

Research Article

Volatile Organic Compounds Characterization: A Case Study of a Tank Farm in the United States

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Abstract

Tank Farms are among the major sources of VOCs. Because VOCs are dangerous, there is often a requirement to monitor their concentrations; however, current VOC monitoring techniques (spot sampling) are often of low resolution to determine their representative concentrations. In this study, we conducted continuous measurement of aggregate concentrations of VOC in two boreholes at a Tank Farm site in U.S. The measurement was done on hourly sampling basis using an in-borehole gas monitor called Gasclam. A Tenax TA sorbent tube incorporated into and to work in parallel with this instrumentation was used to adsorb bulk concentrations of VOC and subsequently desorbed (for characterisation) using thermal desorption/gas chromatography-mass spectroscopy (TD/GC-MS) technique. Gasclam result showed aggregate VOC concentrations of 7570 ppm and 705 ppm in boreholes 1 and 2 respectively over the monitoring period. The total concentration of adsorbed VOCs in boreholes 1 and 2 are 96.3 mg/m³ and 129 mg/m³ respectively. Among the identified VOCs are those recognised to be hazardous to health and the environment. A comparison of the concentration of some specific VOCs in this site and the international standard shows that they have passed the set limits. Site clean-up was therefore recommended.

INTRODUCTION

The need to characterisation volatile organic compounds (VOCs) is majorly because of their significant human health and environmental effects [1-3]. These effects of VOCs are intensified by their variety, variability, ubiquity, volatility and solubility making them easily available and susceptible to human inhalation and ready contaminants of controlled waters [4]. Two VOCs, namely benzene and formaldehyde, have been recognized as human carcinogens by the International Agency for Research on Cancer [5]. VOCs are also implicated in the formation of ozone and photochemical oxidants associated with urban smog [6].

Therefore, a better understanding of their subsurface distribution, via monitoring, is to be encouraged. Monitoring of VOCs in contaminated sites ideally should involve measurement of both VOC concentration and flux. This is because; while VOC concentration determines their worst case scenario in contaminated sites, VOCs flux determines when and at what concentration they will reach the receptor [7,8].

In this study, we have characterised a former Tank Farm located in Bangor, United States with special emphasis on VOCs

concentrations. The aim is to determine their specificity and quantity. Whilst specific VOCs would help to determine whether they are amongst the ones considered to be hazardous to health, their quantity on the other hand would determine if they have passed the regulatory limits.

Site description

This is a Tank Farm which provides bulk storage of jet fuel for operations at the City-owned International Airport. This Tank Farm previously provided fuel for the former Dow Air Force Base. The Tank Farm has been storing and supplying jet fuels for over 60 years. There are a few monitoring wells at the tank farm, but no active remediation system. The monitoring wells indicate little contamination at this site. A second Gasclam was placed in a pit which allows access to the piping between the Tank Farm and Airport. At the time that the Gasclam was installed to record data, an abandoned pipe was open and emitting small amounts of vapour in this pipeline pit.

Methodology

The Gasclam was designed to operate remotely; specifically in 50 mm ID monitoring wells. It monitors and records the

following: CH₄, CO₂, O₂, CO, H₂S, VOCs, atmospheric pressure, borehole pressure, pressure differential, temperature and water level. It is made from stainless steel and is also intrinsically safe. It is environmentally sealed and has ingress protection rated IP-68. The Gasclam is battery operated and can be powered for up to three months whilst operating on an hourly sampling frequency. Target applications for the Gasclam ground gas monitor include landfill for long term profiling, Brown field sites for development issues, monitoring for coal mine fires, leakage of crude/petroleum, solvent storage and filling stations, oil refineries for local compliance/regulation, and for below ground carbon capture and storage monitoring regime.

The Gasclam has the following technical information: (i) it has a memory which can record and store 65,000 time/date stamped readings, (ii) it weighs 7kg (13.2 lbs), (iii) It has overall length of 85cm (33.5 inches), (iv) the head diameter is 10.8 cm (4.25 inches), (v) its operation temperature range is -5 to +50°C or 41°F to 122°F, (vi) it is powered by Duracell 1.5v LR20 MN1300 cells or a rechargeable battery pack.

