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# The Utility of a Dual Monitoring Methodology to Determine Concentration of Specific Vocs at High Temporal Resolution

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**Abstract:** Gasclam – an In-borehole ground-gas monitor was redesigned to see the if it can be used to determine the concentration of specific Volatile Organic Compound (VOCs) by combining two technologies - a Photoionization detector (PID) and a Tenax TA sorbent. The above technologies were connected to work in parallel inside the Gasclam. With this new methodology, it is now not only possible to determine concentration of specific VOCs but also their variability at high temporal resolution. Before this research, it was only aggregate VOC concentration that Gasclam was able to detect; however, VOCs vary not only in concentration but also in type, behaviour and toxicity. There was a requirement for specific VOCs to be identified – a problem that has been solved by the current methodology. The high temporal resolution offered by this method has also helped to determine when the concentrations of specific VOCs exceed standard limits.

**Key words:** Gasclam · Continuous PID · Tenax TA · Environmental controls · Variability · Periodic measurement · Time series concentration

## INTRODUCTION

The previous research has shown that a Photoionization detector (PID) can be used to monitor VOCs at a temporal resolution that matches their variability in the environment. Such a capability reduces uncertainty in attempts to detect or predict worst case concentrations of VOCs. Whilst the uncertainty in assessing the health risks of VOC are, therefore, even at low concentration [1], it may still be high because of the wide variety of compounds that cause a PID to respond. The many different compounds susceptible to photo-ionisation need not share the same toxicity or mobility. Consequently, effective VOC monitoring must include not only recording temporal variability [2] of VOC but that of specific compounds. Furthermore, because of the acute toxicity of some of these compounds PID may not have sufficiently low detection limits; there is a requirement to have an alternative or additional detection system to that of PID alone [3].

Presently, gas chromatography (GC) is the device used for specific VOCs identification [3] but it is not often used in-situ. The reasons are (i) most GCs are not portable; (ii) the portable ones are very expensive. Hence, the need to collect a sample in-situ and transfer it to the laboratory for analysis by GC. To achieve this requires a device which can concentrate and retain VOC samples. These properties are found in sorbent materials [3]. The capability of adsorbent materials to allow pre-concentration of VOC sample serves to enrich the VOCs in the sample since they are generally found in trace amounts in air samples [4].

**Aims:** The **aim**s of this chapter are: (1) to determine whether the two technologies (that is, PID and sorbent) can be combined to form a dual monitoring technique, (2) to determine if the dual technique can be an effective methodology.

In order to determine if PID and sorbent can be combined to form a dual VOC monitoring methodology, it is important to recall how gas flows through the instrument (Gasclam) which houses the PID (see chapter 1). Also, in order for the Gasclam (a device capable of unmanned high temporal resolution PID monitoring in-situ) to perform its numerous functions, it was designed in such a way that its interior is tightly packed with

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pneumatics and electronics, leaving little space for further incorporation of any other device such as the sorbent. There is therefore, a requirement to choose an appropriate sorbent which can fit into the Gasclam gas path if dual monitoring will be possible.

**Objective for Aim 1:**

- To select an appropriate sorbent for incorporation into the Gasclam containing PID to form a dual VOC monitoring technique.

**Selection of Appropriate Sorbents – Factors to Consider:** The type of sorbent used determines the range of target compounds that would be adsorbed [4],[5] and removed [6] from the VOC sample. The variety of sorbents currently available allows the sampling of gaseous compounds from very volatile organic compounds (VVOCs) to semi-volatile organic compounds. However, none of the existing sorbents is capable of retaining all compounds, so either a combination of sorbents with different characteristics (multi-bed tubes) or one sorbent specifically chosen for the actual analytical problem has to be used. In the case of this work which involves sampling in a borehole environment and analysis by thermal desorption, the factors to consider include sorbent size (must fit into the Gasclam), be able to work in parallel with the PID in a borehole environment, sorbent strength, inertness, hydrophobicity, artefacts, thermal stability, mechanical strength, and particle size [7, 8].

**Sorbent Size:** The many available sorbents currently used for VOC sampling can fit into the Gasclam gas path; however, Tenax TA adsorbent has shown to have the best fit.

**Sorbent Strength:** The sorbent or sorbents selected must be sufficiently strong to retain target analytes during sampling/concentration, but must be sufficiently weak to release them efficiently during thermal desorption phase [9]. Sorbent strength is usually measured with respect to retention or breakthrough volumes [10]. Retention volume is the standard volume of the sorbent tube whilst breakthrough volume is the volume of the gaseous sample that can be drawn through a sample tube before an analyte is eluted from the tube [11]. Validated retention and breakthrough volumes information for a wide range of common sorbent/sorbate combinations and how they can be determined experimentally can be found in literature [12, 13]. The reasons for breakthrough volume include high sampling speed, too high analyte concentration, and retention ability of the sorbent for the targeted amount of analyte. The solution would be to use safe sampling volume (SSV) and the right sampling temperature. SSV is usually defined as 70% of the 5% breakthrough volume [14]. If for a given sample, the sample volume is lower than SSV of the lowest boiling compounds in that sample; it can be assumed that all the compounds were quantitatively retained in the tube. The SSV for numerous compounds depending on the sampling temperature is published on the Scientific Instrument Services Website [15].

**Inertness:** The material contents of some sorbents are chemically active. For example, carbon blacks, whose materials are derived originally from natural charcoal and contain trace metals, are in this category. They are generally unsuitable for labile species like sulphur compounds, terpenes, and amines [16].

**Hydrophobicity:** Most common weak and medium strength sorbents have been recognised to be highly hydrophobic and as a result do not compromise their sorbent strength even when sampling at high (>80%) relative humidity. Conversely, most strong sorbents do compromise some form of carbonised molecular sieve, with sorbents strength sometimes reduced to up to a factor of 10 at 90% relative humidity [17]. If large amount of water retained on the tube is not selectively eliminated prior to sample analysis, the result can be adversely affected [18, 19].

**Artefacts:** There is variability in the inherent artefact levels of different sorbents. Example, porous polymers such as the Chromosorb® Century series, PoraPak ™ and HaySep™ series have relatively high artefacts with several peaks at 5-10ng, whilst Tenax® TA has reduced artefacts with minimum levels between 0.1 and 1 ng for well-conditioned materials [20]. Both carbon blacks and carbonised molecular sieves are excellent in terms of inherent artefacts [20].

**Thermal Stability:** Different sorbents offer different thermal stability for VOCs analysis [20]. The range of adsorbed compounds (sample size) can therefore be limited by the thermal stability of the sorbent [21, 22]. This is because some compounds or analytes may be lost due to decomposition on the sorbent surface at elevated temperatures. For example, the choice of silane-like materials (example, glass/quartz woo or small sieves) which help to retain the sorbents in the tubes is very crucial [23]. This is because, glass or stainless steel tubes contain hydroxyl groups which at elevated thermal

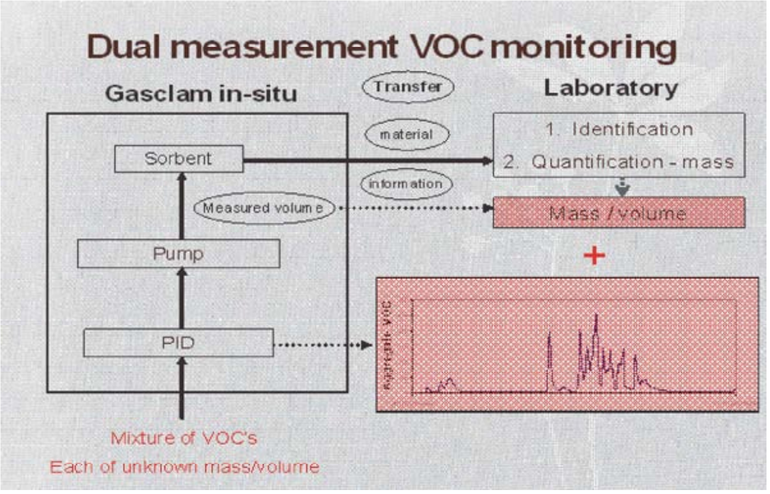

Fig. 1: Dual VOC monitoring methodology

desorption temperatures (example, 250°C) can be released and attack the VOCs and displace them. These salinization agents are often found in chromatograms [23].

