Appendix D – Technical analysis, inter-day evaluation of odour control systems, regarding methanethiol, dimethyl sulfide and dimethyl disulfide.

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

Wet Biological Scrubbing Towers

The wet-bio scrubber towers (WBST) on-site WWTP1 are used as the first line of odour control after autothermal thermophilic aerobic digestion (ATAD) of the wastewater, which typically contains high levels of malodourous compounds including the reduced sulfur compounds, methanethiol, dimethyl sulfide and dimethyl disulfide which will be the focus of this discussion. The VOC measurements were taken at the foul air outtake from the ATADs (S1) and before treatment by the WBST, after treatment from the first tower (S3), and after treatment from the second tower (S4). The sampling points are shown in photos (Figure 1). The gas stream after treatment by the WBST passed through a chemical scrubber sampled as S5 and will be discussed in the next section.

The six ductwork sampling days span from August 2022-February 2024, measurements were typically taken every two months. Figures 2, 3 and 4 display the concentrations of

Figure 1: (Top-Left) Photo of ATADs treatment location at WWTP1, (Top-Right) Ductwork coming from ATADs foul air, sample point 1. (Bottom-Left) Photo of Sample point 3 ductwork coming from WBST1 into WBST2, (Bottom-Mid) Photo of ductwork sample point 4, leaving WBST2.

methanethiol, dimethylsulfide, and dimethyl disulfide from the ATAD foul air stream illustrating the range of input concentrations and scrubber efficiency.

This untreated foul air stream (S1) is coming directly from the headspace of the enclosed ATAD system and represents the highest concentrations of malodourous compounds at this facility. Figure 2 shows the concentration of methanethiol (*m/z* 49.01) from ATADs normally ranges between 3000-4000 ppb_v with one sampling day showing elevated concentrations > 7000 ppb_v (mean=3790 ppb_v, %RSD=47). 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 ppbv in the ATADs foul air stream.[70] These concentrations are also in the range of previous work done at the WWTP from 2019-2020, which had 25-75 percentile ranges of methanethiol concentrations from 3000-7000 ppb_v.[67]

The concentrations of methanethiol after the first and second bio scrubber towers are depicted in the subsequent panels of Figure 2. The concentration range for methanethiol at S3 was typically recorded between 1000-4000 ppb_v (mean=2500 ppb_v, %RSD=50), these values are lower than but comparable to previous concentrations recorded from 2019-2020 with 25-75 percentile measurement ranges between 4000-5000 ppb_v.[67] The concentrations of methanethiol were lower by 60-70% after WBST1 compared to the incoming foul air on three of the six sampling days (May 2023, Nov 2023, and Feb 2024) recorded in Table 1. However, the methanethiol levels were not being brought down by the first bio scrubber tower on three other sampling days (Aug 2022, Mar 2023, and Sep 2023), indicating inefficient removal at WBST1 and suggesting that it is a possible source on some occasions.

Wet bio scrubber 1 had removal efficiencies of MeSH in Aug 2022, Mar 2023, and Sep 2023 from -12 to -25% indicating a higher concentration after treatment. This data was brought to the attention of the engineers and operators on-site.

The median concentration ranges of MeSH at S4 (post WBST2) were generally lower 600-3700 ppb_v (mean=1800 ppb_v, %RSD=63) than observations at S3 suggesting further removal. These results are in the range of the measurements made in 2019-2020, with an overall median concentration of 3200 ppb_v.[67] The second bio scrubber tower lowered the concentrations of methanethiol significantly (40-60%) on three sampling days (Aug 2022, Mar 2023, and Sep 2023) which are the same days noted above where WBST1 was ineffective, thus passing higher loads to wet bio scrubber 2.

On sampling day 3 (May 2023) the bio scrubber towers were both working giving removal efficiencies of MeSH at 62% and 47% from WBST1 and WBST2, respectively.

This was following alterations in water flow rates made by the operation staff at the WWTP.

During sampling day 5 (Nov 2023) when elevated methanethiol concentrations in excess of 7000 ppbv were observed, WBST1 was working well at bringing down concentrations by 64% while the WBST2 appeared to become a source of methanethiol with a removal efficiency of -44% (Table 1). Similar observations were made on day 6 (Feb 2024), where concentrations were higher after WBST2 than WBST1, although concentrations were still below the input concentrations from the ATAD foul air (Figure 2). Operators were informed that the WBST2 was not working properly and to confirm this we captured both gas streams onto sorbent tubes at S3 (WBST1) and S4 (WBST2).

The results from the additional sorbent tube sampling are summarized in Figures 25 and 26, which confirmed our on-site observations from PTR-TOF-MS.

Other bio trickling filters similar to WBST1 and WBST2 have been evaluated and found at best 70% removal efficiency of methanethiol from the gas streams.[71] The overall efficiencies for both wet bio-scrubber towers in tandem was from 27-80% removal, indicating that these systems when plumbed in-line are lowering the concentrations of methanethiol from S1 to S4 over the whole sampling campaign (Table 1). This suggests that depending on the microbial communities which live in the wet bio scrubber tower and the operation of the WBSTs, they may be able to remove a portion of methanethiol.[71]

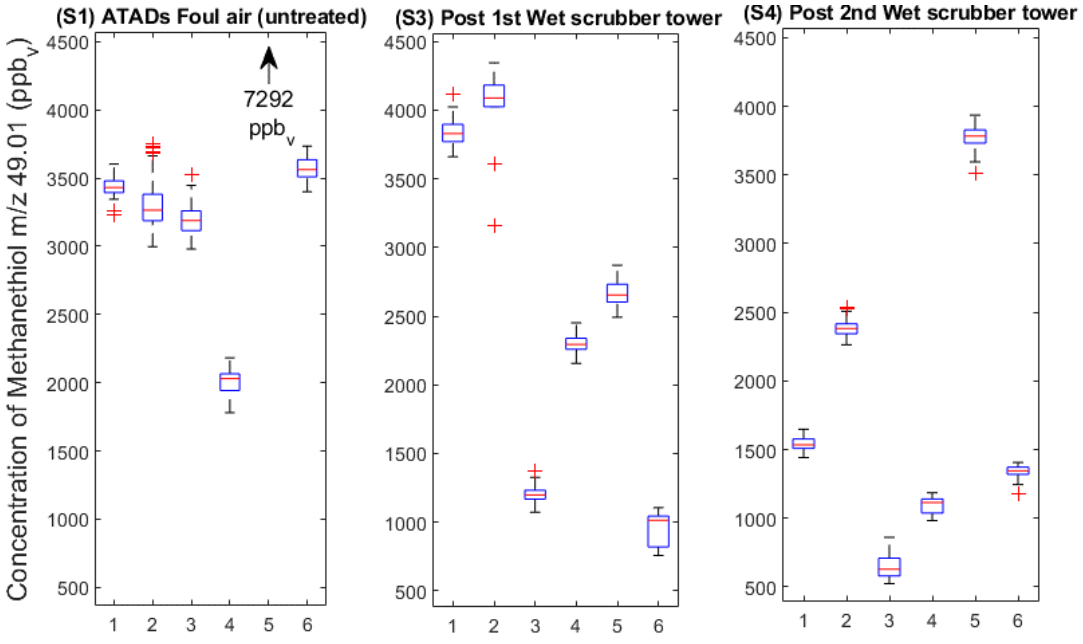

Figure 2: Methanethiol concentrations from wet bio scrubber towers. Sampling days 1-6, 1-August 2022, 2-March 2023, 3- May 2023, 4-Sept 2023,5- November 2023, 6- February 2024. Boxplots show concentration ranges from ATAD foul air stream at S1 (untreated), S2, and S3 (after wet bio scrubbers).

Table 1 % Removal of methanethiol from bio wet scrubber towers 1 and 2 from all sample days. (S3, S4)

Median concentrations and %Removal for Methanethiol from odour controls						
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
S1→S4 (%)	55	27	80	45	48	62

-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment.

The concentrations of dimethyl sulfide (*m/z* 63.02) were tracked during the 6 on-site sampling days showing a high range of variability from the ATAD headspace shown in Figure 3 with a median value of 1290 ppb_v (mean=2300 ppb_v, %RSD=160).

The concentration medians from the whole sampling campaign for S3 (mean=900 ppb_v, %RSD=100) and S4 (mean=550 ppb_v, %RSD= 70) were 770 and 440 ppb_v, respectively for DMS. These were higher than previous measurements from 2019-2020 with medians of DMS for S1, S3 and S4 at 400, 500 and 400 ppb_v, respectively.[67]

The first and second wet bio scrubber tower were not functioning properly to eliminate DMS during the first sampling day (Aug 2022), with removal efficiencies from WBST1 at -87% and -29% from WBST2 (Table 2).

During sampling day 2 (Mar 2023) the WBST1 and WBST2 were effectively bringing down DMS concentrations by >70% at each WBST step. On sampling day 3 and 4 (May 2023, Sept 2023) the WBST1 was slightly eliminating DMS from the ATAD foul air stream with removal efficiencies of <5-19% and WBST2 was working better then WBST1 at 22-49% removal efficiencies (Table 2).

On day 5 (Nov 2023) WBST1 and 2 had removal efficiencies of 37% and -27%, respectively. On sampling day 6 (Feb 2024) WBST1 was working with good efficiency >70% reduction of DMS concentration, yet WBST2 was still not functioning properly and was a source of DMS (-149% removal efficiency) similar to sampling day 1 and 5 (Aug 2022, Nov 2023), which was reported to the operational staff so they could make appropriate changes.

The overall removal efficiencies from both wet bio-scrubber towers in tandem were from 20%-96%, except on day 1 (Aug 2022) with an efficiency at -140%, which shows most days the WBSTs were able to lower concentrations of DMS from S1 to S4 when used together (Table 2).

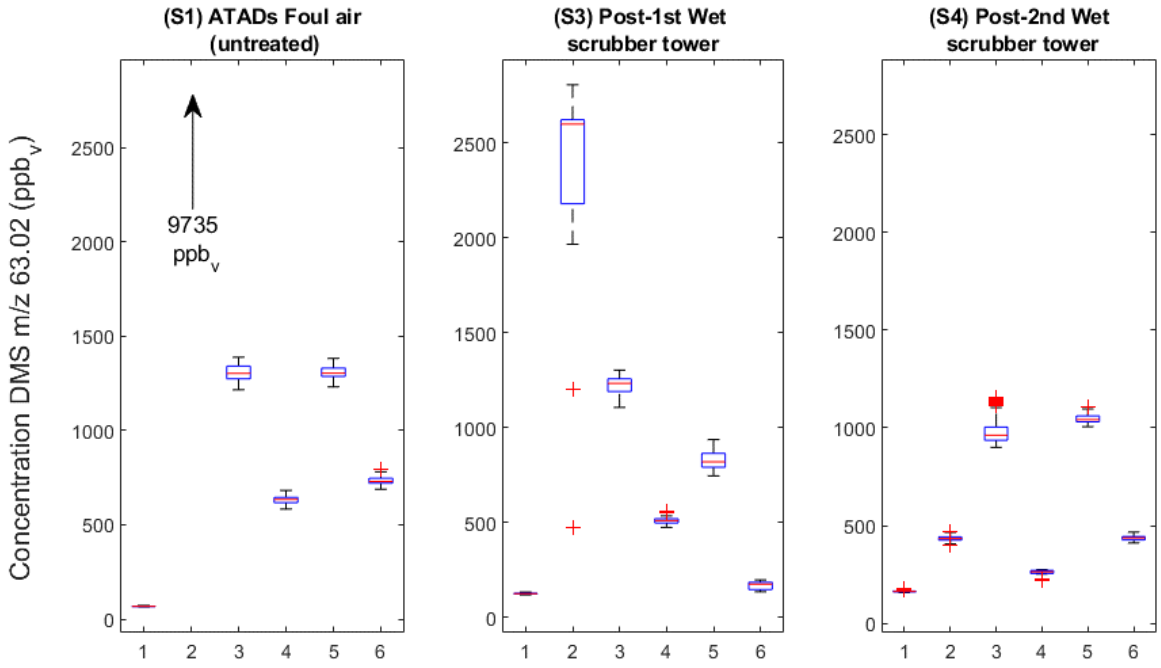

Figure 3: Dimethylsulfide concentration from wet bio scrubber towers. Sampling days 1-6, 1-August 2022, 2-March 2023, 3-May 2023, Sept 2023, 5- November 2023, 6- February 2024. Boxplots show concentration ranges of DMS from ATAD foul air (untreated), post WBST1, and post WBST2

Table 2: % Removal of dimethyl sulfide from bio wet scrubber towers 1 and 2 from all sample days. (S3, S4)

% Removal of DMS from odour controls						
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)	68	9735	1302	633	1304	730
S3 (ppb_v)	126	2598	1233	511	821	175
S1→S3 (%)	-87	73	0	19	37	76
S4 (ppb_v)	162	433	962	263	1042	436
S3→S4 (%)	-29	83	22	49	-27	-149
S1→4 (%)	-140	96	26	58	20	40

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

The concentration medians from the whole sampling campaign for dimethyl disulfide (DMDS) at S1 (mean=300 ppb_v, %RSD=55), S3 (mean=280 ppb_v, %RSD=85) and S4 (mean=260 ppb_v, %RSD 60) were 290, 245 and 240 ppb_v, which were very comparable to the medians from the sampling done in 2019-2020, with medians of 300, 300, 200 ppb_v respectively (Figure 4).[67]

During sample day 1 (Aug 2022) detection of dimethyl disulfide (*m/z* 94.99) was below 100 ppb_v in the ATADs foul air stream (S1) and subsequently higher at sample points S3

and S4, there was an increase in concentration following both wet scrubber treatment, this is likely from the treatment becoming a source of DMDS (Table 3).

On sampling days 2-5 (Mar, May, Sept, Nov 2023) an average of 400 ppb_v dimethyl disulfide was detected in the ATADs foul air steam as the input to the wet bio scrubbers.

On sample day 2 (Mar 2023) the WBST1 was not functioning adequately regarding elimination of the dimethyl disulfide, although in WBST2 the concentrations were reduced by 80% from WBST1 showing good efficiency from WBST2 (Table 3).

Sampling day 3 (May 2023) was the only day both towers were removing DMDS together and followed a downward trend between the sample points from S1 to S4 which indicated the processes were working, although concentrations through WBST2 were still moderately high above 200 ppb_v (Figure 4 and Table 3).

On sampling day 4 (Sept 2023) dimethyl disulfide concentrations were negligibly lower from ATADs foul air through WBST1, nor did the WBST2 lower the concentrations further. On this day S4 was found to have a higher concentration of DMDS comparatively to both S1 and S3, indicating S4 was a possible source of DMDS at the time of sampling and was further investigated by TD-GC-MS on the next sampling day (Figure 5, 26).

During sampling day 5 (Nov 2023) WBST1 was negligible in removing DMDS with a removal efficiency of <5%, while WBST2 was poorly operational with a removal efficiency of -86%. Sampling day 6 (Feb 2024) showed good efficiency for removal from WBST1 at 77% while WBST2 was a source of DMDS with a removal efficiency of -360% (Table 3).

The possibility of conversion from methanethiol to dimethyl disulfide during treatment could be responsible for the elevated levels of DMDS in the gas stream post treatment as proposed in Equation 3. The overall removal efficiencies for DMDS from both WBSTs found that half the days sampled (Mar 2023, May 2023, Sept 2023) a positive removal efficiency was seen from 17-71%, indicating that this system in some cases does remove a portion of the DMDS from S1 to S4 (Table 3). On sample days 1, 5 and 6 (Aug 2022, Nov 2023, Feb 2024) the overall removal efficiencies were poor ranging from negligible removal efficiency of <5% to increased concentrations from S1 to S4 of 79-190% (Table 3).

