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DETERMINATION OF VOLATILE ORGANIC COMPOUNDS AT A MARINE TERMINAL IN UNITED STATES USING IN-BOREHOLE GAS MONITORING

A. N. Nwachukwu
Department of Physics/Geology/Geophysics, Faculty of Science, Alex Ekwueme Federal University, Ndufu-Alike Ikwo (AE-FUNAI), Ebonyi State, Nigeria., arthurdeconvenantchild@yahoo.com

C. U. Uwa
Department of Biology, Faculty of Science, Alex Ekwueme Federal University, Ndufu-Alike Ikwo (AE-FUNAI), Ebonyi State, Nigeria.

K. E. Nwagu
Alex Ekwueme Federal University, Ndufu-Alike Ikwo (AE-FUNAI), Ebonyi State, Nigeria

B. E. Ephraim
Department of Geology, Faculty of Science, University of Calabar, Calabar, Cross River State, Nigeria.

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DETERMINATION OF VOLATILE ORGANIC COMPOUNDS AT A MARINE TERMINAL IN UNITED STATES USING IN-BOREHOLE GAS MONITORING

A. N. Nwachukwu, C. U. Uwa, K.E. Nwagu, and B. E. Ephraim

Key words: Gasclam, TD/GC-MS, Tenax TA sorbent, environmental releases, carcinogens, emission limits, VOCs, United States, remediation.

ABSTRACT

A time-series study was conducted to determine both the aggregate and specific Volatile Organic Compounds (VOCs) concentrations at a Marine Terminal. An in-situ aggregate data of VOC concentrations and some environmental parameters were logged by means of an in-borehole gas monitor called Gasclam (Ion Science, UK). A *Tenax TA* sorbent tube incorporated into and to work in parallel with the Gasclam was used to adsorb bulk concentrations of VOCs and subsequently desorbed (for characterization) using Thermal Desorption/Gas Chromatography-Mass Spectroscopy (TD/GC-MS) technique. The result shows aggregate VOC concentrations of 31385 ppm and 17140 ppm in wells I and II respectively over the monitoring period. The total concentrations of adsorbed VOCs in wells I and II are 4.17×10^2 mg/m^3 and 1.12×10^3 mg/m^3 respectively. Among the identified VOCs (many of which exceeded their standard limits) are those considered to be hazardous to human health and environment. The study revealed that the marine terminal site is potentially hazardous, and hence, requires active remediation.

I. INTRODUCTION

VOCs comprise of a group of organic compounds which are volatile under normal atmospheric temperature and pressure (Katy et al., 2009). They can come from a variety of natural sources (Ramirez et al., 2010), however; their presence in the environment is mainly due to spillage/leakage of solvents or fuels associated with industrial and commercial activities such as their production, storage, distribution, and uses in industrial processing (Department of Environment, 1995; Tillman and Weaver, 2005; Steinmann, 2008; Katy et al., 2009). Accordingly, VOCs have been observed to be among the most frequently detected contaminants in soil and ground water around landfills and brownfield sites (West et al., 1995; EA, 2004). They can also be found in former gas works (Thomas and Lester, 1994; Dor et al., 2001; Allen, 2002), oil refineries (Cetin et al., 2003; Pandya et al., 2006; Tiwari et al., 2010), and even in homes (from furnishings and consumer household products) (Steinmann, 2008; BS ISO 16000-9, 2006; BS ISO 16000-10, 2006; Venn et al., 2001; Hers et al., 2001; Coward et al., 2001; Coward et al., 2002).

In marine terminals, significant quantities of VOCs are often released into the atmosphere during the loading, offloading and transportation of crude oil by ships (Howard and Nikolas, 2001; Tamaddoni et al., 2014; Choi et al., 2018). Buhaug et al., (2009) explained that about 2.4 million tons of VOCs, representing approximately USD 700 million in value, are lost every year in the transportation of crude oil. These emissions constitute not only economic losses but also threat to both human health (HSE, 2000; ATSDR, 2001; IARC, 2004; Rowe et al., 2007; Argyropoulos et al., 2010) and the environment (Kesselmeier et al., 2000; Possanzini et al., 2002; IPCC, 2007).