Two Gasclam units with PID sensors were modified by incorporating a sorption tube containing Tenax TA (poly-2, 6-diphenyl-p-phenylene oxide) adsorbent [1,2]. This particular sorbent was chosen based on its outstanding selective properties in adsorption and desorption of VOCs over others gases [9]. These properties include high thermal stability [10], high hydrophobicity and rapid desorption kinetics [11-16], high breakthrough volume [17-22], inertness towards most pollutants, high mechanical strength, and a good adsorption range of VOCs [23]. It has a surface area of 35m²g⁻¹ and a pore volume of 2.4 cm³g⁻¹ [9]. VOCs adsorbed on Tenax TA sorbent tube are analysed by thermal desorption /gas chromatography mass spectroscopy (TD/GC-MS); a method which has already been standardised internationally [24].

In-situ VOC sample collection

The two units were installed to monitor continuously on hourly sampling intervals for up to one month. The in-situ continuous data from the Gasclam was downloaded while the sorbent tubes were removed from the Gasclam and sealed for subsequent TD/GC-MS analysis.

Ex-situ sample analysis

Analyses of the samples were conducted by heating the sorbent tube to 300°C. The volatile components were then trapped on a cold trap, held at -10°C, prior to desorption onto the GC column. Desorption of the TD tubes was carried out using a Markes International 50:50 TD system coupled to an Agilent GC/MS. Data acquisition in scanning mode was via a PC running Agilent Chemstation software.

The mass of each of the identified VOCs was calculated relative to the standard by assuming that the area of their peaks on the chromatogram is proportional to their masses (Table 1). The relationship is shown below:

$$A_{is}/Q_{is} = A_x/Q_x \quad (1)$$

Where A_{is} is the area of internal standard on the chromatogram, Q_{is} is the amount of internal standard = 500ng,

A_x is the area of specific VOC on the chromatogram and Q_x is the amount of specific VOC =? The VOCs analytical result is shown in the appendix.

RESULTS AND DISCUSSION

The multi-parameter time series data obtained from the studied site displayed changes in VOCs concentrations which are in the ranges of 10 ppm to 68 ppm in borehole 1 and 0 ppm to 25 ppm in borehole 2. The aggregate concentration of VOCs over the monitoring period is 7570 ppm and 705 ppm in boreholes 1 and 2 respectively. This shows that the concentration of VOCs in borehole 2 is higher than that in borehole 1. However, the high bulk VOCs concentration recorded in borehole 2 may not be proportional to the concentration of adsorbed VOCs since the used sorbent tubes have breakthrough volume above which the adsorbed concentration of VOCs begins to elude the tube [17].

The total concentration of adsorbed VOCs in Borehole 1 is 96.3 mg/m³ whilst in Borehole 2; it is 129 mg/m³. Undecane and butane have the highest and lowest concentrations of 7.38 mg/m³ (7.66%) and 1.95 x 10⁻² mg/m³ (0.0203%) respectively among the identified VOCs in Borehole 1; whilst in Borehole 2, the highest concentration of 5.47 mg/m³(4.25%) was recorded for Undecane and the lowest concentration of 4.80 x 10⁻² mg/m³ (0.0373%) for Dimethyldiazene (Table 2).

Most of the identified VOCs are among USEPA list of 107 compounds whose toxicity and volatility produce a potentially unacceptable inhalation risk to receptors. The risk of anyone being exposed to a significant amount of the contaminant is very high. This is because; an abandoned pipe was open and emitting small amounts of vapour in this site – a potential for exposure. Therefore, it can be concluded that these wells are potentially dangerous. The result also shows that the total concentration of VOCs adsorbed from Borehole 2 is 32.7 orders of magnitude higher than that from Borehole 1 during the monitoring period. This implies that although the 2 boreholes contain hazardous VOCs, Borehole 2 is actually more dangerous on the basis of the quantity of these VOCs it contains. This type of information can be helpful during risk assessment in understanding the regime and distribution of VOCs at different locations on a given site.