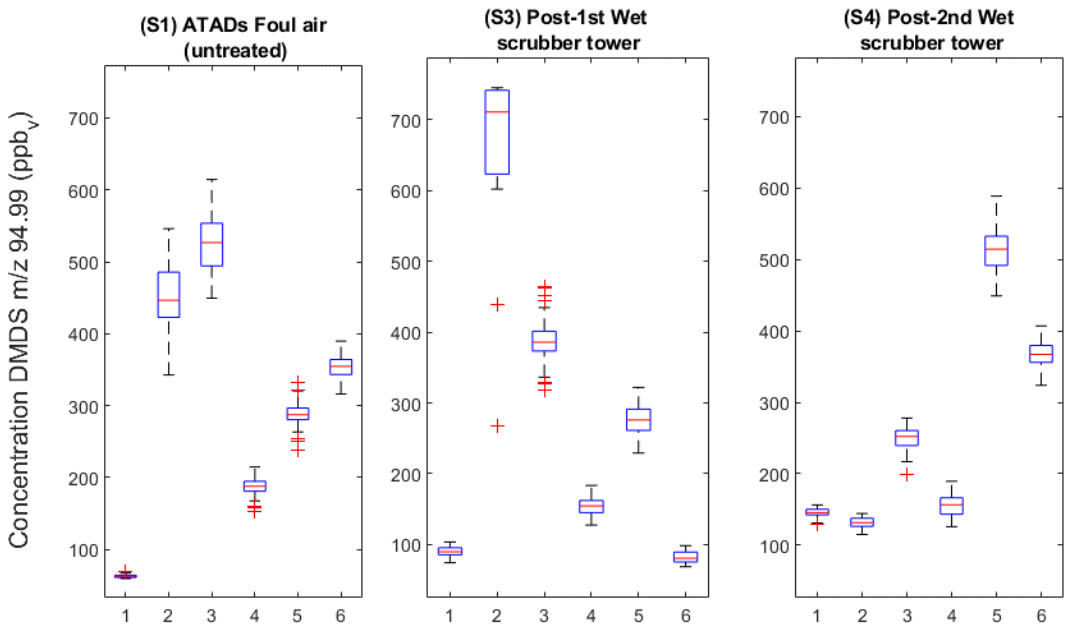

Figure 4:Dimethyl disulfide conc. from wet bio scrubber towers. Sampling days 1-6, 1-August 2022, 2-March 2023, 3- May 2023,4- Sept 2023, 5- November 2023, 6- February 2024. Boxplots show concentration ranges of DMDS from ATAD foul air (untreated), post WBST1, and post WBST2.

Table 3: % Removal of dimethyl disulfide from bio wet scrubber towers 1 and 2 from all sample days. (S3, S4)

Median concentrations and % Removal of DMDS from odour controls						
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)	50	446	526	188	287	354
S3 (ppb_v)	90	710	382	154	276	80
S1→S3 (%)	-80	-59	27	18	0	77
S4 (ppb_v)	145	131	252	156	514	367
S3→S4 (%)	-61	82	34	0	-86	-356
S1→S4 (%)	-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.

During sample day 5, November 2023, we deployed a set of sorbent tubes to collect the gas streams from S3 and S4 to evaluate and confirm our observations showing a trend that the bio scrubber towers were not functioning properly and to help characterize if S4 was a source of the three reduced sulfur compounds methanethiol, DMS and DMDS. The chromatograms and mass spectra taken from the TD-GC-MS runs are shown in Figure 5 for WBST1 (S3) and in Figure 6 for WBST2 (S4).

The sorbent tubes were deployed in similar manners with the same type of sorbent tube used and loaded with equal amounts of air samples. The chromatograms are slightly shifted from each other as these samples tend to be quite humid and can affect retention times in the GC-MS, although confirmatory mass spectra were evaluated to ensure correct peaks were chosen to represent the compounds of interest, listed in Table 4.

Similar to other work done using gas chromatography the main reduced sulfur compounds were eluted in the first ten minutes, with the same order, methanethiol first, then DMS and DMDS last.[40] In Figure 5 major peaks are seen at RT 1.69 and 3.65 min coordinated to DMS and DMDS, with peak heights of $6x10^5$ and $3.5x10^6$ and a minor peak at 1.45 min for Methanethiol with peak height of $3.3x10^4$.

In Figure 6 major peaks were identified at 1.48 and 3.5 min for DMS and DMDS giving peak heights of $7.6x10^5$ and $1.63x10^6$ and a minor peak at 1.28 min for methanethiol with a peak height of $3x10^6$ also described in Table 4.

These spectra are not as reliable on proper quantification as the instrumentation has not been calibrated and methanethiol is prone to oxidize into DMDS and DMTS during transport and analysis. Although, DMS is a more reliable measure to compare the two samples as it is not prone to degradation or transformation during analysis.[35] An increased signal of DMS between WBST1 and WBST2 from figures 25 to 26, was seen agreeing with PTR-TOF-MS measurements S3 median concentration 820 ppb_v and S4 median concentration of 1020 ppb_v (Figure 3). This was also done to assess the portion of dimethyl sulfide and ethanethiol which belong to signal *m/z* 63.02 in the PTR-ToF-MS analysis and was found that only negligible amounts of ethanethiol were present and most of the signal will belong to DMS in our measurements (Table 4).

Using PTR-TOF-MS analysis for methanethiol and DMDS is a preferred method as direct measurement of these gases decreases the chance of transformation and improper designation of concentrations so together with the GC-MS method it can be shown that it is most likely the case that S4 has become a source of these reduced sulfur compounds during sampling days 5 and 6.

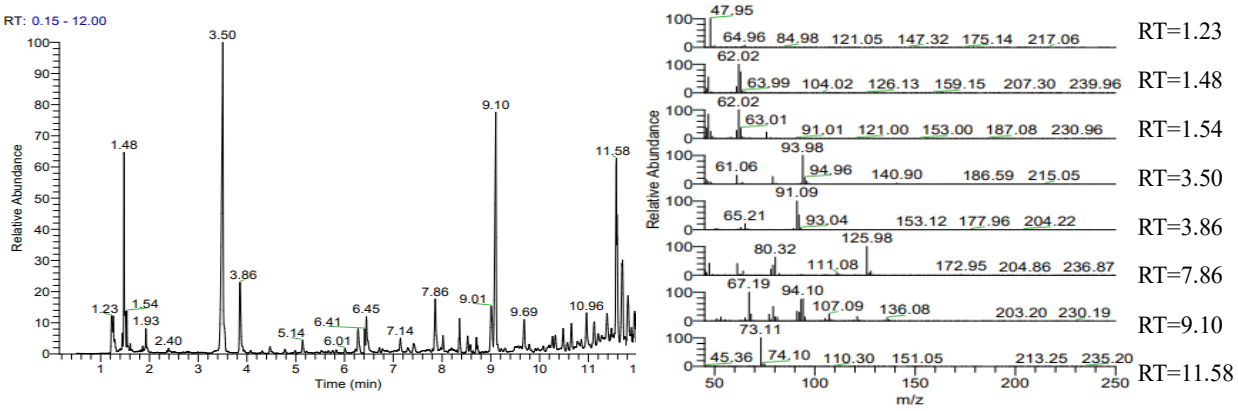

Figure 5: S3-Post-WBST1, Chromatogram and Main peaks EI-MS from TD-GC-MS

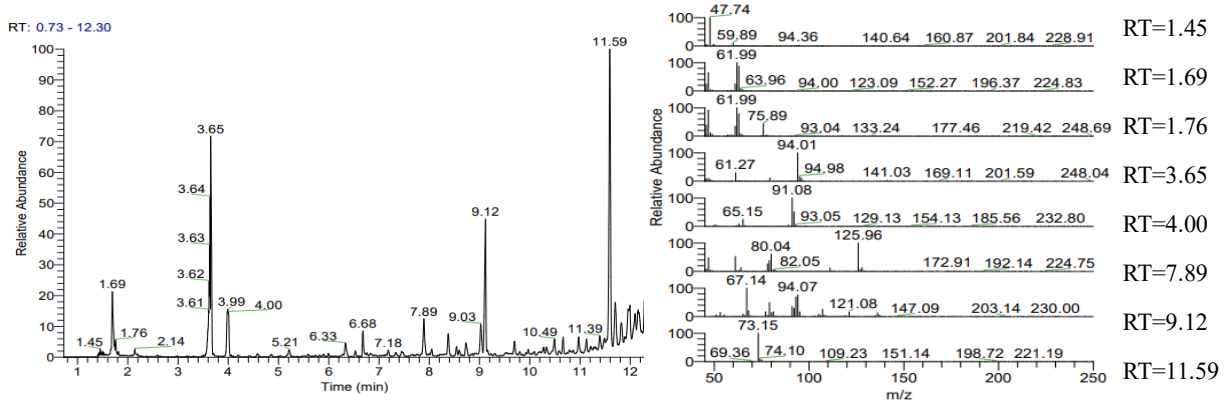

Figure 6: S4-Post WBST2, FCPCC Nov 6, chromatogram from TD-GC-MS, accompanying peaks of interest. RT (retention time)

Table 4: List of Probable compounds from GC-TD-MS Figures 25 and 26 EI-MS for WBSTs foul air.

Compound	Chemical formula	Retention time (min) (WBST 1)	Retention time (min) (WBST 2)	Peak height WBST1	Peak height WBST2
Methanethiol	CH_3SH	1.45	1.23	$3.3x10^4$	$3x10^5$
Dimethyl sulfide	CH_3SCH_3	1.69	1.48	$6x10^5$	$7.6x10^5$
Ethanethiol	CH_3CH_2SH	1.76	1.54	$9.6x10^4$	$3.9x10^4$
Dimethyl disulfide	CH_3SSCH_3	3.65	3.50	$3.5x10^6$	$1.6x10^6$
Toluene	C_7H_8	4.00	3.86	$6.2x10^5$	$3.7x10^5$
Dimethyl trisulfide*	CH_3SSSCH_3	7.89	7.86	$2.15x10^5$	$1.52x10^5$
Monoterpene	$C_{10}H_{16}$	9.12	9.10	$7.2x10^5$	$2.8x10^5$
Butanal*	C_4H_8O	11.59	11.58	$5.4x10^6$	$1.7x10^6$

*-Mass spectral library match was used to confirm the presence of these compounds

The information from this sampling campaign was able to further inform the operations team at the WWTP on how the wet-scrubber systems were working and gave them the insight needed to make changes in their treatment systems operations. Some changes included adjusting water circulation flows in the system, replacing the media in the towers and cleaning accumulated sludge in the system. The operations of the wet-bio-scrubbers may be influencing the concentrations found in the gas streams, as in most cases the WWTP recycles some of its effluent through the WBST to give extra nutrients to the WBST flora and as a water saving tactics strategy.

The process which eliminates the VOCs in the gas stream is highly dependent on mass transfer into the bulk liquid solution, which is then treated by the microbial community which resides on the inert substrate inside the scrubbing tower. These processes can be variable in efficiency, as it depends on the flow of the water solution, and the health of the microbial community and the total load of VOCs which is in contact with the scrubber. The dynamic nature of wastewater treatment can prove to add challenges in the foul air treatment network operations and may need on-going monitoring and optimization to keep systems running efficiently. Overall, the challenging nature of measuring gases in an operational plant should be considered when evaluating treatment systems.

Chemical Scrubber

The chemical scrubber is used in-line after the wet-bio scrubber towers (Figure 7). The scrubbing solution changed part-way through the study in December 2022 from Caustic soda 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 used for most of the study. The technology was used intermittently during the campaign as it was undergoing maintenance. We used the MMSL and collected some sorbent tubes pre and post chemical scrubber throughout the study to complement our analysis.

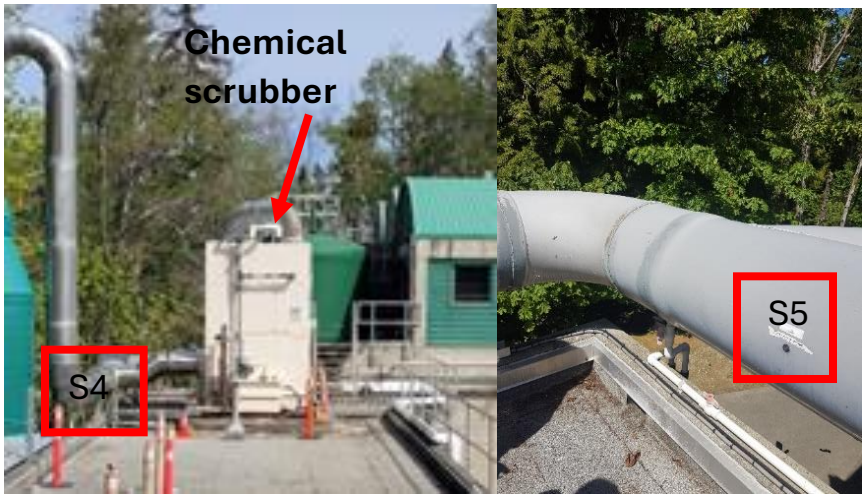

Figure 7: (Left) Photo of Chemical scrubber unit and ducting coming from WBSTs. (Right) Ductwork leaving chemical scrubber, sample point 5.

The concentrations of methanethiol were evaluated pre and post chemical scrubber gas stream, showing variability between sampling days, with sampling day 3 (May 2023) the chemical scrubber was offline for maintenance (Figure 8). Concentration ranges for the input to the chemical scrubber were from 500-3750 ppb_v methanethiol, which encompasses a large range which the chemical scrubbers must work at (mean=1800 ppb_v, %RSD=60).

The S5 median concentration of methanethiol was 1230 ppb_v (mean=1300 ppb_v, %RSD=75), much higher than during the previous sampling done in 2019-2020, with a median at S5 of 250 ppb_v.[67] The post scrubber gas stream also had a variable range (%RSD=75) of concentrations of methanethiol, with some removal of methanethiol seen on days 1, 2 , 5 and 6 (Aug 2022, Mar 2023, Nov 2023, Feb 2024), although it was offline on day 3 (May 2023) so no comparison could be made for that day (Table 5). On day 4 (Sept 2023) the system became a source of methanethiol with a removal efficiency of -81% and was reported to operational staff (Table 5). After operational staff were informed, they changed dosages of the scrubbing solution in November 2023, leading to improved removal of methanethiol.

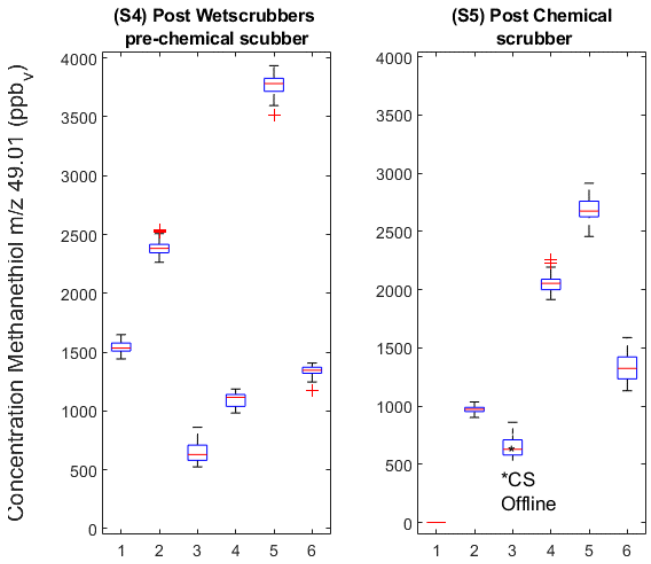

Figure 8:Methanethiol concentrations from post-wet bio scrubber towers, pre-chemical scrubber and post-chemical scrubber treatment. Sampling days 1-5, 1-August 2022, 2-March 2023, 3- May 2023, 4-Sept 2023,5- November 2023, 6- February 2024. Boxplots show concentration ranges of MeSH from pre and post Chemical scrubber treatment, Chemical scrubber (CS) was offline on x-axis 3 (May 2023).

Table 5: % Removal of methanethiol from chemical scrubber from all sample days. (S5)

% Removal of methanethiol from odour control						
Treatment between S#	Aug/22 (day 1)	Mar/23 (day 2)	May/23 (day 3)	Sept/23 (day 4)	Nov/23 (day 5)	Feb/24 (day 6)
S4 (ppb_v)	1534	2381	629	1115	3828	1347.8
S5 (ppb_v)	2	973	629	2013	2679	1193
S4→S5 (%)	100	59	N/A	-81	30	11

-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. N/A indicates chemical scrubber was non-operational that day.

The chemical scrubber performance was similar in the removal of methanethiol as DMS. On sample day 1 (Aug 2022) a removal efficiency of 99% was seen showing optimal performance of the system (Table 6). This was when a caustic scrubbing solution was used in the system, this was changed to ReNew A & B in December 2022.

Modest removal was recorded on days 2 and 5 (Mar 2023, Nov 2023) of 45% and 21% removal and negligible treatment on day 6 (Feb 2024) (Table 6). The median concentration for DMS at S5 was 600 ppb_v (mean=430 ppb_v, %RSD=75), about 200 ppb_v higher than the median reported in 2019-2020 at 400 ppb_v (Figure 9).[67]

Similar to methanethiol, the concentrations on day 4 (Sept 2023) were higher after chemical treatment suggesting improper treatment conditions in the chemical scrubber on that day resulting in a removal efficiency of -137% (Table 6). After operational changes

to dosing of the scrubbing solution, better results were achieved from -137% in September to 21% removal in November.