For example, VOCs are flammable and can cause fire (HSE, 2000). At elevated concentrations in the environment, VOC can also be a concern to human health because of their potential as carcinogens (IARC, 2004; Rowe et al., 2007). In the presence of sunlight, VOCs can react with oxides of nitrogen (NO_x) to produce ground level ozone and photochemical smog[1]. The main organs adversely affected by VOCs include the liver, kidneys, spleen, and stomach, as well as the nervous, circulatory, reproductive, immune, cardiovascular, and respiratory

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Paper submitted 09/20/18; revised 10/23/18; accepted 04/27/20. Corresponding Author: A. N. Nwachukwu (Email: arthurdeconvenantchild@yahoo.com)

[1] *Department of Physics/Geology/Geophysics, Faculty of Science, Alex Ekwueme Federal University, Ndufu-Alike Ikwo (AE-FUNAI), Ebonyi State, Nigeria.*
[2] *Department of Biology, Faculty of Science, Alex Ekwueme Federal University, Ndufu-Alike Ikwo (AE-FUNAI), Ebonyi State, Nigeria.*
[3] *Department of Geology, Faculty of Science, University of Calabar, Calabar, Cross River State, Nigeria.*

[1] www.coatings.org.uk

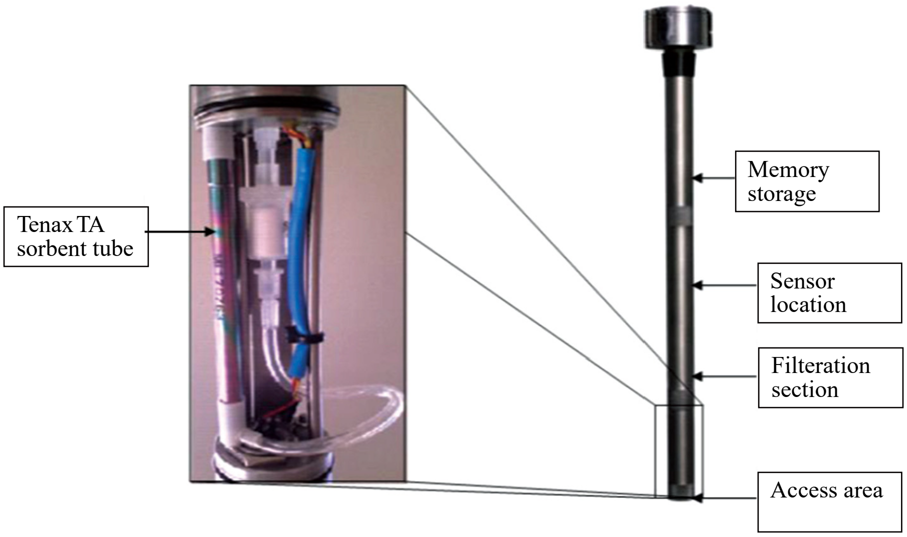

Fig. 1. Inclusion of a sorption cartridge into the basal section of a Gasclam unit

systems (Rowe et al., 2007). There is, therefore, an increasing concern about VOCs emission due to their toxicity and widespread occurrence (Ott *et a*l., 1978; Lynge et al., 1997; Srivastava et al., 2005; Maximilian et al., 2009; Sergio et al., 2012; Nwachukwu, 2014; Nwachukwu and Henry, 2016).

Given the economic, human health and environmental effects of VOCs released from marine terminals; the International Maritime Organization (IMO) regulated VOC emissions from ships through the 15th regulation of MARPOL Annex VI 2010 (International Convention for the Prevention of Pollution from Ships, 2008, Standards for vapour emission control systems, Guidelines for the development of a VOC management plan, 2009). This regulation requires the use of a government-approved vapour emission control system for the loading of crude oil or petroleum products. A variety of studies have been conducted to determine the best techniques for VOC control systems by considering the economic and environmental effects (Khan and Ghoshal, 2000; Shonnard and Hiew, 2000; Howard and Nikolas, 2011; Huang et al., 2011; Lee et al., 2013). However, many countries have adopted Marine Vapour Recovery Systems (MVRSs) to meet IMO regulations.

Whilst a lot of research has been conducted on VOCs emissions recovery, there is no single research on the quantification of VOCs from the surroundings of marine terminals. Note that the quantity of VOCs emitted and recovered directly depends on the amount of VOCs spilled/leaked. Apart from loading, unloading and transportation activities, VOCs can be spilled/leaked into the water body and the surrounding soils by many other ways, including the following[2]:

- *Construction activity: Ports and terminals are frequently situated on reclaimed, low-lying land, with imported fill, which sometimes contains contaminated materials.*
- *Storage facilities: Liquid bulk tanks with connecting pipelines could be subject to sudden and accidental structure failure, or gradual ground seepage and leakage.*
- *Ancillary operations: Tank cleaning, ballast water treatment, shipbuilding, ship repairing or demolition, metal finishing and plating, fire protection activities, paint shops, foundries, and manufactured gas works all present environmental exposures.*

It is, therefore, not enough to monitor only the amount of VOCs released into the atmosphere; there is, also, a requirement to take into consideration those released into the surrounding environment as they are much closer to the receptors. It was sequel to this that this research was conducted.

