

Odour Emission Ability (OEA) Method Development and Evaluation

Author(s): Xinguang Wang, Eric Sivret, and Richard M. Stuetz



5 August, 2014

water@
UNSW
water research centre

DOCUMENT STATUS RECORD

Project Title: SP3: Odour measurement and assessment, evaluation of odour treatment technologies
Client:
Document Title: Odour Emission Ability (OEA) Method Development and Evaluation
Document Number:
File Name:

Issue No.	Date of Issue	Description	Signatures		
			Authors	Checked	Approved
1	5-08-2014	Final	E Sivret, X Wang	R Stuetz	R Stuetz

Notes

Disclaimer:

1. The Water Research Centre has taken all reasonable steps to ensure that the information contained within this report is accurate at the time of production. In some cases, we have relied upon the information supplied by the client.
2. This report has been prepared in accordance with good professional practice. No other warranty expressed or implied is made as to the professional advice given in this report.
3. The Water Research Centre maintains no responsibility for the misrepresentation of results due to incorrect usage of the information contained within this report.
4. This report should remain together and be read as a whole.
5. This report has been prepared solely for the benefit of the client listed above. No liability is accepted by the Water Research Centre with respect to the use of this report by third parties without prior written approval.

Contact Details:

UNSW Water Research Centre
School of Civil and Environmental Engineering
The University of New South Wales

Name: Dr. Eric Sivret
Email: e.sivret@unsw.edu.au

Physical:

Building H22, Vallentine Annexe
Botany Street Gate 11
Kensington.

Postal:

UNSW, Sydney, 2052

Telephone: (02) 9385 5017

Fax: (02) 9313 8624

© Water Research Centre

Font Name: Optima LT Std

Executive Summary

The Odour Emission Ability (OEA) technique, a simple and cost effective means of assessing odorants contained within a liquid sample, was evaluated to determine its effectiveness and suitability for identifying sewer odorants. An overview of the OEA method is provided in this report along with the results of both laboratory and field based method performance evaluations.

In addition to determining that the use of a dynamic injection technique as part of the OEA method enhanced compound recovery, the results of the laboratory assessment indicated that:

- good recoveries and sample reproducibility were obtained when applying the OEA method to create samples using VSC and VOC standards; and
- it was possible to generate odour samples using complex odorant mixtures in a reproducible manner using this methodology.

Results of the field trial to evaluate the potential application of the OEA method to sewage samples to identify specific odorants present in sewer headspace air indicated:

- sample stability is dependent on the sample matrix and will be difficult to predict;
- storage of the samples prior to analysis is not recommended;
- filtration of sewage samples prior to analysis is not recommended; and
- analysis of sewage samples using the OEA method is not a good predictor of VOCs/VSCs present in the sewer headspace air.

As it has been demonstrated that the OEA method can generate reproducible odorant and odour samples, the primary opportunity for future application of this method is to enhance the quality control of field data used to support odour abatement process selection and design. Specifically by the generation of complex sample matrices that provide a better simulation of field samples than the current practices of using a single

compound (n-butanol or hydrogen sulphide) would enhance existing quality control procedures where “standard” samples are included in the samples provided to laboratories as a check on the impact of sample handling, storage and analysis procedures on data quality. The possibility also exists for the OEA method to provide a simple, more cost effective means of implementing inter-laboratory evaluations that could provide the wastewater industry with an understanding of, and the ability to account for, variability introduced into datasets when samples have been analysed by different analytical service providers.

Table of Contents

Executive Summary	i
Table of Contents	iii
List of Figures	iv
List of Tables	iv
1.0 Overview	1
2.0 OEA Development and Evaluation Methodology Overview	2
2.1 Injection Technique Evaluation Methodology	4
2.2 OEA Validation Methodology	6
2.2.1 Validation under laboratory conditions	6
2.2.2 Validation under field conditions	7
3.0 Methodology Development and Evaluation	9
3.1 Injection Technique Evaluation	9
3.1.1 Key Results	10
3.2 Laboratory Validation	10
3.2.1 Key Results	14
3.3 Field Trials	14
3.3.1 Evaluation of Liquid Sample Stability	14
3.3.2 Evaluation of Identification of Key Odorants/Interferents	17
3.3.3 Key Results	18
4.0 Closure	20

List of Tables

Table 1 Compounds/mixtures used in the laboratory evaluation of the OEA method....	6
Table 2 Recovery rates (%) for validation tests using standard solutions of dimethyl trisulfide and bis(methylthio)methane.....	9
Table 3 Laboratory evaluation of OEA method - recovery rates and reproducibility ...	11
Table 4 Evaluation of stability of refrigerated liquid (sewage) samples	16
Table 5 Comparison of VOCs Identified in Field Samples and via OEA method.....	17
Table 6 Comparison of VSCs Identified in Field Samples and via OEA method	18

List of Figures

Figure 1 Dynamic injection system.....	4
Figure 2 Comparison of dynamic and static injection techniques.....	10
Figure 3 OEA method reproducibility: olfactory assessment of VOC mixture	12
Figure 4 OEA method reproducibility: olfactory assessment of VSC mixture.....	12
Figure 5 OEA method reproducibility: olfactory assessment of mixture of VOC and VSC	13
Figure 6 Variation in odour panel sensitivity (based on n-butanol standard)	13
Figure 7 Stability of refrigerated liquid (sewage) samples	15
Figure 8 Stability of liquid (sewage) samples during storage.....	16

1.0 Overview

The Odour Emission Ability (OEA) technique was developed at the University of New South Wales as a simple and cost effective means of assessing odorants contained within a liquid sample. This technique provides a means of identifying key odorants while only requiring a relatively small sample that could easily be transported and would be expected (if stored at constant temperature and pressure) to be relatively stable compared to gas samples.

This technique allows industry to utilise relatively simple (and less time/effort intensive) sampling techniques yet still leverage the suite of analytical techniques developed as part of the SCORE project. The OEA method lends itself well as a screening method for identifying key odorants and interferents (compounds that may interact with odour abatement processes) present in a liquid. Combining this knowledge with the set of gas composition criteria for the selection of gas phase odour abatement technologies for sewer emission sources (developed as part of SP3) could support the technology selection component of odour abatement process design (one of the key SCORE project goals).