As can be observed in Table 3 (see appendix), propylbenzene which was not present in borehole 2 exceeded its Emission Limit (EL) in borehole 1. p-Xylene on the other hand exceeded its EL in the two boreholes. Toluene was not found in borehole 1, however; in borehole 2, it exceeded its emission standard. Whilst 1,2,3-trimethylbenzene passed its EL in borehole 2, in borehole 1, it did not. 1,2,4-trimethylbenzene was only found in borehole 1 in which it exceeded its set limit. Whilst 1,3,5-trimethylbenzene passed its EL in the two boreholes; n-Hexane and methylcyclohexane did not in any of the boreholes. Ethylbenzene passed its EL in borehole 2 but absent in borehole 2. Most of the identified VOCs are the same with those recorded in similar sites according to literatures [1-3].

CONCLUSIONS

- The concentrations of VOC in the two boreholes were variable in concentration. The values range from 10 - 68 ppm in borehole 1 and 0 - 25 ppm in borehole 2.

Table 1: Volatile Organic Compounds Analytical Results Sample: MI 148956 (Borehole 1).

S/N	Name of compounds	Individual TIC peak Area	Total mass (mg)	Total concentration (mg/m ³)	% of the total area	Cumulative % of total area
1	Undecane	4.11E+09	1.56E-01	7.38E+00	7.66E+00	7.66E+00
2	1,3,5-Trimethylbenzene	1.36E+09	5.16E-02	2.44E+00	2.53E+00	1.02E+01
3	3-Methyldecane	1.02E+09	3.87E-02	1.83E+00	1.89E+00	1.21E+01
4	p-Xylene	7.33E+08	2.79E-02	1.32E+00	1.37E+00	1.35E+01
5	3-Methylheptane	7.31E+08	2.78E-02	1.31E+00	1.36E+00	1.48E+01
6	1-Methyl-2-pentylcyclohexane	6.82E+08	2.60E-02	1.23E+00	1.27E+00	1.61E+01
7	Nonane	6.13E+08	2.34E-02	1.10E+00	1.14E+00	1.72E+01
8	2-Methyldecane	5.73E+08	2.18E-02	1.03E+00	1.07E+00	1.83E+01
9	Methylcyclohexane	5.48E+08	2.09E-02	9.85E-01	1.02E+00	1.93E+01
10	5-Methyldecane	5.25E+08	2.00E-02	9.44E-01	9.80E-01	2.03E+01
11	2-Cyclohexylundecane	5.24E+08	2.00E-02	9.42E-01	9.78E-01	2.13E+01
12	2,6-Dimethylnonane	4.82E+08	1.84E-02	8.66E-01	8.99E-01	2.22E+01
13	1-Ethyl-3-methylbenzene	4.52E+08	1.72E-02	8.12E-01	8.43E-01	2.30E+01
14	Heptane	3.91E+08	1.49E-02	7.02E-01	7.29E-01	2.38E+01
15	2,6-Dimethyldecane	3.85E+08	1.47E-02	6.91E-01	7.18E-01	2.45E+01
16	2-Methylheptane	3.49E+08	1.33E-02	6.28E-01	6.52E-01	2.51E+01
17	2,5-Dimethylheptane	3.42E+08	1.30E-02	6.15E-01	6.39E-01	2.58E+01
18	2-Ethyl-1-hexanol	3.21E+08	1.22E-02	5.77E-01	5.99E-01	2.64E+01
19	Octane	3.15E+08	1.20E-02	5.66E-01	5.87E-01	2.70E+01
20	1,2,4-Trimethylbenzene	3.06E+08	1.16E-02	5.49E-01	5.70E-01	2.75E+01
21	3-Methyloctane	2.90E+08	1.10E-02	5.21E-01	5.41E-01	2.81E+01
22	4-Methyldecane	2.87E+08	1.09E-02	5.15E-01	5.35E-01	2.86E+01
23	3-Methylnonane	2.75E+08	1.05E-02	4.93E-01	5.12E-01	2.91E+01
24	1,2-Dipropylcyclopentane	2.62E+08	1.00E-02	4.72E-01	4.90E-01	2.96E+01
25	2-Methylhexane	2.53E+08	9.65E-03	4.55E-01	4.72E-01	3.01E+01
26	3-Methyldecane	2.52E+08	9.61E-03	4.53E-01	4.71E-01	3.05E+01
27	4-Ethyloctane	2.36E+08	9.00E-03	4.24E-01	4.41E-01	3.10E+01
28	3-Methylhexane	2.32E+08	8.85E-03	4.17E-01	4.33E-01	3.14E+01
29	4-Methylnonane	2.32E+08	8.84E-03	4.17E-01	4.33E-01	3.19E+01
30	2,6-Dimethylheptane	2.30E+08	8.77E-03	4.14E-01	4.30E-01	3.23E+01
31	Propylbenzene	2.21E+08	8.41E-03	3.97E-01	4.12E-01	3.27E+01
32	1-Ethyl-2-methylbenzene	1.65E+08	6.30E-03	2.97E-01	3.09E-01	3.30E+01
33	1-Ethyl-3-methylbenzene	1.63E+08	6.20E-03	2.93E-01	3.04E-01	3.33E+01
34	1,2-Dipropylcyclopentane	1.45E+08	5.54E-03	2.62E-01	2.72E-01	3.36E+01
35	1,3-Dimethylcyclohexane	1.44E+08	5.49E-03	2.59E-01	2.69E-01	3.38E+01
36	2,6-Dimethyloctane	1.35E+08	5.14E-03	2.42E-01	2.52E-01	3.41E+01
37	2,6-Dimethylundecane	1.07E+08	4.08E-03	1.92E-01	2.00E-01	3.43E+01
38	2,4-Dimethylheptane	1.07E+08	4.08E-03	1.92E-01	2.00E-01	3.45E+01
39	1-Methyl-2-pentylcyclohexane	1.07E+08	4.06E-03	1.91E-01	1.99E-01	3.47E+01
40	5-Methyldecane	1.03E+08	3.91E-03	1.84E-01	1.91E-01	3.49E+01
41	1-Methyl-4-propylbenzene	8.14E+07	3.10E-03	1.46E-01	1.52E-01	3.50E+01
42	2,6-Dimethyldecane	8.10E+07	3.09E-03	1.46E-01	1.51E-01	3.52E+01
43	1,2-Dibromo-2-methylundecane	7.92E+07	3.02E-03	1.42E-01	1.48E-01	3.53E+01
44	1-Tetradecyne	7.08E+07	2.70E-03	1.27E-01	1.32E-01	3.55E+01