Whilst there is often a requirement to monitor VOCs as in this case; current VOC monitoring techniques are often of low resolution to determine their representative concentrations (Nwachukwu and Anonye 2012). An in-borehole monitor (*Gasclam)* which collects aggregate VOCs concentration at high temporal resolution was deployed whilst a *Tenax TA* sorbent tube incorporated into and to work in parallel with this instrumentation was used to adsorb bulk concentrations of VOCs and subsequently desorbed (for characterization) using Thermal Desorption/Gas Chromatography-Mass Spectroscopy (TD/GC-MS) technique.

Gasclam was developed by Salamander Ltd – a company founded by Dr Stephen Boult of The University of Manchester in 1996. Gasclam won the Innovation Technology prize in the Northwest Business Environment Awards in 2007[3]. Gasclam was designed to operate remotely; specifically in 50 mm ID monitoring wells. Gasclam is an improvement upon existing measurement technologies as it allows continuous collection of information about the movement and build-up of underground gases. This is unlike other ground-gas monitors which only take spot measurements. Gasclam monitors and records the following: CH_4, CO_2, O_2, CO, H_2S, VOCs, atmospheric

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[2] Marsh.com

[3] https://www.manchester.ac.uk/discover/news/ground-gas-gizmo-boosts-brownfield-building/

Table 1. Volatile Organic Compounds Analytical Results, Sample: MI 14859 (Marine Terminal – 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	2.69E+09	9.42E-02	1.96E+01	4.71E+00	4.71E+00
2	Methylcyclohexane	1.04E+09	3.62E-02	7.54E+00	1.81E+00	6.52E+00
3	4-Methyl-1-hexene	1.01E+09	3.53E-02	7.36E+00	1.77E+00	8.28E+00
4	2,6,10-Trimethyldadecane	8.98E+08	3.14E-02	6.54E+00	1.57E+00	9.85E+00
5	Dadecamethylene glycol	8.33E+08	2.91E-02	6.07E+00	1.45E+00	1.13E+01
6	3-Methylhexane	7.34E+08	2.57E-02	5.35E+00	1.28E+00	1.26E+01
7	3-Methylheptane	7.33E+08	2.56E-02	5.34E+00	1.28E+00	1.39E+01
8	Ethylbenzene	6.69E+08	2.34E-02	4.87E+00	1.17E+00	1.50E+01
9	3-Methyldecane	6.65E+08	2.32E-02	4.84E+00	1.16E+00	1.62E+01
10	2-Methylhexane	6.58E+08	2.30E-02	4.79E+00	1.15E+00	1.73E+01
11	Heptane	5.96E+08	2.08E-02	4.34E+00	1.04E+00	1.84E+01
12	1,2-Dipropylcyclopentane	5.37E+08	1.88E-02	3.91E+00	9.38E-01	1.93E+01
13	1,3,5-Trimethylbenzene	5.36E+08	1.87E-02	3.90E+00	9.36E-01	2.03E+01
14	4-Methylheptene	5.33E+08	1.87E-02	3.89E+00	9.32E-01	2.12E+01
15	2-Methylheptane	5.28E+08	1.85E-02	3.85E+00	9.23E-01	2.21E+01
16	Methylcyclopentane	4.67E+08	1.63E-02	3.40E+00	8.16E-01	2.29E+01
17	1-Methyl-2-pentylcyclohexane	4.65E+08	1.63E-02	3.39E+00	8.13E-01	2.37E+01
18	Dadecane	4.61E+08	1.61E-02	3.36E+00	8.05E-01	2.45E+01
19	3-Methyloctane	4.61E+08	1.61E-02	3.36E+00	8.05E-01	2.54E+01
20	2,5-Dimethylheptane	4.53E+08	1.58E-02	3.30E+00	7.91E-01	2.61E+01
21	2-Methylundecane	4.41E+08	1.54E-02	3.21E+00	7.71E-01	2.69E+01
22	5-Methyldecane	4.37E+08	1.53E-02	3.18E+00	7.63E-01	2.77E+01
23	2-Methylpentane	4.37E+08	1.53E-02	3.18E+00	7.63E-01	2.84E+01
24	2-Cyclohexylundecane	4.15E+08	1.45E-02	3.03E+00	7.26E-01	2.92E+01
25	2,6-Dimethylnonane	4.11E+08	1.44E-02	3.00E+00	7.19E-01	2.99E+01
26	2,6-Dimethyldecane	4.10E+08	1.43E-02	2.98E+00	7.16E-01	3.06E+01
27	2-Methyldecane	4.01E+08	1.40E-02	2.92E+00	7.01E-01	3.13E+01
28	2,6-Dimethyloctane	3.73E+08	1.30E-02	2.72E+00	6.52E-01	3.20E+01
29	Hexane	3.55E+08	1.24E-02	2.58E+00	6.20E-01	3.26E+01
30	Ethylcyclohexane	3.38E+08	1.18E-02	2.47E+00	5.91E-01	3.32E+01
31	4-Methyldecane	3.34E+08	1.17E-02	2.43E+00	5.83E-01	3.37E+01
32	Octane	3.17E+08	1.11E-02	2.31E+00	5.54E-01	3.43E+01
33	3-Methylundecane	3.06E+08	1.07E-02	2.23E+00	5.35E-01	3.48E+01
34	2,3-dimethyloctane	2.96E+08	1.04E-02	2.16E+00	5.17E-01	3.54E+01
35	2,6-Dimethyldecane	2.77E+08	9.69E-03	2.02E+00	4.84E-01	3.58E+01
36	4-Methylundecane	2.75E+08	9.61E-03	2.00E+00	4.80E-01	3.63E+01
37	2-Hexyl-1-decanol	2.42E+08	8.45E-03	1.76E+00	4.22E-01	3.67E+01
38	cis-1,3-Dimethylcyclohexane	2.37E+08	8.28E-03	1.72E+00	4.14E-01	3.72E+01
39	4-Methyloctane	2.33E+08	8.14E-03	1.69E+00	4.06E-01	3.76E+01
40	1-Tridecene	2.31E+08	8.07E-03	1.68E+00	4.03E-01	3.80E+01
41	3-Methylpentane	2.05E+08	7.16E-03	1.49E+00	3.58E-01	3.83E+01
42	Chlorobenzene	2.02E+08	7.07E-03	1.47E+00	3.53E-01	3.87E+01