**Mechanical Strength:** Some sorbents like graphitised carbon blacks are extremely friable and prone to formation of fines [20]. Therefore, care should always be taken not to over compress the sorbents during packing and to avoid sharp knocks once the tubes are packed. It has been observed that as the carbon packing ages, the formation of fines increase tube impedance (back pressure) beyond the limits of some pumps [20]. Most sorbents are mechanically strong, however, Tenax® TA can have high % of fines when new and may require sieving before use [24]. The recommended mesh sizes [20] for sorbent in standard 4-5mm bore sampling tubes range from 30 to 80 mesh (˜0.6-0.2mm particle diameter) [25].

Based on the available sorbents, **Tenax TA (poly-2, 6-diphenyl-p-phenylene oxide)** adsorbent (Markes International) stands-out because of its (i) size and (ii) outstanding properties in adsorption and desorption of VOCs over other adsorbents [26, 27]. These properties include high thermal stability [25], high hydrophobicity and rapid desorption kinetics [28, 29], high breakthrough volume [4, 30-33], inertness towards most pollutants, high mechanical strength, and adsorption of a good range of VOCs [25]. It has a surface area of 35$m^2$ $g^{-1}$ and a pore volume of 2.4 $cm^3$ $g^{-1}$ [32]. 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 [34, 35].

**Design of Dual VOCs Monitoring Methodology:** Measurement of VOCs concentration from the subsurface can be a difficult task because of the complexity of soil air matrix. A mixture of VOCs each of unknown mass/volume from the ground is measured directly as time resolved aggregate VOCs concentration (ppm) by photoionisation detector (PID). With the aid of Gasclam pump, the mixture is now passed across the sorbent which adsorbs them. The sorbent is transferred into the laboratory for their individual identification and quantification as mass using GC-MS. This mass is now divided with the known volume of the gases obtained when passed through the pump, and the concentration is realised as time averaged individual VOC concentration. So, while the **PID** resolves the problem of temporal variability of aggregate VOCs concentration, the **sorbent** tackles that of variability of type, hence a dual measurement VOC monitoring (Figure 1.1).

**Design of the Dual Monitoring System:** In other to demonstrate the ability of the Gasclam to perform dual VOC monitoring which refers to PID measurement in-situ, parallel with sorption of VOCs onto media which can be subsequently analysed ex-situ; Gasclam units with PID sensor have been modified by incorporating sorption tubes containing Tenax TA (poly-2, 6-diphenyl-p-phenylene oxide) adsorbent (Markes International) (Figure 2).

While dual monitoring technique may be a useful method; its usefulness can be compromised if the response time of Gasclam - an instruent that is installed for extended periods and re-used, cannot be determined. This is because VOCs may be retained in the Gasclam

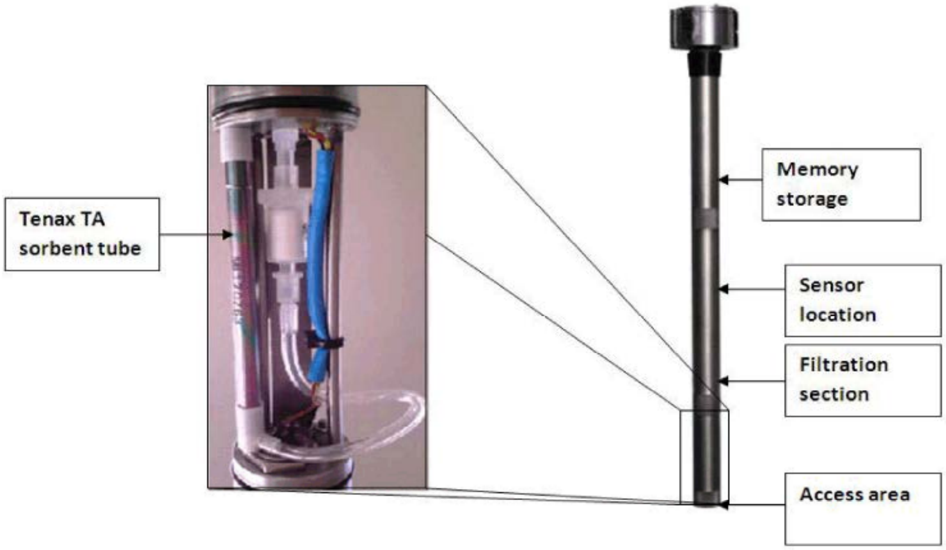

Fig. 2: Inclusion of a sorption cartridge into the basal section of a Gasclam unit

each time it is used for contaminated site investigation and might be a problem. Therefore, the measurement made by the instrument may not be a measurement of exterior environment but could be of the interior, which is an artefact. If this is established, the response time of Gasclam to VOCs need to be ascertained so as to know exactly when it will be clean for use in the next site. Also, the volume of air which would be required to completely remove them from the Gasclam after each time the instrument is used needs to be determined. This however may vary depending on the amount of VOCs retained. The amount of VOCs that could be retained, on the other hand, will largely depend on the length of time the Gasclam is used and the level of site contamination.

The measurement made by the Gasclam itself can be used to determine whether it is contaminated. There are two measurement systems in the Gasclam; PID and sorbent tube. The latter is more sensitive than the former but the former gives real time readings. A zero reading on the PID should translate into a zero reading on the sorbent if the Gasclam is completely clean. In order to determine the response time of the Gasclam, there are requirements to:

- Establish if VOCs are retained in the instrument and also
- Determine the volume of air that would be required to remove the VOCs from it.

To determine if dual monitoring technique is an effective method; there is a requirement to compare it with the present instrumentation. PID performs periodic VOCs measurement; however, it has been shown (in chapter 3) that it can be used effectively for time series VOCs concentration measurement. Sorbent tube on the other hand gives time-integrated concentration of specific VOCs even in low concentrations (ppb – ppt) but does not supports the determination of time series concentration of specific VOCs as a stand-alone instrument. There is therefore, a requirement to determine the time series of specific VOCs. This is because; the time series of specific VOCs would help to ascertain when during their monitoring periods they passed their standard limits.

**Objective for Aim 2:**

- To attempt to measure time series of specific compounds.

In other to try to obtain the time series of specific VOCs, there is a requirement to compare the adsorbed VOCs concentration with their corresponding PID concentration. However, before this can be done, it is important to establish how VOCs respond to PID.

The PID will react to anything the lamp fitted will energise. PIDs work by exposing the air going into the analyser to UV light at a specific energy, such as 9.8 eV or the more usual 10.6 eV. For example all BTEX and most chlorinated solvents will be ionised by an 11.7 eV lamp, but the10.6 eV lamp will not ionise many chlorinated solvents. So, first thing to know is what the lamp energy is.