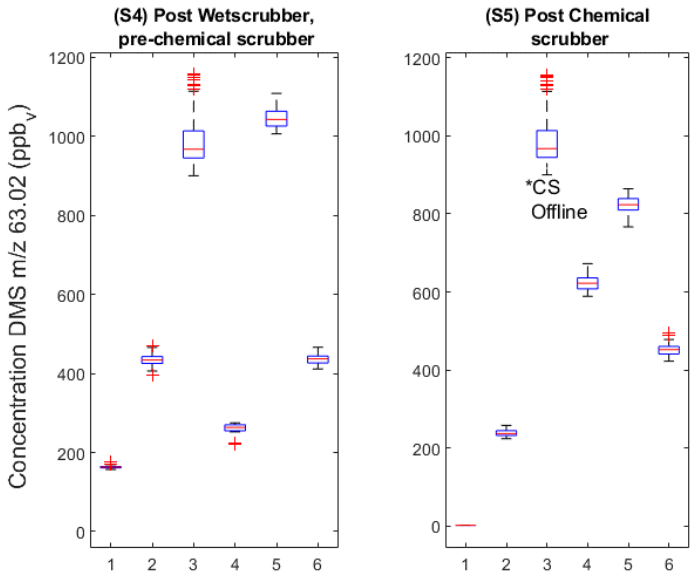

Figure 9:Dimethyl sulfide concentrations from post-wet bio scrubber towers, pre-chemical scrubber and post-chemical scrubber treatment. Sampling days 1-5, 1-August 2022, 2-March 2023, 3- May 2023, 4-Sept 2023,5- November 2023, 6- February 2024. Boxplots show concentrations from pre and post chemical scrubber, chemical scrubber was offline sample point 3 (May 2023).

Table 6: % Removal of dimethyl sulfide from chemical scrubber from all sample days. (S5)

Median concentration and % Removal of dimethyl sulfide from odour control						
Treatment between S#	Aug/22 (day 1)	Mar/23 (day 2)	May/23 (day 3)	Sept/23 (day 4)	Nov/23 (day 5)	Feb/24 (day 6)
S4 (ppb_v)	162	433	962	263	1042	436
S5 (ppb_v)	2	237	962	624	822	454
S4→S5 (%)	99	45	N/A	-137	21	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.

The chemical scrubbers input range was variable for DMDS (mean=260 ppb_v, %RSD=60) similar to DMS (mean=550, %RSD=70) and methanethiol (mean=1800 ppb_v, %RSD=60).

The performance for DMDS removal was similar to methanethiol and dimethyl sulfide with 3 of 6 days (Aug 2022, Mar 2023, Nov 2023) showing modest removal of DMDS and day 6 (Feb 2024) showing negligible removal of DMDS (Figure 10 and Table 7). During day 1 caustic soda scrubbing solution was being used and was changed to a new scrubbing solution, ReNew A & B™ in December 2022.

The system became a source of DMDS on day 4 (Sept 2023), which could indicate problems in the system and was the same case for the DMS and methanethiol on that day (Table 7). As with the DMS and MeSH improvements for removal efficiency was observed after an operational change before the November 2023 sampling, where dosing of the scrubbing solution was changed. The median concentration for DMDS at S5 was 340 ppb_v (mean=250 ppb_v, %RSD=70), higher than the previous sampling campaign in 2019-2020, which was 200 ppb_v.[67]

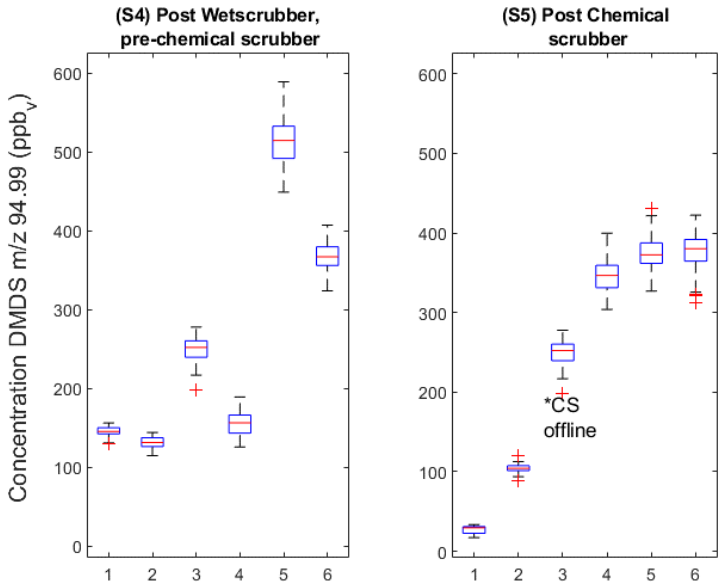

Figure 10:Dimethyl disulfide concentrations from post-wet bio scrubber towers, pre-chemical scrubber and post-chemical scrubber treatment (CS). Sampling days 1-5, 1-August 2022, 2-March 2023, 3- May 2023, 4- Sept 2023, 5-November 2023, 6-February 2024. Boxplots show pre and post chemical scrubber treatment, no detect (ND) at S5 sample point 1 (August 2022), CS offline sample point 3 (May 2023).

Table 7: % Removal of dimethyl disulfide from chemical scrubber from all sample days. (S5)

Median concentration and % Removal of dimethyl disulfide from odour control						
Treatment between S#	Aug/22 (day 1)	Mar/23 (day 2)	May/23 (day 3)	Sept/23 (day 4)	Nov/23 (day 5)	Feb/24 (day 6)
S4 (ppb_v)	145	131	252	156	514	367
S5 (ppb_v)	29	104	252	347	372	380
S4→S5 (%)	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.

During day 5 (Nov 2023) sorbent tubes were deployed at S5 to evaluate and confirm PTR-TOF-MS measurements speciation, which showed similar compounds to S3 and S4 (Table 4 and 10) and ranges peak heights we close in values, although this technique is not the best suited for precise measurements of methanethiol and DMDS and the

treatment processes are variable so that can introduce variation in the sample measurement (Figure 11).

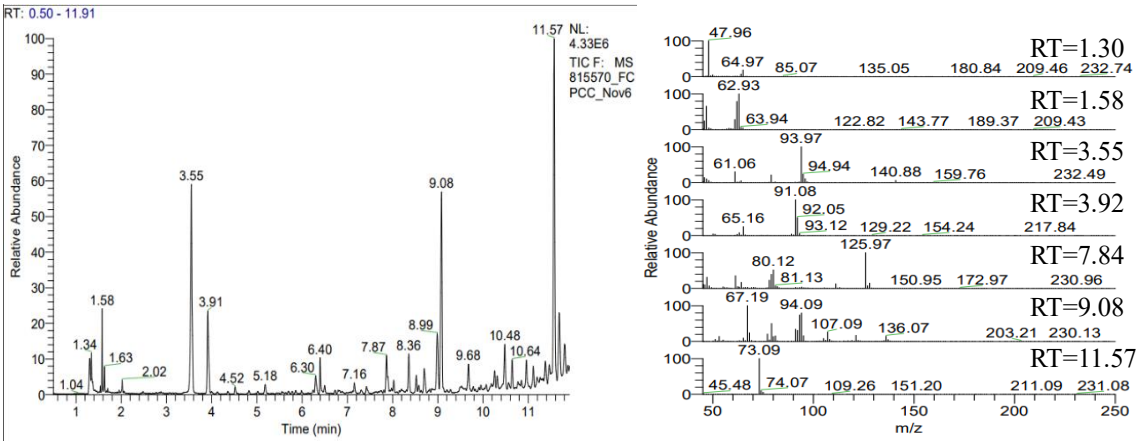

Figure 11: (S5) Post-chemical scrubber gas stream chromatogram and select EI-MS from TD-GC-MS, Nov 6, 2023.

*Table 8: Main peaks from chromatogram of S5, chemical scrubber TD-GC-MS.*Compound likely from mass spectral data.*

Compound	Chemical formula	Retention time (min) (WBST 1)	Peak height WBST1
Methanethiol	CH_3SH	1.30	$2.78x10^5$
Dimethyl sulfide	CH_3SCH_3	1.58	$2.98x10^5$
Dimethyl disulfide	CH_3SSCH_3	3.55	$3.5x10^6$
Toluene	C_7H_8	3.92	$3.93x10^5$
Dimethyl trisulfide*	CH_3SSSCH_3	7.84	$1.84x10^4$
Monoterpene	$C_{10}H_{16}$	9.08	$3.84x10^5$
Butanal*	C_4H_8O	11.57	$2.94x10^6$

Biofilter

A simplistic biofilter was used to trap and eliminate malodours after the de-wetting step which is done to the solids accumulated throughout the wastewater treatment process. The biofilter consists of woodchips and shells which are kept hydrated to give a substrate for oxidizing bacteria (Figure 12). This area of the plant is noticeably odourous while de-wetting processes are running. This process is not continuous and runs in a batch process where fans draw out the foul air and pass it through the filter when in

operation. Some days while sampling, operations were not running, so concentrations are much lower but still not negligible and will be clearly labeled in the data displayed. The concentration ranges from the pre-biofilter were captured while the exhaust fan was running, but once the sampling lines were changed to post-biofilter the fans stopped on some occasions. 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 12: (Left) Photo of ductwork after de-wetting, sample point 6. (Right) Photo of Biofilter, sample location 7.

The sampling at the de-wetting centrifuge foul air exhaust pre-biofilter was evaluated on 6 days, where the post-biofilter measurements were affected by the exhaust fans not running on sampling days 1, 4 and 5 (Aug 2022, Sept 2023, Nov 2023), which show low concentrations of methanethiol those days and high removal efficiencies (Table 9). This showed that the biofilter itself is a constant source of odour even when not running (Figure 13).

The average pre-treatment exhaust was around 1500 ppb_v methanethiol (%RSD=60) while the average concentrations through the biofilter were 300 ppb_v (%RSD=70) while the exhaust fan was running (Mar 2023, May 2023, Feb 2024). The biofilter had an average reduction and dilution through the substrate of 70%. On day 3 (May 2023) the removal efficiency was -20% showing an increase in concentration from post treatment (Figure 13).

The 3rd quartile ranges from 2019-2020 were from 0-70 ppb_v with some outlier days up to 500 ppb_v for (S6), and for (S7) 0-29 ppb_v was recorded, which is typically much lower

than the concentrations recorded during this campaign for methanethiol.[67] A similar sampling was done at a WWTP in California, which uses a similar seashell biofilter to treat wastewater foul air, they found input concentrations of methanethiol from 68-650 ppb_v, and concentrations through the biofilter post treatment below 5 ppb_v, they used GC-MS analysis and this may have impacted their results, or configurations of biofilter setups could be different.[72] The biofiltration process is relatively simple and requires very low maintenance and energy input, so this is an alluring option if it can eliminate odourous VOCs to an acceptable concentration which will not impact the community.

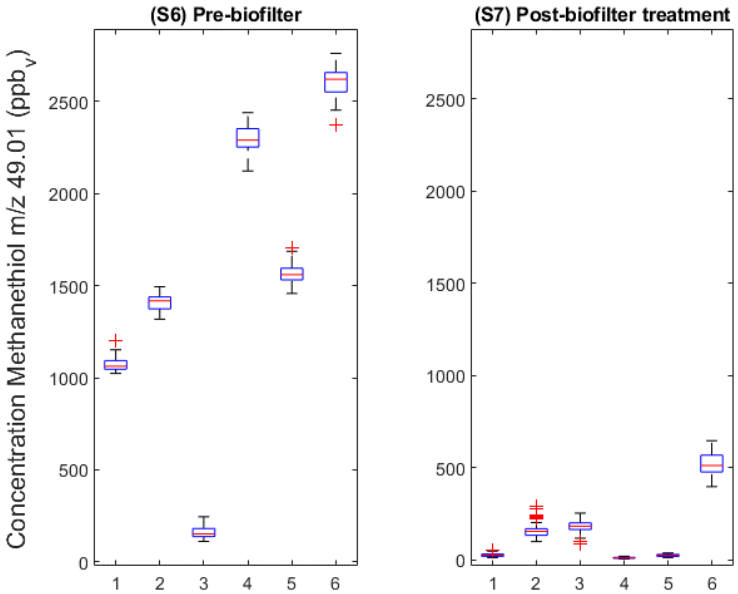

Figure 13:Methanethiol concentrations from pre-biofilter foul air, post-biofilter treatment. Sampling days 1-5, 1-August 2022, 2-March 2023, 3- May 2023, 4-Sept 2023,5- November 2023, 6- February 2024. Boxplots from days 1, 4 and 5 from post biofilter did not have the exhaust fan running while sampling.

Table 9: % Removal of methanethiol from biofilter from all sample days. (S7)

Median concentration and % Removal of methanethiol from odour control						
Treatment between S#	Aug/22 (day 1)	Mar/23 (day 2)	May/23 (day 3)	Sept/23 (day 4)	Nov/23 (day 5)	Feb/24 (day 6)
S6 (ppb_v)	1062	1416	153	2289	1559	2617
S7 (ppb_v)	25	155	183	11	24	513
S6→S7 (%)	100*	59	-20	100*	98*	80

*-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. *Days where exhaust fan was not running during sampling at S7.*

Since the exhaust fans were not operational during sampling days 1, 4 and 5 (Aug 2022, Sept 2023, Nov 2023) their concentrations were not representative of the typical operation. Sample days 2 and 6 (Mar 2023, Feb 2024) showed removal efficiencies for DMS of >40% and day 3 (May 2023) showed poor efficiency of <-100% (Table 10). The average output to the biofilter was around 250 ppb_v (%RSD=50) dimethyl sulfide which

was brought down to an average of 100 ppb_v DMS (%RSD=80), showing a good reduction of 50% DMS through the biofilter (Figure 14 and Table 10).

These findings are similar for S7 from work done in 2019-2020, although concentrations of DMS were much lower 0-60 ppb_v at S6 during the 2019-2020 work at this WWTP. During the sampling days 1 and 4 (Aug 2022, Sept 2023) there was a non-trivial amount of DMS desorbing off the biofilter while the fan was non-operational, with concentrations up to 120 ppb_v, which could potentially be a concern for creating odour complaints. During a sampling campaign done in California utilizing GC-MS measurements looking at DMS through a simple biofilter found input concentrations from 9-29 ppb_v and post-treatment concentrations below 5 ppb_v.[72] Since low concentrations were measured at the pre-treatment side of the biofilter in California, it is likely that this method would bring down the concentrations below 5 ppb_v, yet the input concentrations from WWTP1 biofilter were quite high and is likely not able to handle the flux of DMS through the filter to efficiently lower concentrations below 5 ppb_v.[72]

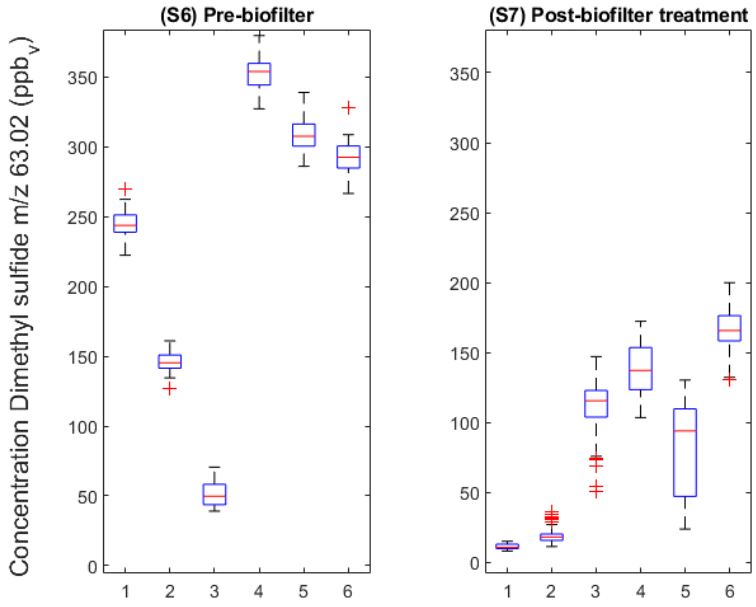

Figure 14: Dimethyl sulfide concentrations from pre-biofilter foul air, post-biofilter treatment. Sampling days 1-5, 1-August 2022, 2-March 2023, 3- May 2023, 4-September 2023,5- November 2023, 6- February 2024. Boxplots from days 1, 4 and 5 from post biofilter did not have the exhaust fan running while sampling.