Table 1. (Continued)

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
43	Xylene	1.64E+08	5.72E-03	1.19E+00	2.86E-01	3.90E+01
44	4-Methylnonane	1.60E+08	5.59E-03	1.16E+00	2.79E-01	3.92E+01
45	1-Methyl-2-propylcyclohexane	1.57E+08	5.48E-03	1.14E+00	2.74E-01	3.95E+01
46	Nonane	1.50E+08	5.24E-03	1.09E+00	2.62E-01	3.98E+01
47	2-Methyloctane	1.47E+08	5.13E-03	1.07E+00	2.56E-01	4.00E+01
48	3-Methylnonane	1.28E+08	4.47E-03	9.30E-01	2.23E-01	4.03E+01
49	3-Ethyl-2-methylheptane	1.25E+08	4.39E-03	9.14E-01	2.19E-01	4.05E+01
50	2,6-Dimethylundecane	9.77E+07	3.42E-03	7.12E-01	1.71E-01	4.06E+01
51	Phytol	9.12E+07	3.19E-03	6.64E-01	1.59E-01	4.08E+01
52	Pentane	8.67E+07	3.03E-03	6.31E-01	1.51E-01	4.10E+01
53	1-Ethyl-2-methylbenzene	5.55E+07	1.94E-03	4.04E-01	9.69E-02	4.11E+01
54	2-Methylbutane	4.71E+07	1.65E-03	3.43E-01	8.23E-02	4.11E+01
55	2-Butyl-1,1,3-trimethylcyclohexane	2.38E+07	8.31E-04	1.73E-01	4.15E-02	4.12E+01
56	Unidentified compounds	3.37E+10	1.18E+00	2.45E+02	5.88E+01	1.00E+02

∑ PID VOCs signal (ppm)	∑ VOC mass (mg)	Total vol. (m^3)	∑VOCs conc.(mg/m^3)
31385	2.00E+00	4.80E-03	4.17E+02

Table 2. Volatile Organic Compounds Analytical Results, Sample: MI 148960 (Marine Terminal – Borehole 2)

