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Original Article

Volatile Organic Compound Concentrations at a former Gasworks in North Lancashire, UK

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ABSTRACT

Former Gasworks often create an extensive contaminant source in the subsurface. When acted upon by environmental controls, the contaminants (example, VOCs) volatilize into the indoor and ambient environments. Since VOCs are toxic both to human health and the environment, there is often a requirement to monitor their concentration, however; current monitoring technique is of low resolution as it only involves spot sampling. To improve on this, an in-borehole gas monitor called *Gasclam* (capable of high temporal measurement of VOC concentrations alongside their environmental controls) was used to obtain the aggregate VOC concentrations whilst 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 characterization) using Thermal Desorption/Gas Chromatography-Mass Spectroscopy (TD/GC-MS) technique. The result showed aggregate VOC concentrations of 30157 ppm and 5504 ppm in boreholes I and II respectively over the monitoring period. The total concentrations of adsorbed VOCs in boreholes I and II are 3.03 x 10^2 mg/m^3 and1.44 x 10^2mg/m^3 respectively. Among the identified VOCs

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were those considered to be hazardous to health such as Toluene, Chlorobenzene, Xylene, Ethylbenzene, Methylcyclohexane and Acetaldehyde. Site remediation was therefore recommended.
Keywords: Gasclam, Tenax TA, TD/GC-MS, Carcinogens, Ozone formation.

INTRODUCTION

Former Gasworks, also known as 'Manufactured Gas Plants' (MGP) were used to produce gas for lightening, heating and cooking between 1820 and the early 1950s (Palanisami et al., 2011). While the manufacturing processes have been gradually phased out (USEPA, 2000a; USEPA, 2000b), they have left behind a legacy of coal tar and other residues in the subsurface. Gasworks tars are normally made up of a complex blend of organic and inorganic contaminants (Palanisami et al., 2011), such as VOCs (benzene, toluene, ethylbenzene and xylene) and semi-volatile organic compounds, polycyclic aromatic hydrocarbons (PAHs), heterocyclic aromatic hydrocarbons (HETs), phenols, cyanides, thiocyanates, metals (arsenic, chromium, copper, lead, nickel, and zinc), ammoniacal contaminants, nitrates, and sulphate/sulphides (Thomas and Lester, 1994; Zamfirescu, 2000; Lundstedt, 2003; Lundstedt *et al*., 2003; Reddy *et al*., 2006; Markus *et al*., 2011).

The presence of such a cocktail of mixed contaminants presents a significant challenge for remediation efforts of MGP sites (Palanisami *et al*., 2011), especially given the wide range of physical and chemical properties of the contaminants (Maria *et al*., 2011). Most former MGP sites have unique features with respect to their release history and/or their geochemical, mineralogical and hydrogeological characteristics (Maria *et al*., 2011). Any remediation effort will require effective risk assessment through intrusive site investigation to be able to delineate the extent of contamination and remedial targets. However; while most of the published studies on characterization of former gasworks sites mainly focused on concentrations of PAHs (Palanisami *et al*., 2011) and its co-occurrence with heavy metals (Thomas and Lester, 1994; Lundstedt, 2003; Lundstedt *et al*., 2003; Reddy *et al*., 2006), not many people have studied the concentrations of volatile organic components of gasworks facilities.

The characterization of VOCs in former gas works is important because of their significant human health and environmental effects. The effects of VOCs are

aggravated by their variety, variability, ubiquity, volatility and solubility making them easily available and susceptible to human inhalation and ready contaminants of controlled waters (Harold, 1998). Two VOCs, namely benzene and formaldehyde, have been recognized as human carcinogens by the International Agency for Research on Cancer (IARC, 2004). VOCs also play an important role in the formation of ozone and photochemical oxidants associated with urban smog (Possanzini *et al*., 2002). 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 (Boult *et al*., 2011; Nwachukwu and Ugwuanyi, 2012).

In this study, we characterised a former gasworks located in North Lancashire, United Kingdom with special emphasis on VOCs concentrations. The aim was to determine the subsurface regime and the species of VOC on this site.

MATERIALS AND METHODS

The materials and methods used in this work were first introduced by Nwachukwu and Ugwuanyi (2012 in a conference proceeding and later applied by Nwachukwu (2014) in his PhD research aimed at improving the prediction of risk due to hazardous ground-gas. Similar materials and methods were used in these studies (Nwachukwu, 2015a; Nwachukwu, 2015b; Nwachukwu, 2015c; Nwachukwu and Henry, 2016).

Gasclam was one of the materials used. It was designed to operate remotely; specifically in 50 mm ID monitoring wells. It monitors and records the following parameters: CH_4, CO_2, O_2, CO, H_2S, VOCs, atmospheric pressure, borehole pressure, pressure differential, temperature and water level. It was made from stainless steel and also intrinsically safe (rated to ATEX/BASEEFA Standards). It was environmentally sealed and had ingress protection rated IP-68. The Gasclam was 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 included 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 had the following technical specifications: (i) it had an on-board memory which can record and store 65,000 time/date stamped readings, (ii) it weighs 7kg (13.2 lbs), (iii) It had an overall length of 85cm (33.5 inches), (iv) the head diameter is 10.8 cm (4.25 inches), (v) its operational temperature range was –5 to +50 °C or 41°F to 122°F and (vi) it was powered by 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 (Markes International) (see Fig. 1). This particular sorbent was chosen based on its outstanding selective properties in adsorption and desorption of VOCs over other gases (Nwachukwu, 2014). These properties included high thermal stability [17], high hydrophobicity and rapid desorption kinetics (Nwachukwu, 2015b; Nwachukwu, 2015c; Nwachukwu and Henry, 2016; Kroupa *et al*., 2004; Brown, 1996; Baro *et al.*, 2009), high breakthrough volume (Lee et al., 2006; Singer et al., 2007; Schripp et al., 2007; Baro et al., 2005; Saba et al., 2001; Baya and Siskos, 1996) inertness towards most pollutants, high mechanical strength, and a good adsorption range of VOCs (Rothweiler and Wager, 1991; Borusiewicz and Zieba, 2007; Ras and Borull, 2009; Gallego et al., 2010; ISO 16000-6, 2011). It had a surface area of 35m^2 g^{-1} and a pored volume of 2.4 cm^3 g^{-1}[16]. VOCs adsorbed on Tenax TA sorbent tube were analyzed by TD/GC-MS; a method which has already been standardized internationally (Borusiewicz and Zieba, 2007).