Table 10: % Removal of dimethyl sulfide from biofilter from all sample days. (S7)

Median concentration and % Removal of dimethyl sulfide from odour control						
Treatment between S#	Aug/22 (day 1)	Mar/23 (day 2)	May/23 (day 3)	Sept/23 (day 4)	Nov/23 (day 5)	Feb/24 (day 6)
S6 (ppb_v)	243	145	50	354	307	291
S7 (ppb_v)	11	18	115	137	94	166

S6→S7 (%)	99*	45	-130	61*	69*	43

*-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. *Days where exhaust fan was not running during sampling at S7.*

During the sampling visits dimethyl disulfide (DMDS) was measured at an average input of 80 ppb_v DMDS (%RSD=80) and was modestly removed by the biofilter treatment (S7) (mean=70 ppb_v, %RSD=130) by 21% on day 2 (Mar 2023), and on sampling day 3 and 6 (May 2023, Feb 2024) where concentrations were observed equal to or higher than the input of DMDS. This could occur from the process changing during sampling or could be from conversion of methanethiol to DMDS (Table 11).[36] A comparison to the data collected from this WWTP in 2019-2020 showed DMDS concentrations in the 0-50 ppb_v and 0-5 ppb_v range for S6 and S7 respectively, which were substantially lower than this sampling campaign.

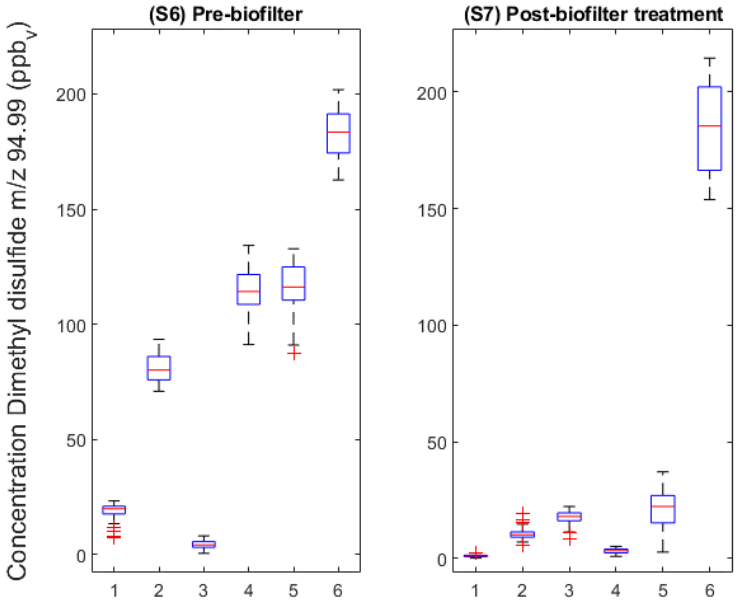

Figure 15:Dimethyl disulfide concentrations from pre-biofilter foul air, post-biofilter treatment. Sampling days 1-5, 1-August 2022, 2-March 2023, 3- May 2023, 4- Sept 2023, 5- November 2023, 6- February 2024. Boxplots from days 1, 4 and 5 from post biofilter did not have the exhaust fans running while sampling.

Table 11: % Removal of dimethyl disulfide from biofilter from all sample days. (S7)

Median concentration and % Removal of dimethyl disulfide from odour control						
Treatment between S#	Aug/22 (day 1)	Mar/23 (day 2)	May/23 (day 3)	Sept/23 (day 4)	Nov/23 (day 5)	Feb/24 (day 6)
S6 (ppb_v)	19	80	4	114	116	184
S7 (ppb_v)	1	10	18	3	22	188
S6→S7 (%)	80*	21	-350	97*	81*	0

*-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. *Days where exhaust fan was not running during sampling at S7.*

This is a variable process so not every day is the same, depending on the load to the de-wetting centrifuge, how long it has been running, and quality of the biofilter bed can all influence concentration ranges for the input and above the biofilter bed. The quality of the substrate in regard to moisture, packing and microbial content can affect the outcomes of treatment. Being a dynamic situation where the plant is constantly changing can cause inherent problems in sampling. Between sample points and even during sampling a process can change and cause fluctuations in the measurement. This odour control method can be effective in removing some VOCs during operations although characterization of the process during normal operations has influenced the results in this case.

UV-Advanced Oxidation Pilot Study

During the sampling campaign a pilot study was done using a proprietary technology which uses advanced oxidation technology. This odour control was achieved using multiple banks of UV-lights and modified activated carbon filters, producing a 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 some measurements of Ozone post-treatment. The measurements taken were also compared to the biofilter concentrations pre- and post-treatment, as this technology would replace the existing biofilter.

The pilot sized unit was plumbed into the exhaust from the de-wetting centrifuge foul air and was sampled at this point and after treatment by the photo oxidative treatment (Figure 17). During four sampling days the inputs to the odour control unit were variable but had an average pre-treatment concentration of 900 ppb_v (%RSD=70) of methanethiol and an average low <5 ppb_v (mean=1 ppb_v, %RSD=60) of methanethiol post-treatment showing good continual 99% average removal of methanethiol across all sampling days with some small deviations during high loads of VOCs as seen on May 24th and 29th, where removal dipped to 98% removal (Figure 17). Similar to methanethiol, dimethyl sulfide input to the odour control unit was variable with an average of 230 ppb_v DMS (%RSD=70) and a post-treatment average concentration <5 ppb_v (mean=2 ppb_v, %RSD=120). The dimethyl disulfide was similar to the DMS with lower concentration inputs to the treatment system at an average of 40 ppb_v (%RSD=100) and a post-treatment concentration below 2 ppb_v (mean=0 ppb_v, %RSD=50) DMDS (Figure 17 and Table 12).

All together this system worked very well at eliminating all three reduced sulfur compounds investigated with removals >95% across all three sulfur compounds measured. This method greatly improves on the removal efficiency of the biofilter treatment, although does require more energy input and annual maintenance (Table 12). This technique can generally eliminate most odour problems. Even with release at low ppb_v they are still prone to dilution and transformation in the atmosphere before leaving the fence line. A photo of the system is show in Figure 16. Additional information from the pilot study is available in the supplemental information Appendix A.

Figure 16: Photo of Advanced UV oxidation unit for odour control, Inlet on the left of unit and outlet at the right.

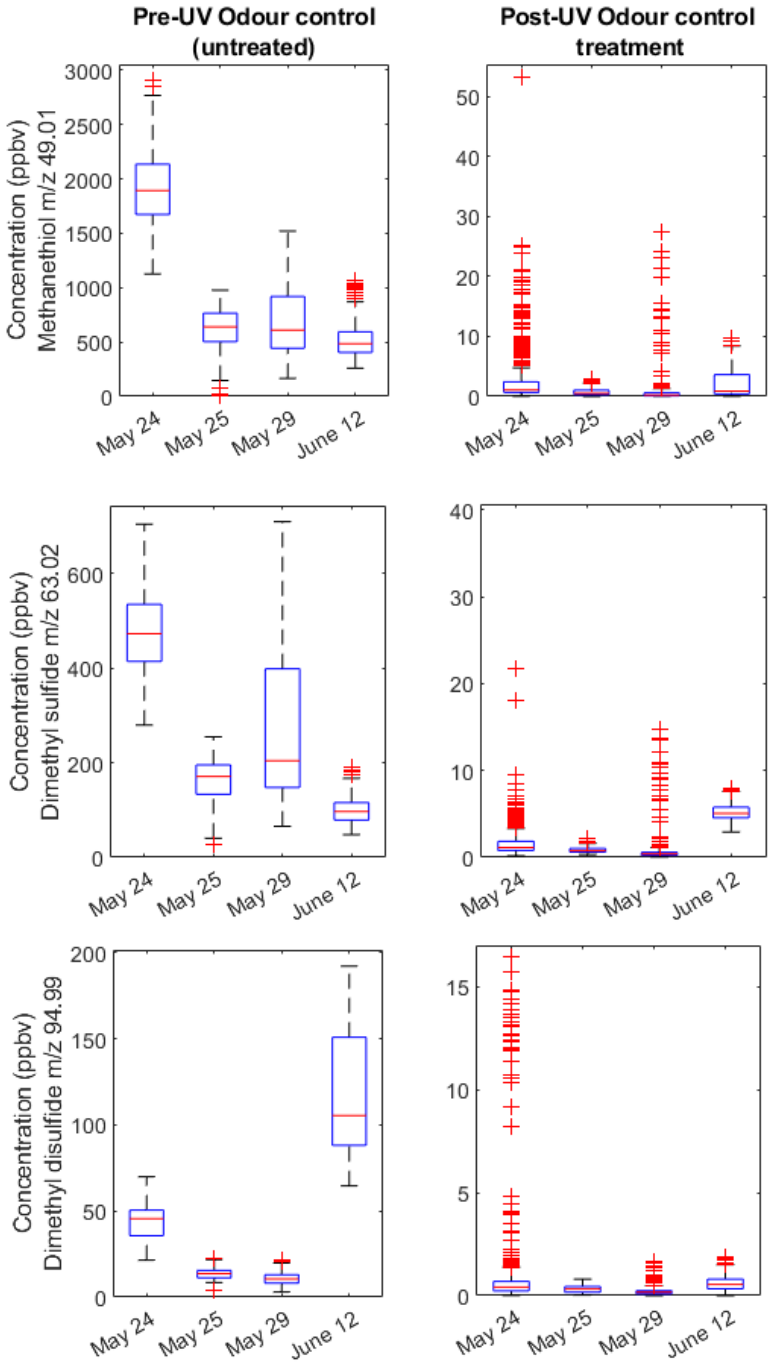

Figure 17: Boxplots from Odour unit trial, Odour unit uses UV/0_3 oxidation, the four sampling days show ranges of concentrations at the inlet and outlet of the odour control unit. Y-axis is scaled differently on each group of boxplots.

Table 12: % Removal of reduced sulfur compounds from AOP odour control unit trial.

% Removal from odour control				
Chemical compound	May 24, 2023	May 25, 2023	May 29, 2023	June 12, 2023
Methanethiol Median Inlet conc. (ppb_v)	1894	640	610	485
Methanethiol Median Outlet conc. (ppb_v)	1.1	0.5	0.2	0.9
Methanethiol % Removal	99.9	99.9	99.97	99.8
Dimethyl sulfide Median Inlet conc. (ppb_v)	473	171	204	97
Dimethyl sulfide Median Outlet conc. (ppb_v)	1.1	0.8	0.4	5.1
Dimethyl sulfide % Removal	99.8	99.5	99.8	94.7
Dimethyl disulfide Median Inlet conc. (ppb_v)	46	14	11	106
Dimethyl disulfide Median Outlet conc. (ppb_v)	0.3	0.2	0.1	0.4
Dimethyl disulfide % Removal	99.3	98.6	99.1	99.6

Conclusions for WWTP1

The treatment of foul air at WWTP1 was effective at reducing the malodourous VOC load compared to the untreated foul airstream, although malodourous VOCs were still emitted above their odour thresholds, with post-treatment concentrations from each exhaust point ranging from an average of 1500 ppb_v methanethiol from (S5) post wet bio scrubber towers coupled with chemical scrubber, an average of 150 ppb_v from the biofilter and the less discussed headworks and trickling filter wastewater treatment room air exhaust outputting around 100 ppb_v of methanethiol very close to the previous work done which had a median of 150 ppb_v (Figure 18).[67] The concentrations recorded are all much higher than odour detection thresholds and could all potentially drive odour complaints in the neighborhood (Figure 18).

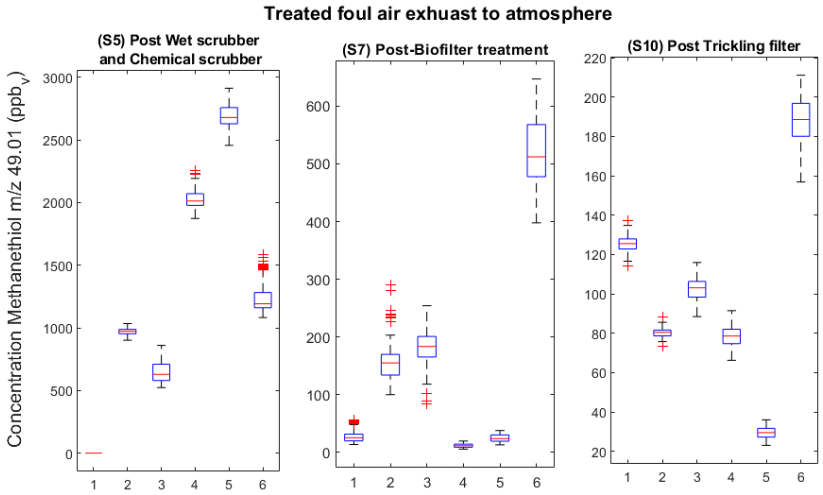

Figure 18: Methanethiol concentrations from exhaust points at WWTP1, post-chemical scrubber, post-biofilter treatment and post trickling filter room treatment. Sampling days 1-5, 1-August 2022, 2-March 2023, 3- May 2023, 4-Sept 2023,5- November 2023, 6- February 2024. Boxplots from days 1, 4 and 5 from 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.

The most concerning exhaust point is from the output of the treated ATAD foul airstream by WBSTs and the chemical scrubber (S5) which has 10x the output as the other exhaust locations onsite. The three main reduced sulfur compounds were treated by the odour control systems with higher efficiencies for methanethiol compared to DMS and DMDS. The wet bio-scrubber towers had removal efficiencies for MeSH averaged at 50% across all days with no negative removal efficiencies suggesting that this system works consistently to lower MeSH emissions, while the chemical scrubber also had an average positive removal efficiency of 50%, it suffered one of the sampling days giving a -80% removal efficiency, thus not working consistently to removal methanethiol each day.

The biofilter on days where operations were normal the average positive removal efficiencies for methanethiol was 70%, although on one of the days it also had a removal efficiency of -20%, indicating this system does not always work to remove methanethiol. The removal efficiencies for DMS had similar ranges for all three odour controls from 40-50%, although all three systems also had one sampling day with a negative removal efficiency of <-100%, indicating that on most days these systems can reduce the DMS load, although in some conditions they may not remove dimethyl sulfide.

The removal efficiencies for DMDS were low from all three systems with the WBSTs and chemical scrubber having an average positive removal efficiency at >30%, but the WBSTs had 2 days, and the chemical scrubber had 1 day with negative removal efficiencies <-100%, which suggests these systems are capable of lowering DMDS inputs although some operational conditions may not support removal of DMDS.

The average positive removal efficiency from the biofilter during normal operational conditions for DMDS was low at 10% and had one day at <-100%, which indicates this system only will remove minor portions of DMDS and may support production of DMDS in some cases.

The pilot odour control study using AOPs worked well across all three reduced sulfur compounds with removal efficiency of >99%, this method of odour control does use an energy intensive process and may have operational maintenance and running costs which may hinder the use of this technology, furthermore the study was done over a two-week period and may have unknown challenges with use beyond the characterized period.

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 work done by Davison J. which encompasses the 2019-2020 data is for reference although during the time from that sampling to now, alterations in operations have occurred onsite and there has been more growth in the area and combined total influent flow went from $3.6x10^6$ m^3 to $3.8x10^6$ m^3 from 2020 to 2023.[67,73]

An average of 1500 ppb_v of methanethiol was observed to be coming from sample point 5 over the sampling campaign, which exhausts to the atmosphere, 1500 ppb_v at STP is 2951.53 $\mu g/m^3$, with an estimated average flow rate of 3050 m^3/hr, is 9.00g/hr flux of methanethiol or 78.85 kg/year. An average of 600 ppb_v of dimethyl sulfide was observed which is 1524.66 $\mu g/m^3$, with an average flux of 4.65 g/hr and 40.65 kg/year. Dimethyl

disulfide had an average of 340 ppb_v or 1309.94 µg/m^3, which gives an estimated flux of 34.9 kg/year (Table 13). The three reduced sulfur compounds yearly flux reported in terms of sulfur is calculated at 97.37 kg/year. Equation 16 is used to calculate yearly emissions.

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

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

Table 13: Estimated flux rates from exhaust from S5 for methanethiol, dimethyl sulfide and dimethyl disulfide.

Compound	Average concentration (ppb_v)	Molecular weight (g/mol)	Average flux (kg/hr)	Yearly emissions (kg/year)	Total moles/yr
Methanethiol	1500	48.11	0.0090	78.9	1640.0
Dimethyl sulfide	600	62.13	0.0047	40.7	655.1
Dimethyl disulfide	340	94.2	0.0040	34.9	370.49
Total Sulfur from MeSH, DMS and DMDS	----------	32.065	----------	97.4	3036.1

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

Stand-alone Modular Activated carbon scrubber units

Onsite WWTP2, two standalone Activated carbon scrubbers were used to eliminate malodours in the foul air streams. This chapter includes the one located at the screening room area where influent is passed through an initial coarse filter before continuing to the primary settling pond. The foul air from the room is collected and passed through the activated carbon scrubber system, which includes multiple beds of activated carbon and modified activated carbon (Figure 19).

