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Original Research Paper

Volatile Organic Compounds at a Gasoline Retail Site in the United States

Physical Sciences

KEYWORDS : Gasclam, TD/GC-MS, VOCs characterisation, carcinogens, ozone formation, photochemical smog.

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ABSTRACT

Gasoline stations are important source of Volatile Organic Compounds (VOCs) emission especially in metropolitan cities. These VOCs react photochemically in the atmosphere leading to various health (example, cancer) and environmental hazards (ozone depletion). Growing environmental awareness has put up stringent regulations to control VOCs emission. Consequent upon this, there is often a requirement to monitor VOCs concentration from their sources; however, current VOC monitoring techniques are often of low resolution to determine their representative concentrations. In this study we used a more representative approach to measured and analyse aggregate concentrations of VOC and their individual components at a Gasoline Station in the U.S. Continuous measurement of aggregate concentrations of VOC was conducted at the site on hourly sampling basis using an in-borehole gas monitor called Gasclam 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 characterisation) using thermal desorption/gas chromatography-mass spectroscopy (TD/GC-MS) technique. Gasclam result shows VOC in the site to range from 1555 ppm to 2155 ppm with average concentration of 1733 ppm over the monitoring period. The total concentration of adsorbed VOCs in the site is 5.23 x 102 mg/m3. Among the identified VOCs (many of which exceeded their standard limits) are those considered to be hazardous to health and the environment. Although various types of remediation have been done on this site; our result shows they were not effective. Further remediation is therefore recommended.

1.0 Introduction

Volatile organic compounds (VOCs) belong to a very heterogeneous group of chemicals characterized by their relatively high vapour pressures (Isabel *et al*., 2010). Exposure to these compounds can bring about a variety of adverse health effects, including asthma, headaches, mucosal symptoms (Steinemann, 2008) and, in some cases (example benzene), an increased risk of cancer (Nwachukwu and Ugwuanyi, 2012; Ott *et al*., 1978; Lynge *et al*., 1997). VOCs are also indirectly implicated because of their role as precursors of ozone and other photochemical pollutants (Amrita and Anjali, 2011; Rui Li, 2011; Sergio *et al*., 2012), hence the requirement to always ensure clean air.

Since the passage of the novel Clean Air Act in 1963, U.S. state and federal governments have implemented numerous policies designed to reduce human exposure to ground-level ozone pollution (Maximilian and Ryan, 2009). Ozone is an odourless, colourless gas that has been linked to several human health problems (Maximilian and Ryan, 2009). Ozone can aggravate the symptoms of asthma, increase susceptibility to pneumonia and bronchitis, and cause airway irritation and pain during physical exertion (Maximilian and Ryan, 2009). These effects are particularly pronounced amongst children and the elderly (Maximilian and Ryan, 2009). Moreover, ozone is destructive to crops and natural vegetation (Bell *et al*., 2004; EPA 2006; Moretti and Neidell, 2008; Neidell, 2004, 2009).

Although ozone is not emitted directly by any source, the two classes of chemicals that react in the atmosphere to produce ozone—volatile organic compounds (VOCs) and oxides of nitrogen (NOx)—are pollutants produced partly through human activity (Maximilian and Ryan, 2009). Ozone control programs have targeted a wide array of VOC and NOx emission sources, including motor vehicles, electricity generators, and large industrial emitters such as cement plants (Maximilian and Ryan, 2009). Despite more than 40 years of regulatory effort, however, many areas of the U.S. continue to experience ambient air concentrations of ozone that exceed standards set by the Environmental Protection Agency (EPA) (Maximilian and Ryan, 2009). This however, could be because the control programmes were not effective in ensuring that the regimes of the two major gases that react to form ozone are robustly determined from their sources. This study focuses on VOCs regime only.

In urban areas especially in the U.S., the main source of VOCs is usually traffic. Additional sources are gasoline stations and small-scale industries (paint and adhesives,) which use organic compounds as solvents (Isabel *et al*., 2010).

Gasoline stations as emission sources of VOCs have been the subject of considerable study, a particular interest being those related to the design and evaluation of control systems in an attempt to diminish emissions (Uren, 1997; Ohlrogge *et al*., 2000), those related to their effects on workers (Brugnone *et al*., 1997; Periago and Prado, 2005) and environmental studies to evaluate associated air quality (Gonzalez-Flesca *et al*., 2002; Palmgren *et al*., 2001; Srivastava *et al*., 2005; Fernández-Villarrenaga *et al*., 2005).