SITE DESCRIPTION

The site under study is a previously used town's gasworks which lasted for about 105 years (1845-1950). It is a sub-site of a 6.6 Ha land that has a long history of industrial

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

use having being in use since 1800s. Industrial activities have resulted in significant land contamination. Large parts of the site are either vacant or derelict.

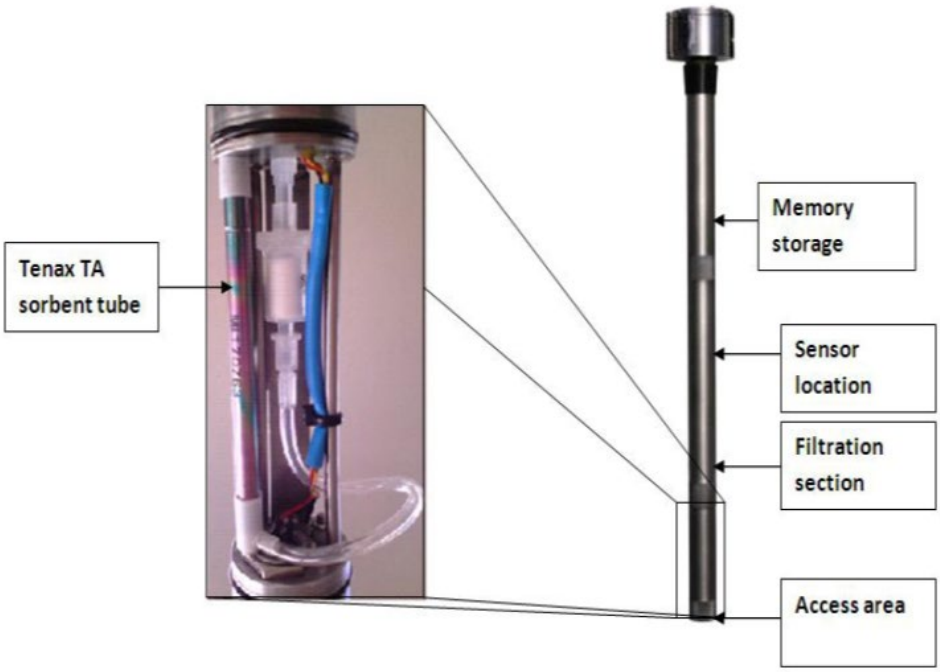

Fig. 1 Inclusion of a sorption cartridge into the basal section of a Gasclam unit

Local council reports from land contamination studies have revealed widespread and substantial problems of land contamination across the whole area of the site. The following risk were supposedly posed by the site: (i) contaminants in the ground and within in-situ below-ground structures (including soil gases) pose intolerable risks to future residents, and potentially pose risks to present site occupiers, (ii) contaminants in the soil and groundwater constitute a risk of pollution to controlled waters, most especially the River Lune, a salmond quality watercourse located 40m north of the site boundary. The contaminants are believed to be leaching into groundwater beneath the soil and that the contaminated water in the sand and gravel stratum beneath the site poses a pollution risk to the people living adjacent River Lune, with ammonia discharging into the river, (iii) contaminants in the soil and groundwater constitute potentially risks to the fabric of buildings and infrastructure (Nwachukwu, 2014).

Given the above potential risks, associated with the study site, the Local Authority, Lancaster City Council, required that a satisfactory clean-up exercise be conducted on the whole site. This was to ensure that all risks to human health and the environment were properly addressed and either removed or mitigated. VHE Construction Limited is the most recent of the companies awarded a contract to clean up the site. The remediation exercise will surely diminish the impending adverse effects arising directly from the works on the public in terms of public amenity and also to ensure public health and safety. The potential adverse effects were as follows: (i) public health – volatilization of contaminants and dusts, (ii) public safety –safety provisions for workers and the surrounding public and site security, and (iii) environmental – pollution of controlled water.

IN-SITU VOC MEASUREMENT

The two units were installed to monitor continuously VOC concentration for up to one week on hourly sampling intervals. The in-situ continuous data from the PID (Fig. 2) were downloaded while the sorbent tube was removed from the Gasclam and sealed for subsequent ex-situ TD/GC-MS analysis.

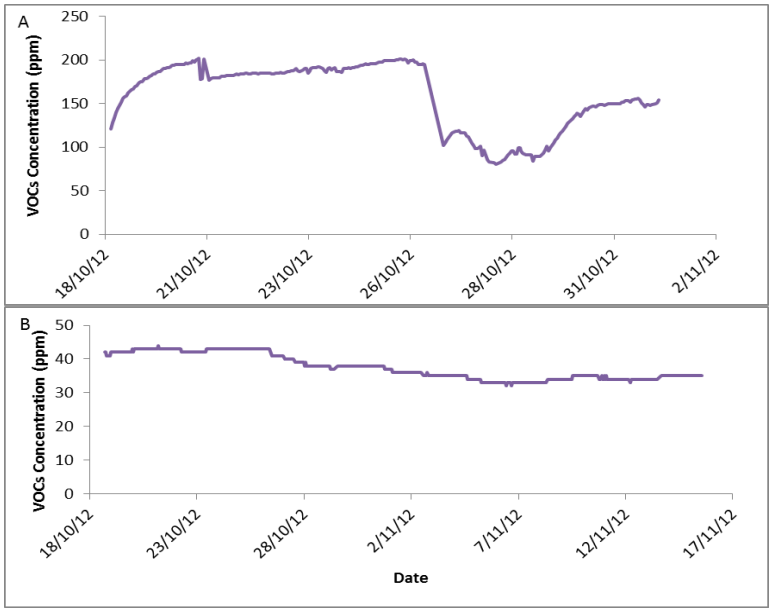

Fig. 2 Time series VOCs concentration datasets from boreholes 1 (A) and 2 (B) in the studied site.