Figure 19: (Left) Photo of Mobile Mass Spec Lab on-site WWTP2 at sample locations 2 & 3, Modular activated carbon scrubber 1 to left of the MMSL. (Right) Photo of exhaust stack from Modular scrubber, sample point 3.

Sampling days on-site consisted of 8 days showing the variability of the VOC concentrations pre-treatment at S2 (%RSD=75) (Figure 20). The methanethiol concentrations were averaged pre-treatment above 10 ppb_v from the 8 sampling days. The stand-alone modular activated carbon scrubber worked well over the 8 sampling days for eliminating methanethiol concentrations to below 0.5 ppb_v (%RSD=80) at S3. Concentrations were detected close to detection limits of the instrumentation, giving a an average removal efficiency of 98% for MeSH (Table 14).

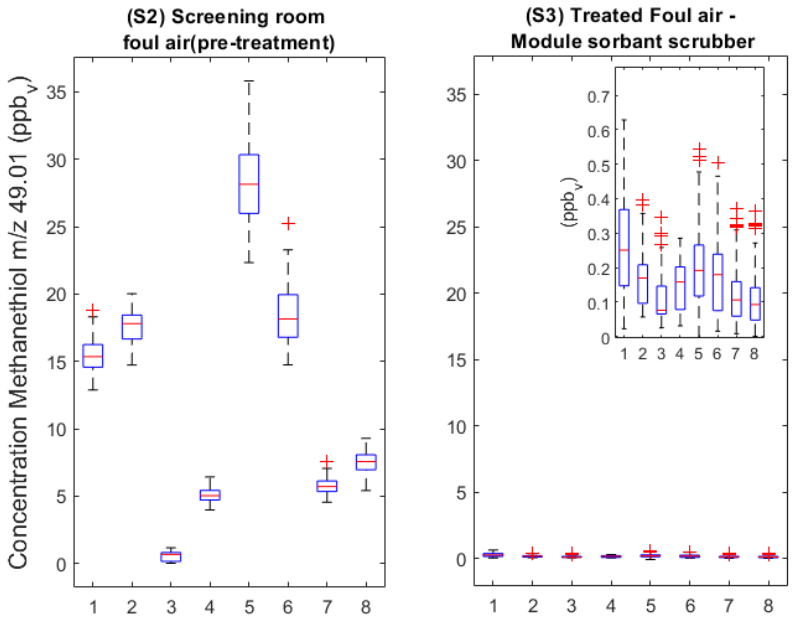

Figure 20: Boxplots showing concentrations of methanethiol from modular activated carbon scrubber on sample days,1-August 2022,2-Nov 2022,3-Jan 2023, 4-April 2023,5-June 2023,6-Sept 2023,7-Nov 2023,8-Feb 2024

Table 14: % Removal of methanethiol from module activated carbon odour control (S3)

Median concentration and % Removal of methanethiol from odour control								
Sample site	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)
S2 (ppb_v)	15	17	0.7	5	28	18	5.5	7.6
S3 (ppb_v)	0.25	0.2	0.1	0	0	0.2	0.1	0.1
S2→3 (%)	98	99	86	100	100	99	98	99

The dimethyl sulfide concentrations recorded throughout the 8 days on-site were relatively low pre-treatment (mean=2 ppb_v, %RSD=100) with sampling day 2 (Nov 2022) recorded slightly elevated concentrations compared to the other days (Figure 21, Table 15).

The modular activated carbon scrubber (S3) did not reduce the DMS by any substantial amount except on day 2 (Nov 2022) which the concentration was reduced by >70% (Table 15). This data shows the incompatibility for total removal of DMS during treatment with the concentrations post-treatment (S3) (mean=1 ppb_v, %RSD=50) remaining relativelty low and comparible with the input concentrations (S2) (Figure 21). When working properly on 5 of the 8 days (Aug 2022, Nov 2022, Jun 2023, Sept 2023, Nov 2023), the removal efficiencies from S3 were 33% to 71% (Table 15). On days 3 and 8 (Jan 2023, Feb 2024) a negative removal efficiency was recorded at -67% and -38% indicating a higher concentration of DMS post-treatment (S3) (Table 15).

The concentrations of DMS were relatively low for S3 at <2 ppb_v which may not pose a great risk of causing odour complaints offsite as they are subjected to further dilution and transformation in the atmosphere before they reach the fenceline (Figure 21).

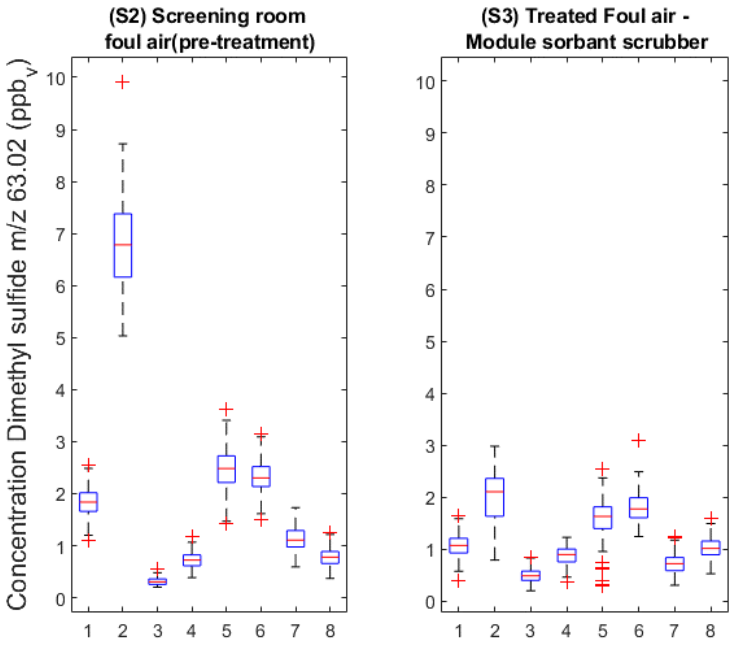

Figure 21:Boxplots showing concentrations of dimethyl sulfide from modular activated carbon scrubber on sample days,1-August 2022,2-Nov 2022,3-Jan 2023, 4-April 2023,5-June 2023,6-Sept 2023,7-Nov 2023,8-Feb 2024

Table 15: % Removal of dimethyl sulfide from module activated carbon odour control (S3)

Median concentration and % Removal of dimethyl sulfide from odour control								
Sample site	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)
S2 (ppb_v)	2	7	0.3	1	3	2.5	1	0.8
S3 (ppb_v)	1	2	0.5	1	2	1.5	0.5	1.1
S2→3 (%)	50	71	-67	0	33	40	50	-38

-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment.

The dimethyl disulfide concentrations were low <2ppb_v across input (S2) (mean=0, %RSD=80) and post-treatment (S3) (mean=1 ppb_v, %RSD=85) for all 8 sampling days (Figure 22). The elimination of DMDS during this treatment is negligible as most concentrations recorded were either the same as the input ranges or in the case on sampling days 6-8 (Sept 2023,Nov 2023, Feb 2024) were slightly elevated from the input concentrations (Table 16).

This is consistent with other observations seen in this work from activated carbon scrubbing technology where DMDS is not removed, and the sorbent may likely become a source of DMDS from conversion of methanethiol to DMDS on the substrate.[36]

On 5 days (Aug 2022, Nov 2022, Jan 2023, Apr 2023, Jun 2023) the removal efficiency was 0-50% indicating a minor reduction of DMDS post treatment although these concentrations were low and close to the input concentrations (Table 16). The high volatility of DMDS makes it less compatible with sorption-based scrubbers as it is prone to quick breakthrough and desorption.[35]

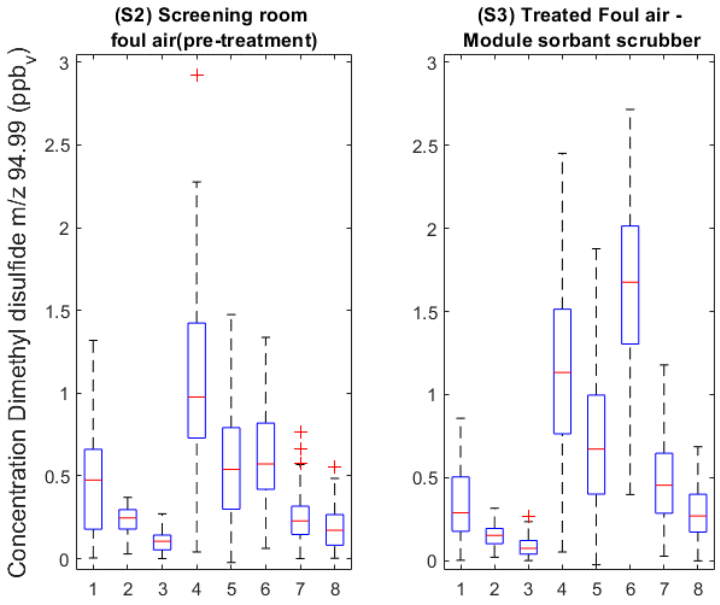

Figure 22:Boxplots showing concentrations of dimethyl disulfide from modular activated carbon scrubber on sample days,1-August 2022,2-Nov 2022,3-Jan 2023, 4-April 2023,5-June 2023,6-Sept 2023,7-Nov 2023,8-Feb 2024

Table 16: % Removal of dimethyl disulfide from module activated carbon odour control (S3)

Median concentration and % Removal of dimethyl disulfide from odour control								
Sample site	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)
S2 (ppb_v)	0.5	0.24	0.1	1	1	0.5	0.2	0.2
S3 (ppb_v)	0.25	0.15	0.1	1	1	1.5	0.5	0.3
S2→3 (%)	50	38	0	0	0	-200	-150	-50

-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment.

Module carbon scrubber 2

Activated carbon scrubber 2 is located at the de-wetting room where collected solids have their water removed by centrifugation and foul air collected from this process is passed through the activated carbon scrubber system seen in Figure 23. Measurements are taken pre and post treatment at each site, although the screening site which uses activated carbon scrubber 1 is continuous and undergoes fluxes with influent quantities and the de-wetting process is a batch process like at WWTP1. Not all days had this process running, or it is only running for some periods throughout the day.

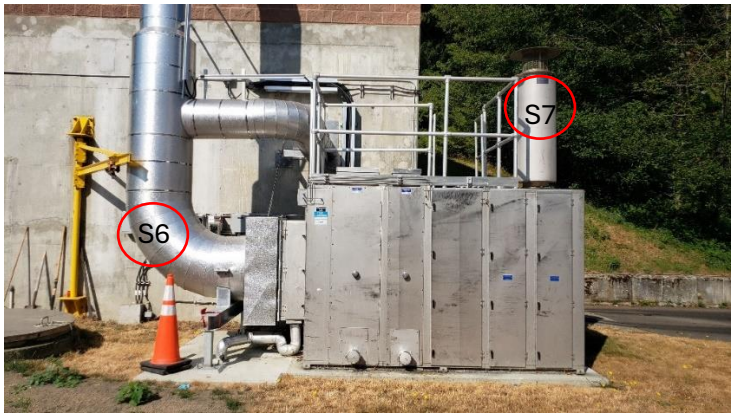

Figure 23: Photo of Modular activated carbon scrubber 2 from de-watering building, sample points 6 & 7.

During the 8 sampling days concentrations were recorded pre (S6) and post treatment (S7), showing some variability in the VOC concentration in the foul air. Throughout the sampling days input concentrations averaged low <1.5 ppb_v (%RSD=110) methanethiol, and the output through the modular scrubber averaged <0.3ppb_v (%RSD=110) which indicated the system was working efficiently to remove the trace methanethiol introduced

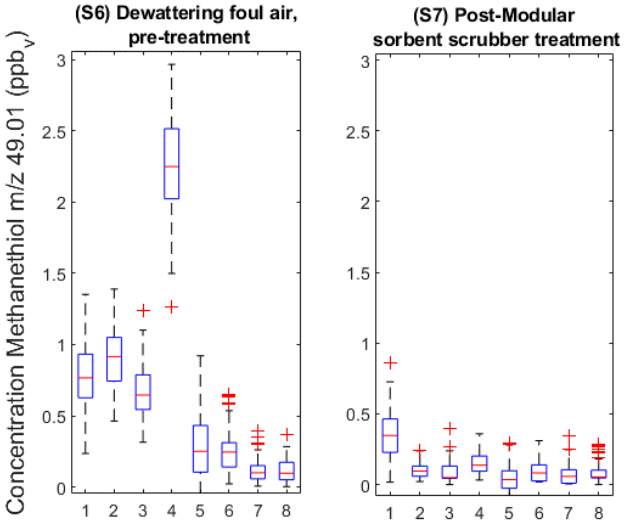

Figure 24: Boxplots showing concentrations of methanethiol from modular activated carbon scrubber 2 on sample days,1-August 2022,2-Nov 2022, 3-Jan 2023, 4-April 2023,5-June 2023,6-Sept 2023,7-Nov 2023,8-Feb 2024

to the scrubber system (Figure 24). On days 1-4 (Aug 2022, Nov 2022, Jan 2023, Apr 2023) removal efficiencies of 55-100% was observed for methanethiol. On days 5-7 (Jun 2023, Sept 2023, Nov 2023) no signifigant removal (<5%) was observed by the system (Table 17). On day 8 (Feb 2024) the blower was offline so only ambient amounts of air were travelling through the system and is not representitive of the normal operations (Figure 24). Sampling day 8 can be used as an example to what the concentrations are when the system is being left not running.

Table 17: % Removal of methanethiol from module activated carbon odour control (S7)

Median concentration and % Removal of methanethiol from odour control								
Sample site	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)
S6 (ppb_v)	0.76	0.91	0.6	2	0	0.2	0.1	0.1
S7 (ppb_v)	0.34	0.01	0.1	0	0	0.2	0.1	0.1
S6→7 (%)	55	99	83	100	0	0	0	0

Figure 25 shows the variability of dimethyl sulfide in the gas stream going to the scrubber system (mean=1 ppb_v, %RSD=130). The pre- and post-treatment concentrations were similar in magnitude which indicated an incompatibiliy with the scrubber system, similar to the previous modular scrubber system from the screening room foul air shown in Figure 21. There was a small reduction in median concentrations although including the variability at each day the concentrations were not effectively eliminated. The average median values for S6 were 1.3 ppb_v and S7 was 0.95 ppb_v (%RSD=140), with a removal efficiencies for days 1-4 (Aug 2022, Nov 2022, Jan 2023, Apr 2023) at 13-100% and days 5-7 (Jun 2023, Sept 2023, Nov 2023) showing <5% removal efficiencies (Table 18). The sampling day 8 (Feb 2024) with the blowers not running may indicate the amount of residual VOCs being desorped from the treatment system.

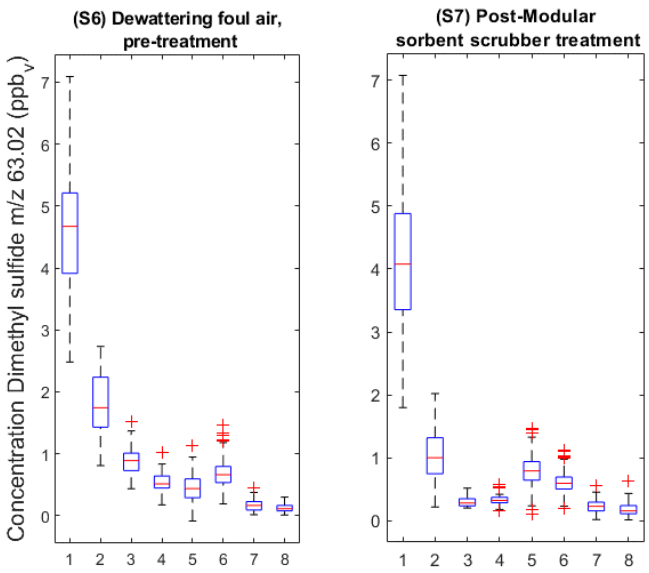

Figure 25:Boxplots showing concentrations of dimethyl sulfide from modular activated carbon scrubber on sample days,1-August 2022,2-Nov 2022,3-Jan 2023, 4-April 2023,5-June 2023,6-Sept 2023,7-Nov 2023,8-Feb 2024

Table 18: % Removal of dimethyl sulfide from module activated carbon odour control (S7)

Median concentration and % Removal of dimethyl sulfide from odour control								
Sample site	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)
S6 (ppb_v)	4.6	1.7	0.9	1	0	0.5	0.2	0.2
S7 (ppb_v)	4	1	0.3	0	1	0.5	0.2	0.2
S6→7 (%)	13	41	67	100	0	0	0	0

The dimethyl disulfide concentrations were on average low <1.5 ppb_v pre-treatment (S6) (mean=1, %RSD=160) and <1ppb_v post treatment (S7) (mean=0 ppb_v, %RSD=80), showing a slight decrease in concentrations but overall negligible removal of dimethyl disulfide similar to the previous modular scrubber (Figure 26). These results could be from non-compatibility with the system to fully eliminate DMDS from the gas stream. On days 2, 3, 4 and 7 (Nov 2022, Jan 2023, Apr 2023, Nov 2023) removal efficiencies were 50-96% (Table 19). Days 1 and 6 (Aug 2022, Sept 2023) showed removal efficiencies of -15% and -50% indicating poor performance of the system, along with no change on day 5 (Jun 2023) (Table 19). On sampling day 8 (Feb 2024) which has the blowers offline can be used as a measure of ambient concentration at the inlet and outlet of the system.