Furthermore, the OEA method is well suited for directly evaluating the performance of liquid phase odour abatement treatments such as chemical dosing. Here the concentration of specific compounds in the liquid phase (measured via conversion of the liquid sample using the OEA method and subsequent chemical analysis) is directly proportional to the abatement performance. The requirement for relatively small liquid samples allows for the evaluation and optimisation of liquid phase odour abatement treatments at pilot scale, reducing the need for more costly full scale trials.

While conceptual development has been previously completed and the technique has been applied for several situations, a need existed to further evaluate the effectiveness of this technique and assess its suitability/usefulness for identifying sewer odorants. An overview of the OEA development and evaluation methodology is provided in **Section 2**. Methodology development and evaluation are presented in **Section 3**. Concluding remarks are provided in **Section 4**.

2.0 OEA Development and Evaluation Methodology Overview

The odour emission ability (OEA) technique determines the potential emissions of odour and odorants from a liquid sample through the transformation of a liquid phase sample into a gas phase sample that is compatible with analysis via gas phase analysis techniques (such as olfactometry and gas chromatography). Gas phase samples are prepared through the evaporation of a known volume (100-200 μ L) of the liquid sample into a sampling bag for filled with either clean air or high purity nitrogen gas. The specific sample and odour bag volumes can be adjusted based upon the appropriate concentration ranges and sample volume requirement for the analytical methodology being employed.

Prepared samples can be analysed using a wide range of analytical techniques suitable for gas phase analysis. For this work, the OEA method was tested for two groupings of compounds (volatile organic compounds – VOCs, and volatile sulfur compounds - VSCs), and for odour concentration. A brief overview of the specific methodologies employed is provided next.

VOC samples were collected onto Tenax-TA sorbent tubes from the prepared sample bags using an SKC AirChek2000 pump at a flow rate of 100 mL/min for 10 min. The VOC samples were analysed using a gas chromatograph equipped with a mass spectrometer detector to identify and quantify the VOCs present in the sample. **VSC samples** were analysed directly from the prepared sample bags using a gas chromatograph equipped with a sulfur chemiluminescence detector. Specific VSCs present in the sample were identified via retention time matching with pure standards (which were also used to provide calibration factors to produce quantitative data).

For additional detail on the VOC and sulfur compound analytical methodologies employed, please refer to the SCORE SP3 project report: *Analytical Methodology Development and Evaluation*.

Odour concentration of prepared bag samples was analysed using a dynamic olfactometer (Odormat™) in accordance with the Australian and New Zealand standard *Air Quality* –

Determination of odour concentration by dynamic olfactometry (AS/NZS 4323.3:2001). A six person panel was used for the assessments. For additional detail on the olfactometry methodology, please refer to the Australian and New Zealand Standard (AS/NZS 4323.3:2001).

OEA Calculations

The results of the analysis of the samples generated using the OEA method can then be converted onto a potential emission basis, i.e. what mass of odour/odorant could be emitted per unit volume of liquid. This quantity facilitates comparison of emission potential to assess the effectiveness of liquid phase treatments. **OEA** can be expressed as the following equation:

$$OEA = \frac{C \cdot V_N}{V_i}$$

Where: OEA = odour emission ability from a liquid source (OU/L);
C = odour concentration (OU/m³);
V_n = volume of gas (air or nitrogen) used to prepare bag sample (m³); and
V_i = volume of liquid sample injected (L).

Similarly, for a specific odorant or compound of interest, the **compound emission ability (CEA)** can be expressed as:

$$CEA = \frac{C \cdot V_N}{V_i}$$

Where: CEA = compound emission ability from a liquid source (mg/L);
C = compound concentration (mg/m³);
V_n = volume of gas (air or nitrogen) used to prepare bag sample (m³); and
V_i = volume of liquid sample injected (L).

As noted previously, two main needs exist with regards to finalising the development of this methodology in order to be suitable for utilisation by the industry. Firstly the injection technique method to be finalised, and secondly the methodology needs to be validated under laboratory and field conditions. A summary of the methodologies followed is provided

in **Sections 2.1** and **2.2** for the injection technique evaluation and method validation, respectively.

2.1 Injection Technique Evaluation Methodology

As the OEA method focuses on transferring compounds from a liquid sample into a gas sample, the means in which this is achieved (injection technique) is a fundamental aspect of the methodology. Two injection techniques were trailed as part of the study: (i) a dynamic injection method, and (ii) a static injection method.

For the **dynamic injection method**, a 15 μL sample of liquid was injected using a dynamic injection system (**Figure 1**). Clean air was generated by an air/nitrogen generator (Dominick Hunter) and filtered through a Supelpure HC filter unit at a flow rate of 300mL/min for 10 minutes into a 5 L Tedlar sample bag.