45	1,5-Dimethylcyclooctane	6.81E+07	2.59E-03	1.22E-01	1.27E-01	3.56E+01
46	1-Ethyl-2-propylcyclohexane	6.50E+07	2.47E-03	1.17E-01	1.21E-01	3.57E+01
47	trans-1-Methyl-4-isopropylcyclohexane	6.45E+07	2.46E-03	1.16E-01	1.20E-01	3.58E+01
48	2,6,10-Trimethyldodecane	5.73E+07	2.18E-03	1.03E-01	1.07E-01	3.59E+01
49	Cyclododecanemethanol	5.35E+07	2.04E-03	9.61E-02	9.98E-02	3.60E+01
50	1,2,3-Trimethylbenzene	5.12E+07	1.95E-03	9.21E-02	9.56E-02	3.61E+01
51	cis-1-Methyl-4-isopropylcyclohexane	5.12E+07	1.95E-03	9.21E-02	9.56E-02	3.62E+01
52	Methylcyclopentane	4.31E+07	1.64E-03	7.74E-02	8.03E-02	3.63E+01
53	1,2-Dimethylcyclooctane	4.27E+07	1.63E-03	7.68E-02	7.97E-02	3.64E+01
54	Isobutyl-3-methylcyclopentane	4.11E+07	1.56E-03	7.38E-02	7.66E-02	3.65E+01
55	Dodecane	3.42E+07	1.30E-03	6.16E-02	6.39E-02	3.65E+01
56	Isobutyl-3-methylcyclopentane	3.18E+07	1.21E-03	5.72E-02	5.93E-02	3.66E+01
57	1,1,2,3-Tetramethylcyclohexane	2.27E+07	8.67E-04	4.09E-02	4.24E-02	3.66E+01
58	2,6-Dimethylundecane	1.99E+07	7.56E-04	3.57E-02	3.70E-02	3.67E+01
59	Hexane	1.55E+07	5.89E-04	2.78E-02	2.88E-02	3.67E+01
60	3-Tridecene	1.44E+07	5.47E-04	2.58E-02	2.68E-02	3.67E+01
61	2-Methylpentane	1.11E+07	4.23E-04	1.99E-02	2.07E-02	3.68E+01
62	Butane	1.09E+07	4.14E-04	1.95E-02	2.03E-02	3.68E+01
63	Unidentified compounds	3.39E+10	1.29E+00	6.09E+01	6.32E+01	1.00E+02
Σ PID VOCs signal (ppm)		Σ VOC mass (mg)		Total vol. (m³)		ΣVOCs conc.(mg/m³)
7570		2.04E+00		2.12E-02		9.63E+01