LABORATORY ANALYSIS OF TENAX TA TUBES BY TD-GC/MS

The Tenax TA tubes were analyzed to determine the types of VOC they contained, following in-situ borehole gas sampling using Gasclam. Analysis of the sample was conducted by heating the sorbent tube to 300^{o}C. The volatile components were then trapped on a cold trap, held at -10^{o}C, prior to desorption onto the GC column (Nwachukwu, 2014). Desorption of the sorbent 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 *for gas chromatography (GC) systems, version G2070BA.*

The ChemStation software is designed to run on IBM-compatible personal computers under Microsoft® Windows XP Professional operating environment. It includes data acquisition, instrument control, data analysis (integration, quantification and reporting), automation and customization for one analytical instrument [2]

RESULTS AND DISCUSSION

The time series datasets of aggregate VOCs concentration obtained with the help of the new instrumentation (Gasclam) from the study site are shown in figure 2. The summation of the *in-situ* PID data from the Gasclam shows that the total VOC concentration adsorbed onto the sorbent materials during the entire monitoring period are 30157 ppm and 5504 ppm for boreholes 1 and 2 respectively. Whilst Table I represents the identified individual VOCs and their concentration from Borehole 1 (closer to the gasworks retort house), Table II on the other hand represents the VOCs from Borehole 2 (some distance away from the retort house).

The result above has validated Local Council reports that there was a widespread and substantial problem of land contamination across the whole area. However, the distribution of the contaminants (VOCs) varied from place to place on the site with more contamination observed closer to the source (that is, the gasworks retort house). Whilst it constitutes the following potential adverse effects (public health –

[2] https://www.agilent.com/cs/library/usermanuals/public/G207091126_Understanding.pdf

volatilization of contaminants and dusts, public safety –safety provisions for workers and the surrounding public and site security, and environmental –pollution of controlled water) as highlighted by the Local Council, there was no report or record of anyone who has been affected by it.

A selection of datasets each collected at hourly intervals from boreholes 1and 2 in the studied site, shows measureable concentrations of VOCs which varied over the monitoring period, (Fig. 2). Borehole 1 (Fig. 2A) was located very close to the gasworks while borehole 2 (Fig. 2B) was further away from it. As expected, the concentration of VOC in borehole 1 was higher than that of borehole 2 given the proximity of borehole 1 to the identified source (Former Gasworks). The value ranged from 40 ppm to 230 ppm for borehole 1 and 32 ppm to 45 ppm in borehole 2. The average concentration of VOCs in boreholes 1 and 2 were 166 ppm and 38 ppm respectively during the monitoring period.

The total concentration of adsorbed VOCs in Borehole 1 is 303 mg/m^3 whilst in borehole 2; it was 144 mg/m^3. p-xylene and n-propane have the highest and lowest concentrations of 9.91 mg/m^3 (3.27%) and 2.27 x 10^{-2} mg/m^3 (0.0075%) respectively among the identified VOCs in borehole 1; whilst in borehole 2, the highest concentration of 4.64 mg/m^3 (3.21%) was recorded for Undecane and the lowest concentration of 1.54 x 10^{-3} mg/m^3 (0.00107%) by acetaldehyde. A good number of specific VOCs found in this site were the same with those observed in previously studied similar sites (Nwachukwu, 2015a; Nwachukwu, 2015b; Nwachukwu, 2015c; Nwachukwu and Henry, 2016).

Unlike in borehole 2, more than half of the identified VOCs in borehole 1 were compounds of benzene. Benzene was classified as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC) – a property which makes the site a potentially dangerous one. The result also showed that the total concentration of VOCs adsorbed from borehole 1 was more than 3 times that from borehole 2. This implied that although the 2 boreholes contain hazardous VOCs, borehole 1 was actually more dangerous in terms of the type and quantity of the specific VOCs detected in it. 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.

The measured concentrations of some selected VOCs were compared with their standard limits in Table III. The table shows p-Xylene to exceed the emission limit by several orders of magnitude in both Boreholes but this was more in borehole I. Whilst Toluene limit was exceeded in Borehole I, in Borehole II; the reverse is the case. In fact, it is 4.85 mg/m^3 higher and 0.46 mg/m^{3}lower than the set limit in Boreholes I and II respectively during the monitoring period. o-Xylene, Ethylbenzene, 1,2,3-Trimethylbenzene, 1,2,4-Trimethylbenzene, 1,2,3,4-Tetramethyl benzene, and 1,2,3,5-Tetramethyl benzene which were only detected in Borehole I, all passed their emission limits with great margins. Conversely, Methylcyclohexane and Acetaldehyde which were observed in Boreholes I and II respectively did not pass their emission limits among the selected compounds in the two Boreholes.

Four of the most recent similar studies (Nwachukwu, 2015a; Nwachukwu, 2015b; Nwachukwu, 2015c; Nwachukwu and Henry, 2016), show aggregate adsorbed VOC concentrations to range from 112.65mg/m^3 to 523mg/m^3. The studies include VOC characterization at (i) an Industrial Lagoon [18], (ii) a Tank Farm [17], (iii) a Drinking-water Well [19], and (iv) a Gasoline Retail Site [20] with aggregate adsorbed VOC concentrations of 240mg/m^3, 112.65mg/m^3, 253mg/m^3, and 523mg/m^3 respectively. The aggregate adsorbed VOC concentration of the current study (223.5mg/m^3) falls within the range of that of the recent studies.

Moreover, many of the identified VOCs in this study were also common to the previously studied sites; however, some of the sites contain specific VOCs which distinguish them from others. For example, it was only in the Industrial Lagoon site that Tetrachloroethylene, Trichloroethylene, Dichloroethylene, Dichloromethylene, and Chloroethylene were found out of the previous studies (Nwachukwu, 2015a; Nwachukwu, 2015b; Nwachukwu, 2015c; Nwachukwu and Henry, 2016) under review and current research. This is because, Chlorinated Hydrocarbon was the main waste deposited in the site by a nearby Chemical Company. Similarly, Benzene and its compounds were found in most of the above sites including this study; however, they

were more in Gasoline Retail Site where above 80% of the identified VOCs are Benzene and its compounds.