Secondly, most PIDs are calibrated using a surrogate standard such as isobutylene and a conversion factor applied. For mixed hydrocarbon mixtures such as petrol, diesel, BTEX, the conversion is a guesstimate because the mixture varies in composition and each individual compounds has a different response factor compared to isobutylene. Therefore, unless you know you have just a single source of a compound you are measuring, do not rely on the result as anything but a sort of guess that at best gives the classification of "not a lot", "some", "quite a lot". In most situations where the PID is used, the composition of the air being sampled is unknown, so the broad classification described above is the best you can hope for. Moreover, the PID measures concentration on a volume basis. This has a big impact on working out if there is a lot of something in the air sample or not a lot.

Since PID readings may be equal to the sum of the concentration of those VOCs it responds to; there is, therefore, a requirement to recalibrate the PID signals relative to the real VOCs collected by means of sorbent tubes. To do this, two cases will need to be considered: (i) if PID responds to all VOCs as isobutylene, (ii) if PID responds differently to different VOCs. The two cases will be compared to determine the best from which the time series concentration of specific VOCs may be obtained.

## Methodology

**Laboratory Experiment to Determine the Response Time of PID:** In order to determine the best practice for Gasclam use, a laboratory experiment has been conducted. Before the experiment, a pre-test was conducted to establish starting condition for a previously used Gasclam. To do this test, a sorbent tube is installed in and run with the Gasclam by allowing Gasclam to take samples of clean air (CKgas, 20% $O_2$ and 80% $N_2$). While the sorbent tube result will help to establish if some VOCs from investigated sites are retained in the Gasclam, the clean air passed through it will help to clean the instrument before starting the experiment. The sorbent tube was then detached and analysed by TD/GC-MS. The pre-test was immediately followed by the laboratory experiment proper.

To conduct the experiment, a sample of VOC concentration was prepared by serial dilution of a VOC (isobutylene) in sample tedlar bag. The concentration of the VOC used is made to be within the detection limit of the Gasclam (0-4000 ppm) and also not too high to be dangerous especially in laboratory environment; therefore, a VOC concentration of 1000 ppm was chosen and was prepared. The materials used include 1 litre of pressurized VOC (isobutylene) cylinder, sample tedlar bags, and a syringe. The prepared VOC concentration was circulated through the Gasclam and the PID readings monitored. A fall in PID reading over time would indicate that VOCs are being retained.

The Gasclam was then purged with clean air until the PID reading falls to zero. Once this is done, sorbent tubes were attached to the Gasclam and clean air passed through them with the 1st for 5 hours and the 2nd for 7 hours (@ 1 hour/sample). More than 1 tube was used since there is no guarantee that the Gasclam will be clean after the 1st purging. The sorbent tubes were also sent to the laboratory for GC-MS analysis.

## Field Investigations

**Sample Collection:** To see if the dual monitoring methodology is effective, Gasclam units were installed to monitor continuously on hourly sampling intervals for different periods at different sites (see chapter 3).The in-situ continuous data from the PID were downloaded while the sorbent tubes were removed from the Gasclam and sealed. The sorbent tubes were subsequently analysed ex-situ for individual VOCs by thermal desorption Gas Chromatography/Mass Spectrometry (GC-MS).

**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. The relationship is shown below:

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

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 **appendix 3**.

## RESULTS AND DISCUSSION

**Laboratory Experiment:** The Gasclam used in this experiment was previously used for VOCs monitoring in site F borehole 1. During the in-situ VOCs monitoring, the

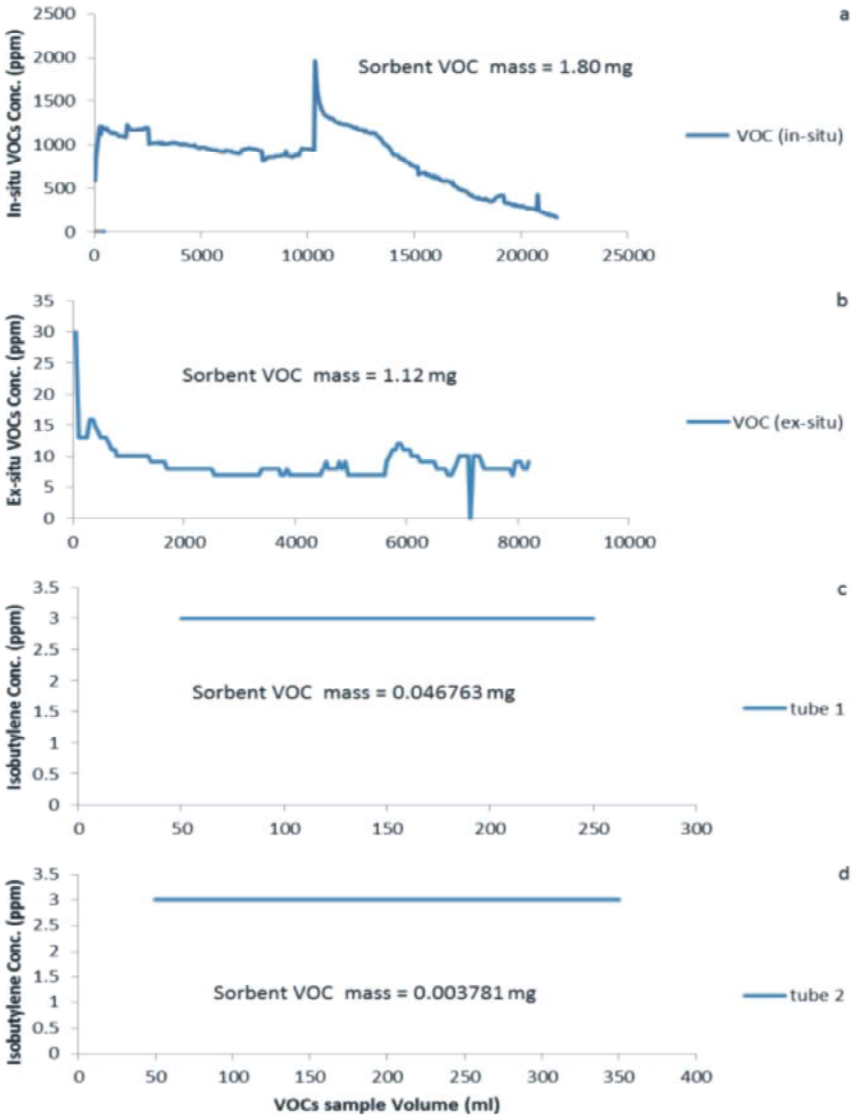

Fig. 3: A graph of (a) In-situ PID VOCs concentration, (b) ex-situ PID VOCs concentration, (c) isobutylene concentration 1and (d) isobutylene concentration 2 against their sample volume.

instrument was set to sample at the rate of 1hour/sample with each sample containing 50ml of air. The volume series PID VOCs data is shown in Figure 3a below. Also attached to the figure is the corresponding total sorbent VOCs concentration of 1.17 mg.

The same day the Gasclam was moved to the laboratory, a new sorbent tube was installed into it and then set to sample every hour. This is to know if VOCs are retained in the Gasclam. The PID data shows an initial VOCs concentration of 30 ppm which dropped sharply to 13 ppm after the 2nd sample and then to 10 ppm where it remained constant for 12 hours. After this period, it dropped further to 9 ppm for 6 hours and then 7 ppm for 17 hours before the data was downloaded (Figure 3b). During this ex-situ VOCs sampling, a total sample volume of 8050ml was collected with the sorbent tube result showing aggregate VOCs mass of 1.12 mg. Many components of the in-situ sorbent VOCs were equally found in the ex-situ sorbent VOCs. These findings suggest that VOCs are retained in the Gasclam. It took a total of 21 hours for the VOCs concentration to drop to 7 ppm during ex-situ sampling.