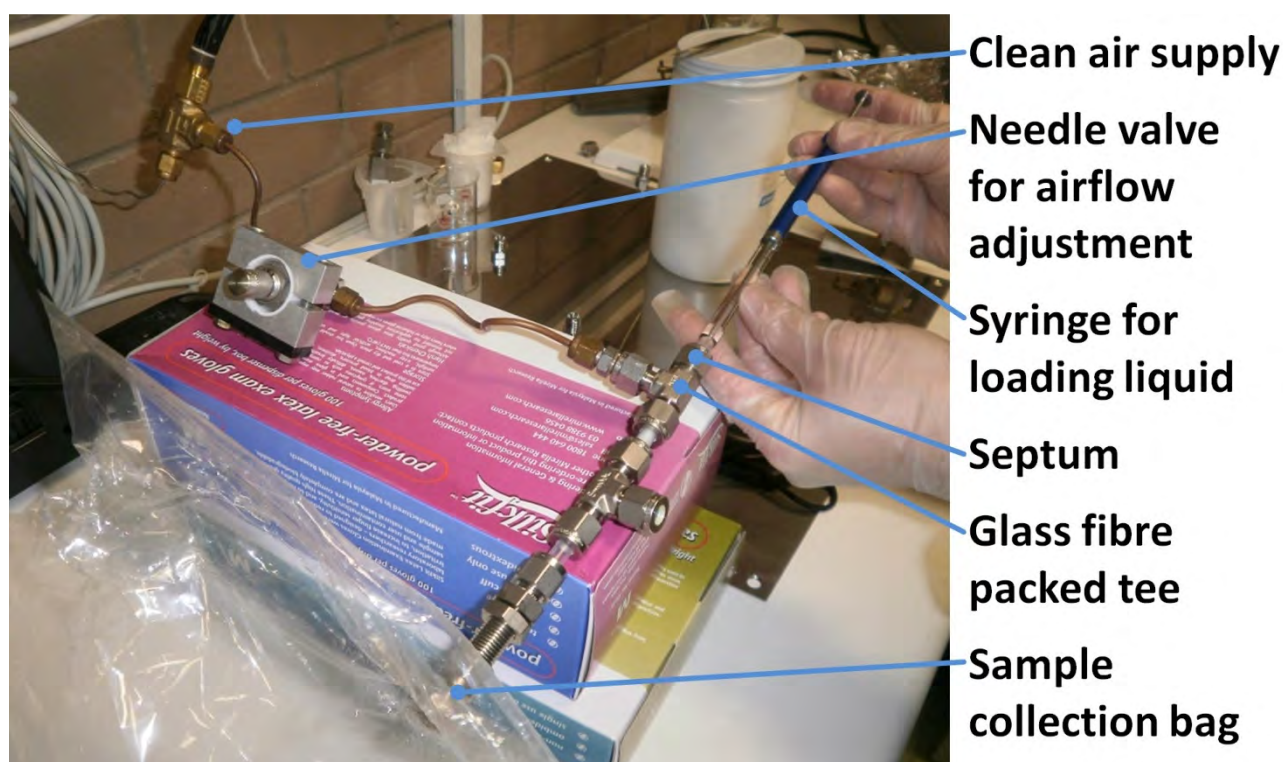


Figure 1 Dynamic injection system

For the **static injection method**, a 15 μL sample of liquid was injected into a 5 L Tedlar sample bag filled with 3 L clean air, generated by an air/nitrogen generator (Dominick

Hunter) and filtered through a Supelpure HC filter unit.

This validation work was conducted using two VSCs, dimethyl trisulfide (DMTS) and bis(methylthio)methane (BMTM). These compounds are relatively stable compared to other sulfur compounds like methyl mercaptan.

Gas samples were prepared from liquid solutions of DMTS and BMTM using both injection methodologies and analysed via GC-SCD as outlined in **Section 2.0**. Both the static and dynamic injection samples were prepared and stored at laboratory temperature conditions (20°C and 45% RH) for 30 minutes prior to analysis.

To determine if evaporation conditions affect the recovery rate in the static injection technique, additional samples were prepared using the DMTS standard and stored for 30 minutes in a climate chamber at two elevated temperatures (50°C and 75°C) prior to analysis.

The GC-SCD data was used to quantify the recovery rates for DMTS and BMTM, which are presented in **Section 3.1**.

2.2 OEA Validation Methodology

2.2.1 Validation under laboratory conditions

The OEA testing methodology was first evaluated under laboratory conditions using a series of standard compounds to assess the methodology on the basis of recovery and reproducibility. This recovery testing (additional to that conducted in the injection technique evaluation) was conducted to assess the methods suitability for a wider range of sulfur compounds and volatile organic compounds of interest.

The validation trial focused on the recovery and reproducibility of specific representative compounds and compound mixtures (**Table 1**). Two groups of compounds were tested (VOCs and VSCs), with three compounds in each group that had a range of volatilities. As field samples from sewer sites contain both sulfur compounds and VOCs, and a final mixture of both the VOC and VSC mixtures was evaluated to assess the reproducibility of odour measurements for samples that are more representative of field samples.

Table 1 Compounds/mixtures used in the laboratory evaluation of the OEA method

Compound(s)	Description	Number of Tests
Bis(methylthio)methane	Low volatility VOSC (bp ~ 147 °C)	5 (VSC)
Dimethyl disulfide	Med Volatility VOSC (bp ~ 109 °C)	5 (VSC)
Dimethyl trisulfide	High Volatility VOSC (bp ~ 58 °C)	5 (VSC)
Sulfur mixture	Bismethylthiomethane, dimethyl disulfide, dimethyl trisulfide	5 (VSC)
Butanoic acid	Low volatility VOC (bp ~ 164 °C)	5 (VOC)
Butanol	Med Volatility VOC (bp ~ 118 °C)	5 (VOC)
Butanal	High Volatility VOC (bp ~ 75 °C)	5 (VOC)
VOC mixture	Butanoic acid, butanol, butanal	5(VOC)
Gas mixture	Sulfur mixture + VOC mixture	5 (Odour)

A series of 5 replicate gas samples were prepared for each specific compound or mixture from liquid standards using the OEA method (using the dynamic injection method which has been identified as the optimal injection technique in **Section 3.1**) For VOC/VSC analysis a 15 µL sample of liquid was injected using the dynamic injection system with clean air

(generated by an air/nitrogen generator (Dominick Hunter) and filtered through a Supelpure HC filter unit) supplied at a flow rate of 300mL/min for 10 minutes to provide a 3 L gas sample that was collected in a 5 L Tedlar sample bag. As a larger sample volume was required for the olfactometry analysis, a 50 µL sample of liquid was injected using the same system, with the clean air supplied for a longer period to generate a 20 L sample that was collected in a 30 L Tedlar sample bag.

These samples were analysed using the methodologies outlined in **Section 2.0**. The methodology reproducibility from an olfactory perspective was also assessed by preparing 5 replicate samples of the gas mixture (sulfur mixture + VOC mixture) that were subsequently analysed vial dilution olfactometry as outlined in **Section 2.0**.

