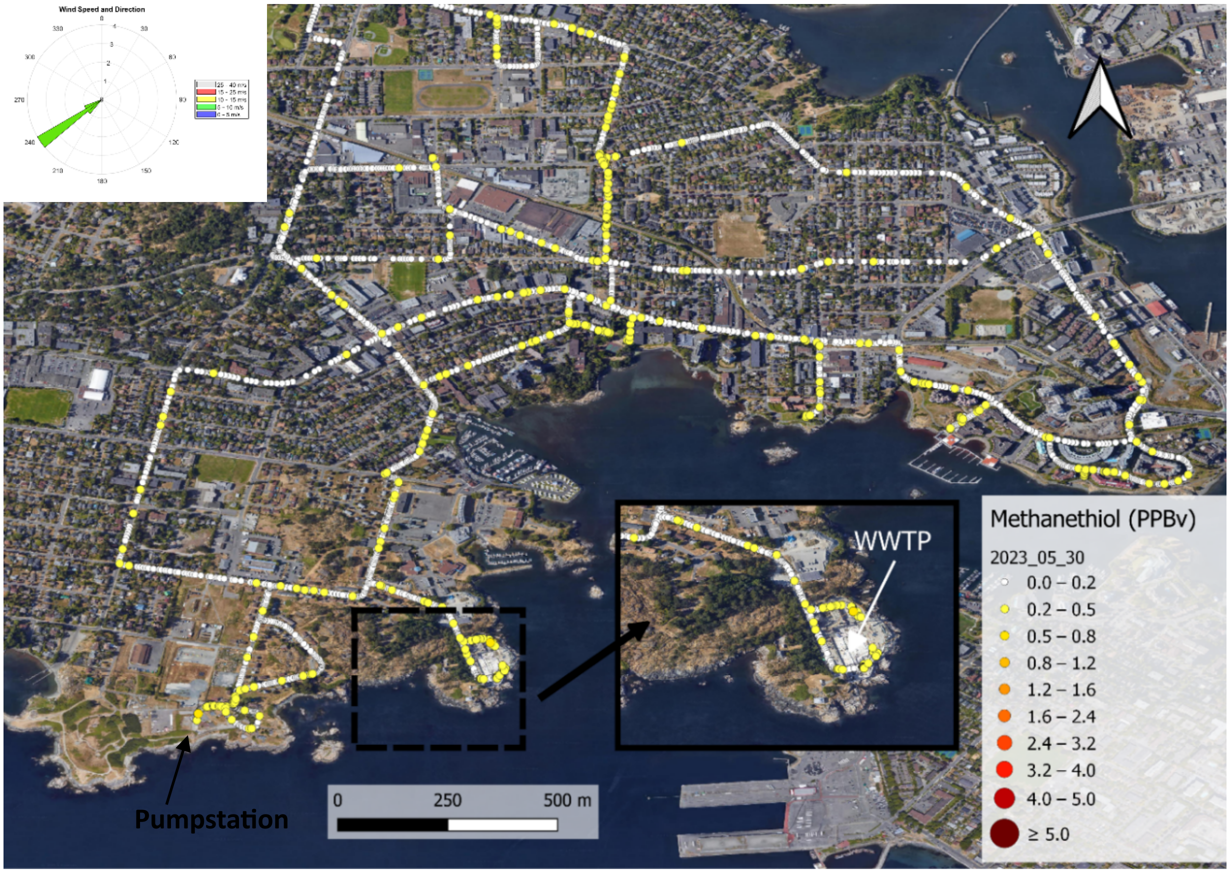

Figure 42: Single day community drive map from WWTP3, plotting concentration of methanethiol taken with MMSL. Windrose shows prevailing windspeed and direction. May 30, 2023.

An example of a single day map showing concentrations of dimethyl sulfide from the community drive around WWTP3 is shown below (Figure 43). During the community drive a consistently elevated concentration of dimethyl sulfide (>0.8 ppb_v) was measured downwind of the WWTP (Figure 43). Most of the elevated concentrations of DMS were centered around the middle of the drive route which was most likely a plume from the WWTP infiltrating into the community. There were two other locations which had elevated DMS that day other than at the WWTP, which included the pumpstation in the southwest portion of the drive route and further east of the plume which was nearby a local brewery which is also a source of DMS and the odour was a noticeable difference near the brewery compared to the plume in the more central location of the drive route (Figure 43). A common smell from the wastewater plant was detected earlier on the drive route by the northwest portion of the drive for a short period of time before the wind shifted to the other observed plume.

This data illustrates the possibility of odour contribution into the local community near the WWTP and was due to a particular meteorological condition, with winds carrying the compounds from the WWTP into the community. This was not a consistent observation over the campaign and was not captured to this extent on any other sampling trips. Additional single day mapping from the campaign is available in the supplementary information appendix B.