Although all these studies have been useful in checkmating the health and environmental effects of VOCs, none of the approaches attempted to monitor VOC concentrations at high temporal resolution – a method which allows the variability of gas concentration to be understood and the long-term average to be determined (which is necessary for assessment of chronic risk such as that of ozone depletion). Also, since VOCs vary both in toxicity and behaviour, they need to be characterised (specifically identified and quantified) – this is also one of the shortcomings of past studies of VOCs emission from gasoline stations.

This study uses a new methodology to try to improve upon the shortcomings of present studies of VOCs emission from gasoline station with a view to add to existing wealth of knowledge on this. Firstly, VOCs regime will be determined and then characterised. Secondly, the type and quantity of VOCs in the investigated site will portend the need for remediation and will be recommended accordingly. This is because if you can stop the causes in their sourc-

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es, you can avert their effects (health and ozone formation) outside their sources.

1.1 Site Information

This property consisting of 1902 m^2 has been used for retail gasoline sales since the mid-1950s. In 1995 the State Department of Environmental Protection was notified of gasoline in the subsurface at this property. The subsequent investigation found fuel in the subsurface of a portion of the property. In one boring 66 cm of product was observed; however, the recharge rate was very slow. Over the years various types of remediation work was performed at the site including pump and treat. No active remediation system is operational at this site at this time. Currently the site is a 7-11 convenience store with three underground storage tanks and a pump island. 3.8 cm of free product was found in the monitoring well at the time in which the Gasclam was removed from the well. Depth to fuel and water was approximately 4.6 to 6.1 metre.

2.0 Methodology

The Gasclam was designed to operate remotely; specifically in 50 mm ID monitoring wells. It monitors and records the following: CH_4, CO_2, O_2, CO, H_2S, 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, 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[1].

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.

A Gasclam unit with PID sensors were modified by incorporating a sorption tube containing Tenax TA (poly-2, 6-diphenyl-p-phenylene oxide) adsorbent (Markes International) (Nwachukwu, 2015a, b). This particular sorbent was chosen based on its outstanding selective properties in adsorption and desorption of VOCs over others gases (Kroupa *et al*., 2004). These properties include high thermal stability (Brown, 1996), high hydrophobicity and rapid desorption kinetics (Barro *et al*., 2009; Lee *et al*., 2006; Singer *et al*., 2007; Schripp *et al*., 2007; Barro *et al*., 2005; Saba *et al*., 2001), high breakthrough volume (Baya and Siskos, 1996; Rothweiler and Wager, 1991; Borusiewicz and Zięba-Palus, 2007; Camel and Caude, 1995; 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).

2.1 In-situ VOC sample collection

A Gasclam unit was installed to monitor continuously on hourly sampling intervals for up to seven days. The in-situ continuous data from the PID (figure 1) was downloaded while the sorbent tube was removed from the Gasclam and sealed. The sorbent tube was subsequently analysed ex-situ for specific VOCs by thermal desorption Gas Chromatography/Mass Spectrometry (TD/GC-MS).

2.2 Ex-situ sample analysis

An analysis of the sample was 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. The relationship is shown below:

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

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 table 1.

3.0 Results and Discussion

The time series data collected from the studied gasoline site on hourly sampling basis is shown in figure 1. It displays measureable concentrations of VOCs which are variable. The concentration of VOCs in the investigated borehole ranges from 1555 ppm to 2155 ppm with average concentration of 1733 ppm over the monitoring period. The summation of the *in-situ* PID data from the Gasclam shows that the total VOC concentration adsorbed onto the sorbent material during the entire monitoring period to be 247754 ppm.

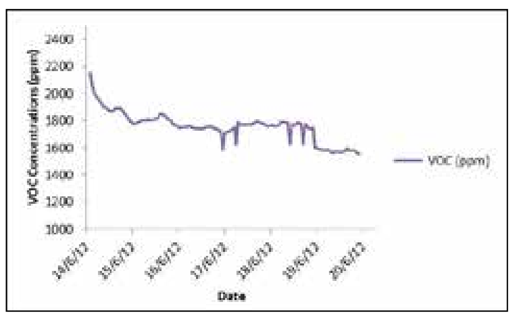

Figure I: Time series data, showing variability in VOCs concentration. The monitoring period is 7 days (14/6/2012 to 20/6/2012).

The specific volatile organic compounds identified and quantified from the single sorbent sample collected from this site are as shown in table I below. The table displays 53 compounds and their quantity including the unidentified ones. More than half of the identified compounds are compound of benzene.