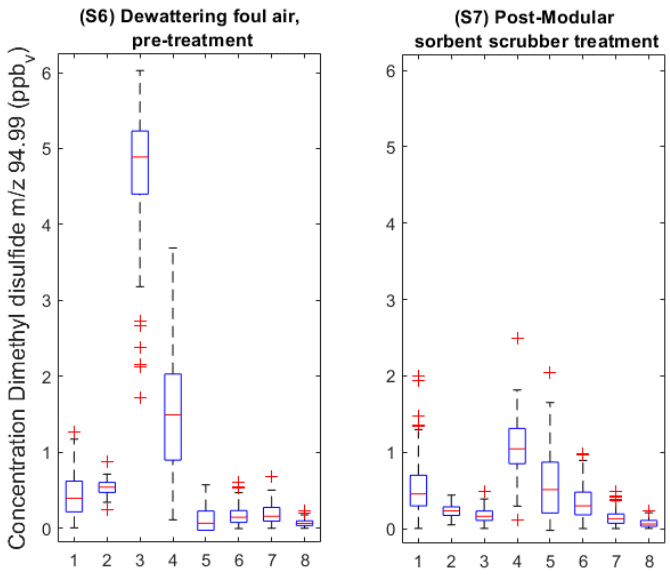

Figure 26:Boxplots showing concentrations of dimethyl disulfide from modular activated carbon scrubber on sample days,1-August 2022,2-Nov 2022,3-Jan 2023, 4-April 2023,5-June 2023,6-Sept 2023,7-Nov 2023,8-Feb 2024

Table 19: % Removal of dimethyl disulfide from module activated carbon odour control (S7)

Median concentration and % Removal of dimethyl disulfide from odour control								
Sample site	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)
S6 (ppb_v)	0.39	0.54	5	2	0	0.2	0.2	0.1
S7 (ppb_v)	0.45	0.23	0.2	1	0.5	0.3	0.1	0.1
S6→7 (%)	-15	57	96	50	0	-50	50	0

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

Bioreactor odour control technology

The main odour control technology onsite is the large bioreactor systems which are two large modular bioreactors which follow the foul airstream after a large wet scrubber/rain tower and before exhausting to the atmosphere (Figure 28, 29). The bioreactors are run in parallel with one another and share the same exhaust tower which sits ~50 ft off the ground, during the sampling campaign we outfit a large sampling line to the top the of the exhaust tower to better sample the combined outputs post treatment (Figure 29). Samples were taken post-wetting/ pre-bioreactor treatment (S8) and at the exhaust stack (S9). The MMSL was used to take measurements of the VOCs at these locations and sorbent tube analysis was done at this location. Photos of the primary treatment and foul air collection which runs to the bioreactor are shown in Figure 27.

Figure 27 (Left) Photo of primary treatment sedimentation. (Right) Foul air collection from primary treatment, ductwork is sample point 4 and is plumbed to the Bioreactor odour treatment system.

Figure 28 Photo of Rain tower, which adds humidity to the airstream before it enters the Bioreactor odour control, Exhaust of Rain tower to the left is sample point 8.

Figure 29: (Left) Photo of Bioreactor exhaust stacks, sample point 9. (Right) Photo of Bioreactors showing ductwork from raintower which is sample point 8.

The foul air collection network pre-treatment (S8) was evaluated across 8 on-site sampling days showing variability in on-site foul air methanethiol concentration, with an average of 130 ppb_v (%RSD=70) of incoming methanethiol to the bioreactor treatment system (Figure 30).

The post-treatment (S9) concentrations of methanethiol were also variable but averaged at 20 ppb_v (%RSD=70). On day 1 (Aug 2022) modest removal efficiency of 30% was recorded. On average the system works well to reduce the methanethiol by >80%, with efficiency still reached during some days with elevated methanethiol concentration inputs seen on days 5 and 6 (Table 20).

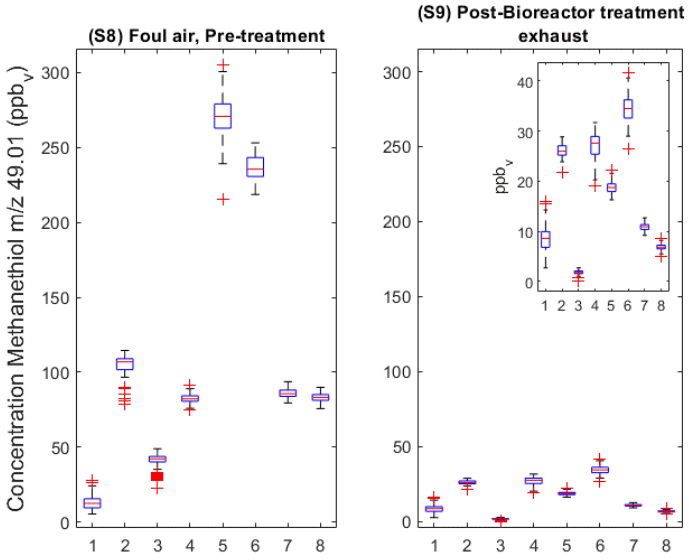

Figure 30:Boxplots showing concentrations of methanethiol from Pre and Post Bioreactor treatment on sample days,1-August 2022,2-Nov 2022,3-Jan 2023, 4-April 2023,5-June 2023,6-Sept 2023,7-Nov 2023,8-Feb 2024

Table 20 % Removal of methanethiol from bioreactor odour control (S9)

Median concentration and % Removal of methanethiol from odour control								
Sample site	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)
S8 (ppb_v)	12.3	106	42	205	271	235	85	83
S9 (ppb_v)	8.6	25.9	2	28	19	34	11	6.9
S8→9 (%)	30	76	95	86	93	86	87	92

Dimethyl sulfide concentrations from the foul air network (S8) were highly variable (%RSD=95) with half the sampling days >100 ppb_v and the other half <40 ppb_v dimethyl sulfide (Figure 31).

The post-treatment (S9) concentrations of DMS were also variable (%RSD=100) throughout the study period showing some days with modest removal of this gas, days 1, 3, 5 and 8 (Aug 2022, Jan 2023, Jun 2023, Feb 2024) having removal efficiencies from 28-46% (Table 21). Days 6 and 7 (Sept 2023, Nov 2023) have negligible amount of removal efficiency up to 17% and on days 2 and 4 (Nov 2022, Apr 2023) an increased concentration was observed giving removal efficiencies of -12 and -56%, respectively (Table 21).

The overall average removal efficiency was 10% for DMS (Table 21). The high variability of the efficiency suggests inconsistent compatibility for removal of DMS using the bioreactor system.

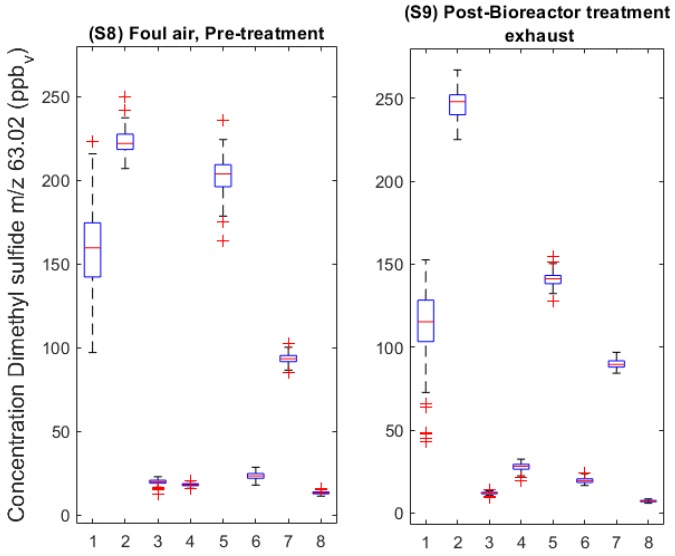

Figure 31:Boxplots showing concentrations of dimethyl sulfide from Pre and Post Bioreactor treatment on sample days,1-August 2022,2-Nov 2022,3-Jan 2023, 4-April 2023,5-June 2023,6-Sept 2023,7-Nov 2023,8-Feb 2024

Table 21: % Removal of dimethyl sulfide from bioreactor odour control (S9)

Median concentration and % Removal of dimethyl sulfide from odour control								
Sample site	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)
S8 (ppb_v)	159	221	20	18	204	23	93	13.5
S9 (ppb_v)	115	248	12	28	141	19	89	7.3
S8→9 (%)	28	-12	40	-56	31	17	0	46

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

The dimethyl disulfide concentrations recorded during the sampling campaign pretreatment (S8) (mean=6 ppb_v, %RSD=70) and post-treatment (S9) (mean=6 ppb_v, %RSD=90) highlight non-compatibility of the system for removal of DMDS (Figure 32, Table 22). Although only modest increases of DMDS concentration post treatment observed on days 4 and 6 (Apr 2023, Sept 2023) of 17 and 67%, which could be from production of DMDS or come from the variability in input to the system as they fall in the range of the input concentrations (Figure 32 and Table 22). Sample days 1, 2, 3 and 8 (Aug 2022, Nov 2022, Jan 2023, Feb 2024) had removal efficiencies from 34-75% (Table 22). Day 5 (Jun 2023) showed no change in concentration from treatment and day 7 (Nov 2023) showed a slight decrease of 23% (Table 22).

It is important to consider the overall concentrations were quite low (mean=6 ppb_v) at the exhaust even with inconsistent efficiencies (Figure 32). Similar to adsorption-based systems like the activated carbon scrubbers, this is not an effective treatment to eliminate all DMDS concentrations but may not provide as much of a source of this gas from treatment.

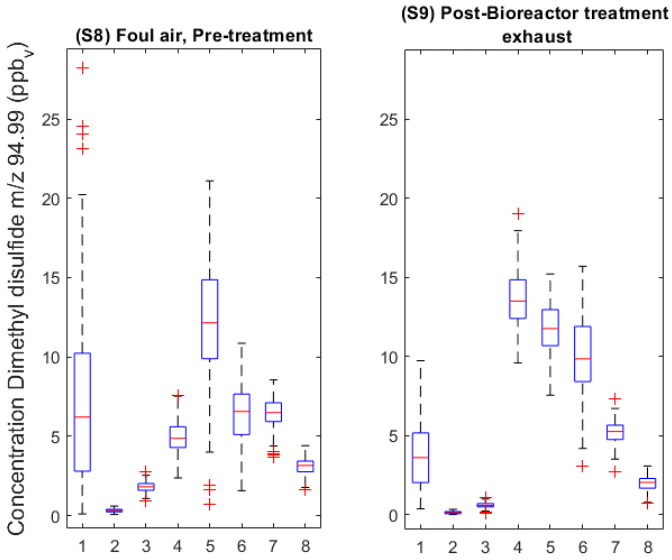

Figure 32:Boxplots showing concentrations of dimethyl disulfide from Pre and Post Bioreactor treatment on sample days,1-August 2022,2-Nov 2022,3-Jan 2023, 4-April 2023,5-June 2023,6-Sept 2023,7-Nov 2023,8-Feb 2024

Table 22: % Removal of dimethyl disulfide from bioreactor odour control (S9)

Median concentration and % Removal of dimethyl disulfide from odour control								
Sample site	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)
S8 (ppb_v)	6	0.3	2	12	12	6	6.5	3.2
S9 (ppb_v)	3.5	0.1	0.5	14	12	10	5	2.1
S8→9 (%)	42	67	75	-17	0	-67	23	34

-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment.

The average flow rate at the exhaust stack is 18,650 m^3/hr. Average fluxes are in Table 23 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 23: Estimated flux of methanethiol, dimethyl sulfide and dimethyl disulfide from exhaust stack (S9) at STP.

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	48.11	39.55	0.000378	6.46	134.31
Dimethyl sulfide	50.18	62.13	127.51	0.0024	20.83	335.29
Dimethyl disulfide	6.21	94.2	23.93	0.00044	3.9	41.4
Total sulfur (from MeSH, DMS and DMDS)	----------	32.065	----------	----------	17.71	552.4

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. Using a biological treatment system can reduce costs associated with replenishing sorbents and high energy consumption from advanced controls like photo-oxidation.

Mass spectra from sample points 8 and 9 are shown in Figure 33. The distribution of mass to charges is similar for both S8 and S9 although signal intensities are greatly reduced in S9 from S8 showing that a variety of VOCs are being removed from the foul air stream post treatment. Mass-to-charges at 45, 49 and 59, are likely due to acetaldehyde, methanethiol and acetone, respectively, and are greatly reduced from S8 to S9. The bioreactor/filter treatment reduced the amount of these compounds out of the air stream. Methanethiol, dimethyl sulfide and dimethyl disulfide are labelled on the Mass spectra (Figure 33). Mass spectra can be used to identify the mixture of compounds in the gas stream and may allow for identification of a chemical fingerprint for each exhaust point.

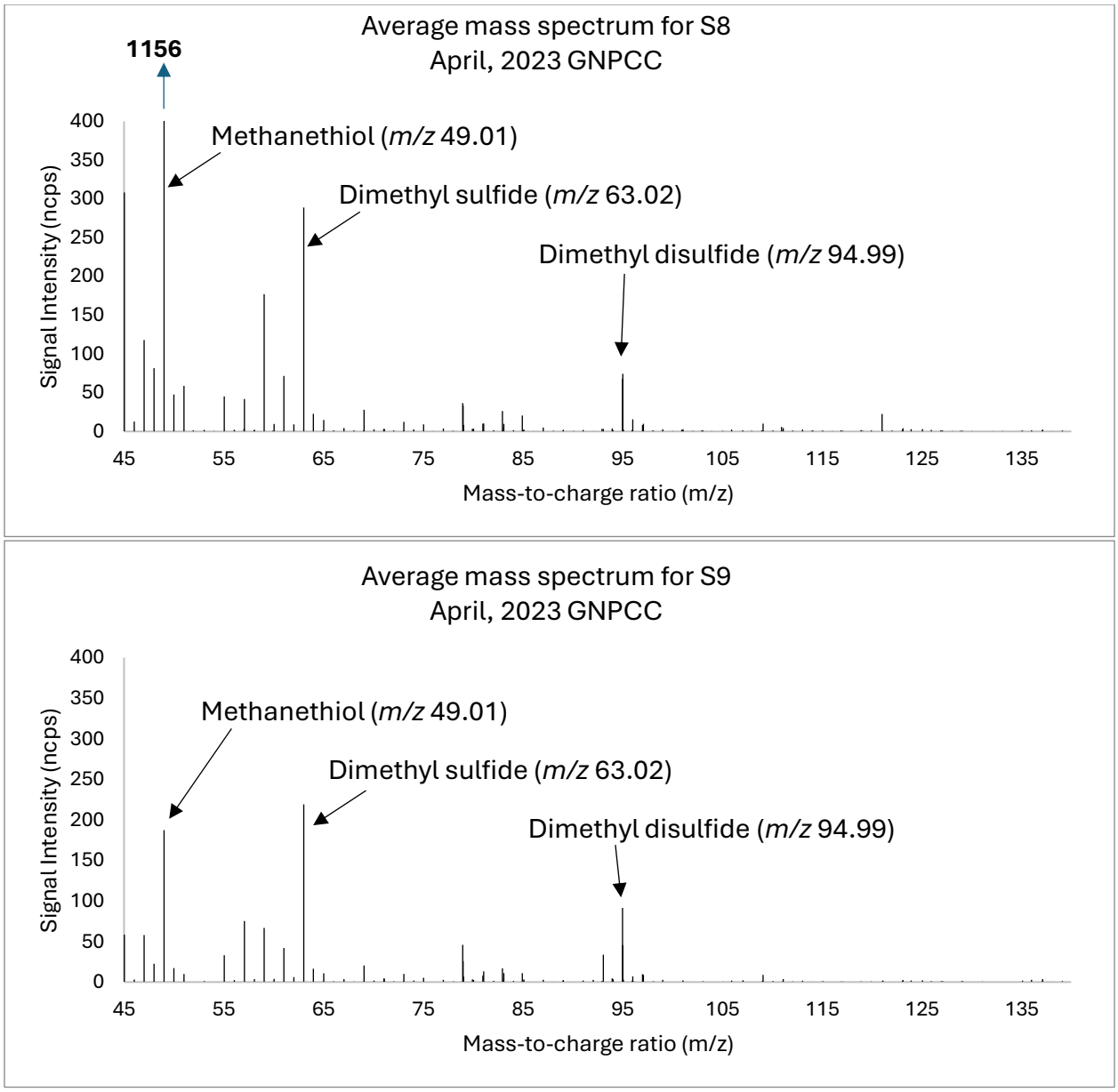

Figure 33: Average Mass spectra from S8-pre-bioreactor (top) and S9-post-bioreactor (bottom) during April 2023 on-site sampling day 4.