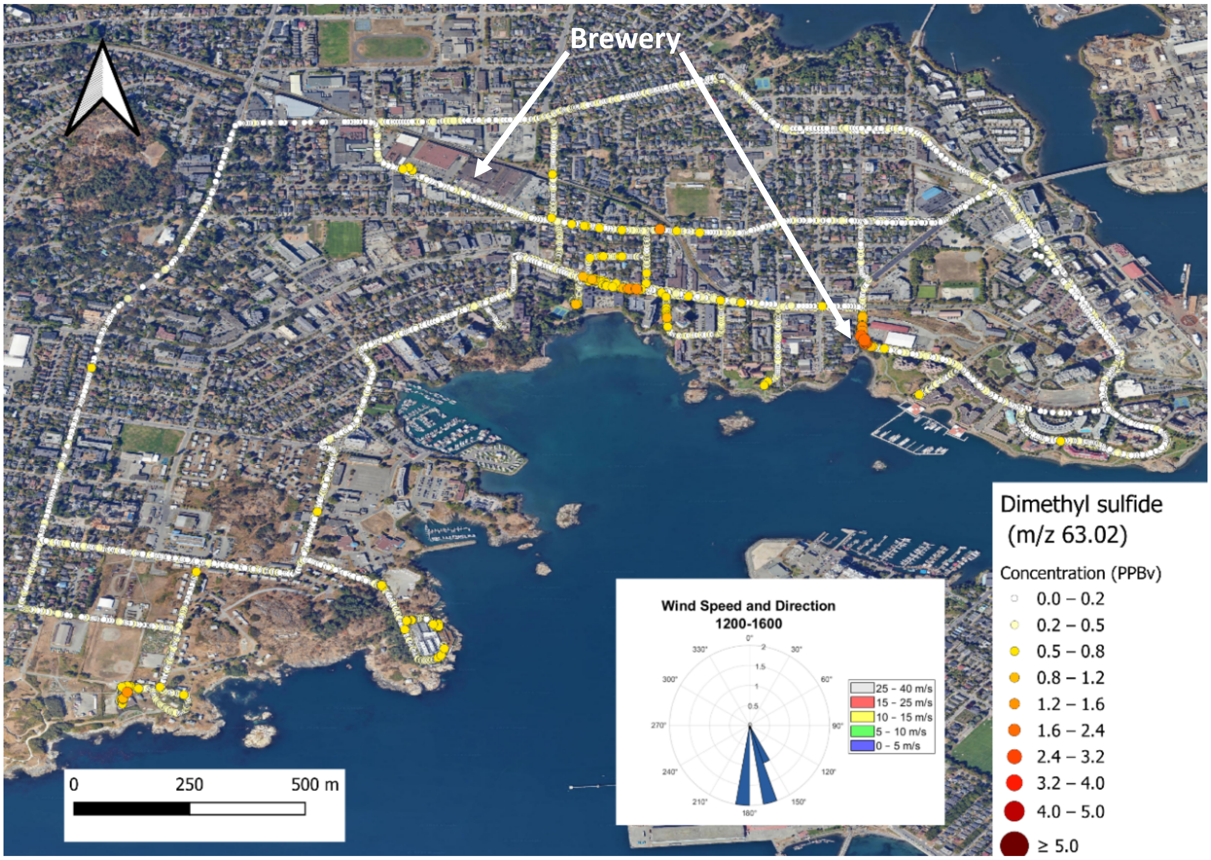

Figure 43: Single day community drive map from WWTP3, plotting concentration of dimethyl sulfide taken with MMSL. This day a clustering of elevated concentrations in taking place near the middle of the drive route. Windrose shows prevailing windspeed and direction during sampling time. June 18, 2024.

4.4.2 Geospatial Averaging Maps and Interpolation mapping using IDW for WWTP3

The geospatially averaged gridded maps are shown below including methanethiol, dimethyl sulfide, dimethyl disulfide and methane (Figure 44). The mean concentrations observed at each 50m x 50m box is plotted using compiled data from the whole sampling campaign consisting of over 60 hours of drive data (>200,000 observations). This data shows where areas may be more consistently influenced by these compounds.