2.2.2 Validation under field conditions

The suitability of the OEA method as a means of identify key gas phase odorants and/or interferences present in using sewage samples was evaluated by collecting grab samples of sewage simultaneous to gas phase sample collection from the sewer headspace. This assessment was conducted for two sewer sites (S-1: undosed sewer with 34 ML/d ADWF and >95% domestic wastewater, and S-2: sewer dosed with Odorlok with a 230 ML/d ADWF and ~90% domestic wastewater) that, based on the results of the routine field monitoring program, fall within the typical range of odorant emissions from sewer sites in Sydney. The assessment focused on two objectives:

- i) assess the stability of liquid samples in terms of storage; and
- ii) determine the level of applicability of the OEA method to identify key odorants/interferences that would appear in the sewer headspace air.

The **stability** of the liquid samples was assessed to identify limitations with regards to the storage of these samples and to determine an appropriate time limit for analysis based on sample stability. Stability was assessed by storing the sewage samples in a refrigerator at 5 °C and withdrawing liquid aliquots at specific time intervals for conversion into gas phase samples via the OEA method. As the potential exists for the solid/biologically active material

to cause transformation in the odorants over time, both unfiltered and filtered (using a 0.45 µm filter) sewage samples were stored and evaluated. Samples were assessed immediately upon receipt of the sewage samples (sewer headspace air samples were also assessed at this time to provide a reference) and 1, 2, 5, and 9 days following collection. The generated gas samples were analysed via dynamic olfactometry to determine the odour concentration as outlined in **Section 2.0**.

The **applicability** of the OEA method to identify key odorants/interferents in sewer headspace air was assessed on site S-2 (described previously) by converting freshly collected sewage samples into gas samples using the OEA method for analyses via GC based analytical techniques (outlined in **Section 2.0**) to identify the VOCs and VSCs present. As the potential exists for background VOCs in sample bags, VOC samples were loaded directly from the dynamic injection system into Tenax TA sorbent tubes for analysis. VSC samples were collected in sample bags for subsequent analysis.

The identified dominant VOCs and VSCs were compared with those identified from sewer headspace air samples that were collected at the time of collection of the sewage samples. As the actual concentrations of volatile compounds in the sewer headspace is dependent on a range of factors (for example volatility, level of turbulence in the system, air intrusion rates) a strictly quantitative correlation is beyond the scope of this work and the compounds identified in the samples were compared in a semi-quantitative manner to assess if 1) the same compounds were identified in the sewage as in the sewer headspace, and 2) if the order of the compounds (i.e. which compounds are dominant) was similar.

3.0 Methodology Development and Evaluation

3.1 Injection Technique Evaluation

The validation testing results for both the dynamic and static injection methods are presented in **Table 2**. Results are also presented in this table that assess the impact of different evaporation conditions on the recovery using the static injection method. A comparison of the two injection methods is provided as **Figure 2** for dimethyl trisulfide and bis(methylthio)methane.

Table 2 Recovery rates (%) for validation tests using standard solutions of dimethyl trisulfide and bis(methylthio)methane

Test	Dimethyl trisulfide				Bis(methylthio)methane	
	Dynamic Injection	Static injection			Dynamic Injection	Static Injection*
		Lab Condition*	50°C**	75°C***		
Test 1	98.7	109.0	86.4	44.0	99.8	62.0
Test 2	102.8	110.9	91.0	53.7	106.4	68.7
Test 3	109.6		92.2	50.8	99.0	71.8
Test 4	101.2		90.8		106.5	71.1
Test 5	108.0		87.9		108.4	74.8
Average	104.1	109.9	89.7	49.5	104.0	69.7
Standard Deviation	0.015		0.008	4.98	0.013	0.014

*22°C, RH 45% and evaporated for 1 hour

**evaporated inside environmental chamber controlled at 50°C and RH 20%

***evaporated inside environmental chamber controlled at 75°C and RH 20%

The results demonstrate that for both compounds, the dynamic injection method achieved higher recovery rates than the static injection method. This could be due to incomplete evaporation or decomposition of the target compounds during the static injection and subsequent stabilisation period. Static injections at higher temperatures to increase evaporation resulted in increased decomposition and lower recovery.

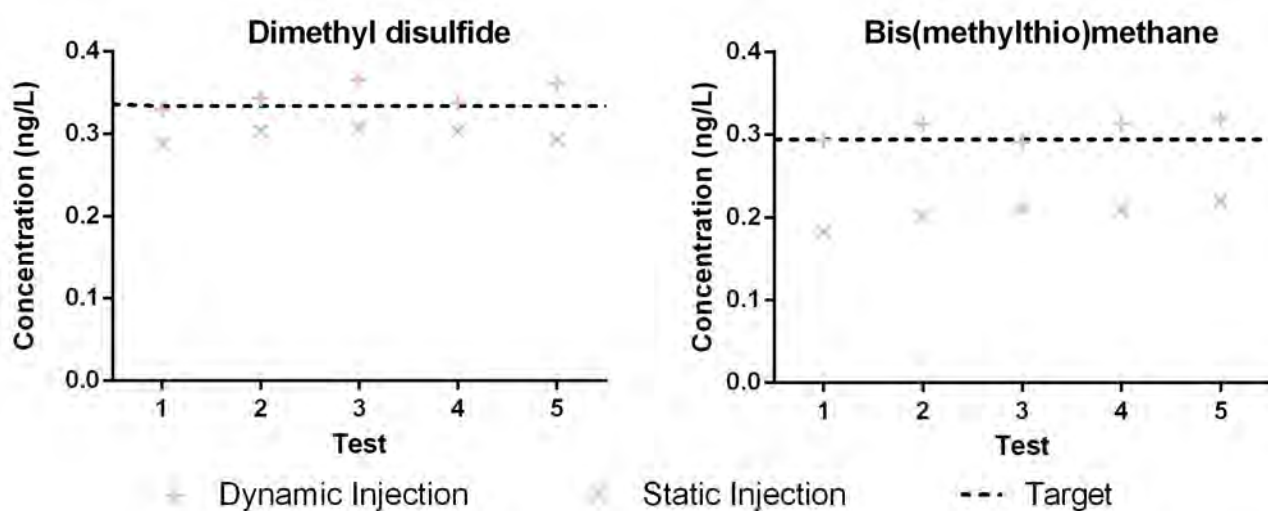


Figure 2 Comparison of dynamic and static injection techniques

Overall, the recovery rates for BMTM were lower than for DMTS. This may be a function of the volatility of the compounds; the boiling point for BMTM (147°C) is higher than that for DMTS (41°C), thus BMTM is less volatile than DMTS and more difficult to evaporate. The dynamic injection technique was less impacted by the volatility of the compounds than the static injection technique, which emphasised the most volatile compound. It is likely that this would also be the case for complex odorant mixtures.