Conclusions from WWTP2 odour controls

The concentration of methanethiol, DMS and DMDS from the post treatment air from the modular activated carbon scrubbers was very low (<2 ppb_v) and were mostly recorded at detection limits of our equipment. The removal of methanethiol by the activated carbon scrubbers was 80-95% removal efficiency, 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, yet they were not definitively 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.

The bioreactor system works well at eliminating a large portion of malodourous methanethiol from the foul air stream at an average of 80% removal yet showed an inconsistent removal of DMS at an average of 30% removal efficiency with two sample days having a negative removal efficiency of <-10%. The average removal efficiency for DMDS was 40% on 6 of the 8 sample days, while two days had a negative removal efficiency of <-20%.

These findings indicate 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 emitted above their odour detection thresholds but are not excessively high, <20 ppb_v, and will be diluted by the atmosphere after release. This WWTP study consisted of over 17 hours of on-site evaluation including over 61,000 observations and gives a glimpse into the workings of odour control technologies onsite.

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

Foul air from primary treatment

During the sampling campaign, 11 on-site days were evaluated at the inlet and outlet of the primary treatment odour control which has an inline bio trickling filter then activated carbon scrubber towers. This was done to evaluate the variability in the VOC concentrations from the primary treatment and the scrubbing efficiency of the odour controls (Figure 30-52). High variability was observed across the sampling period with a range of 200-1200 ppb_v (mean=520 ppb_v, %RSD=70) methanethiol (MeSH) in the foul air stream pre-treatment (1A) (Figure 34). The high variability in the primary treatment foul air has also been noted in previous work done on concentrations of methanethiol dissolved in wastewater. [40]

The post treatment gas stream (1C) was also variable in methanethiol concentrations although was always <100 ppb_v and an average of 30 ppb_v (%RSD=70) (Figure 30). The average removal efficiency for methanethiol was >90% removal which would suggest good compatibility with the system (Table 24). Although the post-treatment concentrations are still much higher than the odour thresholds (ODT MeSH=0.02ppb_v), yet they would still be subject to further dilution and transformation in the atmosphere (Table 24). The removal efficiency for MeSH is similar to work done by Shammay *et al*, which found that activated carbon had good removal efficiency >90%, measuring systems which averaged at 130 ppb_v MeSH input concentrations and had input concentration ranges of systems similar to WWTP3 ranging from 80-740 ppb_v.[74]

From the work done at WWTP3 and WWTP2 it suggests activated carbon is an effective method for removal of odourous methanethiol with removal efficiencies consistently >80%.

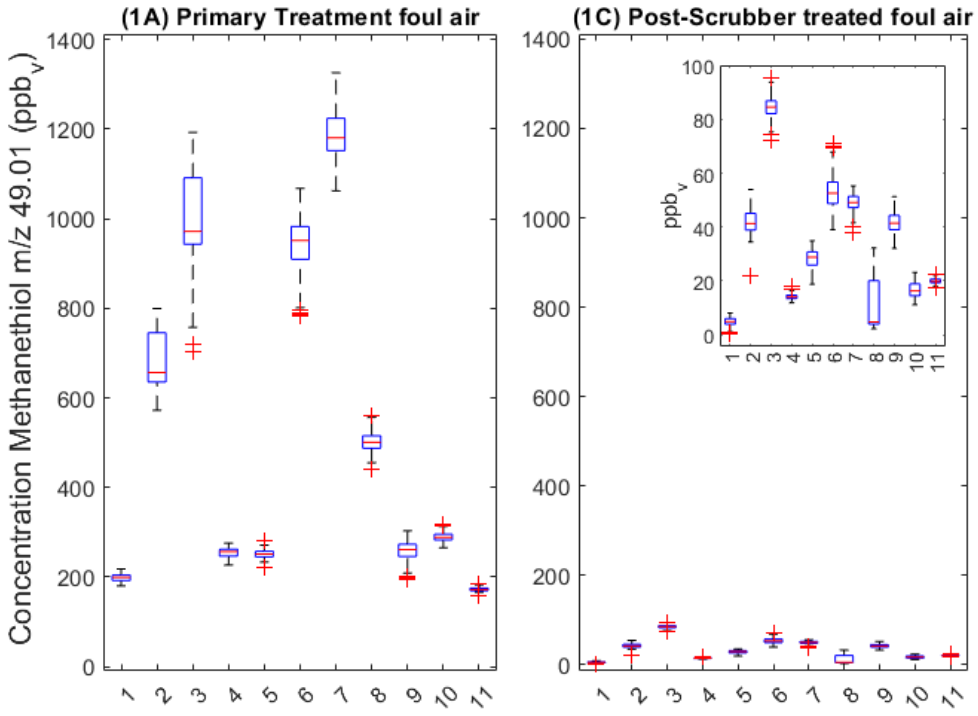

Figure 34: Boxplots of concentrations of methanethiol from sample points 1A and 1C, from the primary treatment foul air odour control. 1-April 2022, 2-November 24, 2023, 3-November 25, 2023, 4-February 2023, 5-April 2023, 6-May 2023, 7-July 2023, 8-August 2023, 9-October 2023, 10-November 2023, 11-February 2024.

Table 24: % Removal of methanethiol from activated carbon scrubber odour control (1C)

Median concentration and % Removal of methanethiol from odour control (1A→1C)											
Sample site	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 (ppb_v)	199	681	1003	254	251	941	1189	502	261	289	172
1C (ppb_v)	5	42	85	14	28	53	49	11	42	16	20
%	98	94	92	94	89	94	96	98	84	94	88

During the 11 days of on-site sampling some variability was observed in the incoming foul air to the activated carbon scrubbers (1A) with an average of 40 ppb_v (%RSD=70) dimethyl sulfide (DMS) (Figure 35).

Modest DMS removal was observed on some sampling days (up to 40%), the average post-treatment (1C) concentration was 30 ppb_v (%RSD = 40) (Table 25). Overall, the primary odour treatment with activated carbon appears to have little affect on the DMS concentration over the study period examined here with most days showing negligible

amounts of removal. These findings were similar to activated carbon scrubbing systems evaluated from WWTP2, this could be an incompatibility issue with the odour treatment system for removal of DMS.

The average removal efficiency was -10% for DMS from this system. On six sampling days (Nov 2022, Apr 2023, Oct 2023, Nov 2023) negative removal efficiencies were recorded ranging from <5% to -148%, indicating elevated DMS concentrations were observed in the post-treatment gas stream (Table 25).

On the days 1, 4, 6, 7 (Apr 2022, Feb 2023, May 2023, Jul 2023) where removal of DMS was occurring, the efficiencies ranged from 16-44% removal and on day 11 (Feb 2024), 0% removal efficiency was recorded (Table 25).

These observations are consistent with observations by Shammay *et al*, which found removal efficiency of DMS from activated carbon is poor, with average removal efficiency around 10%, with some instances of negative removal efficiency, similar to this study.[73]

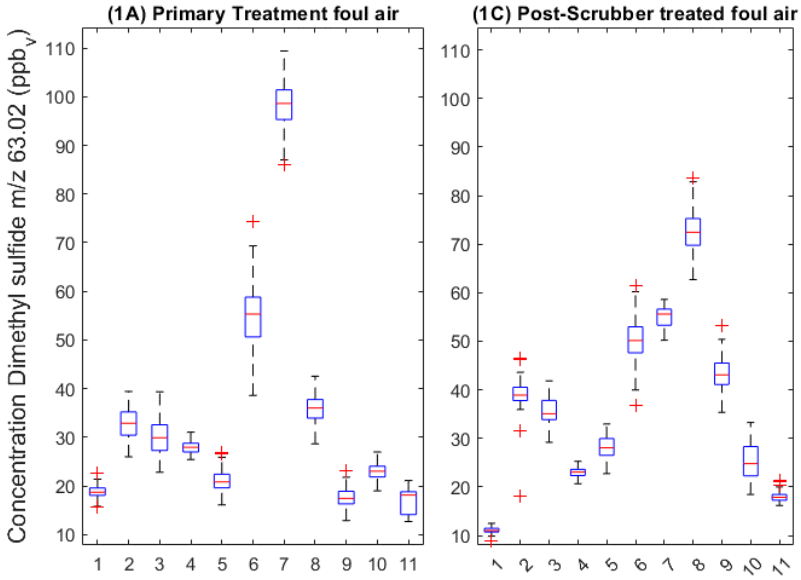

Figure 35: Boxplots of concentrations of dimethyl sulfide from sample points 1A and 1C, from the primary treatment foul air odour control. 1-April 2022, 2-November 24, 2023, 3-November 25, 2023, 4-February 2023, 5-April 2023, 6-May 2023, 7-July 2023, 8-August 2023, 9-October 2023, 10-November 2023, 11-February 2024.

Table 25: % Removal of dimethyl sulfide from activated carbon scrubber odour control (1C)

Median concentration and % Removal of dimethyl sulfide from odour control (1A→1C)											
Sample site	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 (ppb_v)	19	33	30	28	21	57	99	35	17	23	18
1C (ppb_v)	11	39	35	23	28	48	55	36	43	25	18
%	40	-18	-18	18	-32	16	44	0	-148	-8	0

-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment.

The input concentration range of DMDS to the activated carbon scrubbers was <80 ppb_v across all sampling days, and an average of 20 ppb_v (%RSD=100). Figure 36 shows that the input concentrations of DMDS are somewhat lower than that of DMS (~ 40 ppbv) and significantly less than methanethiol (~ 500 ppb_v).

The post-treatment concentration ranges were variable and on average 90 ppb_v (mean=110 ppb_v, %RSD=110) greater than the input concentration. This is most likely from contribution of DMDS generated on the sorbent, by chemical conversion of methanethiol to dimethyl disulfide (Equation 3). Sample day 1 (Apr 2022) showed the only positive removal efficiency during these 11 sample days, at a 64% removal efficiency (Table 36).

On days 2-11 (Nov 2022-Feb 2024) removal efficiency was poor, with significant increases in the DMDS observed (Table 36). The elevated concentrations of DMDS may be a good indicator that the sorbent beds are spent and in need of replenishing.

To investigate this phenomenon we obtained some used sorbents from WWTP3 which were placed in a glass TOC vial and were dynamically sampled with zero air into the vial and a line connected to the mass spectrometer, which showed high levels of DMDS coming off the sorbent and much less methanethiol reported in Appendix C. This is unusual unless the methanethiol is converting to DMDS, as input concentrations to the sorbents are much higher for MeSH then DMDS (Table 34 and 36).

After several observations on-site of elevated DMDS post-treatment we decided to examine this further. In addition to similar observations being reported by Andersen *et al.* 2012 and Shammay *et al.* 2016, we obtained fresh sorbent material from engineering staff at WWTP3 to conduct several bench scale trials.[35,74] A small scale benchtop experiment was done to assess the transformation of MeSH to DMDS using the fresh sorbents obtained from WWTP3, where we produced DMDS with only addition of methanethiol to a sorbent packed flow tube. This is discussed in further detail in Appendix C.

This work done at WWTP3 is very similar to findings at other activated carbon scrubbers, where DMDS was poorly removed, and the scrubber was a source of DMDS rather than removing the compound from the gas stream.[74] This suggests these systems

are not well suited for removal of DMDS from the gas stream and may in fact act as a source.

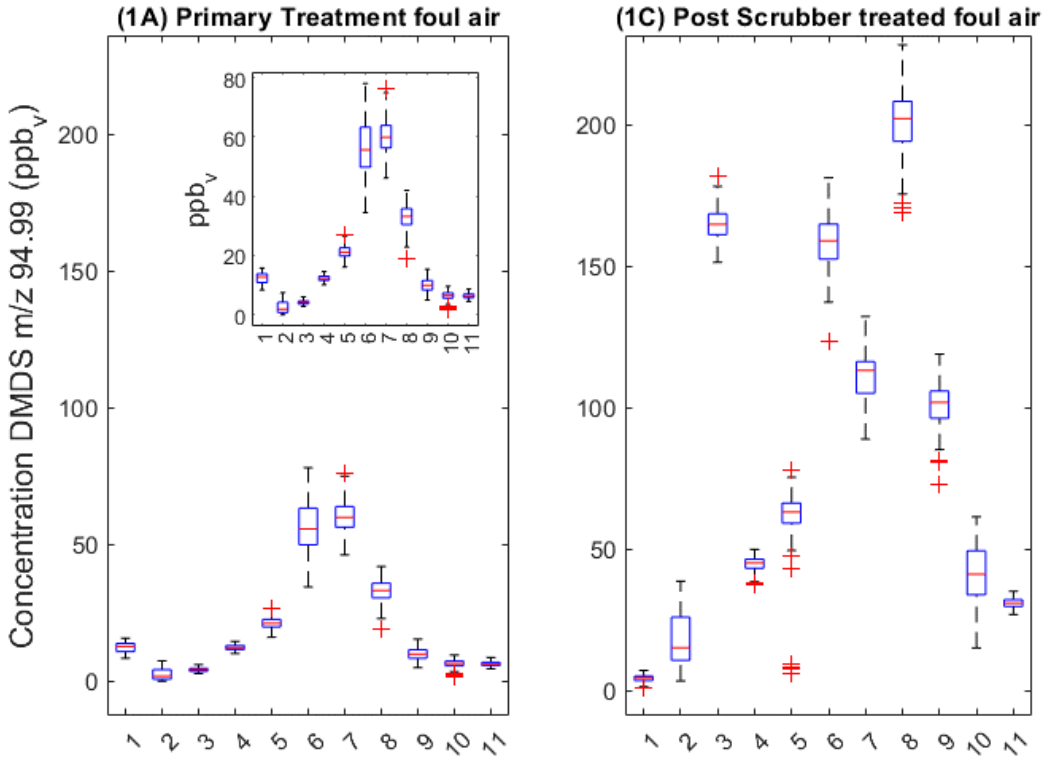

Figure 36: Boxplots of concentrations of dimethyl disulfide from sample points 1A and 1C, from the primary treatment foul air odour control. 1-April 2022, 2-November 24, 2023, 3-November 25, 2023, 4-February 2023, 5-April 2023, 6-May 2023, 7-July 2023, 8-August 2023, 9-October 2023, 10-November 2023, 11-February 2024.

Table 26: % Removal of dimethyl disulfide from activated carbon scrubber odour control (1C)

Median concentration and % Removal of dimethyl disulfide from odour control (1A→1C)											
Sample site	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 (ppb_v)	12	3	4	12	21	57	60	33	10	7	6
1C (ppb_v)	4	18	165	45	60	412	112	200	102	41	31
%	64	-610	-1000	-266	-180	-628	-86	-507	-919	-534	-400

-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. Negative removal efficiency is capped at -1000%.

Additionally, the estimated reduced sulfur flux from primary odour controls using the design flow rate of 17000 m^3/hr and the average concentrations from the sampling campaign was calculated (Equation 16). Total yearly flux of the combined three sulfur compounds reported as sulfur is 55 kg/year (Table 27).

Table 27: Flux data for methanethiol, dimethyl sulfide and dimethyl disulfide from primary odour controls at WWTP3.