All the sites under review (including the current study site) except Drinking-water Well constitute risk both to human health and the environment. This was because they have exposure pathways and receptors. In Drinking-water Well, the risk of anyone being exposed was very low as the only potential for exposure, during sampling which was usually a controlled process. All the sites have been found to contain VOCs identified to be carcinogenic, with more of them (especially group 1 and 2 carcinogens) found in Industrial Lagoon and Gasoline Retail sites.

If just a week data could reveal the high concentration levels of the detected specific VOCs; it would be much more if monitored over a longer period. Whilst the type and properties of the VOCs found on this site imply that it was a very dangerous one; there was, a requirement to allow for an extended monitoring of the VOCs concentration if their subsurface regime must be ascertained. Although, a clean-up exercise was ongoing at the site during the time of this research, further site visits were recommended to establish the success of the exercise. This was because; previous researches have revealed failures of remediation exercises at different VOC contaminated sites (Nwachukwu, 2015a; Nwachukwu, 2015b; Nwachukwu, 2015c; Nwachukwu and Henry, 2016).

CONCLUSIONS

- The measured concentrations of VOC in the site varied from place to place both in bulk and specific (individual) concentrations; however, higher concentrations were detected closer to the source.
- Many of the identified VOCs have been found not only to exceed international set standards but include those recognized to be significantly hazardous to health and the environment even at trace concentrations.
- The method (PID/Tenax enabled Gasclam) used saves time by reducing the number of site monitoring visits and enables a more accurate representation of

sub-surface conditions to be obtained through high frequency monitoring instead of unrepresentative spot sampling.

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CONFLICT OF INTEREST

Note that there is no conflict of interest.

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Table I: VOCs Analytical Results. Sample: H 148951 (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	p-Xylene	2.03E+09	8.42E-02	9.91E+00	3.27E+00	3.27E+00
2	Toluene	1.59E+09	6.59E-02	7.75E+00	2.56E+00	5.83E+00
3	o-Xylene	1.33E+09	5.49E-02	6.45E+00	2.13E+00	7.96E+00
4	Ethylbenzene	1.00E+09	4.15E-02	4.88E+00	1.61E+00	9.57E+00
5	Undecane	9.87E+08	4.09E-02	4.81E+00	1.59E+00	1.12E+01
6	1,2,4-Trimethylbenzene	8.49E+08	3.51E-02	4.13E+00	1.36E+00	1.25E+01
7	1,4-Dimethyl-2-ethyl benzene	8.23E+08	3.40E-02	4.00E+00	1.32E+00	1.38E+01
8	1-Ethyl-3-methylbenzene	7.59E+08	3.14E-02	3.70E+00	1.22E+00	1.51E+01
9	Methylcyclohexane	6.97E+08	2.88E-02	3.39E+00	1.12E+00	1.62E+01
10	2-Cyclohexylundecane	6.76E+08	2.80E-02	3.29E+00	1.09E+00	1.73E+01
11	1-Ethyl-4-methylbenzene	5.74E+08	2.38E-02	2.80E+00	9.23E-01	1.82E+01
12	2,4-Dimethyl-1-ethylbenzene	5.57E+08	2.30E-02	2.71E+00	8.95E-01	1.91E+01
13	2-Chloro-2-methylpentane	5.23E+08	2.16E-02	2.54E+00	8.40E-01	1.99E+01
14	3-Methyldecane	4.85E+08	2.01E-02	2.36E+00	7.79E-01	2.07E+01
15	trans-1,3-Dimethylcyclopentane	4.60E+08	1.90E-02	2.24E+00	7.39E-01	2.14E+01
16	1-Methyl-3-propylbenzene	4.57E+08	1.89E-02	2.22E+00	7.34E-01	2.22E+01
17	Heptane	4.51E+08	1.86E-02	2.19E+00	7.24E-01	2.29E+01
18	1-Ethyl-2-methylbenzene	4.40E+08	1.82E-02	2.14E+00	7.06E-01	2.36E+01
19	Dodecane	4.32E+08	1.79E-02	2.11E+00	6.95E-01	2.43E+01
20	3-Methylundecane	4.15E+08	1.72E-02	2.02E+00	6.67E-01	2.50E+01
21	4-Methylundecane	4.13E+08	1.71E-02	2.01E+00	6.63E-01	2.56E+01
22	6-Methyltridecane	4.10E+08	1.70E-02	2.00E+00	6.59E-01	2.63E+01
23	2-Methylundecane	4.07E+08	1.69E-02	1.98E+00	6.54E-01	2.69E+01
24	2,6-Dimethyldecane	3.86E+08	1.60E-02	1.88E+00	6.19E-01	2.76E+01
25	3-Ethylhexane	3.74E+08	1.55E-02	1.82E+00	6.01E-01	2.82E+01
26	2,6-Dimethyloctane	3.72E+08	1.54E-02	1.81E+00	5.98E-01	2.88E+01
27	Propylbenzene	3.62E+08	1.50E-02	1.76E+00	5.82E-01	2.93E+01
28	2-Methyl-2-cyclopenten-1-one	3.57E+08	1.48E-02	1.74E+00	5.73E-01	2.99E+01
29	Methylcyclopentane	3.53E+08	1.46E-02	1.72E+00	5.68E-01	3.05E+01