3.1.1 Key Results

The sample injection methodology had a significant impact on compound recovery. While both dynamic and static injection techniques can obtain relatively high recovery rates, the dynamic injection technique provided better compound recovery for both compounds studied and is the recommended injection technique for the OEA method.

3.2 Laboratory Validation

With the dynamic injection technique having been previously selected as the optimal technique (over the static injection technique – see **Section 3.1**), the laboratory validation of the OEA method has been completed using that injection technique only. The results of this evaluation (using a series of 5 replicate tests for single compounds and mixtures of compounds) are presented in Table 3.

Table 3 Laboratory evaluation of OEA method - recovery rates and reproducibility

	Recovery Rate (%)		Reproducibility (% Standard Deviation)
	Range	Average	
Single Compounds			
Dimethyl Disulfide	97.7 - 101.3	99.6	1.3
Dimethyl Trisulfide	98.7 - 109.6	104.1	4.6
Bismethylthiomethane	99.8 - 108.4	104.0	4.3
Butanal	81.4 - 117.7	96.7	14.4
1-Butanol	87.9 - 120.3	101.3	14.2
Butanoic Acid	28.4 - 77.8	54.7	20.4
Mixtures			
<i>VOC Mixture</i>			
Butanal	78.4 - 115.8	93.1	12.7
1-Butanol	87.9 - 109.2	95.0	8.2
Butanoic Acid	43.1 - 114.0	75.6	31.1
<i>Sulfur Mixture</i>			
Dimethyl Disulfide	89.2 - 96.8	91.8	3.6
Dimethyl Trisulfide	92.5 - 97.8	94.6	2.0
Bismethylthiomethane	91.3 - 96.7	94.4	1.9

The recovery rates of five of six tested compounds were over 81% with an average recovery rate of more than 96.7% with good reproducibility (ranging from 1.3 to 14% relative standard deviation, with lower deviation for the sulfur compounds). Butanoic acid was the exception, which had poor and highly variable recovery.

For the mixed sample, the recovery rates of individual compounds were slightly lower than that of their single compound. The obtained results also shows that the recovery rates of sulfur compounds were higher than that of the VOCs. The lower recovery of the VOCs may be related to the sampling methodology employed. While the sulfur compounds were directly sampled into the cold trap from the sample bag using an air server, the VOC samples were collected onto sorbent tubes which were then thermally desorbed and then captured onto the cold trap. The recovery of the VOCs would thus also be a function of the capture efficiency of the sorbent tubes.

The second component of the laboratory evaluation focused on the **reproducibility of odour samples generated** using the OEA method. Duplicate odour measurements were made on 5 different days for compound mixes of the three VOCs and three sulfur compounds (**Figure 3** and **Figure 4**, respectively), and for a mixture of the three VOCs and three sulfur compounds

(Figure 5). An identical compound list was used as presented in Table 3. As the makeup of the odour panels varies from day to day due to panellist availability, the potential exists for the panel sensitivity to vary and introduce variability in the results that is not associated with the OEA method. This variability was assessed by analysing a sample of n-butanol (the standard gas used to assess olfactory sensitivity) during each panel session (Figure 6).