Table 2: Volatile Organic Compounds Analytical Results Sample: MI 148957 (Borehole 2).

S/N	Name of compounds	Individual TIC peak Area	Total mass (mg)	Total concentration (mg/m ³)	% of the total area	Cumulative % of total area
1	Undecane	1.01E+09	4.43E-02	5.47E+00	4.25E+00	4.25E+00
2	1,3,5-Trimethylbenzene	6.75E+08	2.96E-02	3.66E+00	2.85E+00	7.10E+00
3	Toluene	5.98E+08	2.63E-02	3.24E+00	2.52E+00	9.62E+00
4	Nonane	5.65E+08	2.48E-02	3.06E+00	2.38E+00	1.20E+01
5	p-Xylene	4.21E+08	1.85E-02	2.28E+00	1.78E+00	1.38E+01
6	Heptane	3.95E+08	1.73E-02	2.14E+00	1.67E+00	1.54E+01
7	Ethylbenzene	3.66E+08	1.61E-02	1.98E+00	1.54E+00	1.70E+01
8	Octane	3.52E+08	1.55E-02	1.91E+00	1.49E+00	1.85E+01
9	2-Methyldecahydronaphthalene	3.40E+08	1.49E-02	1.85E+00	1.43E+00	1.99E+01
10	Phytol	3.21E+08	1.41E-02	1.74E+00	1.35E+00	2.13E+01
11	2-Methyldecane	3.06E+08	1.34E-02	1.66E+00	1.29E+00	2.26E+01
12	Dadecane	2.90E+08	1.27E-02	1.57E+00	1.22E+00	2.38E+01
13	2-Methylhexane	2.84E+08	1.25E-02	1.54E+00	1.20E+00	2.50E+01
14	2-Methylheptane	2.61E+08	1.15E-02	1.42E+00	1.10E+00	2.61E+01
15	3-Methylhexane	2.35E+08	1.03E-02	1.27E+00	9.90E-01	2.71E+01
16	2,6-Dimethylnonane	2.16E+08	9.48E-03	1.17E+00	9.10E-01	2.80E+01
17	2-Methylundecane	1.96E+08	8.63E-03	1.07E+00	8.28E-01	2.88E+01
18	5-Methylundecane	1.96E+08	8.61E-03	1.06E+00	8.27E-01	2.96E+01
19	2-Cyclohexyldecane	1.92E+08	8.43E-03	1.04E+00	8.09E-01	3.04E+01
20	5-Methyldecane	1.85E+08	8.14E-03	1.00E+00	7.81E-01	3.12E+01
21	3-Methyloctane	1.71E+08	7.49E-03	9.25E-01	7.19E-01	3.19E+01
22	2,6-Dimethyldecane	1.61E+08	7.06E-03	8.71E-01	6.77E-01	3.26E+01