30	3-Methylhexane	3.50E+08	1.45E-02	1.71E+00	5.63E-01	3.10E+01
31	4-Methyldecane	3.42E+08	1.42E-02	1.67E+00	5.50E-01	3.16E+01
32	cis-1,4-Dimethylcyclohexane	3.42E+08	1.41E-02	1.66E+00	5.49E-01	3.21E+01
33	2-Methylpentane	3.38E+08	1.40E-02	1.65E+00	5.43E-01	3.27E+01
34	1-Hexene	3.32E+08	1.37E-02	1.61E+00	5.33E-01	3.32E+01
35	4-Cyclohexyldecane,	3.21E+08	1.33E-02	1.56E+00	5.16E-01	3.37E+01
36	3,4-Dimethylpent-2-en-1-ol	3.11E+08	1.29E-02	1.52E+00	5.00E-01	3.42E+01
37	2-Methyldecane	3.08E+08	1.27E-02	1.50E+00	4.94E-01	3.47E+01
38	1,2,3-Trimethylbenzene	3.03E+08	1.25E-02	1.48E+00	4.87E-01	3.52E+01
39	1-Chloro-3-methylbutane	2.84E+08	1.18E-02	1.38E+00	4.56E-01	3.57E+01
40	4-Ethyloctane	2.83E+08	1.17E-02	1.38E+00	4.54E-01	3.61E+01
41	2-Butyl-1-octanol	2.67E+08	1.11E-02	1.30E+00	4.30E-01	3.66E+01
42	1,2,3,4-Tetramethylbenzene	2.63E+08	1.09E-02	1.28E+00	4.22E-01	3.70E+01
43	1-Ethyl-1-methylcyclopentane	2.57E+08	1.06E-02	1.25E+00	4.12E-01	3.74E+01
44	cis-2-Ethyl-2-hexen-1-ol	2.46E+08	1.02E-02	1.20E+00	3.95E-01	3.78E+01
45	Carbonic acid, butyl tetradecyl ester	2.35E+08	9.74E-03	1.15E+00	3.78E-01	3.82E+01
46	1-Methylcyclopentene	2.33E+08	9.62E-03	1.13E+00	3.74E-01	3.85E+01
47	Octacosane	2.32E+08	9.61E-03	1.13E+00	3.73E-01	3.89E+01
48	cis-1,3-Dimethylcyclohexane	2.31E+08	9.56E-03	1.12E+00	3.71E-01	3.93E+01
49	2-Hexyl-1-octanol	2.21E+08	9.15E-03	1.08E+00	3.55E-01	3.96E+01
50	Benzeneacetaldehyde, α-ethyl	2.21E+08	9.13E-03	1.07E+00	3.54E-01	4.00E+01
51	1-Methyl-2-propylcyclopentane	2.09E+08	8.63E-03	1.02E+00	3.35E-01	4.03E+01
52	2,6-Dimethylundecane	1.82E+08	7.53E-03	8.85E-01	2.92E-01	4.06E+01
53	Isopropyltoluene	1.82E+08	7.52E-03	8.85E-01	2.92E-01	4.09E+01
54	1,2,4,5-Tetramethylbenzene	1.80E+08	7.43E-03	8.74E-01	2.88E-01	4.12E+01
55	1,2-Dipropylcyclopentane	1.75E+08	7.25E-03	8.53E-01	2.81E-01	4.15E+01
56	1,3-Diethylbenzene	1.72E+08	7.14E-03	8.40E-01	2.77E-01	4.18E+01
57	4-Isopropylbenzaldehyde	1.63E+08	6.73E-03	7.91E-01	2.61E-01	4.20E+01
58	3,5-Dimethyl-1-ethylbenzene	1.57E+08	6.49E-03	7.63E-01	2.52E-01	4.23E+01
59	1,2-Dimethyl-1-cyclooctene	1.52E+08	6.31E-03	7.42E-01	2.45E-01	4.25E+01
60	Isopropylbenzene	1.51E+08	6.25E-03	7.36E-01	2.43E-01	4.28E+01
61	Decane	1.42E+08	5.89E-03	6.93E-01	2.28E-01	4.30E+01
62	2-Methyl-1-decanol	1.36E+08	5.64E-03	6.64E-01	2.19E-01	4.32E+01
63	2-Propenylbenzene	1.36E+08	5.63E-03	6.63E-01	2.19E-01	4.34E+01

64	3-Ethyl-2-methylheptane	1.26E+08	5.21E-03	6.13E-01	2.02E-01	4.36E+01
65	cis-1-Ethyl-3-Methylcyclopentane	1.19E+08	4.94E-03	5.81E-01	1.92E-01	4.38E+01
66	Tridecanal	1.16E+08	4.81E-03	5.66E-01	1.87E-01	4.40E+01
67	Octane	1.06E+08	4.37E-03	5.14E-01	1.70E-01	4.42E+01
68	1-Bromotriacontane	1.03E+08	4.24E-03	4.99E-01	1.65E-01	4.43E+01
69	1-Sec-butyl-2,4-dimethylbenzene	9.98E+07	4.13E-03	4.86E-01	1.60E-01	4.45E+01
70	3-Propylcyclohexene	9.89E+07	4.09E-03	4.82E-01	1.59E-01	4.47E+01
71	Ethylcyclohexane	9.84E+07	4.07E-03	4.79E-01	1.58E-01	4.48E+01
72	1-Ethyl-2-methylcyclohexane	9.47E+07	3.92E-03	4.61E-01	1.52E-01	4.50E+01
73	4-Methylnonane	9.22E+07	3.82E-03	4.49E-01	1.48E-01	4.51E+01
74	5-Methyldecane	9.19E+07	3.80E-03	4.48E-01	1.48E-01	4.53E+01
75	Ethylcyclopentane	9.19E+07	3.80E-03	4.47E-01	1.48E-01	4.54E+01
76	3-Methylpentane	9.10E+07	3.77E-03	4.43E-01	1.46E-01	4.56E+01
77	cis-1-Isopropyl-4-methylcyclohexane	9.06E+07	3.75E-03	4.41E-01	1.45E-01	4.57E+01
78	1,2-Dimethylcyclohexane	8.72E+07	3.61E-03	4.24E-01	1.40E-01	4.58E+01
79	1-Butyl-1-methyl-2-propylcyclopropane	8.37E+07	3.46E-03	4.07E-01	1.34E-01	4.60E+01
80	7-Hexylicosane	8.24E+07	3.41E-03	4.01E-01	1.32E-01	4.61E+01
81	2-Hexyl-1-decanol	8.11E+07	3.36E-03	3.95E-01	1.30E-01	4.62E+01
82	4-Methyl-2-cyclohexen-1-ol	8.09E+07	3.35E-03	3.94E-01	1.30E-01	4.64E+01
83	Cyclodecane	7.86E+07	3.25E-03	3.82E-01	1.26E-01	4.65E+01
84	cis-4-Decenal	7.81E+07	3.23E-03	3.80E-01	1.25E-01	4.66E+01
85	1,2,3-Trimethylcyclohexane, (1α,2β,3α)	7.57E+07	3.13E-03	3.68E-01	1.22E-01	4.67E+01
86	Nonadecan-1-ol	7.08E+07	2.93E-03	3.45E-01	1.14E-01	4.69E+01
87	(1,3,3-Trimethylnonyl)benzene	7.05E+07	2.92E-03	3.43E-01	1.13E-01	4.70E+01
88	2,2-Dimethylcyclohexyl acetate	6.63E+07	2.74E-03	3.23E-01	1.06E-01	4.71E+01
89	1-Isopropyl-3-methylcyclohexane	6.17E+07	2.55E-03	3.00E-01	9.91E-02	4.72E+01
90	4-Ethyl-3-octene	5.75E+07	2.38E-03	2.80E-01	9.23E-02	4.73E+01
91	cis-2-Nonene	5.65E+07	2.34E-03	2.75E-01	9.07E-02	4.74E+01
92	6-Methyl-2-cyclohexen-1-ol	5.22E+07	2.16E-03	2.54E-01	8.38E-02	4.74E+01
93	2,6,10-Trimethyltetradecane	4.77E+07	1.97E-03	2.32E-01	7.66E-02	4.75E+01
94	Nonacosane	4.13E+07	1.71E-03	2.01E-01	6.63E-02	4.76E+01