In preparation for a laboratory experiment, a pre-test was conducted to determine the start condition of the Gasclam. The Gasclam was flushed with clean air every 3 minutes until the PID reading dropped to 3 ppm and remained constant there. Note that the PID reading dropped to 3 ppm after 6 minutes and further flush did not change this reading. A new sorbent tube was then inserted into the instrument and allowed to sample clean air until 17/05/2013 collecting a total of 105 samples. The result of sorbent tube analysis shows the pre-test sorbent VOCs mass to be 0.350 mg.

The pre-test was followed by a laboratory experiment conducted using a particular VOC called isobutylene. 1000 ppm of this VOC was circulated through the Gasclam. It was then flushed with clean air until the reading on the PID dropped to 2 ppm and could not change further. A sorbent tube was then installed and clean air passed through it 5 times at 15minutes/sample (total sample volume = 250ml). The PID VOCs volume series data and the corresponding sorbent tube mass (0.046763 mg) are shown by Figure 3c. The tube was removed and a second one installed. 7 samples of clean air was passed though the Gasclam at the same sampling frequency as the first (total sample volume = 350ml). The volume series data of the PID VOC concentration and the equivalent sorbent mass (0.003781 mg) are shown by Figure 3d.

Figure 3e below represents PID readings in ppm over time during another laboratory experiment to determine whether VOCs are actually retained in the Gasclam; however, in this case, only isobutylene was used. As can be observed, the concentration of the VOC (isobutylene) used decreased 3 times from initial reading of 1756 ppm to 1755 ppm, 1754 ppm and 1752 ppm with time and then remained constant there during the remaining period of the experiment.

The decrease in VOCs concentration from the last experiment (Figure 4) supports the earlier finding that VOCs are usually retained in the Gasclam. In the case of this experiment, a total of 4 ppm was retained. The result of sorbent tube analysis (from first laboratory experiment) did not reveal any presence of the VOC (isobutylene) used in the experiment. This implies that the VOC used was completely removed from the Gasclam during the cleaning process. However, there is presence of other VOCs in both tubes. The number of these VOCs in the first tube decreased with increase in purging. Most of the identified VOCs can be traced to the last site where the Gasclam was used. Some of these VOCs have their concentrations as high as their concentrations in the site where the instrument was last used. Their concentrations remained very high even after the purgings. This observations suggest that some VOCs stick more to the Gasclam than others, and as a result can be retained for a very long time in their container – a characteristic which suggests them to more dangerous than other gases. The major retained VOCs and their concentrations in-situ and after purgings ex-situ can be seen in Figure 5. Generally, the aggregate sorbent VOCs mass decreased with increase in the volume of clean air passed through the Gasclam. It took 250ml of clean air to reduce 0.350 mg of VOCs to 0.046763 mg and further 350ml to get it down to 0.003781 mg. This implies that with about 1.5L of clean air, the VOCs retained in the Gasclam may be completely removed.

**Calibration of PID Signals to Real VOCs:** In order to recalibrate PID signals to adsorbed VOCs, two cases were considered; they include:

- If PID responds in the same way to each of the characterised VOCs
- If PID responds differently to each VOC

**Case 1:** If PID responds the same way to each of the characterised VOCs

In this case, PID's response to isobutylene is assumed to be same for all VOCs. Therefore, the total PID VOC signal was compared with the total sorbent VOCs concentration by assuming that they are equal (Figure 6).

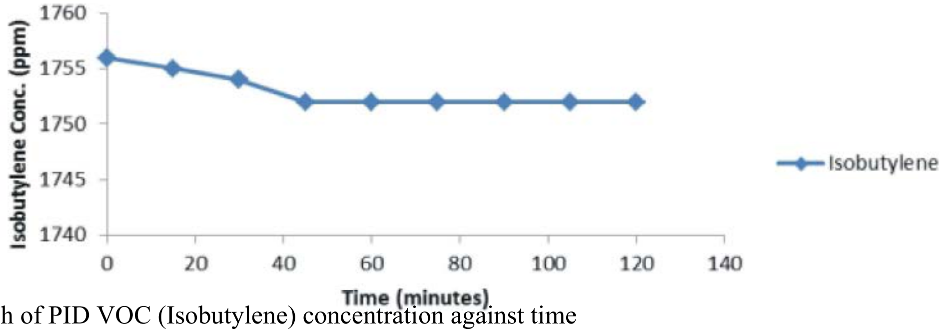

Fig. 4: A graph of PID VOC (Isobutylene) concentration against time

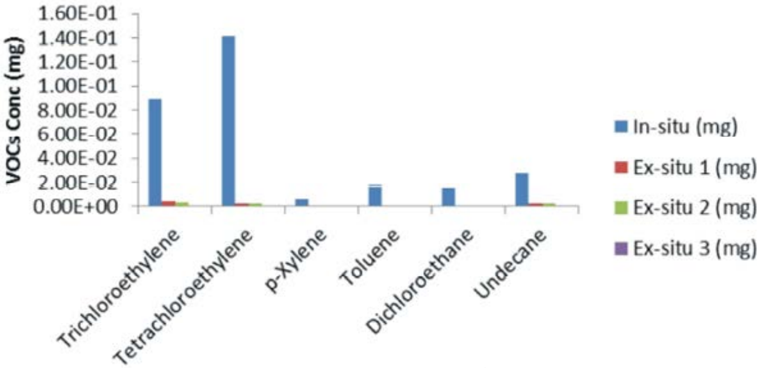

Fig. 5: Major retained VOCs. Ex-situ 1 = retained VOC conc. after 1st purging, Ex-situ 2 = retained VOC conc. after 2nd purging, Ex-situ 3 = retained VOC conc. after 3rd purging.

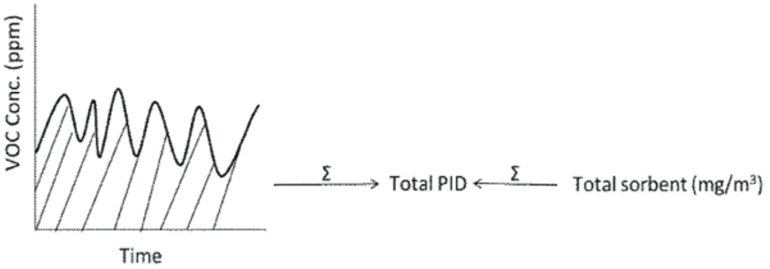

Fig. 6: Comparison of total PID signal (ppm) to total sorbent concentration (mg/m$^3$)

For example, in site C where a total of 50 VOCs were identified and quantified; the total sorbent concentration (523 mg/m$^3$) over this period is assumed to be proportional to the total PID reading of 247754 ppm. Assuming that the letters A, B, and a, represent the bulk concentration of the adsorbed VOCs (mg/m$^3$), the bulk concentration of the PID VOCs (ppm), and the individual concentration of the characterised VOCs (mg/m$^3$) respectively; then the unknown individual PID concentrations, b (ppm), corresponding to each of the characterised VOCs can be calculated by using the equation:

$$b = a\,B/A \text{ (note: if } A = B, \Rightarrow a = b) \qquad (2)$$

Alternatively, b can be calculated by assuming that its % concentration is equal to that of a. For example, since 4.92% of the total sorbent reading (25.80 mg/m$^3$) corresponds to p-xylene; it implies that 4.92% of total PID reading (12190 ppm = 5.30E+04 mg/m$^3$) also corresponds to p-xylene. Case 1 can be very useful provided that PID has the same response to all VOCs.