The methanethiol was not on average elevated (>0.5 ppb_v) in many locations, typically onsite at the WWTP and near the community park, but not detected in the rest of the community (Figure 44). The dimethyl sulfide as found to be slightly elevated in the community (>0.5 ppb_v), with greater on average concentrations (>0.8ppb_v) found at the community park and onsite at the WWTP similar to the methanethiol, and also observed at elevated levels (>0.8ppb_v) near the pump station and on the road near the pump station (Figure 44). Dimethyl sulfide can have other sources in a community and may not all be caused by the WWTP, sources can include diesel exhaust and rotting seaweed and from other industrial sources. The Dimethyl disulfide concentrations were elevated (>0.5 ppb_v) in many regions on the drive route, although these contributions may likely not be from the WWTP and are most likely caused from diesel exhaust and industrial exhaust. The concentrations of DMDS found around the pumpstation and WWTP are likely to originate from those sources and may have an impact into the local community, although DMDS is not an ideal compound to definitively use to identify the odour source from the WWTP (Figure 44).

The methane concentrations were generally ambient (2 ppm) on most of the drive route except near the community park and by the WWTP and pumpstation where they were found above 2.2 ppm (Figure 44). These findings match the reduced sulfur compounds assessed and is likely part of those gas mixtures. In two locations on the road, near the far north and the far west, there were elevated levels of methane (>2.3 ppm), DMS (>0.2 ppb_v) and DMDS (>4 ppb_v) likely caused from high traffic volumes and construction located in those areas (Figure 44).

With all the information given from the mapping it is likely that odours could be caused from the WWTP in the nearby community although other sources can also be impacting the overall air quality in the community.

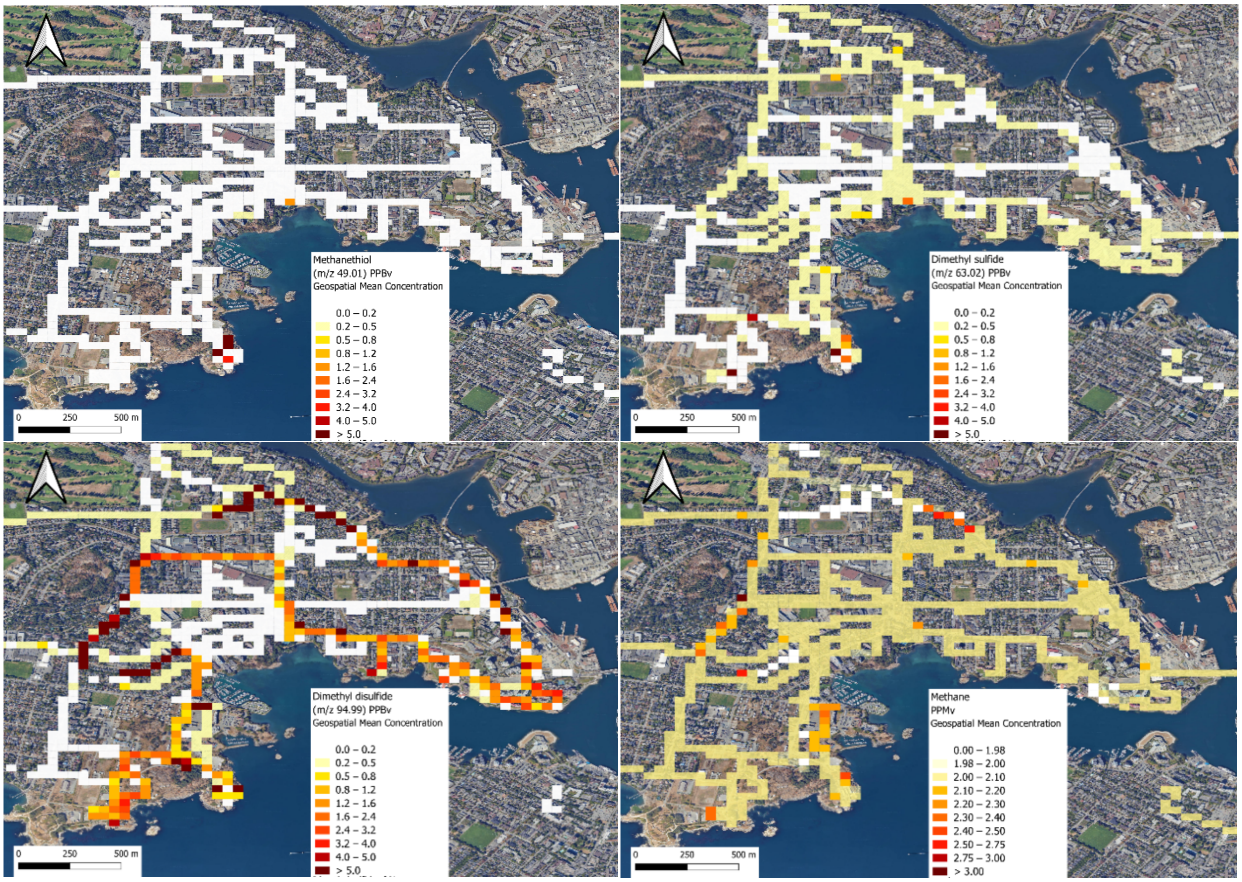

Figure 44:Geospatially averaged maps from WWTP3 community drive, showing concentration means of methanethiol, dimethyl sulfide, dimethyl disulfide and methane. All drive data from campaign is compiled in these figures.