Table I: Volatile Organic Compounds Analytical Results Sample: MI 148958

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	p-Xylene	5.70E+09	1.84E-01	2.58E+01	4.92E+00	4.92E+00
2	1,2,3-Trimethylbenzene	4.00E+09	1.29E-01	1.81E+01	3.46E+00	8.38E+00
3	o-Xylene	3.72E+09	1.20E-01	1.68E+01	3.21E+00	1.16E+01
4	1-Ethyl-3-methylbenzene	3.15E+09	1.02E-01	1.43E+01	2.73E+00	1.43E+01
5	1,4-Dimethyl-2-ethylbenzene	2.78E+09	8.97E-02	1.25E+01	2.40E+00	1.67E+01
6	Toluene	2.73E+09	8.82E-02	1.23E+01	2.36E+00	1.91E+01
7	1,3,5-Trimethylbenzene	2.27E+09	7.34E-02	1.03E+01	1.96E+00	2.10E+01
8	P-Methylallybenzene	2.26E+09	7.31E-02	1.02E+01	1.96E+00	2.30E+01
9	1,2,3,4-Tetramethylbenzene	1.65E+09	5.34E-02	7.46E+00	1.43E+00	2.44E+01
10	1-Ethyl-2-methylbenzene	1.61E+09	5.20E-02	7.27E+00	1.39E+00	2.58E+01
11	1-Methyl-3-propylbenzene	1.47E+09	4.74E-02	6.64E+00	1.27E+00	2.71E+01
12	1, 2-Dimethyl-4-ethylbenzene	1.39E+09	4.51E-02	6.30E+00	1.21E+00	2.83E+01
13	1,2,4-Trimethylbenzene	1.39E+09	4.49E-02	6.28E+00	1.20E+00	2.95E+01
14	2,4-Diethyl-1-methylbenzene	1.26E+09	4.09E-02	5.72E+00	1.09E+00	3.06E+01
15	1,2,3,5-Tetramethylbenzene	1.24E+09	4.01E-02	5.61E+00	1.07E+00	3.17E+01
16	1-Methyl-3,5-diethylbenzene	1.24E+09	4.00E-02	5.60E+00	1.07E+00	3.27E+01
17	1,3-Diethylbenzene	1.19E+09	3.85E-02	5.38E+00	1.03E+00	3.38E+01
18	1,2,4,5-Tetramethylbenzene	1.10E+09	3.55E-02	4.97E+00	9.50E-01	3.47E+01
19	Benzene	1.07E+09	3.45E-02	4.82E+00	9.22E-01	3.56E+01
20	2-Propenylbenzene	1.02E+09	3.30E-02	4.61E+00	8.81E-01	3.65E+01
21	1,1-Dimethylpropylbenzene	8.62E+08	2.78E-02	3.89E+00	7.45E-01	3.73E+01
22	1,4-Diethyl-2-methylbenzene	8.36E+08	2.70E-02	3.78E+00	7.23E-01	3.80E+01
23	6-Ethyl-1,2,3,4-tetrahydronaphthalene	7.98E+08	2.58E-02	3.61E+00	6.90E-01	3.87E+01
24	3-Methylhexane	7.40E+08	2.39E-02	3.34E+00	6.39E-01	3.93E+01
25	2,4-Dimethyl-1-ethylbenzene	7.34E+08	2.37E-02	3.32E+00	6.34E-01	3.99E+01
26	Methylcyclohexane	7.23E+08	2.34E-02	3.27E+00	6.25E-01	4.06E+01
27	1-Methyl-2-propylbenzene	7.10E+08	2.30E-02	3.21E+00	6.14E-01	4.12E+01
28	Undecane	6.67E+08	2.16E-02	3.01E+00	5.76E-01	4.18E+01
29	3-Ethylhexane	6.63E+08	2.14E-02	2.99E+00	5.73E-01	4.23E+01
30	3,5-Dimethyl-4-ethylbenzene	6.55E+08	2.12E-02	2.96E+00	5.66E-01	4.29E+01
31	1-Ethyl-1-methylindane	6.47E+08	2.09E-02	2.92E+00	5.59E-01	4.35E+01
32	1-Ethyl-2,4,5-trimethylbenzene	6.37E+08	2.06E-02	2.88E+00	5.51E-01	4.40E+01
33	1-Sec-butyl-4-methylbenzene	6.30E+08	2.04E-02	2.85E+00	5.44E-01	4.45E+01
34	1,3-Diethyl-5-methylbenzene	5.66E+08	1.83E-02	2.56E+00	4.89E-01	4.50E+01
35	Hexane	4.03E+08	1.30E-02	1.82E+00	3.49E-01	4.54E+01
36	Pentamethylbenzene	3.41E+08	1.10E-02	1.54E+00	2.94E-01	4.57E+01
37	1-Methylnaphthalene	3.33E+08	1.08E-02	1.51E+00	2.88E-01	4.60E+01
38	4,7-Dimethylindane	3.06E+08	9.88E-03	1.38E+00	2.64E-01	4.62E+01
39	1-Sec-butyl-2,4-dimethylbenzene	2.99E+08	9.66E-03	1.35E+00	2.58E-01	4.65E+01
40	2-Methylnaphthalene	2.53E+08	8.17E-03	1.14E+00	2.18E-01	4.67E+01
41	Methylcyclopentane	2.51E+08	8.11E-03	1.13E+00	2.17E-01	4.69E+01
42	2,6-Dimethyloctane	2.22E+08	7.16E-03	1.00E+00	1.91E-01	4.71E+01
43	2-Methylpentane	2.15E+08	6.95E-03	9.72E-01	1.86E-01	4.73E+01
44	1-Ethyl-2-methylcyclohexane	2.00E+08	6.47E-03	9.05E-01	1.73E-01	4.75E+01
45	Isopropylbenzene	1.85E+08	5.99E-03	8.38E-01	1.60E-01	4.76E+01
46	2,6,10-Trimethyltetradecane	1.75E+08	5.66E-03	7.92E-01	1.51E-01	4.78E+01
47	2-Ethylindane	1.04E+08	3.36E-03	4.70E-01	8.99E-02	4.79E+01
48	2-Methylbutane	8.77E+07	2.84E-03	3.97E-01	7.58E-02	4.80E+01
49	1-Chloro-3-methylbutane	8.01E+07	2.59E-03	3.62E-01	6.92E-02	4.80E+01
50	3-Methylpentane	7.47E+07	2.41E-03	3.38E-01	6.46E-02	4.81E+01
51	Butyl benzene	7.41E+07	2.39E-03	3.35E-01	6.40E-02	4.82E+01
52	Butane	3.57E+06	1.15E-04	1.61E-02	3.08E-03	4.82E+01
53	Unidentified compounds	6.00E+10	1.94E+00	2.71E+02	5.18E+01	1.00E+02