S/N	Name of compounds	Individual TIC peak Area	Total mass (mg)	Total concentration (mg/m^3)	% of the total concentration	Cumulative % of total concentration
1	1,3,5-Trimethylbenzene	2.17E+09	8.82E-02	2.05E+01	1.83E+00	1.83E+00
2	Methylisopropylbenzene	1.77E+09	7.19E-02	1.67E+01	1.49E+00	3.32E+00
3	1-Ethyl-2-methylbenzene	1.56E+09	6.36E-02	1.48E+01	1.32E+00	4.63E+00
4	1,4-Dimethyl-2-ethylbenzene	1.51E+09	6.14E-02	1.43E+01	1.27E+00	5.90E+00
5	2,4-Diethyl-1-methylbenzene	1.48E+09	6.03E-02	1.40E+01	1.25E+00	7.15E+00
6	1,2,4,5-Tetramethylbenzene	1.48E+09	6.03E-02	1.40E+01	1.25E+00	8.40E+00
7	1,2,3-Trimethylbenzene	1.42E+09	5.77E-02	1.34E+01	1.20E+00	9.60E+00
8	1,2,4-Trimethylbenzene	1.41E+09	5.73E-02	1.33E+01	1.19E+00	1.08E+01
9	2,6-Dimethylundecane	1.27E+09	5.18E-02	1.21E+01	1.07E+00	1.19E+01
10	1-Methyl-2-propylbenzene	1.15E+09	4.67E-02	1.09E+01	9.67E-01	1.28E+01
11	1, 2,3,4-Tetramethylbenzene	1.12E+09	4.55E-02	1.06E+01	9.42E-01	1.38E+01
12	2,6-Dimethyldecane	1.06E+09	4.31E-02	1.00E+01	8.93E-01	1.47E+01
13	1,3-Diethyl-5-methylbenzene	1.03E+09	4.20E-02	9.76E+00	8.69E-01	1.55E+01
14	2-Ethyl-1,4-dimethyl-Benzene	8.92E+08	3.63E-02	8.44E+00	7.52E-01	1.63E+01
15	1-Phenyl-1-butene	8.54E+08	3.48E-02	8.08E+00	7.20E-01	1.70E+01
16	1-Ethyl-4-isopropylbenzene	8.52E+08	3.47E-02	8.06E+00	7.18E-01	1.77E+01
17	3-Methyl-2-butenyl(1 benzene)	8.52E+08	3.47E-02	8.06E+00	7.18E-01	1.84E+01
18	1-Ethyl-4-isopropylbenzene	8.16E+08	3.32E-02	7.73E+00	6.88E-01	1.91E+01
19	Pentamethylbenzene	7.86E+08	3.20E-02	7.43E+00	6.62E-01	1.98E+01
20	1,3-Diethylbenzene	7.81E+08	3.18E-02	7.40E+00	6.59E-01	2.04E+01

Table 2. (Continued)