**Case 2:** If PID responds differently to specific VOCs

If PID responds differently to specific VOCs, then the concentration of specific VOCs needs to be weighted in terms of the response factor. Note that the higher the response factor of a VOC, the lower the response of PID to that VOC[1]. Therefore, the PID signals of specific VOCs were calibrated to their sorbent concentrations by assuming that the % of their PID concentrations divided by their response factors is proportional to their % contribution to the aggregate sorbent VOCs concentration. Thus, the magnitude of the response factor of a VOC is assumed to be a measure of the contribution of that particular VOC to the total PID VOCs signal.

Table 1 displays the effects of cases 1 and 2 on the concentration of some selected VOCs from sites A to F.

The table shows the effect of different cases of PID response to VOCs. For example, in site A, the time average sorbent concentration of 1, 3, 5-trimethylbenzene and chlorobenzene are 1.45 ppm and 0.57 ppm respectively. When the PID signals of these VOCs are calibrated to their real concentration (sorbent concentration) relative to case 1, they now have concentrations of 0.57 ppm and 0.22 ppm; however, when done in terms of case 2, their concentrations change to 1.30 ppm and 0.55 ppm respectively. Unlike in case 1; the concentrations realised when case 2 is taken into consideration made marked improvement as they are much closer to the sorbent concentrations of the considered compounds. Just like

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[1] (http://www.rkieagle2.com/eagle2_response_factors.pdf)

Table 1: Effects of both cases of PID response on the concentration of some selected VOCs

| | | | | | | PID | |
|---|---|---|---|---|---|---|---|
| | | | | | | PID response | |
| | | | Sorbent | | = ISOB. | = specific VOCs | |
| Site | S/N | Name of compounds | Time ave. conc. (ppm), a | Time ave. conc. (%), b | Time ave.conc. (ppm), c = $T_c$*b | Time ave.conc. (%), d = $(b/rf_s)^*$ | Time ave. conc. (ppm), e = $T_e$*d |
| A | 1 | Total (T) | | 100.00 | 17.42 | 100.00 | 17.42 |
| | 2 | 1,3,5-Trimethylbenzene | 1.45 | 3.26 | 0.57 | 7.47 | 1.30 |
| | 3 | Chlorobenzene | 0.57 | 1.25 | 0.22 | 3.17 | 0.55 |
| B | 1 | Total (T) | | 100.00 | 4.35 | 100.00 | 4.35 |
| | 2 | Toluene | 0.78 | 2.52 | 0.11 | 4.63 | 0.20 |
| | 3 | Ethylbenzene | 0.48 | 1.54 | 0.07 | 2.83 | 0.12 |
| C | 1 | Total (T) | | 100.00 | 1733.00 | 100.00 | 1733.00 |
| | 2 | p-Xylene | 5.38 | 4.92 | 85.30 | 5.33 | 92.40 |
| | 3 | 1,2,3-Trimethylbenzene | 3.33 | 3.46 | 60.00 | 5.62 | 97.40 |
| D | 1 | Total (T) | | 100.00 | 180.42 | 100.00 | 180.42 |
| | 2 | 1,3,5-Trimethylbenzene | 3.78 | 1.83 | 3.30 | 3.54 | 6.39 |
| | 3 | p-Xylene | 0.46 | 0.222 | 0.40 | 0.431 | 0.78 |
| E | 1 | Total (T) | | 100.00 | 177.39 | 100.00 | 177.39 |
| | 2 | p-Xylene | 2.07 | 3.27 | 5.80 | 4.70 | 8.34 |
| | 3 | Toluene | 1.62 | 2.56 | 4.54 | 4.41 | 7.82 |
| F | 1 | Total (T) | | 100.00 | 1204.30 | 100.00 | 1204.30 |
| | 2 | Tetrachloroethylene | 5.79 | 17.90 | 215.60 | 29.40 | 354.10 |
| | 3 | Trichloroethylene | 4.58 | 11.20 | 134.90 | 11.60 | 139.70 |

Where $T_c$ = total time averaged concentration of VOCs (ppm) when PID response is same as Isobutylene, Te = total time averaged concentration of VOCs (ppm) when PID response is equal to specific VOCs, $(b/rf_s)^*$ = ratio of time averaged sorbent concentration, b (%), to the response factors of specific VOCs ($rf_s$) normalized.

those of site A, the PID signals of the considered compounds (that is, toluene and ethylbenzene) in site B were much closer to their sorbent concentrations when analysed in terms of case 2 than in terms of case 1; however, more improvement is observed for those of site A. Both the PID signals of example compounds in site C are much higher than their standard sorbent concentrations. In site D, the PID signals of the considered VOCs are very close to the sorbent concentrations when considered in terms of case 1 than case 2. This is the opposite of what is observed in sites A and B. Just as in site C, the PID signals of the calibrated VOCs in both cases of PID response are of several orders of magnitude higher than their sorbent concentrations in sites E and F.

As can be observed from the table, the lower the total PID signal; the closer the time average signals of specific VOCs to their sorbent concentrations when calibrated in terms of case 2. In other words, when the total PID VOCs signal is low, response factor of the component VOCs play a significant role in improving their signals to match with that of the sorbent. However, when the total time average PID signal is large; the effect of their response factors tends to be ineffective since specific VOCs signals tend to be of several orders of magnitude higher than their sorbent concentrations. These findings suggest that: (i) adsorbents do not always retain all VOCs passed through them (ii) adsorbents are good for detection of very low concentrations of VOCs whilst (iii) PIDs are better when high VOCs concentrations are to be measured. Note that the response factors used in this work was supplied by Ionscience, UK.

**Comparing Cases 1 and 2: Which Is Better?:** Cases 1 and 2 above are useful assumptions; however, one may be more useful than the other. To determine which is better, there is a requirement to determine (i) for case 1, the correlation between the total PID VOCs concentrations (ppm) and the total sorbent VOCs concentrations (mg/m$^3$); (ii) for case 2, the correlation of total PID VOCs concentrations and total sorbent tube VOCs concentrations - obtained as sum of the division of individual VOCs concentration by their response factors (iii) compare the $R^2$ – values of (i) and (ii). The one with the highest positive $R^2$ – value will be considered to be better. This is because; ideally PID VOCs concentration