Mapping was produced using Inverse Distance Weighting, using drive data collected from the whole sampling campaign (Figure 45). These maps were made as an example to visualize the distribution of the VOCs in the local community using modeled data and to compare them with the direct measurements which were geospatially averaged. These IDW maps reflect similar results as the geospatially averaged maps (Figure 44), showing the possibility of the DMS and DMDS migrating into the nearby communities at concentrations >1 ppb_v (Figure 45). Only minor amounts of MeSH are projected on the IDW map like the geospatially averaged maps, with those concentrations focused at the one beach location and the WWTP (Figure 45). These maps provide an easy-to-understand representation of on-ground concentrations and indicate that using models informed by real data could be a valuable tool for better understanding the distribution of VOCs in a community.

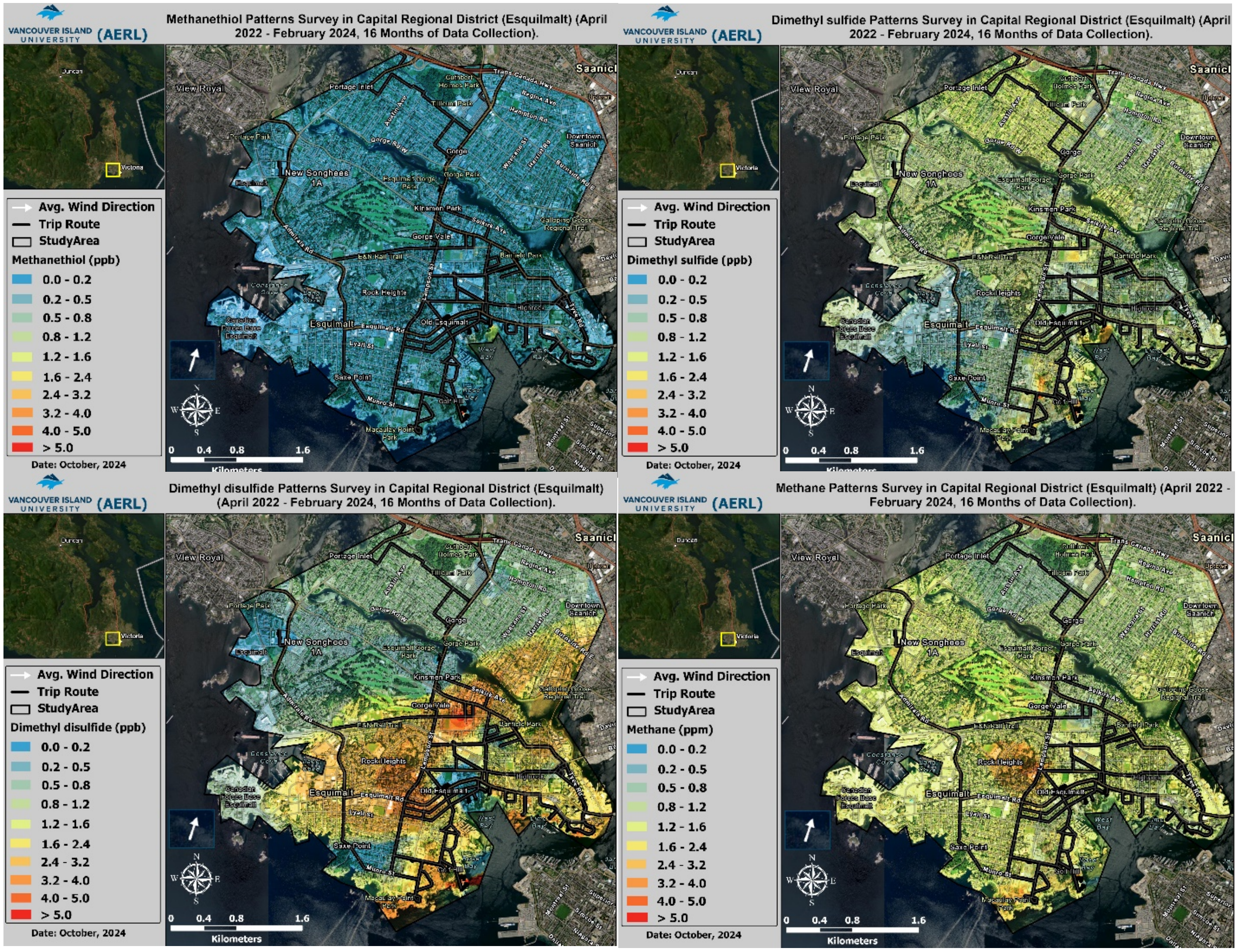

Figure 45: Interpolation maps from WWTP3 community drives, all data from April 2022-Feb 2024 was used to create these interpolation maps. Figure courtesy of Benjamin Ikhuoria Odia (Adv. Dip. GIS).