S/N	Name of compounds	Individual TIC peak Area	Total mass (mg)	Total concentration (mg/m^3)	% of the total concentration	Cumulative % of total concentration
21	2,6-Dimethyloctane	7.40E+08	3.01E-02	7.00E+00	6.23E-01	2.11E+01
22	1-Sec-butyl-2,4-dimethylbenzene	6.25E+08	2.54E-02	5.91E+00	5.27E-01	2.16E+01
23	4-Methyldecane	6.20E+08	2.52E-02	5.87E+00	5.23E-01	2.21E+01
24	Cyclopropylbenzene	5.83E+08	2.37E-02	5.52E+00	4.91E-01	2.26E+01
25	p-Isopropyl benzaldehyde	5.46E+08	2.22E-02	5.17E+00	4.60E-01	2.31E+01
26	1,3-Dimethyl-2-ethylbenzene	5.37E+08	2.18E-02	5.08E+00	4.52E-01	2.35E+01
27	Undecane	5.08E+08	2.07E-02	4.80E+00	4.28E-01	2.39E+01
28	Hexylcyclohexane	4.89E+08	1.99E-02	4.62E+00	4.12E-01	2.44E+01
29	3-Ethylhexane	4.88E+08	1.99E-02	4.62E+00	4.12E-01	2.48E+01
30	2,4-Dimethyl-1-ethylbenzene	4.71E+08	1.92E-02	4.46E+00	3.97E-01	2.52E+01
31	1-Chlorooctane	4.60E+08	1.87E-02	4.36E+00	3.88E-01	2.56E+01
32	1,2-Dimethylbenzene	4.48E+08	1.82E-02	4.24E+00	3.77E-01	2.59E+01
33	1-Sec-butyl-4-methylbenzene	4.22E+08	1.72E-02	4.00E+00	3.56E-01	2.63E+01
34	tert-Pentylbenzene	4.07E+08	1.66E-02	3.85E+00	3.43E-01	2.66E+01
35	Heptane	3.42E+08	1.39E-02	3.24E+00	2.88E-01	2.69E+01
36	1,4-Diethyl-2-methylbenzene	3.41E+08	1.39E-02	3.23E+00	2.87E-01	2.72E+01
37	2,6,10-Trimethyltetradecane	3.37E+08	1.37E-02	3.19E+00	2.84E-01	2.75E+01
38	1-Ethyl-5-methylcyclopentene	3.33E+08	1.36E-02	3.15E+00	2.81E-01	2.78E+01
39	Methylcyclohexane	3.26E+08	1.33E-02	3.08E+00	2.74E-01	2.80E+01
40	(1-Methyldene) cyclobutane	3.23E+08	1.31E-02	3.05E+00	2.72E-01	2.83E+01
41	2-Methylheptane	3.21E+08	1.31E-02	3.04E+00	2.70E-01	2.86E+01
42	Octane	3.13E+08	1.27E-02	2.96E+00	2.64E-01	2.89E+01
43	1,2,3-Trimethylcyclopetene	2.84E+08	1.15E-02	2.68E+00	2.39E-01	2.91E+01
44	2,5-Dimethyl-heptane	2.80E+08	1.14E-02	2.65E+00	2.36E-01	2.93E+01
45	p-Xylene	2.64E+08	1.07E-02	2.50E+00	2.22E-01	2.95E+01
46	Hexane	2.58E+08	1.05E-02	2.44E+00	2.18E-01	2.98E+01
47	2-Chloro-2-methylpentane	2.57E+08	1.04E-02	2.43E+00	2.16E-01	3.00E+01
48	1-Chlorooctadecane	2.51E+08	1.02E-02	2.37E+00	2.11E-01	3.02E+01
49	Cis-1,3-Dimethylcyclohexane	1.99E+08	8.09E-03	1.88E+00	1.68E-01	3.04E+01
50	Heptylcyclohexane	1.95E+08	7.95E-03	1.85E+00	1.65E-01	3.05E+01
51	3-Methylhexane	1.64E+08	6.66E-03	1.55E+00	1.38E-01	3.07E+01
52	1-Heptadecyne	1.61E+08	6.53E-03	1.52E+00	1.35E-01	3.08E+01
53	Ethylcyclohexane	1.49E+08	6.05E-03	1.41E+00	1.25E-01	3.09E+01
54	Methylcyclopentane	1.17E+08	4.77E-03	1.11E+00	9.87E-02	3.10E+01
55	3-Methylcyclopentene	1.06E+08	4.32E-03	1.01E+00	8.95E-02	3.11E+01
56	2-Methylpentane	7.73E+07	3.14E-03	7.31E-01	6.51E-02	3.12E+01
57	2,6,10-Trimethyldodecane	5.72E+07	2.33E-03	5.41E-01	4.82E-02	3.12E+01
58	3-Methylpentane	2.87E+07	1.17E-03	2.71E-01	2.41E-02	3.13E+01
59	Pentane	1.68E+07	6.83E-04	1.59E-01	1.41E-02	3.13E+01
60	2-Methylbutane	2.91E+06	1.18E-04	2.75E-02	2.45E-03	3.13E+01
61	Unidentified compounds	8.16E+10	3.32E+00	7.72E+02	6.87E+01	1.00E+02

∑ PID VOCs signal (ppm)	∑ VOC mass (mg)	Total vol. (m^3)	∑VOCs conc.(mg/m^3)
17140	4.83E+00	4.30E-03	1.12E+03