23	Hexane	1.58E+08	6.93E-03	8.56E-01	6.66E-01	3.33E+01
24	1,2,3-Trimethylbenzene	1.55E+08	6.82E-03	8.42E-01	6.55E-01	3.39E+01
25	Methylcyclohexane	1.45E+08	6.38E-03	7.88E-01	6.12E-01	3.45E+01
26	3-Methyldecane	1.45E+08	6.35E-03	7.85E-01	6.10E-01	3.52E+01
27	2,6-Dimethyloctane	1.41E+08	6.21E-03	7.67E-01	5.97E-01	3.58E+01
28	1-Ethyl-3-methylbenzene	1.36E+08	5.99E-03	7.39E-01	5.75E-01	3.63E+01
29	4-Methyldecane	1.17E+08	5.12E-03	6.32E-01	4.92E-01	3.68E+01
30	4-Methylundecane	1.11E+08	4.86E-03	5.99E-01	4.66E-01	3.73E+01
31	2,6-Dimethylundecane	1.09E+08	4.81E-03	5.93E-01	4.61E-01	3.77E+01
32	2,3-Dimethyloctane	1.09E+08	4.78E-03	5.90E-01	4.59E-01	3.82E+01
33	3-Methylundecane	1.08E+08	4.75E-03	5.87E-01	4.56E-01	3.87E+01
34	2,5-Dimethylheptane	7.86E+07	3.45E-03	4.26E-01	3.31E-01	3.90E+01
35	Ethylcyclohexane	6.71E+07	2.95E-03	3.64E-01	2.83E-01	3.93E+01
36	2,6,10-Trimethyladecane	6.12E+07	2.69E-03	3.32E-01	2.58E-01	3.95E+01
37	2,6-Dimethylheptane	5.68E+07	2.49E-03	3.08E-01	2.39E-01	3.98E+01
38	Tridecane	5.34E+07	2.35E-03	2.90E-01	2.25E-01	4.00E+01
39	2-Methylpentane	5.08E+07	2.23E-03	2.76E-01	2.14E-01	4.02E+01
40	Methylcyclopentane	4.54E+07	1.99E-03	2.46E-01	1.92E-01	4.04E+01
41	3-Methylpentane	4.01E+07	1.76E-03	2.17E-01	1.69E-01	4.06E+01
42	Dimethyldiazene	8.85E+06	3.89E-04	4.80E-02	3.73E-02	4.06E+01
43	Unidentified compounds	1.41E+10	6.19E-01	7.64E+01	5.94E+01	1.00E+02
Σ PID VOCs signal (ppm)		Σ VOC mass (mg)		Total vol. (m³)		ΣVOCs conc.(mg/m³)
705		1.04E+00		8.10E-03		1.29E+02

Table 3: European Union-wide harmonized VOCs Emission Limit ((mg/m³) of some selected compounds and their concentrations in the monitored site. The numbers in red-type depict exceedance of emission limit whilst the one in green shows non-exceedance of emission limit.

S/N	Name of compounds	EU-wide harmonized Emission Limit ((mg/m ³)	Total concentration (mg/m ³) in Borehole 1	Total concentration (mg/m ³) in Borehole 2
1	Propylbenzene	0.95	0.40	-
2.	p-Xylene	0.5	1.32	2.28
3.	Toluene	2.9	-	3.24
4.	1,2,3-Trimethylbenzene	0.45	0.09	0.84
5.	1,2,4-Trimethylbenzene	0.45	0.55	-
6.	1,3,5-Trimethylbenzene	0.45	2.44	3.66
7.	n-Hexane	6	0.03	0.86
8.	Methylcyclohexane	8.1	0.99	0.79
9.	Ethylbenzene	0.85	-	1.98

Source: Joint Research Centre (JRC) Project and European Collaborative Action (ECA) Report 29, 2013 [24].

Also whilst the former has a total VOCs concentration of 7570 ppm; the latter has 705 ppm as its total over the monitoring period.

- The identified VOCs comprise of those recognised to be significantly hazardous to health and the environment. They include toluene, xylene, ethylbenzene, and Propylbenzene.
- A comparison of the individual concentrations of VOCs in this site with the EU-wide Emission Limits shows that they have passed the set limits. The presence of these VOCs constitutes a risk in this site due to the presence of an

exposure pathway and a receptor.

- The use of a PID/Tenax enabled Gasclam enables robust sub-surface VOC gas/vapour monitoring data enabling site zoning and a more effective targeting of remedial efforts on those zones of actual concern leading to savings in both time and money and helping to ensure that the remedial works are more sustainable in line with current guidance.
- They also save frequent “snapshot” monitoring visits enabling a more accurate representation of sub-surface conditions to be obtained.

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