4.4.4 Investigation of seaweed decomposition onshore in drive route.

On the drive route there is a little community park which has a walkway along the beach and a small sandy portion of the beach which has been reported to have frequent malodours associated with it during the summer, especially when seaweed has washed up and is decomposing on hot days. During one of our samplings, we noticed a strong odour originating from the shoreline and investigated the smells further to evaluate the potential this source has for emitting reduced sulfur compounds. An accompanying map from the drive route that day is shown, indicating low concentrations of DMS (<0.5 ppb_v) on the drive route except at the community park which had concentrations of DMS >5 ppb_v, which sparked further investigation that day (Figure 46).

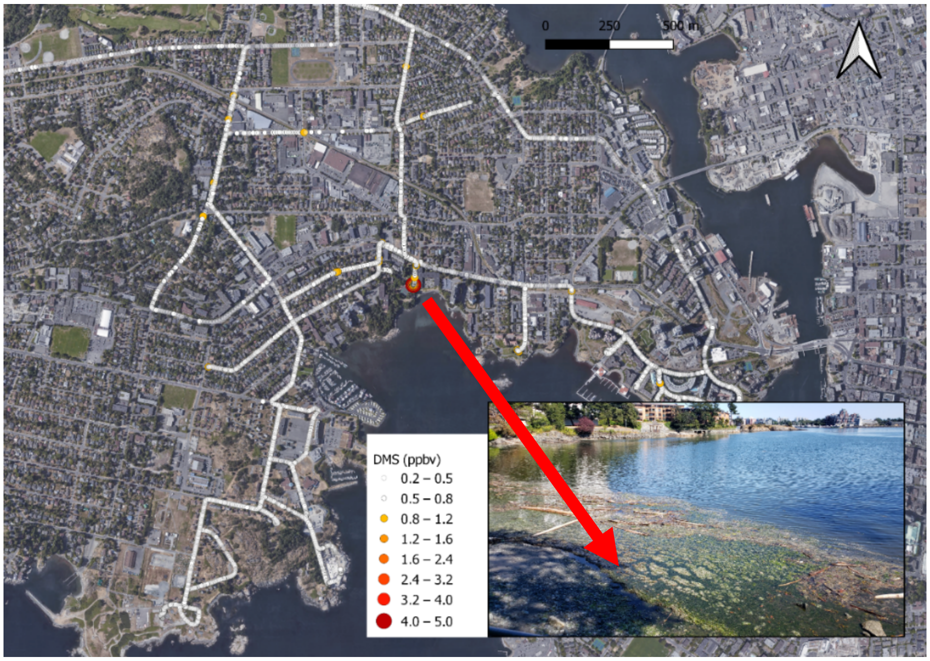

Figure 46: Single day drive from WWTP3 community, plotting dimethyl sulfide concentration during seaweed decomposition event.

Below are boxplots taken from the sampling, where we had brought our sample line from the MMSL close to the beach and sampled for around 5 minutes (Figure 47). Elevated concentrations of methanethiol and dimethyl sulfide were captured (>5 ppb$_v$), with negligible amounts of DMDS present (<0.4 ppb$_v$), and some elevated concentrations of VOCs (>250 ppb$_v$) such as acetaldehyde (*m/z* 45.02) and acetone (*m/z* 59.04) which can also contribute to odours. The concentration ranges for methanethiol and DMS were 2-10 ppb$_v$ and 4-14 ppb$_v$ respectively and were above their odour thresholds and were noticeably odourous by our perception (Figure 47). This work confirmed that these

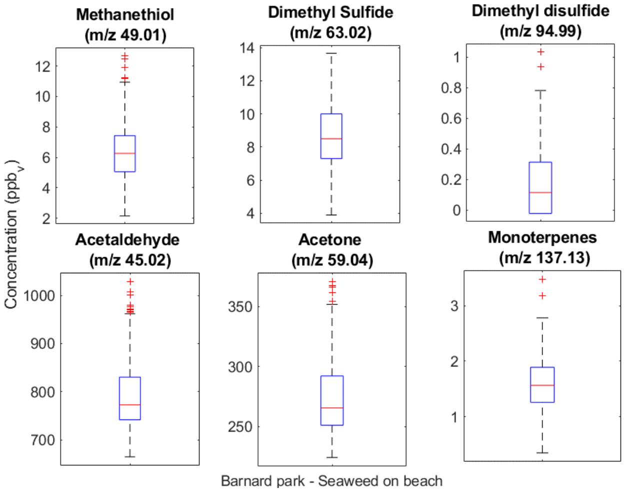

Figure 47:Boxplots from beachfront sampling using MMSL, during a seaweed decomposition even, which was noticeably smelly.

events could potentially contribute to the odour complaints in this area at certain times when seaweed is decaying on the beach.