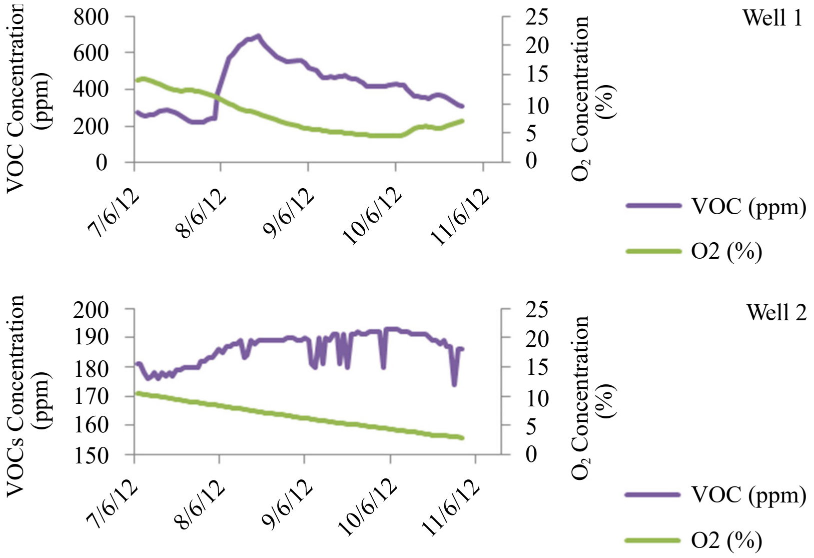

Fig. 2. Time series data from boreholes 1 and 2; showing variability in VOCs and O_2 Concentrations. The monitoring period is for five (5) days (7:6:201 – 11:6:2012).

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. 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, brownfield 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[4].

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 (Nwachukwu, 2015a, b, c; Nwachukwu and Ugwuanyi, 2012).

1. Monitored Site Information

This is a Maine marine terminal with less than 200,000 barrels of storage capacity and situated at 601 Danforth Street Portland, ME 04102 along the eastern coast of the United States. It is also known as Merrill's Marine Terminal after the owner Paul D. Merril. It is in an industrial section of the town with other industrial companies bordering its property. This property has been used as a marine terminal for over 36 years. No active remedial systems are active or planned and there has not been any significant spills reported at this site in the past ten years.

II. MATERIALS AND METHODS

Two Gasclam units, equiped with PID sensors were each modified by integrating a sorption tube containing Tenax TA (poly-2, 6-diphenyl-p-phenylene oxide) adsorbent (see Figure 1) (Nwachukwu, 2015a, b, c). This particular sorbent was chosen based on its outstanding selective properties in adsorption and desorption of VOCs over others gases (Kroupa et al., 2004). Some of such properties include high thermal stability (Brown, 1996), high hydrophobicity and rapid desorption kinetics (Rothweiler and Wager, 1991; Saba et al., 2001; Barro et al., 2005; Lee et al., 2006; Singer et al., 2007; Schripp et al., 2007; Barro et al., 2009), high break-through volume (Camel and Caude, 1995; Baya and Siskos, 1996;; Borusiewicz and Zięba-Palus, 2007; Ras and Borrull, 2009; Gallego et al., 2010), inertness towards most pollutants, high mechanical strength, and a good adsorption range of VOCs (Woolfenden, 2010). It has a surface area of 35m^2 g^{-1} and a pore volume of 2.4 cm^3 g^{-1} (Kroupa et al., 2004). VOCs adsorbed on Tenax TA sorbent tube were analysed by thermal desorption/gas chromatography-mass spectroscopy (TD/GC-MS); a method which has already been standardised internationally (ISO 16000-6, 2004).

1. In-situ VOC sample collection

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[4] (www.ionscience.com/products/gasclam)

The modified Gasclam units were installed to monitor VOC concentrations continuously on an hourly sampling basis for up to five days from 7/6/2012 to 11/6/2012. The in-situ continuous data from the PID (figure 1) were downloaded while the sorbent tubes were detached from the Gasclam and sealed. The sorbent tubes were subsequently analysed ex-situ for specific VOCs by Thermal Desorption/Gas Chromatography-Mass Spectrometry (TD/GC-MS).

2. Ex-situ VOC sample analysis

Analyses of the samples were conducted by heating the sorbent tubes 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. The relationship is shown below:

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

Where A_{is} is the area of the 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 unknown amount of specific VOCs. The VOCs analytical results are shown in Tables 1 and 2 respectively.

III. RESULTS AND DISCUSSION

Figure 2 represents the time series datasets obtained from two boreholes in the investigated site. The datasets show significant variability in VOCs concentration. The range of VOCs concentration in borehole 1 is 220 ppm to 692 ppm with an average concentration of 327 ppm whilst in borehole 2; it ranges from 174 ppm to 193 ppm with an average concentration of 179 ppm. As observed, the concentration of VOCs in borehole 1 is much higher than that in borehole 2, both in range and average concentration. An inverse relationship appeared to exist between VOCs concentration and atmospheric oxygen in borehole 1, but such relationship is not clearly portrayed in borehole 2. The inverse relationship suggests atmospheric pressure to be a control on the variability of VOC concentration in borehole 1.