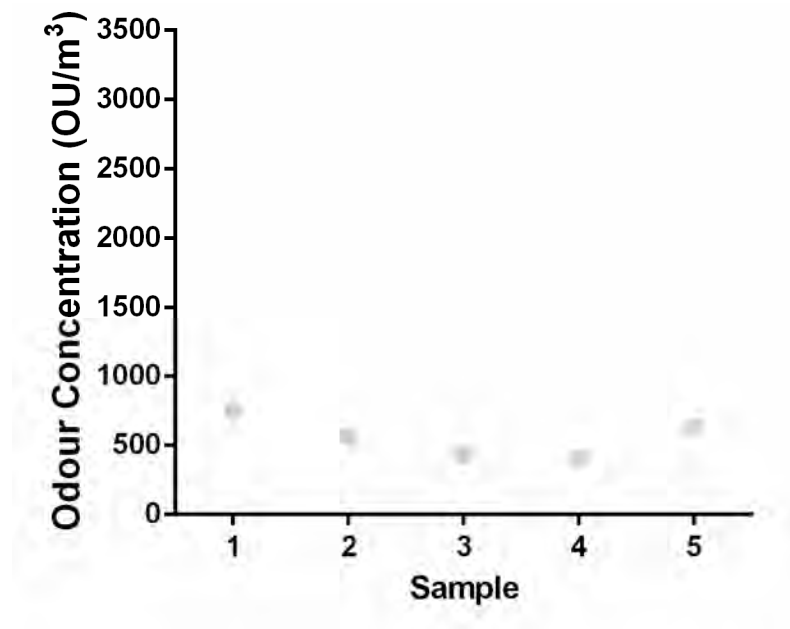


Figure 3 OEA method reproducibility: olfactory assessment of VOC mixture

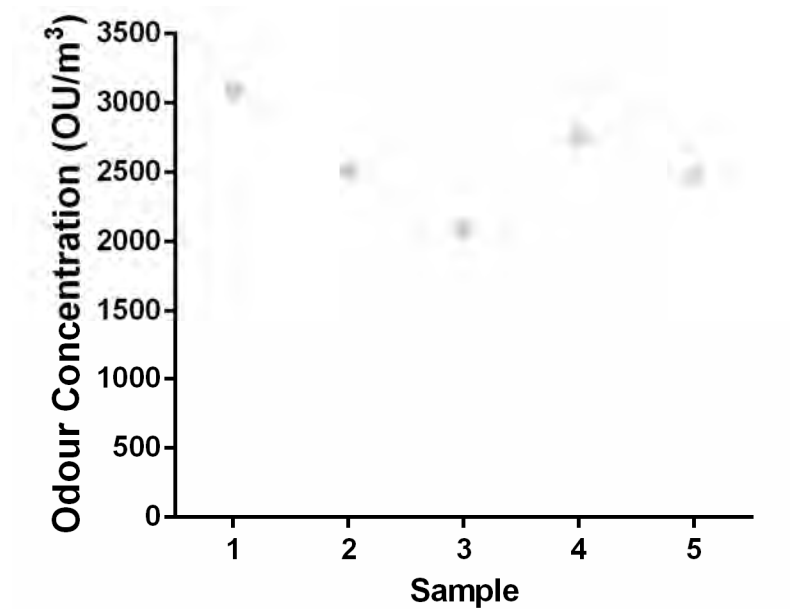


Figure 4 OEA method reproducibility: olfactory assessment of VSC mixture

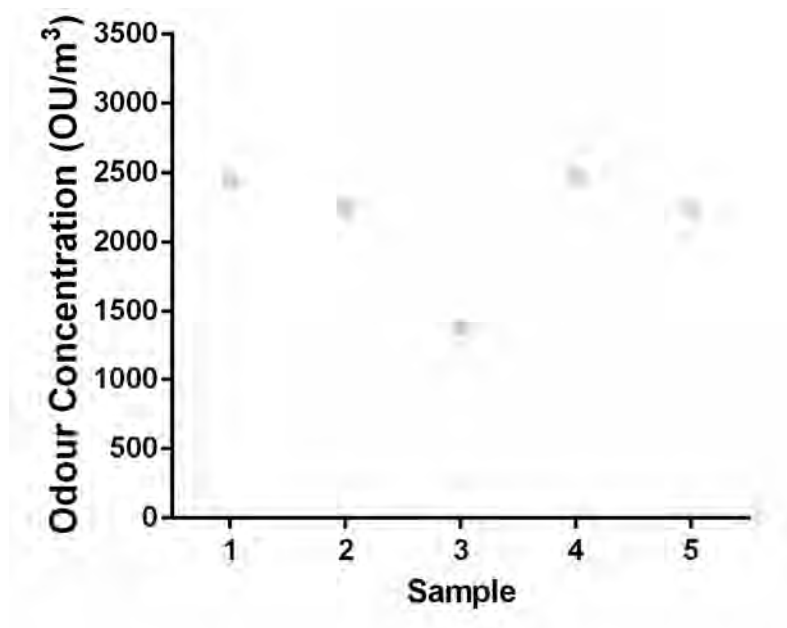


Figure 5 OEA method reproducibility: olfactory assessment of mixture of VOC and VSC

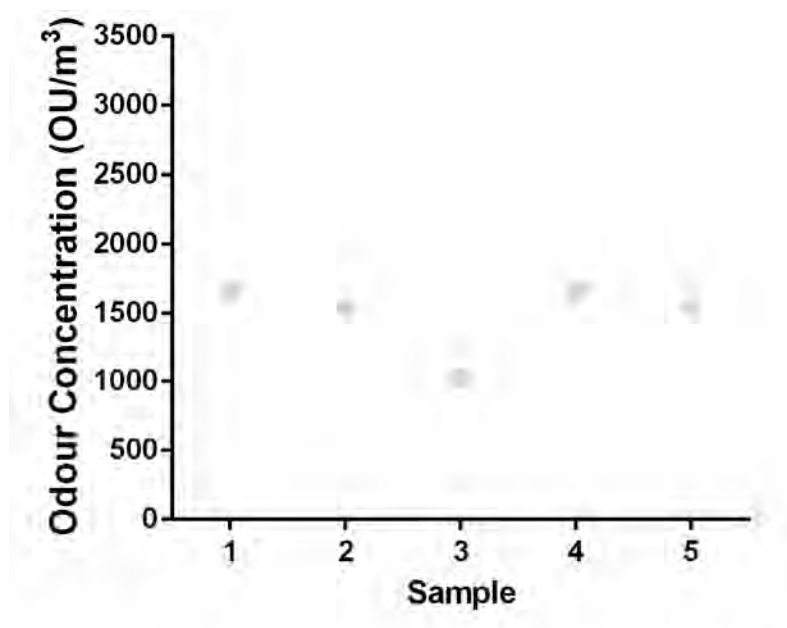


Figure 6 Variation in odour panel sensitivity (based on n-butanol standard)

There was some variation between the odour concentrations measured from successive replicate samples. For the VOC mixture, the sulfur mixture, and the VOC/sulfur mixture, the measured concentration ranges were $558 \text{ OU} \pm 30.3\%$, $2158 \text{ OU} \pm 25.3\%$, and $2584 \text{ OU} \pm 19.4\%$, respectively. It should be noted that the odour concentration variations had a similar pattern as the sensitivity of the odour panel (**Figure 6** – based on n-butanol), indicating that a significant component of the observed variability was associated with the olfactometry

methodology and not the OEA method. It should be noted that the measured odour panel sensitivity range (1486 OU \pm 21.7%) is within the range allowed under the Australian and New Zealand olfactometry standard (AS/NZS 4323.3: 2001).

3.2.1 Key Results

Good recoveries and sample reproducibility has been observed for samples created using sulfur compounds and VOCs using the OEA method. Reproducibility of odour samples is of similar quality as analysis of the n-butanol standard, and well within the error range allowable by the olfactometry methodology.

3.3 Field Trials

3.3.1 Evaluation of Liquid Sample Stability

The first component of the field trial was to assess the **stability of the liquid (sewage) samples** collected from the field assessed based upon the measured odour emission ability (OEA). Both filtered and unfiltered sewage samples were evaluated over a 10 day period (**Figure 7**). To provide further context, sewer headspace air samples were also collected from each of the sites and analysed for odour concentration via dynamic olfactometry, with average concentration measurements of 4944 OU/m³ for site S-1, and 7745 OU/m³ for site S-2.