95	1-Isobutyl-3-methylcyclopentane	4.11E+07	1.70E-03	2.00E-01	6.60E-02	4.76E+01
96	3-Methylenepentane	4.10E+07	1.70E-03	1.99E-01	6.58E-02	4.77E+01
97	Heptacosane	3.42E+07	1.41E-03	1.66E-01	5.49E-02	4.78E+01
98	7-Hexadecanal	3.41E+07	1.41E-03	1.66E-01	5.47E-02	4.78E+01
99	2-Nitrohept-2-en-1-ol	3.33E+07	1.38E-03	1.62E-01	5.35E-02	4.79E+01
100	trans-1-Ethyl-3-Methylcyclopentane	3.07E+07	1.27E-03	1.50E-01	4.93E-02	4.79E+01
101	Diisooctyl phthalate	2.43E+07	1.01E-03	1.18E-01	3.90E-02	4.80E+01
102	Cyclopropylmethanol	7.52E+06	3.11E-04	3.66E-02	1.21E-02	4.80E+01
103	n-Propane	4.67E+06	1.93E-04	2.27E-02	7.51E-03	4.80E+01
104	Unidentified compounds	3.24E+10	1.34E+00	1.58E+02	5.20E+01	1.00E+02

∑ PID VOCs signal (ppm)	**∑ VOC mass (mg)**	**Total vol. (m^3)**	**∑VOCs conc.(mg/m^3)**
30157	2.58E+00	8.50E-03	3.03E+02

Note: 2.58E+00 = 2.58 x 10^0, 8.50E-03 = 8.50 x 10^{-3}, 3.03E+02 = 3.03 x 10^2

Table II: VOCs Analytical Results. Sample: H 148952 (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	1.24E+09	3.94E-02	4.64E+00	3.21E+00	3.21E+00
2	Methylcyclohexane	7.01E+08	2.24E-02	2.63E+00	1.82E+00	5.04E+00
3	Toluene	6.51E+08	2.08E-02	2.44E+00	1.69E+00	6.73E+00
4	Hexylcyclohexane	6.33E+08	2.02E-02	2.38E+00	1.65E+00	8.38E+00
5	4-Methyl-1-hexene	5.05E+08	1.61E-02	1.90E+00	1.31E+00	9.69E+00
6	2-Methylhexane	4.61E+08	1.47E-02	1.73E+00	1.20E+00	1.09E+01
7	Decane	4.34E+08	1.39E-02	1.63E+00	1.13E+00	1.20E+01
8	3-Methylhexane	3.83E+08	1.22E-02	1.44E+00	9.96E-01	1.30E+01
9	Heptane	3.79E+08	1.21E-02	1.42E+00	9.86E-01	1.40E+01
10	2-Methylheptane	3.75E+08	1.20E-02	1.41E+00	9.76E-01	1.50E+01
11	3-Methyldecane	3.73E+08	1.19E-02	1.40E+00	9.70E-01	1.59E+01
12	1-Methyl-2-	3.58E+08	1.14E-02	1.34E+00	9.31E-01	1.69E+01