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	30	48.11	59.0	0.0010	8.79	182.72
Dimethyl sulfide	30	62.13	76.2	0.0012	11.35	182.72
Dimethyl disulfide	110	94.2	423.8	0.0072	63.11	669.98
Total sulfur (MeSH, DMS and DMDS)	---------	32.065	----------	--------	54.68	1705.42

Foul air scrubber towers from secondary waste treatment

The foul air from the secondary treatment system was evaluated during the 11 days of on-site sampling (photo in Figure 40) showing the concentrations in the foul air system (2A) (Figures 53-55). Methanethiol was found to be quite variable from 50-800 ppb_v (mean=350 ppb_v, %RSD=80) (Table 23). Half of the sampling days (Apr 2022-Feb 2023, Oct 2023, Feb 2024) were relatively low MeSH concentration <200 ppb_v compared to the other half the days >600 ppb_v (Apr 2023-Aug 2023, Nov 2023) (Figure 37, Table 28). Although, the post-treatment air stream (2B) was less variable showing good removal of methanethiol (>90%) with an average concentration across all days of <15 ppb_v (mean=10 ppb_v, %RSD=95) (Figure 37, Table 28). Throughout the study methanethiol removal efficiencies were >90% (Table 28). These findings are similar to the activated carbon scrubber from the primary treatment and also from previous work done showing removal efficiencies >90% for methanethiol.[74] The activated carbon scrubber systems have been quite robust in their efficiency of methanethiol removal across all technologies discussed in this chapter including these stacks, which the output always <40 ppb_v from the treated secondary foul air stream and removal efficiencies above 90%.

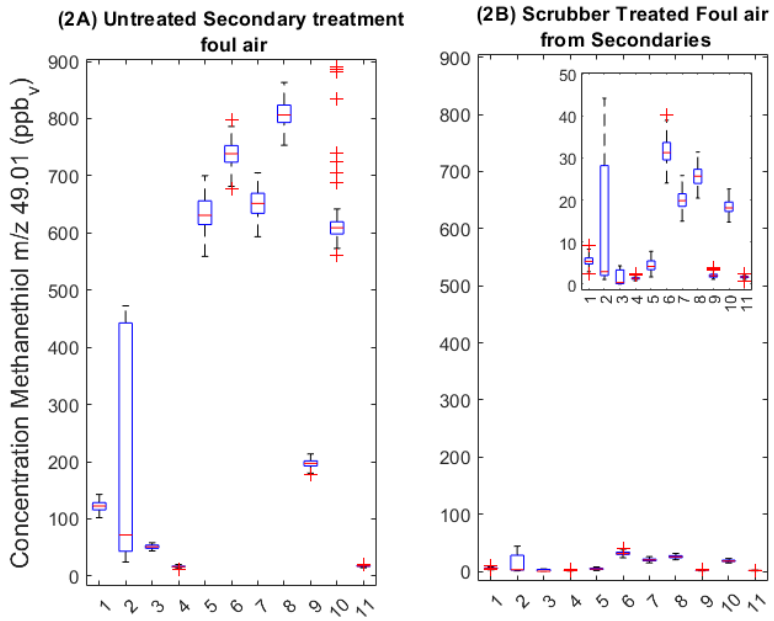

Figure 37: Boxplots of concentrations of methanethiol from secondary treatment foul air odour control sample points 2A and 2B. 1-April 2022, 2-November 24, 2023, 3-November 25, 2023, 4-February 2023, 5-April 2023, 6-May 2023, 7-July 2023, 8-August 2023, 9-October 2023, 10-November 2023, 11-February 2024.

Table 28: % Removal of methanethiol from activated carbon scrubber odour control (2B)

Median concentration and % Removal of methanethiol from odour control (2A→2B)											
Sample site	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)
2A (ppb_v)	126	230	51	16	634	567	650	719	196	609	18
2B (ppb_v)	5	12	2	1	4	31	20	20	2	18	2
%	96	95	97	91	99	95	97	97	99	97	90

During the sampling campaign the secondary treatment foul air stream (2A) was evaluated for DMS concentrations, showing a variable concentration range across the 11 sampling days (mean=50 ppb_v, %RSD=80) (Figure 38).

The post-treatment (2B) concentrations were also variable (mean=40 ppb_v, %RSD=100). The removal efficiencies for days 1-3 (Apr 2022-Nov 2022) and 5-11 (Apr 2023-Feb 2024) also showed variable treatment efficiency ranging from 6-72% (Table 29). Day 4 (Feb 2023) showed an elevated concentration with a removal efficiency of -240% (Table 29).

This system may be more optimized for DMS removal then some of the other discussed activated carbon scrubbers as it uses a modified activated carbon enhanced with oxidants (photo in Figure 40). Removal efficiencies are still relatively low showing 72% decrease at best and an average 11% removal efficiency was observed (Table 29).

These findings are corroborated by the findings by Shammay *et al*, describing poor removal efficiencies for DMS by activated carbon, with removal efficiencies recorded in the 3rd quartile range of best 40%.[74] The evidence from the study shows the minor compatibility of these systems for DMS removal, although better than the non-modified activated carbon scrubber towers used at sample location 1C. A different treatment approach may be more applicable to consistently remove more DMS from the gas stream.

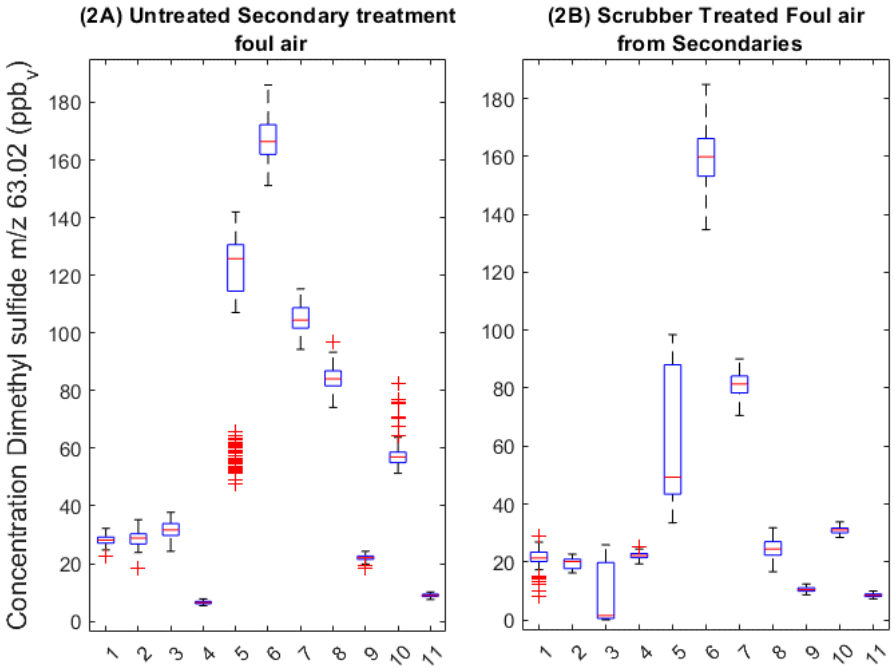

Figure 38:Boxplots of concentrations of dimethyl sulfide from secondary treatment foul air odour control sample points 2A and 2B. 1-April 2022, 2-November 24, 2023, 3-November 25, 2023, 4-February 2023, 5-April 2023, 6-May 2023, 7-July 2023, 8-August 2023, 9-October 2023, 10-November 2023, 11-February 2024.

Table 29: % Removal of dimethyl sulfide from activated carbon scrubber odour control (2B)

Median concentration and % Removal of dimethyl sulfide from odour control (2A→2B)											
Sample site	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)
2A (ppb_v)	28	29	32	7	96	134	105	71	22	57	9
2B (ppb_v)	21	20	9	22	55	126	81	32	11	31	9
%	25	32	72	-240	43	6	23	56	52	46	0

-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment.

The dimethyl disulfide concentrations at 2A were similar to the DMS concentrations, although on the lower side with an average of 40 ppb_v (%RSD=190), showing variability in the untreated foul air stream (Figure 39).

The DMDS concentration in the treated air stream (2B) was variable (mean=60 ppb_v, %RSD=100) and was systematically increasing over several visits, possibly indicating the nature of the sorbent was degrading and becoming spent, most likely from increased loads of methanethiol which could convert to DMDS within the sorbent bed (Figure 39).

On days 1,2 (Apr 2022-Nov 2022) and 7-11 (Jul 2023-Feb 2024) removal efficiencies were poor ranging from -31 to -666% indicating the treatment system was not working properly for DMDS removal (Table 30). On days 3 and 4 (Nov 2022, Feb 2023) greater negative removal efficiencies were recorded at <-1000% (Table 30).

Sample days 5 and 6 (Apr 2023, May 2023) had some removal of DMDS at <50% efficiency (Table 30). Typical measurements showed that the treatment was a source of DMDS, indicating the incompatibility with DMDS and the odour control technology (Figure 39).

The overall average removal efficiency was <-360% for DMDS, indicating a higher concentration of DMDS on average post-treatment. On some individual days there was minor removal of DMDS and concentration ranges should be considered when evaluating removal efficiencies. These concentrations and removal efficiency is similar to previous work done at WWTPs which had DMDS inputs ranging up to 120 ppb_v, and a median removal efficiency of <-50%, indicating the activated carbon is a common source of DMDS, as seen also in our bench scale experiment and our sampling of spent sorbent (Appendix C).[74]

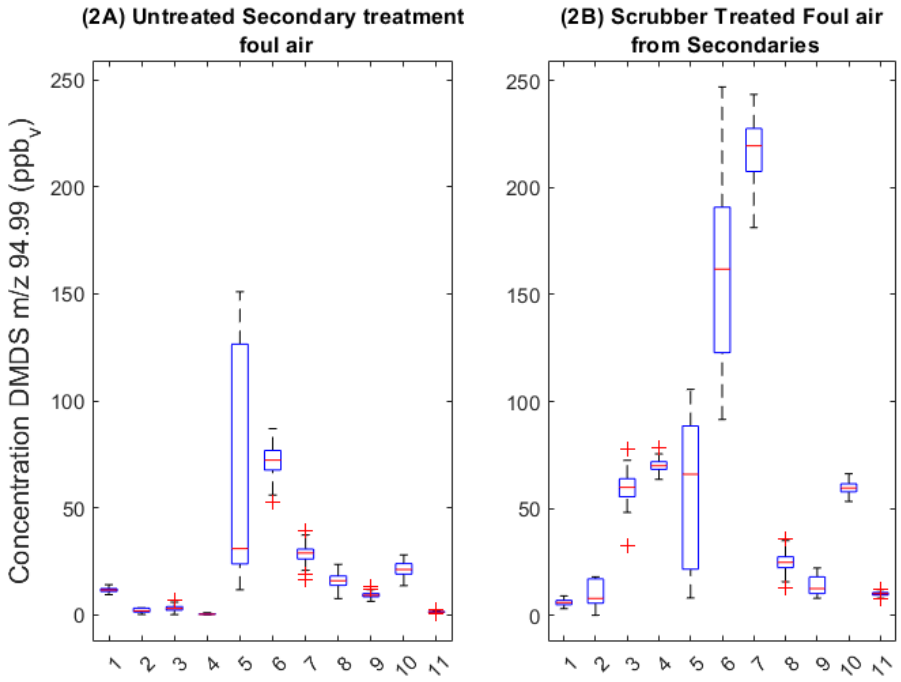

Figure 39: Boxplots of concentrations of dimethyl disulfide from secondary treatment foul air odour control sample points 2A and 2B. 1-April 2022, 2-November 24, 2023, 3-November 25, 2023, 4-February 2023, 5-April 2023, 6-May 2023, 7-July 2023, 8-August 2023, 9-October 2023, 10-November 2023, 11-February 2024.

Table 30: % Removal of dimethyl disulfide from activated carbon scrubber odour control (2B)

Median concentration and % Removal of dimethyl disulfide from odour control (2A→2B)											
Sample site	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)
2A (ppb_v)	11	2	3	0	63	237	28	16	10	21	1
2B (ppb_v)	15	10	60	70	58	126	217	29	16	60	10
%	-31	-381	-1000	-1000	9	47	-666	-87	-64	-181	-629

-Boxes highlighted in grey show negative removal efficiencies, indicating higher concentrations post-treatment. Negative removal efficiency is capped at -1000%.

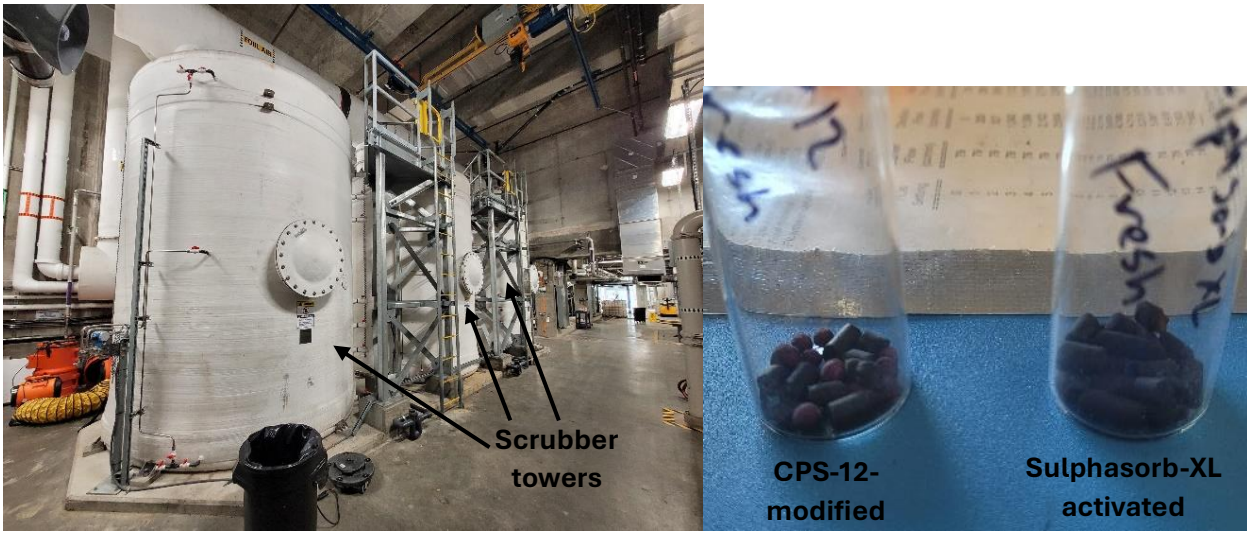

Figure 40: (Left) Photo of Activated carbon scrubbers for Secondary treatment foul air stream. (Right) Photo of activated carbon sorbents from towers, CPS-12 modified activated carbon and Sulphasorb-XL.

The recorded negative removal efficiencies for DMS and DMDS are either from variability in the input concentrations or may indicate that the sorbents are becoming a source of the VOCs or becoming spent and allowing for breakthrough and desorption of DMS and possible conversion of sulfur containing VOCs to DMDS in the process (Appendix C). The performance to remove methanethiol was good >90% for both scrubber towers while DMS was better removed by the modified activated carbon tower (2B). This modification which included oxidants mixed with the activated carbon (CPS-12, Trane) enhanced the ability of the sorbent to remove DMS but may have impacted the production of DMDS from partial oxidation of MeSH as seen in our bench scale experiment (Appendix C).

Additionally, the estimated flux of reduced sulfur compounds from secondary 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 31). The average estimated yearly flux of the three compounds reported as sulfur, is 60 kg/year.

Table 31: 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 ($\mu g/m^3$)	Average flux (kg/hr)	Yearly flux (kg/year)	Yearly moles (mole/year)
Methanethiol	10	48.11	19.68	0.0006	5.32	110.53
Dimethyl sulfide	40	62.13	101.64	0.0031	27.47	442.12
Dimethyl disulfide	60	94.2	231.17	0.0071	62.47	663.18
Total sulfur (from MeSH, DMS and DMDS)	----------	32.065	----------	----------	60.25	1879.01

Conclusions from odour control study at WWTP3

The odour control systems at WWTP3 work very well for methanethiol removal. Both activated carbon scrubber towers (1C and 2B) can eliminate large volumes of malodourous methanethiol at >90% removal efficiency. Minor amounts of dimethyl sulfide (DMS) were removed on half of the sampling days at >20% removal efficiency from activated carbon scrubber 1C and half of the sampling days <-20% removal efficiency, indicating an inconsistent ability to remove DMS. This may originate from the condition of the sorbent bed which does not use a blended modified activated carbon like the scrubber tower at 2B. The DMS removal from the modified activated carbon scrubber 2B was much better showing an average removal efficiency of 35%, with only one day when scrubber 2B was acting as a source of DMS.

The dimethyl disulfide removal efficiency for scrubber tower at 1C and 2B averaged at <-300%, indicating these systems do not work well for removal of DMDS and in fact were more likely to be a source. When the scrubber systems are not working

optimally it is shown that production/release of dimethyl disulfide is found in the systems and may be due to the partial oxidation of methanethiol on the sorbents as seen in the bench scale experiments and in literature (Appendix C).[36]

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 with over 43 hours of onsite evaluation including >154,000 observations to aid in decisions on how to manage these systems or plan for modifications/upgrades.