4.5 Summary from community scale mobile monitoring

During the sampling campaigns, on-road measurements taken with the MMSL were recorded and compiled to assess potential sources of odours in the community including from the WWTPs. From each of the WWTPs studied, malodourous VOCs were detected outside the property and on some occasions with specific meteorological conditions they were measured above their odour thresholds and creating a plume into the nearby community.

In addition, we observed other sources of odours in the community from decomposing seaweed, manholes, pumpstations and vehicular exhaust. These observations serve to inform the operators of the WWTPs in their impacts to the local air quality in the communities and contribute to the knowledge base for the distribution and concentrations of these selected VOCs.

From the overall geospatial assessments of mean concentrations of the discussed VOCs it has shown that minimal levels of VOCs (<4 ppb$_v$) are infiltrating the local communities, however even at low concentrations they are typically above odour thresholds (ODT=0.02 ppb$_v$ MeSH and DMDS, 0.39 ppb$_v$ DMS) and can pose a risk of causing odour problems. Generally, from the on-road mobile measurements it has been shown that concentrations can be elevated (>0.5 ppb$_v$) up to 2 km away from the WWTPs at certain times indicating that sporadic weather events can exacerbate the extent of the impacts from the WWTPs. The methane concentrations are valuable information as it indicates that emissions of methane are collocated with the emissions of the reduced sulfur compounds and could potentially be used as a proxy for the three reduced sulfur compounds and wastewater foul air in general.

Chapter 5: Summary

5.1 On-site evaluation of odour controls at WWTPs

The work done at the WWTPs to evaluate ductwork and exhaust concentrations has given the operation and management staff crucial information to inform operations of the wastewater treatment plants. Over the whole campaign at the three WWTPs over 80 hours of time (>280,000 observations) was spent on-site taking samples of the foul air networks and exhausts. This study encompassed a wide range of odour controls including activated carbon media scrubbers, wet-scrubbers, chemical scrubbers, bio filters and reactors. The wastewater treatment plants also ranged in their treatment technologies, wastewater loadings, plant size and operations. The concentrations observed at the WWTPs are not extremely high in comparison to other WWTPs previously studied although impacts from exhausting the treated foul air to the atmosphere can still pose an odour risk on-site and off-site in the local communities.[71]

During the sampling campaigns the operations and management staff were updated with technical reports to guide them in assessing their impacts and aid in the decision-making regarding operations. The exhaust stack concentrations spanned a range across all WWTPs with concentrations of methanethiol generally ranging from 20-2000 ppb_v at exhaust stacks with higher input concentrations ranging from 200-3500 ppb_v. Some odour treatment technologies reduced the concentrations to below 2 ppb_v although these locations typically had low input concentrations into their odour control systems from 5-30 ppb_v. Overall, the percent decrease of methanethiol from all the odour control methods were >80%, which suggests that these treatment methods were effective in lowering the concentrations in the air streams but did not completely remove methanethiol.

The odour control technologies generally did not eliminate dimethyl sulfide and dimethyl disulfide efficiently with some of the better results only reducing the concentration at best by <40% for DMS and DMDS. The one technology which was done as a pilot study, using UV photo oxidation was an outlier as it was able to reduce concentrations of all 3 analytes by 99% but this was only studied over a two-week period at one location at WWTP1 and there could be instances which this technology does not work well at other locations and further investigation is encouraged.

The total sulfur emissions were estimated from the three WWTPs investigated. Given that these rates do not include fugitive emissions on-site, they are considered conservative estimates over the study period (Figure 48). These emission rates can be used to inform global atmospheric budgets and land use regression models.

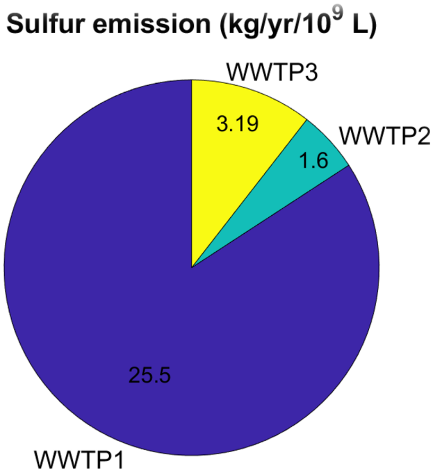

Figure 48: Total sulfur emissions in kg per billion liters of water treated, from WWTP1,2,3 derived from stack emissions.