	pentylcyclohexane					
13	3,3-Dimethyloctane	3.42E+08	1.09E-02	1.28E+00	8.89E-01	1.78E+01
14	2-Hexyldodecanol	3.39E+08	1.08E-02	1.27E+00	8.81E-01	1.86E+01
15	Undecane, 2-cyclohexyl	3.29E+08	1.05E-02	1.23E+00	8.55E-01	1.95E+01
16	2-Methyldecane	3.22E+08	1.03E-02	1.21E+00	8.37E-01	2.03E+01
17	3-Methyloctane	3.15E+08	1.01E-02	1.18E+00	8.20E-01	2.12E+01
18	1-Decanol, 2-hexyl-	3.12E+08	9.97E-03	1.17E+00	8.12E-01	2.20E+01
19	5-Methyldecane	3.08E+08	9.82E-03	1.16E+00	8.00E-01	2.28E+01
20	Methylcyclopentane	3.01E+08	9.61E-03	1.13E+00	7.83E-01	2.36E+01
21	2,5-Dimethylheptane	2.81E+08	8.96E-03	1.05E+00	7.30E-01	2.43E+01
22	2,6,10-Trimethyldodecane	2.78E+08	8.87E-03	1.04E+00	7.23E-01	2.50E+01
23	4-Methyl-1-heptene	2.71E+08	8.64E-03	1.02E+00	7.04E-01	2.57E+01
24	4-Methyldecane	2.60E+08	8.30E-03	9.76E-01	6.76E-01	2.64E+01
25	2,6-Dimethylheptane	2.57E+08	8.19E-03	9.64E-01	6.67E-01	2.71E+01
26	p-Xylene	2.47E+08	7.89E-03	9.28E-01	6.43E-01	2.77E+01
27	2-Methylundecane	2.46E+08	7.86E-03	9.25E-01	6.40E-01	2.83E+01
28	2,6-Dimethyloctane	2.32E+08	7.39E-03	8.69E-01	6.02E-01	2.89E+01
29	Tetradecyloxirane	2.26E+08	7.21E-03	8.48E-01	5.87E-01	2.95E+01
30	1-Ethyl-2-propylcyclohexane	2.20E+08	7.03E-03	8.27E-01	5.73E-01	3.01E+01
31	4-Methyloctane	2.20E+08	7.02E-03	8.26E-01	5.72E-01	3.07E+01
32	Ethylcyclohexane	2.19E+08	7.01E-03	8.24E-01	5.71E-01	3.12E+01
33	Nonane	2.08E+08	6.62E-03	7.79E-01	5.40E-01	3.18E+01
34	cis-1,3-Dimethylcyclohexane	2.07E+08	6.59E-03	7.76E-01	5.37E-01	3.23E+01
35	3-Ethyl-2-methylheptane	1.91E+08	6.11E-03	7.19E-01	4.98E-01	3.28E+01
36	4-Methylnonane	1.91E+08	6.09E-03	7.16E-01	4.96E-01	3.33E+01
37	Octane	1.91E+08	6.08E-03	7.16E-01	4.96E-01	3.38E+01
38	1,5-Diisopropyl-2,3-dimethylcyclohexane	1.88E+08	6.00E-03	7.05E-01	4.89E-01	3.43E+01
39	2,3-Dimethylhexane	1.83E+08	5.84E-03	6.87E-01	4.76E-01	3.48E+01
40	9-methylheptadecane	1.82E+08	5.82E-03	6.85E-01	4.75E-01	3.52E+01
41	Cyclododecanemethanol	1.82E+08	5.80E-03	6.83E-01	4.73E-01	3.57E+01

42	1-Decanol, 2-hexyl-	1.81E+08	5.79E-03	6.81E-01	4.72E-01	3.62E+01
43	n-Hexane	1.79E+08	5.72E-03	6.73E-01	4.66E-01	3.67E+01
44	1-Methyl-2-propylcyclohexane	1.78E+08	5.67E-03	6.68E-01	4.62E-01	3.71E+01
45	1-Decanol, 2-hexyl-	1.75E+08	5.60E-03	6.58E-01	4.56E-01	3.76E+01
46	2-Methylpentane	1.75E+08	5.59E-03	6.58E-01	4.55E-01	3.80E+01
47	2-Octyl-1-decanol	1.68E+08	5.38E-03	6.32E-01	4.38E-01	3.85E+01
48	trans-Decahydronaphthalene	1.68E+08	5.35E-03	6.30E-01	4.36E-01	3.89E+01
49	2-Methyloctane	1.65E+08	5.26E-03	6.19E-01	4.29E-01	3.93E+01
50	1,2,4-Trimethylcyclopentane	1.55E+08	4.93E-03	5.80E-01	4.02E-01	3.97E+01
51	trans-1,2-Dimethylcyclohexane	1.54E+08	4.91E-03	5.78E-01	4.00E-01	4.01E+01
52	1-Ethyl-3-methylbenzene	1.50E+08	4.78E-03	5.62E-01	3.90E-01	4.05E+01
53	3-Ethyl-2-methylheptane	1.50E+08	4.78E-03	5.62E-01	3.89E-01	4.09E+01
54	1-Methyl-2-propylcyclopentane	1.49E+08	4.75E-03	5.59E-01	3.87E-01	4.13E+01
55	5-Methylnonane	1.49E+08	4.75E-03	5.59E-01	3.87E-01	4.17E+01
56	3-Butyl-cyclohexanone	1.49E+08	4.74E-03	5.58E-01	3.87E-01	4.21E+01
57	trans-1,3-Dimethylcyclohexane	1.46E+08	4.67E-03	5.49E-01	3.80E-01	4.25E+01
58	3-Methylnonane	1.45E+08	4.62E-03	5.43E-01	3.76E-01	4.28E+01
59	Tridecanal	1.44E+08	4.61E-03	5.42E-01	3.75E-01	4.32E+01
60	trans-1-Ethyl-3-Methylcyclopentane	1.44E+08	4.60E-03	5.41E-01	3.75E-01	4.36E+01
61	Diisooctyl phthalate	1.40E+08	4.46E-03	5.24E-01	3.63E-01	4.39E+01
62	cis-1,4-Dimethylcyclohexane	1.31E+08	4.18E-03	4.92E-01	3.41E-01	4.43E+01
63	2,4-Dimethylheptane	1.23E+08	3.91E-03	4.60E-01	3.19E-01	4.46E+01
64	Chlorobenzene	1.14E+08	3.64E-03	4.28E-01	2.97E-01	4.49E+01
65	4-Methylnonane	1.13E+08	3.60E-03	4.24E-01	2.94E-01	4.52E+01
66	1-Nonadecene	1.11E+08	3.54E-03	4.17E-01	2.89E-01	4.55E+01