∑ PID VOCs signal (ppm)	∑ VOC mass (mg)	Total vol. (m3)	∑VOCs conc. (mg/m3)
247754	3.74E+00	7.15E-03	5.23E+02

The total concentration of adsorbed VOCs in this site is 5.23 x 10^2 mg/m^3. p-Xylene and butane have the highest and lowest concentrations of 25.8 mg/m^3 (4.92%) and 1.61 x 10^{-2} mg/m^3 (0.003%) respectively among the identified VOCs in the site.

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Most of the identified VOCs are derivatives of benzene (a compound which has been recognised as human carcinogens) and also among 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.

Table II: European Union-wide harmonized VOCs Emission Limit ((mg/m^3) 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
	Benzene	0.001	4.82
1	p-Xylene	0.5	25.8
2	o-Xylene	0.5	16.8
3	Toluene	2.9	12.3
5	1,2,3-Trimethylbenzene	0.45	18.1
	1,2,4-Trimethylbenzene	0.45	6.28
6	1,3,5-Trimethylbenzene	0.45	10.3
7	1,2,3,4-Tetramethyl benzene	0.5	7.46
8	1,2,3,5-Tetramethyl benzene	0.5	5.61
9	n-Hexane	6	1.82
10	Methylcyclohexane	8.1	3.27

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

The result as can be observed in Table II shows that Benzene to exceed the emission limit by several order of magnitude. In fact, it is about 4819 times higher than the set limit. p-Xylene and o-xylene emission limits were exceeded during the monitoring period. The measured concentration of p-xylene and o-xylene were more than 51 and 33 times their limits respectively. Similarly, Toluene, 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 all passed their emission limits with several order of magnitudes. It was n-Hexane and Methylcyclohexane that did not pass their emission limits among the selected compounds.

4.0 Conclusions

This site is a potentially dangerous one especially to the owners and customers of the Convenience store. This is because, most of the identified VOCs here are derivatives of benzene – a compound widely known for its carcinogenicity.

Moreover, a comparison of the individual concentrations of VOCs in this site with the EU-wide harmonized standard shows that they have passed the set limits. The site is therefore recommended for further remediation especially to save people living close to it from potential VOC (especially benzene) hazards.

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.

Recommendation: The data represented in this work were collected over a period of one week. Whilst the data are enough for the purpose of identifying specific VOCs in the studied site, more data need to be collected over time so as to determine how the concentrations of VOC will change in future. More data would have been collected on the course of this research if not that the volume of the sorbent tube used is such that it would not have been able to adsorb more VOCs else it would attain breakthrough volume ((Baya and Siskos 1996; Rothweiler and Wager 1991; Borusiewicz and Zięba-Palus 2007; Camel and Caude 1995; Ras and Borrull 2009; Gallego *et al*. 2010). Breakthrough volume is the volume above which the adsorbed VOCs begin to elute the tube.

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