Whilst bulk VOC concentration automatically depicts that a particular site constitutes risk; it does not define the level of risk until the bulk VOC concentration is resolved into its specific components. This implies also that a site may contain lower bulk VOC concentrations than another but at the same time be more hazardous. Due to this, the bulk VOC concentrations of 31385 ppm and 17140 ppm from boreholes 1 and 2 respectively were characterised into their specific components as shown in Tables 1 and 2.

The specific volatile organic compounds identified and quantified from the sorbent samples collected from this site are as shown in Tables 1 and 2 below. The Tables display 56 and 61 compounds for boreholes I and II respectively, and their quantity including the unidentified ones.

The total concentration of adsorbed VOCs in Borehole I is 4.17 x 10^2 mg/m^3 whilst in Borehole II, it is 1.12 x 10^3. Undecane and 2-Butyl-1, 1, 3-trimethylcyclohexane have the highest and lowest concentrations of 19.60 mg/m^3 (4.71%) and 0.173 mg/m^3 (0.042%) respectively among the identified VOCs in Borehole I. In Borehole II; 1, 3, 5-Trimethylbenzene and 2-Methylbutane have the highest and lowest concentrations of 20.05 mg/m^3 (1.83%) and 0.028 mg/m^3 (0.003%) respectively among the identified VOCs.

A good number of the identified VOCs in the site are included in the USEPA list of 107 compounds whose toxicity and volatility produce a potentially unacceptable inhalation risk to receptors – a property which makes the site a potentially dangerous one. The highest in occurrence among the VOCs are derivatives of benzene - a compound which has been recognized as human carcinogen (IARC, 2004). They were observed mostly in Borehole II (see Table II). This result was expected since the borehole is closest to the terminal unlike borehole I which is some distance away from it. This is typical of a site contaminated by gasoline (Choi et al., 2018) and similar to the findings of Nwachukwu and Dick (2016), Nwachukwu (2015a) and Nwachukwu (2015b). Although bulk VOC concentration does not immediately determine risk level; in the case of this site, borehole II which had higher bulk VOC concentration also has higher number of very dangerous specific VOCs. This observation, together with the relative closeness of borehole II to the terminal, points to the fact that the risk due to VOC emission at the site reduces away from the terminal. Indication is that people working within the terminal are more susceptible to VOC risk, and hence requires personal protective equipments.

Whilst identification of specific VOCs can be useful in defining the extent of risk constituted by a site or borehole in comparison to others, their quantification can be more useful especially when compared to set standards. An example is shown in Table 3 for some selected dangerous specific VOCs.

As shown in Table 3, Ethylbenzene displays a value of 4.87 mg/m^3 in Borehole I, and this value is 4.02 mg/m^3 higher than the set limit of 0.85 mg/m^3. Indication is that Ethylbenzene exceeded the emission limit by several orders of magnitude in Borehole I – the only well it was detected in. Similarly, p-Xylene which was observed in the two wells had its emission limit exceeded by 0.69 mg/m^3 and 2.0 mg/m^3 in Boreholes I and II respectively during the monitoring period. The same thing applies to 1,2,3-Trimethylbenzene, 1,2,4-Trimethylbenzene, 1,3,5-Trimethylbenzene, 1,2,3,4-Tetramethyl benzene, and 1,2,3,5-Tetramethyl benzene, as these VOCs exceeded their emission limits with wide margin. On the other hand, only n-Hexane and Methylcyclohexane displayed values that were lower than their emission limits among the selected compounds in the two Boreholes (Table 3).

IV. CONCLUSIONS

- This site is a potentially unsafe one especially to the operators and customers of the Marine terminal. This is because; most of the identified VOCs are included in the USEPA list of VOCs recognised to constitute risks both to human health and the environment.
- Moreover, a comparison of the individual concentrations of VOCs in this site with the EU-wide harmonized standard shows most of them have passed the set limits. The site is therefore recommended for remediation specifically to save the operators and people living close to it from potential VOC (especially benzene) hazards.
- The use of a PID/Tenax enabled Gasclam allows robust sub-surface VOC gas/vapour data collection, 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.

RECOMMENDATION

The data represented in this work were collected over a period of five days. Whilst the data are enough to identify specific VOCs in the studied site, more data need to be collected over time to determine how the concentrations of VOC will change in future.

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