67	5-Methyloctane	1.07E+08	3.41E-03	4.01E-01	2.78E-01	4.58E+01
68	Ethylcyclopentane	1.03E+08	3.29E-03	3.87E-01	2.68E-01	4.60E+01
69	trans, cis-1,2,4-Trimethylcyclohexane	1.02E+08	3.26E-03	3.83E-01	2.66E-01	4.63E+01
70	1-Ethyl-4-methylcyclohexane	9.45E+07	3.02E-03	3.55E-01	2.46E-01	4.65E+01
71	1,1,2,3-Tetramethylcyclohexane	9.44E+07	3.01E-03	3.55E-01	2.46E-01	4.68E+01
72	1,4-Dimethyl-4-pentenyl acetate	9.28E+07	2.96E-03	3.48E-01	2.41E-01	4.70E+01
73	1,2-Dipropylcyclopentane	9.19E+07	2.93E-03	3.45E-01	2.39E-01	4.73E+01
74	cis-1-Ethyl-3-Methylcyclopentane	9.13E+07	2.91E-03	3.43E-01	2.38E-01	4.75E+01
75	cis-1-Ethyl-3-methylcyclohexane	9.10E+07	2.90E-03	3.42E-01	2.37E-01	4.77E+01
76	1,2,4-Trimethylcyclohexane	8.94E+07	2.85E-03	3.36E-01	2.32E-01	4.80E+01
77	Ethyl Acetate	8.88E+07	2.83E-03	3.34E-01	2.31E-01	4.82E+01
78	2,7-Dimethyloctane	8.80E+07	2.81E-03	3.30E-01	2.29E-01	4.84E+01
79	3-Methylpentane	8.12E+07	2.59E-03	3.05E-01	2.11E-01	4.86E+01
80	Propylcyclohexane	8.09E+07	2.58E-03	3.04E-01	2.10E-01	4.89E+01
81	1-Ethyl-2,3-dimethylcyclohexane	7.90E+07	2.52E-03	2.97E-01	2.05E-01	4.91E+01
82	Undecane	7.89E+07	2.52E-03	2.96E-01	2.05E-01	4.93E+01
83	Dodecane	7.81E+07	2.49E-03	2.93E-01	2.03E-01	4.95E+01
84	Oleyl alcohol, trifluoroacetate	7.29E+07	2.33E-03	2.74E-01	1.90E-01	4.97E+01
85	2,6,11-Trimethyldodecane	7.03E+07	2.25E-03	2.64E-01	1.83E-01	4.98E+01
86	2,4,6-Trimethylheptane	7.03E+07	2.24E-03	2.64E-01	1.83E-01	5.00E+01
87	Cyclohexanepropanol	6.80E+07	2.17E-03	2.55E-01	1.77E-01	5.02E+01
88	1-Ethyl-2-methylcyclohexane	6.13E+07	1.96E-03	2.30E-01	1.60E-01	5.04E+01
89	1-Isopropyl-3-methylcyclohexane	5.95E+07	1.90E-03	2.23E-01	1.55E-01	5.05E+01
90	1-Tridecene	5.48E+07	1.75E-03	2.06E-01	1.43E-01	5.07E+01

91	2-Ethyl-1,3-dimethylcyclohexane	5.40E+07	1.72E-03	2.03E-01	1.40E-01	5.08E+01
92	1,2-Dimethylcyclooctene	5.38E+07	1.72E-03	2.02E-01	1.40E-01	5.09E+01
93	2,3-Dimethylheptane	5.28E+07	1.68E-03	1.98E-01	1.37E-01	5.11E+01
94	trans-1,2,3-Trimethylcyclohexane	5.04E+07	1.61E-03	1.89E-01	1.31E-01	5.12E+01
95	2-Hexyl-1-octanol	4.87E+07	1.56E-03	1.83E-01	1.27E-01	5.13E+01
96	1-(4-Bromobutyl)-2-piperidinone	4.39E+07	1.40E-03	1.65E-01	1.14E-01	5.15E+01
97	2-Hexyl-1-decanol	4.29E+07	1.37E-03	1.61E-01	1.12E-01	5.16E+01
98	1,2,3-Trimethylcyclohexane	3.88E+07	1.24E-03	1.46E-01	1.01E-01	5.17E+01
99	Isopropylcyclopentane	3.70E+07	1.18E-03	1.39E-01	9.61E-02	5.18E+01
100	1,2,3-Trimethylcyclopentane	3.44E+07	1.10E-03	1.29E-01	8.94E-02	5.18E+01
101	1-Decanol, 2-hexyl-	3.43E+07	1.10E-03	1.29E-01	8.93E-02	5.19E+01
102	Acetone	3.28E+07	1.05E-03	1.23E-01	8.53E-02	5.20E+01
103	1-Isopropyl-cis-4-methylcyclohexane	3.10E+07	9.90E-04	1.17E-01	8.07E-02	5.21E+01
104	1-Dodecanesulfonyl chloride	2.97E+07	9.49E-04	1.12E-01	7.73E-02	5.22E+01
105	cis-1,2,3-Trimethylcyclohexane	2.80E+07	8.93E-04	1.05E-01	7.28E-02	5.23E+01
106	1-Ethyl-2-methylbenzene	2.76E+07	8.80E-04	1.04E-01	7.17E-02	5.23E+01
107	1,2-Diethylcyclohexane	2.35E+07	7.51E-04	8.83E-02	6.12E-02	5.24E+01
108	2-Butyl-1-octanol	2.30E+07	7.35E-04	8.65E-02	5.99E-02	5.24E+01
109	1-Monolinoleoylglycero	1.80E+07	5.76E-04	6.77E-02	4.69E-02	5.25E+01
110	Acetaldehyde	4.10E+05	1.31E-05	1.54E-03	1.07E-03	5.25E+01
111	Unidentified compounds	1.83E+10	5.83E-01	6.86E+01	4.75E+01	1.00E+02

∑ PID VOCs signal (ppm)	∑ VOC mass (mg)	Total vol. (m^3)	∑VOCs conc.(mg/m^3)
5504	1.23E+00	8.50E-03	1.44E+02

Note: 1.23E+00 = 1.23 x 10^0, 8.50E-03 = 8.50 x 10^{-3}, 1.44E+02 = 1.44 x 10^2

Table III: 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 I	Total concentration (mg/m^3) in Borehole II
1	p-Xylene	**0.5**	9.91	0.928
2	Toluene	**2.9**	7.75	2.44
3	o-Xylene	**0.5**	6.45	-
4	Ethylbenzene	**0.85**	4.88	-
5	1,2,3-Trimethylbenzene	**0.45**	1.48	-
6	1,2,4-Trimethylbenzene	**0.45**	4.13	-
7	1,2,3,4-Tetramethyl benzene	**0.5**	1.28	-
8	1,2,4,5-Tetramethyl benzene	**0.5**	0.874	-
9	Acetaldehyde	**1.2**	-	0.00154
10	Methylcyclohexane	**8.1**	3.39	-

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