In addition, methane was measured in the ductwork and total yearly stack emissions were estimated for the WWTPs ranging from 3.5-25 tonnes/year. This methane data is critical in understanding the range of emissions from wastewater treatment facilities.

Overall, the odour remediation technologies onsite greatly reduced the concentrations of methanethiol from the initial concentrations throughout the WWTP, but were typically still observed above its extremely low odour threshold (0.02 ppb_v). Generally, the odour controls did not work as well for DMS and DMDS and other options for eliminating these gases should be investigated. Odour contributions from these three reduced sulfur compounds in post-treatment stack emissions were estimated using Equation 18. This highlights the relative contributions of compound/s contributing to the odour coming from each WWTP (Figure 49).

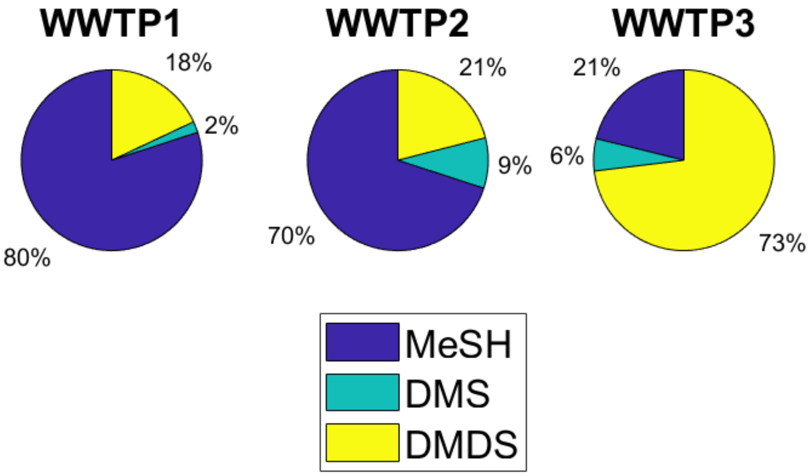

Figure 49: Odour contributions from MeSH, DMS, DMDS based on stack emissions from WWTPs, derived from Equation 18.

5.2 Community scale mobile monitoring summary

The data collected during the community drives is a valuable data bank for assessing the impacts to the local communities and in determining the fate and distribution of methanethiol, dimethyl sulfide and dimethyl disulfide in the community. The study includes over 100 hours of on-road community sampling from the three WWTPs investigated (>360,000 observations). This work illustrates the possibility of odour impacts from the WWTPs to the local communities and shows the influence that windspeed and direction play in how the gases are distributed from the WWTPs. Furthermore, additional sources of odours in the community were assessed, indicating the possible influence on air quality from vehicular emissions, biogenic sources and conveyance lines.

The additional information gained from this work was the possibility of using methane sensors as a proxy for the reduced sulfur compounds and malodours from WWTPs, giving a much more cost-effective option for further studies of this kind.

In general, concentrations (>0.5 ppb_v) of malodourous VOCs were found up to 2 km away from the WWTPs above their odour thresholds (ODT=0.02 ppb_v MeSH and DMDS, 0.39 ppb_v DMS). This indicates that WWTPs may have a role in the local air quality in communities which are located around WWTPs. Furthermore, additional sources of odour are found in the community, from conveyance lines, pump stations and biogenic sources. Engaging individuals from the community in the monitoring process by reporting odour complaints promotes citizen involvement in air quality concerns. Although using only complaint data can be a challenge with variability in reporting from individuals. A data driven approach rather than based solely on odour complaints by the public has allowed WWTP operators and management to have an unbiased assessment of their potential impact on the community. This information has served as a valuable tool in process management and understanding community impacts.

5.3 Future work

Additional measurements of transformation products taken on-road and in the ductwork could aid in a better understanding of the total contribution of sulfur compounds to the atmosphere in addition to other VOCs which may cause odours in the community. Using full scan mass spectrometry fingerprinting of sources on-site at the WWTPs could be done to help evaluate the contributions of particular locations on-site to concentrations measured off-site and potentially for source apportionment.