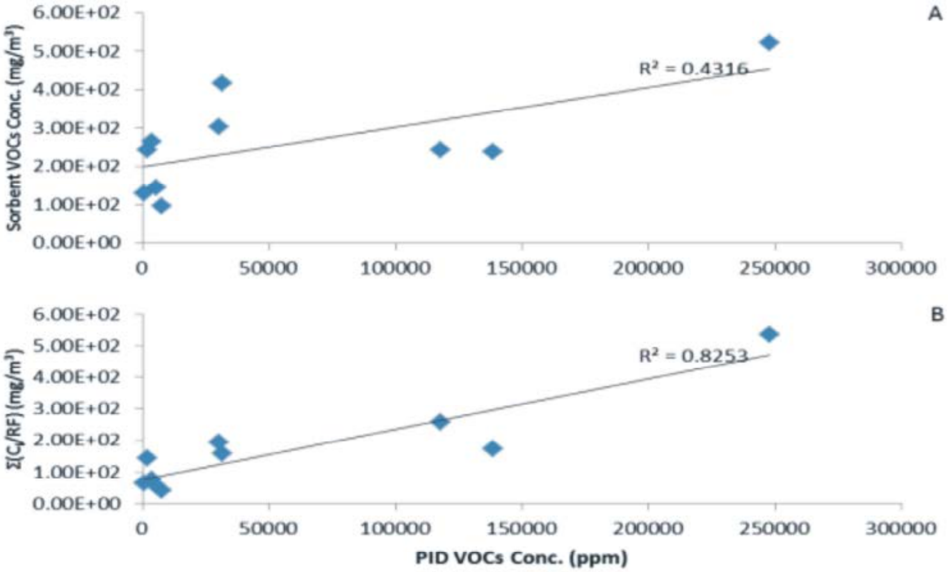

Fig. 7: Graphs of (A) total sorbent VOCs Concentration and (B) calibrated sorbent VOCs concentration against aggregate PID VOCs concentration. Ci = concentration of individual VOCs, RF = response factor of individual VOCs.

is expected to be proportional to the total concentration of sorbed VOCs. Figure 7a below shows the correlations between aggregate PID VOCs concentration and the aggregate sorbent VOCs concentration when the effect of their response factors is neglected (that is, case 1). Figure 7b on the other hand displays the $R^2$ – value between PID VOCs concentrations and their corresponding sorbent tube concentration when the effect of their response factors is taken into consideration. Note that a response factor of 1 was chosen for the unidentified complex mixtures. As can be observed, Figure 7b displays much higher positive $R^2$ – value (0.8253) than Figure 7a (0.4316). This suggests that case 2 is better than case 1 – implying that response factors play a major role in determining the PID VOCs concentration. It also means that PID VOC reading may be a reflection of the total concentration of those VOCs which respond to PID. Therefore, aggregate PID VOCs readings are not expected to be proportional to the sorbent VOCs concentrations provided that there are some individual components of the sorbed VOCs whose response factor to PID is zero. The above correlation may have been higher had it been that (i) all the response factors of the characterised VOCs are known, (ii) the unidentified complex mixtures of the sorbed VOCs are known.

**Determination of Time Series Concentration of Individual VOCs:** The ability of the Gasclam to make continuous measurement of VOCs concentration has been able to allow for their prediction and also to understand the effect of their controls on them. However, as detailed before, bulk VOCs concentration is not a good indicator of risk; therefore, the need for information on their components to be understood. The ability to identify and quantify individual VOCs from their bulk concentration became the needed dramatic advance to solving this problem but not completely. This is because, while this methodology can give time averaged individual VOCs concentration, it was difficult to obtain their time resolved behaviour and possibly the effect of their controls on them. However, assuming that the total percentage concentration of each of the identified VOCs is constant for every sample taken by Gasclam PID, it is now possible to get their continuous behaviour over the monitoring periods by considering all the samples taken. With this, both the short-time and long-time exposure limits of the individual VOCs can be identified for each of the VOCs.

Figures 8 – 9 below show the variability in the concentration of some selected VOCs over the monitoring periods assuming that (i) PID responds differently to them and (ii) their concentrations are invariant over the monitoring period. The ability to determine the time series behaviour of specific VOCs allows the understanding of whether their exposure limits (short-term or long-term) have been exceeded by comparison with standard limits [36]. For example, Figure 8 shows that both the long-term exposure limits (LEL) of 1, 3, 5-trimethylbenzene (25 ppm) and p-xylene (100 ppm) were not exceeded during the

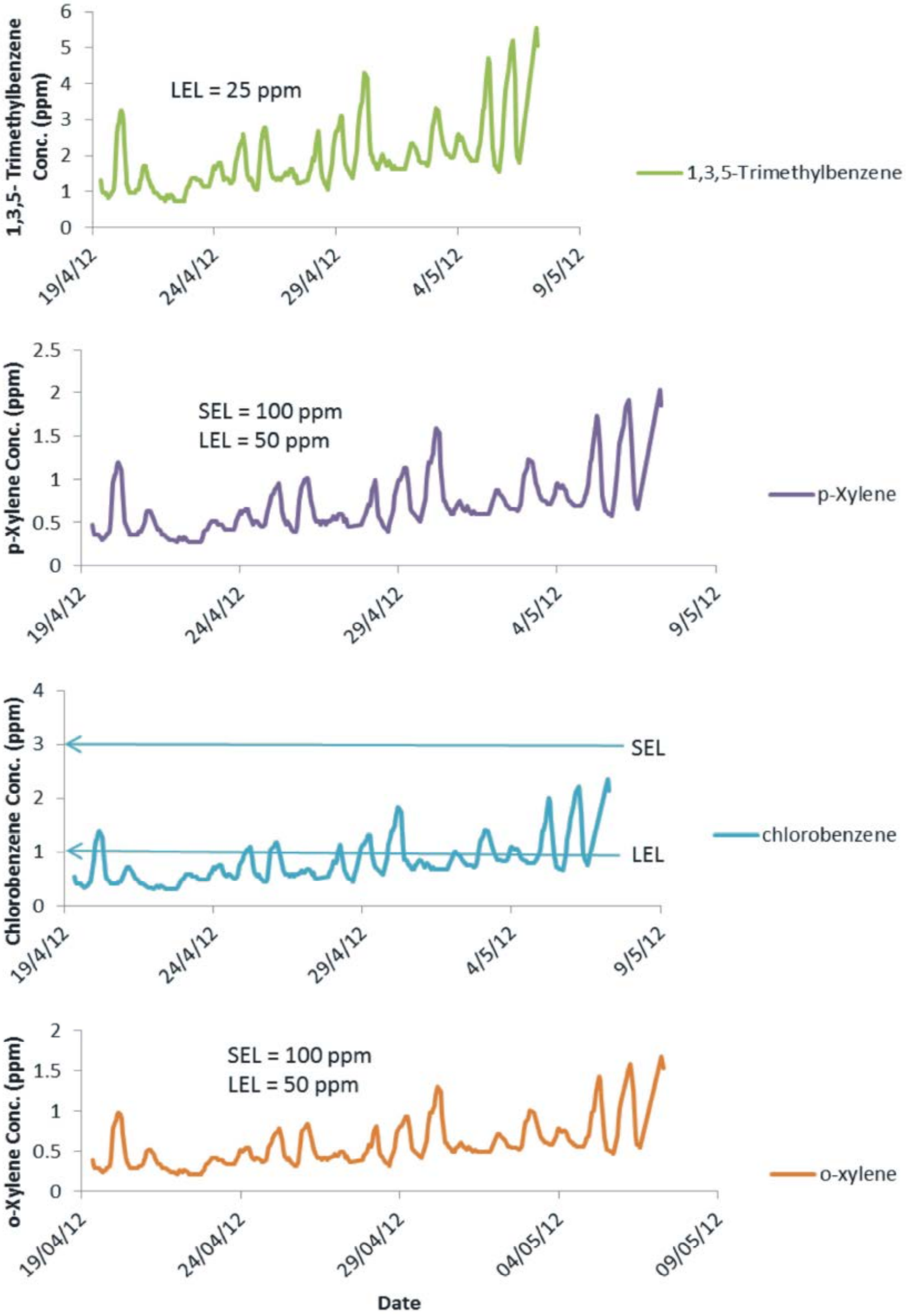

Fig. 8: Time series concentration of 4 of the identified VOCs in site C, assuming that (i) PID responds differently to different VOCs (ii) their concentrations are invariant over the monitoring period. LEL and SEL stand for long-term and short-term exposure limits.