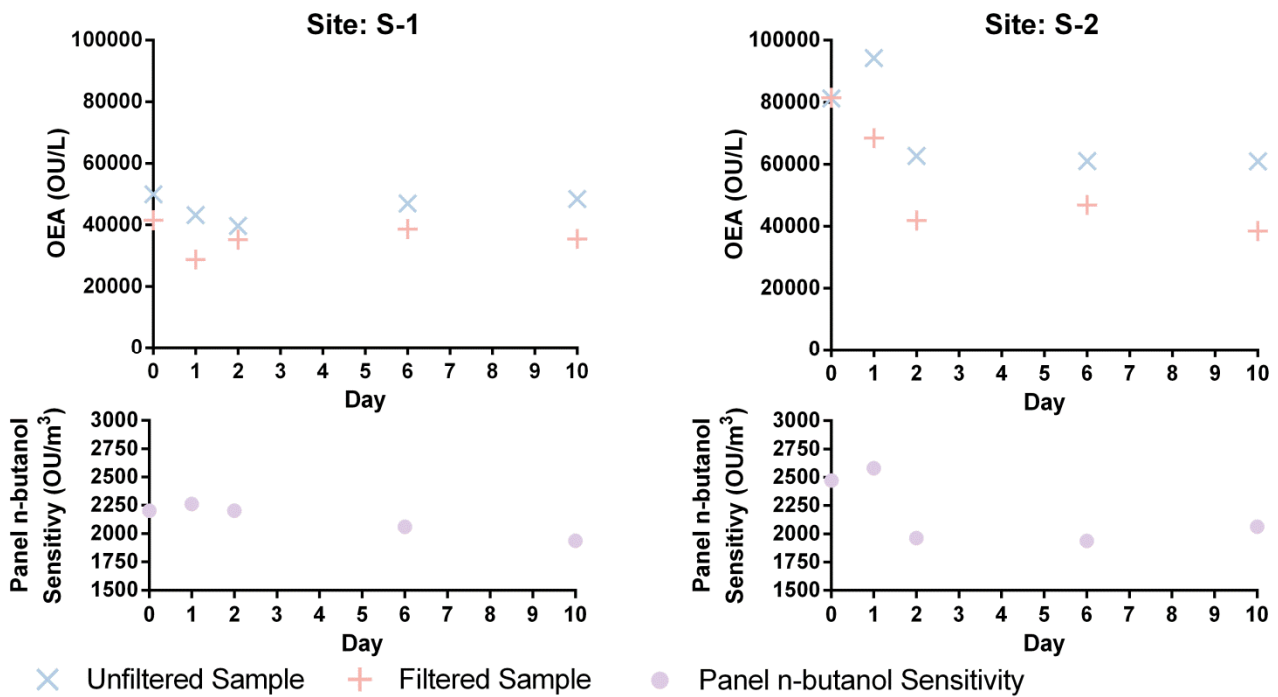


Figure 7 Stability of refrigerated liquid (sewage) samples

As expected, the filtered samples had consistently lower odour emission ability (a measure of the potential odour emissions) than the unfiltered samples, i.e. some odorous material was filtered out. In general, the changes in OEA from the filtered and unfiltered samples were similar over the time frame studied, indicating that filtration did not enhance the sample stability.

Overall sample stability during storage was evaluated by assessing the deviation in OEA from the baseline value over a period of 10 days (**Table 4** and **Figure 8**). Deviations from the baseline OEA would likely be the result of a combination of odorant generation or degradation via chemical or biological reactions occurring within the sample during storage. As seen in **Figure 8**, stability results were mixed with regards to the samples assessed. The measured OEA for site S-1 was generally stable over the 10 day period assessed, however significant changes in OEA were observed over the first 48 hours at site S-2, but was relatively stable afterwards, with changes mirroring changes in panel sensitivity.

Sample stability is thus likely dependent upon the stability of the specific odorants in each sample along with the presence of other compounds that may interact with these odorants. The stability is expected to vary depending upon the sample matrix and will be difficult to

predict. As such the samples should be analysed as soon as possible to minimise degradation/transformation of odorants in the liquid phase, storage of the samples for subsequent analysis is not recommended.

Filtration of the sample reduced the measured OEA and has the potential to modify the nature of the odorants present in the sample), but does not increase sample stability. Filtration of the liquid samples prior to analysis is not recommended.

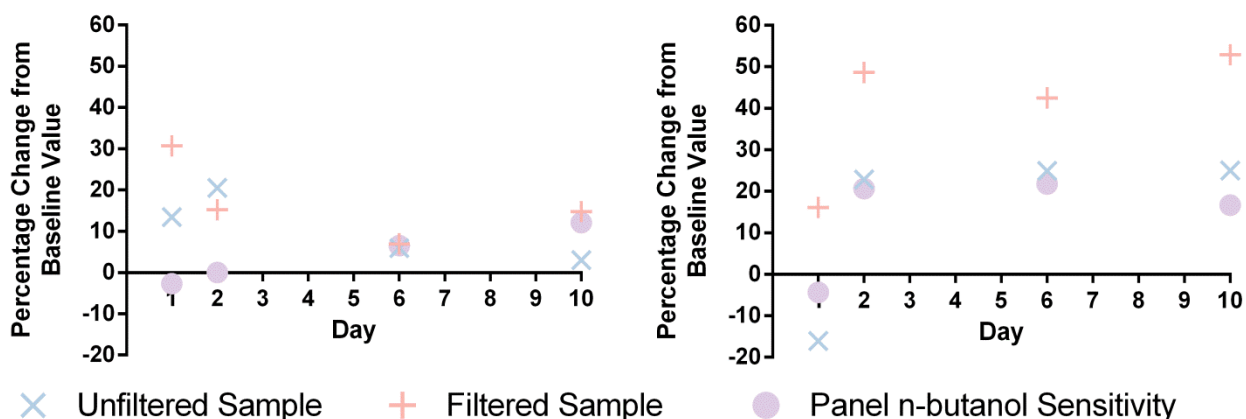


Figure 8 Stability of liquid (sewage) samples during storage

Table 4 Evaluation of stability of refrigerated liquid (sewage) samples

Day	% Change from Day 0					
	S1			S2		
	Raw Sample	Filtered Sample	Panel n-butanol Sensitivity	Raw Sample	Filtered Sample	Panel n-butanol Sensitivity
1	13.4	30.7	-2.7	-16.1	16.1	-4.4
2	20.5	15.2	0	22.8	48.6	20.6
6	5.9	6.9	6.5	24.9	42.5	21.7
10	3.0	14.7	12.1	25.0	52.9	16.6

It should be noted that while there were changes in panel sensitivity from day to day (reflecting random nature of panellist selection) the panel sensitivity on all days fell within the specifications required by the applicable Australian Standard, *The Determination of Odour Concentration by Dynamic Olfactometry* (AS/NZS 4323.3:2001).