Further investigation of emerging odour control technologies would add to the knowledge base described here and could provide WWTPs with additional information on how to eliminate malodourous VOCs. DMS and DMDS were poorly removed by most of the technologies assessed in this work, so I would suggest that additional work be focused on cost-effective mitigation of these compounds. This would help reduce odour complaints from the surrounding community. Conducting more studies looking at chemical transformation of the reduced sulfur compounds would be valuable, regarding their fate and their compatibility with certain odour control techniques. Finally, assessing contributions from biogenic sources and other non-point sources can assist in the attribution of odours to specific sources/activities.

Also, the evaluation of using methane as a proxy sensor for reduced sulfur compounds and odours from WWTPs is worth further investigation as methane is detected by less expensive equipment than a mass spectrometer. In many cases methane and the malodourous compounds are collocated and may be an applicable screening tool to evaluate potential migration of wastewater VOCs offsite, rather than direct measurement of the trace VOCs. This could open more opportunities for plume tracking from WWTPs. Furthermore, using fence line sensors could potentially aid in tracking the exfiltration from WWTPs to offsite locations and could potentially be integrated into WWTPs operations to better deal with impacts to nearby neighbours and the community.

Dispersion modelling using real data from the on-site monitoring would be a next step in understanding the distribution of VOCs in the communities. Using on-road data to test, train and compare with modelled data could allow for better optimization. In addition, using models could help with collection of on-road data, as it could allow forecasting of when the optimal days for sampling would be in a certain area. Further modelling of the fate of the VOCs would be a useful next step. Integrating chemical fate modeling to understand the variety of compounds which could be influenced by these emissions would be interesting.

Equations

(1) $Air\ quality\ health\ index\ (AQHI) =$

$$10/(10.4 * \left(100 * \left(e^{(0.000871*NO_{2a})}\right) - 1 + e^{(0.000537*O_{3a})} - 1 + e^{(0.000487*PM_{2.5a})} - 1\right))$$

NO_{2a}, O_{3a}, $PM_{2.5a}$ = Trailing 3-hr average measurements of concentration

(2) General enzymatic process of amino acid decomposition:

$$HS - CH_2 - (R) + H_2O \rightarrow_{desulphydrase}^{Cysteine} \rightarrow CH_3CO - COOH + HS^-_{(aq)} \ + NH_4^+{}_{(aq)}$$

$$-(R) \ = \ H_2N - CH - COOH$$

(3) General reaction of mercaptans to disulfides:

$$2(CH_3 - (CH_2)_n - SH) \xrightarrow{Air+Activated\ carbon} CH_3 - (CH)_2 - S - S - (CH_2)_n - CH_3$$

(4) % Removal efficiency = $(C_{in} - C_{out})/(C_{in})\ x\ 100$

(5) Hydrogen sulfide oxidation reaction with sodium hydroxide:

$$\mathrm{H_2S\ +\ 2NaOH \rightarrow\ Na_2S\ +\ 2H_2O}$$

(6) Oxygen photolysis: $O_2\ +\ hv \rightarrow 2O$

(7) Ozone formation reaction: $O + O_2 \rightarrow O_3$

(8) Ozone photolysis: $O_3 + hv \rightarrow O_2 + O^{1D}$

(9) Hydroxyl radial formation: $O^{1D} + H_2O + hv \rightarrow 2OH^{\cdot}$

(10) Hydrogen abstraction: $OH^{\cdot} + VOC \rightarrow R^{\cdot}$

(11) Oxygen addition to form peroxyl radicals: $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$

(12) Oxygen abstraction and subsequent oxidations $RO_2^{\cdot} \rightarrow RO^{\cdot} \rightarrow RCHO \rightarrow CO_2$

(13) General sulphide oxidation mechanism:

$$HS^-(aq) + 2O_2 + H_2O \rightarrow SO_4^{-2}(aq) + H_3O^+$$

(14) General proton-transfer reaction $H_3O^+ + R \rightarrow RH^+ + H_2O$

(15) $$DL_{a,ppb} = 3\ x\ (\tfrac{s_{a,zero}}{Slope_a})$$

(16) Emission rate (@ STP) = Concentration x flow rate=

$$\frac{Kg}{year} = \left(\frac{ppb_v * MW}{24.45}\right) * \left(\frac{m^3}{hr}\right) * \left(\frac{1kg}{1x10^9ug}\right) * \left(8760\,\frac{hours}{year}\right)$$

(17) $$LOQ = 10\ x\ (\tfrac{s_{a,zero}}{Slope_a})$$

(18) $$Total\ RSC\ odour\ potency = a_{MeSH}[MeSH] + a_{DMS}[DMS] + a_{DMDS}[DMDS]$$

$$a_{RSC} = \frac{ODT_{highest}}{ODT_{RSC}}$$

$$ODT_{highest} = ODT_{DMS} \qquad ODT_{RSC} = ODT_{MeSH}, ODT_{DMS}, ODT_{DMDS}$$

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