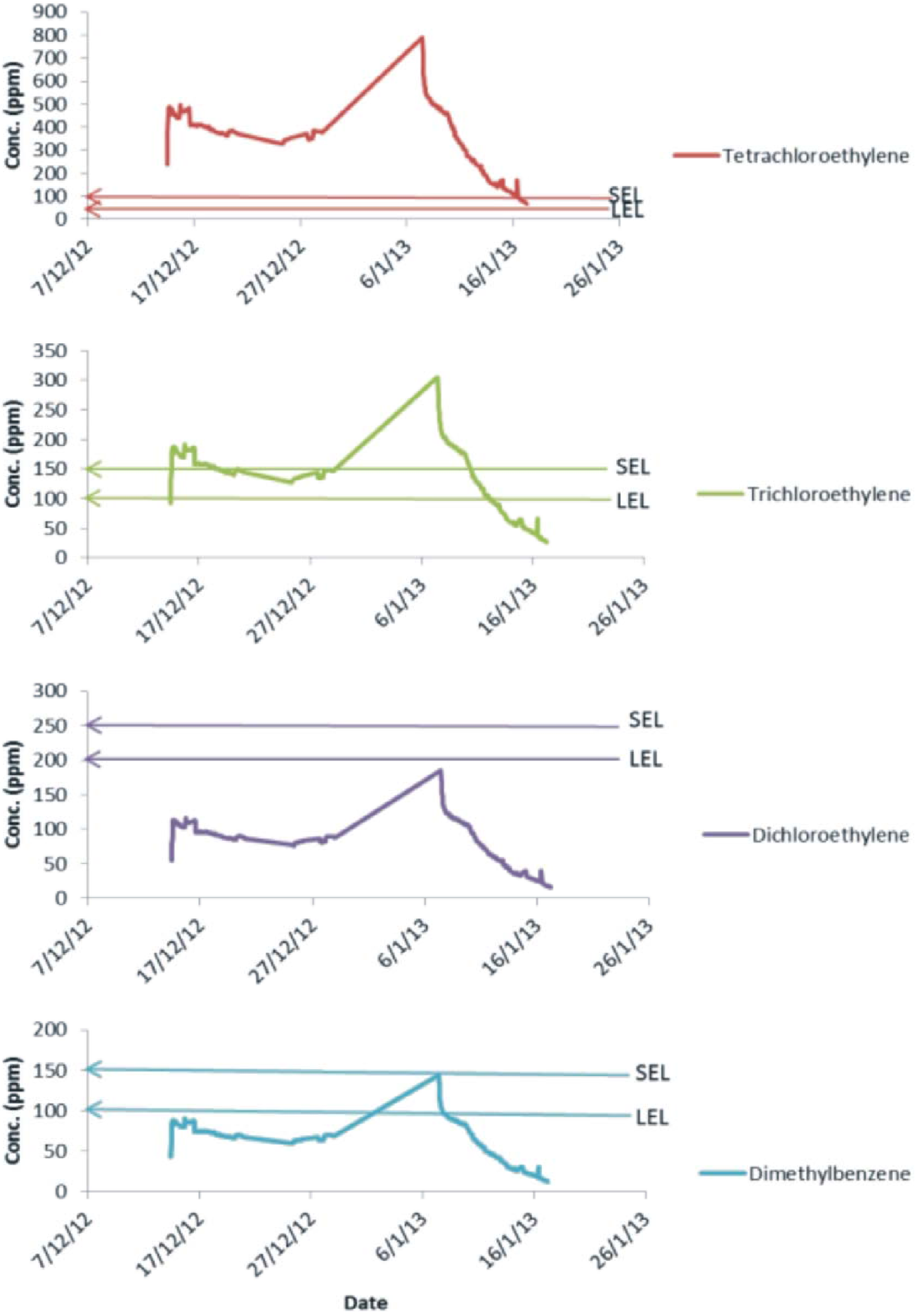

Fig. 9: Time series concentration of 4 of the identified VOCs in site F (well 2), assuming that (i) PID responds differently to different VOCs and (ii) their concentrations are invariant over the monitoring period. LEL and SEL stand for long-term and short-term exposure limits.

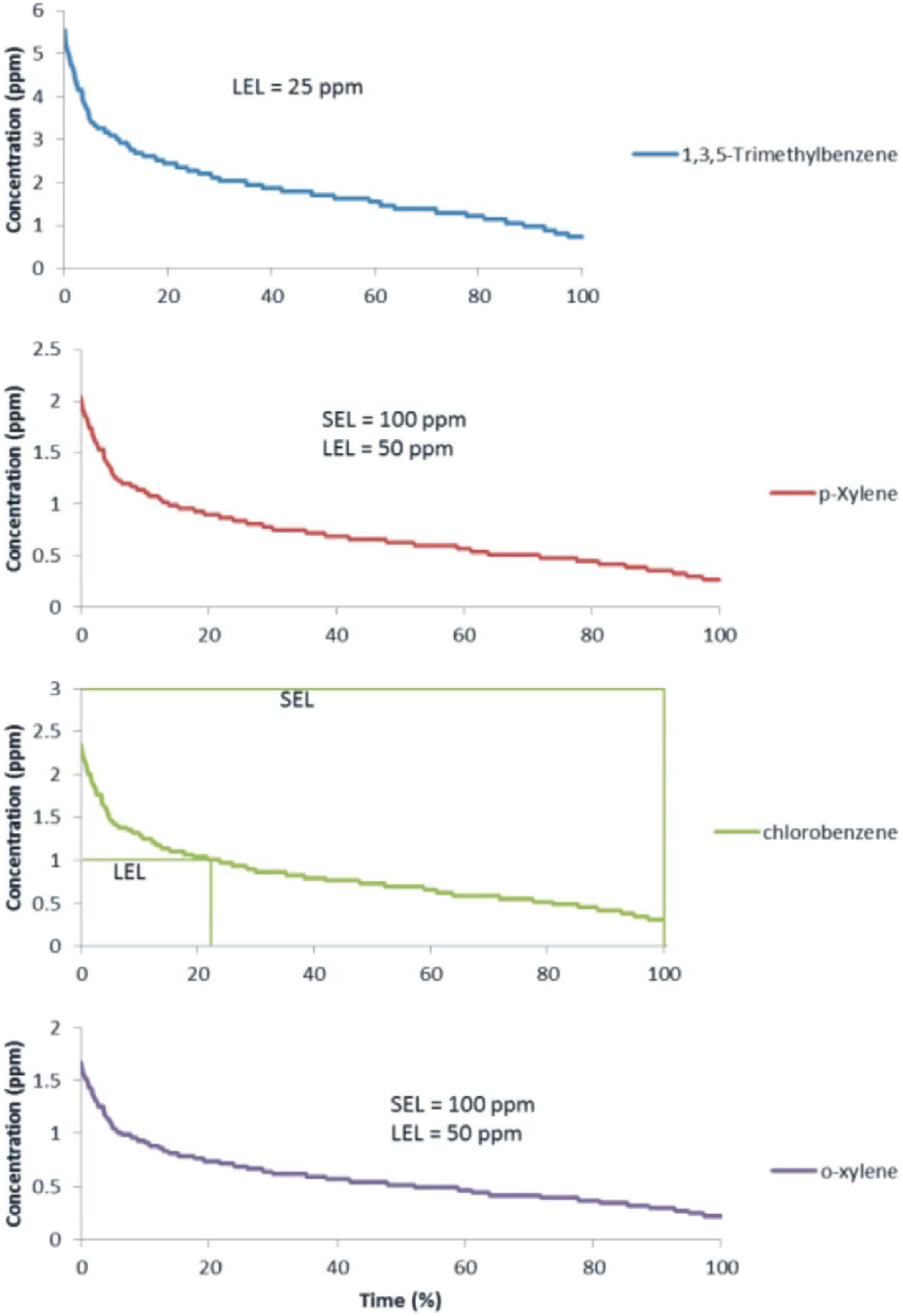

Fig. 10: Concentration duration curves of 4 of the identified VOCs in site C. LEL and SEL stand for long-term and short-term exposure limits.