Furthermore, it should also be noted that the OEA is not directly comparable to the odour

concentrations in the sewer headspace air since the OEA method volatilises all odorants present in the sample, while the types of odorants (and corresponding concentrations) in sewer headspace air will be depended upon a range of factors including (but not limited to) volatility, dilution by air intrusion/ventilation, and other parameters that influence mass transfer such as the amount of turbulence (such as structure types) and liquid surface area.

3.3.2 Evaluation of Identification of Key Odorants/Interferents

The applicability of the OEA method to identify key odorants/interferents in sewer headspace air was conducted on site S-2 for both VOCs (**Table 5**) and VSCs (**Table 6**). As discussed in **Section 2.2.2**, a strictly quantitative correlation is beyond the scope of this work and the compounds identified in the samples are presented in the tables in a semi-quantitative manner to determine if similar compounds were identified in the sewage as in the sewer headspace, and if similar compound rankings in terms of abundance were observed.

Table 5 Comparison of VOCs Identified in Field Samples and via OEA method

	Sewer Headspace Air	Samples Generated via OEA Method
VOCs identified in sample arranged by decreasing abundance	Trimethyloctane 7-Methylpentadecane Hexadecane Trichloromethane Toluene Tetrachloroethene o-Xylene	Undecane Dodecane Benzaldehyde Toluene o-Xylene Benzene Dimethylbenzene

While o-xylene and toluene were detected in both samples, the VOCs detected in the sample generated from sewage via the OEA method did not appear to be a good predictor of the specific VOCs present in the sewer headspace, nor of which VOCs would be dominant.

Table 6 Comparison of VSCs Identified in Field Samples and via OEA method

	Sewer Headspace Air	Samples Generated via OEA Method
VSCs identified in sample arranged by decreasing abundance	Hydrogen sulfide Methyl mercaptan Dimethyl disulfide Carbonyl sulfide Dimethyl sulfide Carbon disulphide Dimethyl trisulfide Diethyl disulphide Dimethyl disulphide Ethyl mercaptan	Hydrogen sulphide Methyl mercaptan Dimethyl sulfide

The VSCs identified in the sample generated from sewage using the OEA method were representative of the top three dominant VSCs present in the sewer headspace air (hydrogen sulphide, methyl mercaptan, and dimethyl sulphide) as well as the relative order. However, the compounds detected at lower concentrations in the sewer headspace air were not detected.

It was observed that the measured concentrations of VSCs in the sample generated by the OEA method were on average 100 times lower than those measured in the sewer headspace samples. This is likely associated with the ratio of dilution gas to sample injection volume required by the methodology to volatilise the water present in the sample (3 L of dilution gas for a 15 µL sample). With this high level of dilution, it is possible that the concentrations of the less dominant VSCs are reduced below the method detection limit.

As such the OEA method is not likely sufficiently sensitive to evaluate the full range of VSCs that might be present in the sewage, although the possibility exists that it could be used as an indicator of the changes in levels of the highest concentration VSCs (primarily hydrogen sulphide and methyl mercaptan). Additional evaluation over a wider range of sewage samples would be required to fully assess its applicability in such situations.

3.3.3 Key Results

In general the results of the field evaluation indicate that the analysis of liquid (sewage)

samples using the OEA method is not a good predictor of VOCs/VSCs present in the sewer headspace air. While not suitable for this specific application, the possibility exists for the OEA method to be applied for the evaluation of the effectiveness of liquid phase odour abatement processes by determining the changes in concentrations of specific odorants/odorant precursors in the sewage, provided that the compound concentrations are above the method detection limits.

4.0 Closure

The OEA method for generation of gas phase samples from liquid samples was assessed under both laboratory and field conditions. The results of the laboratory analysis were used to finalise the methodology and assess its performance, and it was observed that:

- sample injection methodology had a significant impact on compound recovery;
- dynamic injection provided better compound recovery and is the recommended injection technique;
- good recoveries and sample reproducibility were obtained when applying the OEA method to create samples using VSC and VOC standards; and
- it was possible to generate odour samples using complex odorant mixtures in a reproducible manner using this methodology.

A field trial was conducted to evaluate the stability of odorants in sewage samples and assess the potential of these samples to be used as an indicator of specific odorants present in sewer headspace air. Field trial results indicated that:

- specific sample stability is dependent on the sample matrix and will be difficult to predict; to minimise degradation/transformation of odorants in the liquid phase, storage of the samples for subsequent analysis is not recommended;
- filtration of sewage samples prior to analysis is not recommended as it does not increase sample stability, reduces the measured OEA, and has the potential to modify the nature of the odorants present in the sample; and
- analysis of sewage samples using the OEA method is not a good predictor of VOCs/VSCs present in the sewer headspace air.

As it has been demonstrated that the OEA method can indeed generate reproducible odorant and odour samples, the opportunity exists to apply this method to enhance the quality control of field data used to support odour abatement process selection and design. Specifically, the generation of complex sample matrices that provide a better simulation of field samples than the current practices of using a single compound (n-butanol or hydrogen

sulphide) would enhance existing quality control procedures where “standard” samples are included in the samples provided to laboratories as a check on the impact of sample handling, storage and analysis procedures on data quality. The possibility also exists for the OEA method to provide a simple, more cost effective means of implementing inter-laboratory evaluations that could provide the wastewater industry with an understanding of, and the ability to account for, variability introduced into datasets when samples have been analysed by different analytical service providers.