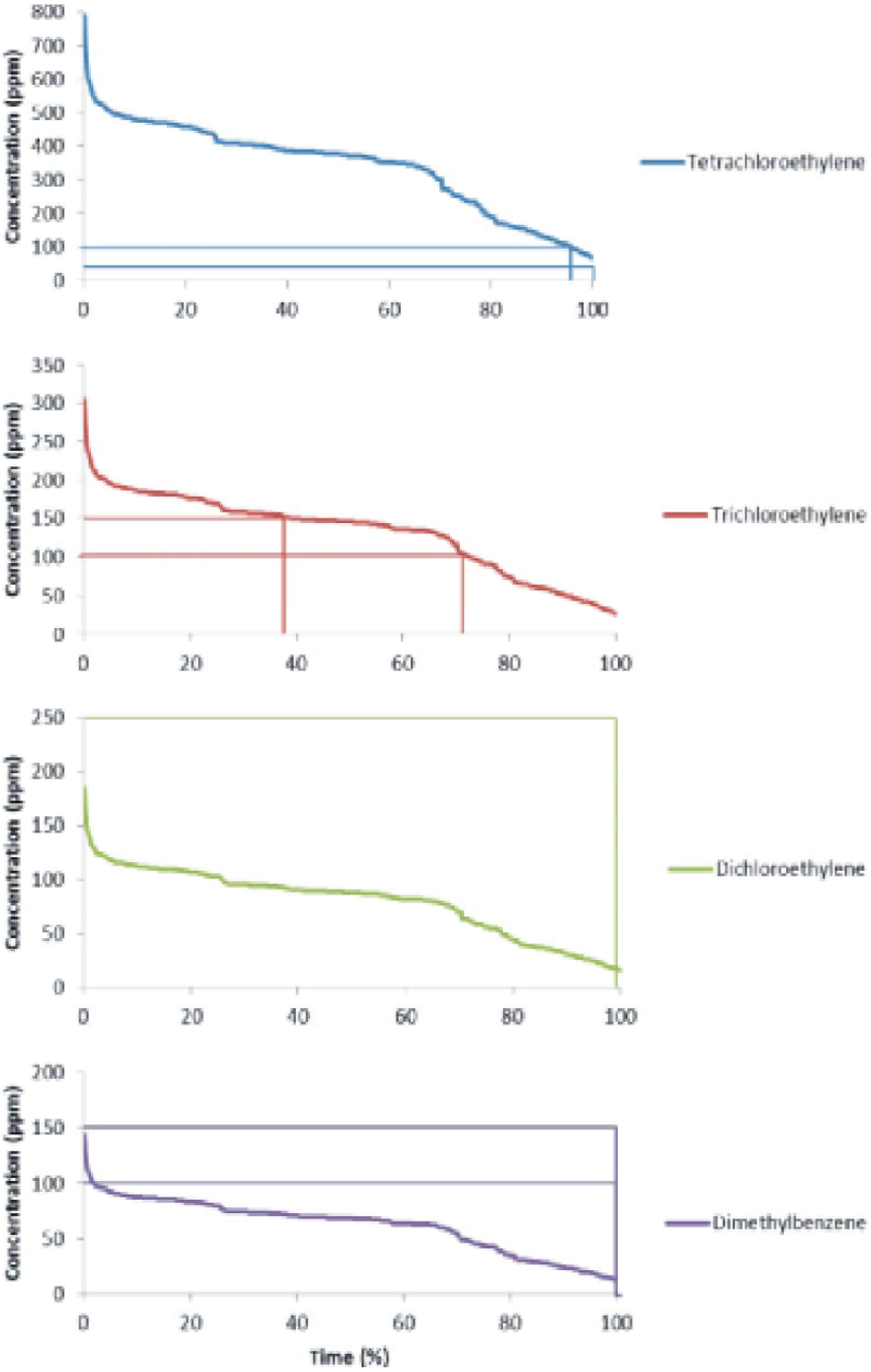

Fig. 11: Concentration duration curves of 4 of the identified VOCs in site F. LEL and SEL stand for long-term and short-term exposure limits.

entire monitoring period. The short-term exposure limit (SEL) of p-xylene was also not exceeded during same period. The figure also shows that while chlorobenzene exceeded its SEL of 3 ppm over the monitoring period and its LEL of 1 ppm for about 22% (Figure 10) of the monitoring period; o-xylene on the other hand did not exceed both the SEL and LEL during the entire monitoring period. Figure 9 shows that whilst tetrachloroethylene exceeded the SEL of 100 ppm for about 92% (Figure 11) of the monitoring period and the LEL of 50 ppm for the entire period; trichloroethylene exceeded both the SEL (150 ppm) and LEL (100 ppm) for about 34% and 71% of the monitoring period respectively. On the other hand, while dichloroethylene exceeded both its SEL of 250 ppm and LEL of 200 ppm during the monitoring period; dimethylbenzene surpassed the SEL of 150 ppm over the same period and LEL of 100 ppm for only 2% of the time.

## CONCLUSIONS

- Photoionization detector (PID) and sorbent tube were successfully combined to derive a dual VOCs monitoring technique. Tenax TA was the adsorbent chosen because of its outstanding qualities over other adsorbents in adsorption and desorption of VOCs. Another factor considered in the choice of the sorbent used is its ability to fit into the Gasclam – an instrument which is tightly packed with pneumatics and electronics.
- The laboratory experiment to determine the response time of the Gasclam showed that VOCs stick to the instrument. Some of these VOCs are traceable to the last site in which the instrumentation was used. Ex-situ VOCs sampling showed that the PID reading dropped from 30 ppm to 7 ppm after 21 hours with the sorbent tube mass equal to **0.350 mg.** It took 250ml of clean air to reduce them from **0.350 mg** to **0.046763 mg** and further 350ml to get them down to **0.003781 mg**. This suggests that with about **1.5L** (that is, 30 samples) of clean air, these VOCs could be removed from the Gasclam.
- The dual VOCs monitoring methodology has proven to be effective. This is because; the time series of specific VOCs concentration during the monitoring periods were successfully obtained. To do this, PID VOCs signal calibrated relative to isobutylene was recalibrated to the real (adsorbed) VOCs by taking into account the response factors of specific VOCs. With the time series of specific VOCs, it is now possible to determine when during the monitoring period each VOC passed the standard exposure limit.
- This new method is therefore very key to ensuring effective VOCs risk assessment as it would provide clear and reliable information that is needed for a more effective monitoring and remediation of sites contaminated by VOCs. Therefore, dual VOCs monitoring measurement is likely to lead to changes in the best practice for ground-gas monitoring.

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