

HOW TO IMPROVE PREDICTION OF RISK FROM GROUND VOCs USING IN-BOREHOLE GAS MONITORING

¹Nwachukwu, A. N and ²Ugwuanyi, J. U

¹University of Manchester, UK.

²University of Agriculture, Makurdi Nigeria.

Abstract

Volatile organic compounds (VOC's) have a variety of negative impacts on human health (Harold, 1998; Barbara *et al*, 2007), some (e.g. benzene and formaldehyde,) are known to be human carcinogens (IARC, 2004). There is, therefore, often a pressing requirement to monitor these compounds. However, monitoring these compounds is not straightforward as their concentrations vary with environmental parameters such as temperature, barometric pressure and groundwater movement. Because of this, the sampling frequency that is used at present is ineffective for determining their representative concentration; therefore, a device which can be left in-situ to collect high temporal resolution data has been developed (Gasclam, Ionscience, UK). VOC's are measured by Photoionisation detector (PID), however; PID measures aggregated VOC concentration. Because VOC's have differing toxicities and behaviours, individual identification is required, therefore, a sample must be collected. In order to do this, a sorbent material must be used to transfer the sample to the GC-MS for identification. The sorbent material must be appropriate for the range of VOC's and of sufficient capacity for extended exposure (BS EN ISO 16017-1:2001). To solve these problems, an optimum VOC monitoring methodology known as **dual measurement VOC monitoring** has been developed following the incorporation of a suitable sorbent into the latest in-borehole monitoring device, the Gasclam (Ionscience, UK).

Keywords: Dual VOCs measurement; risk prediction; carcinogenicity; sorbent material; photoionisation detector (PID).

1.0 Introduction

VOC is an acronym for volatile organic carbon/compound. VOCs have been defined in different ways by different people based on their environment and circumstances, however; there is this consensus that they are organic compounds which are volatile under normal atmospheric/environmental conditions irrespective of the state or form in which they exist (CIRIA 766). They can undergo vapour intrusion, emission and/or vapour release at normal temperature and pressure.

VOCs are made up of diverse mixture of different products which vary in their chemical framework, resulting in a huge variation in their toxicity, mobility and breakdown properties of different products. They are however, of three categories:

- i. Petroleum (non-halogenated) hydrocarbons, for example, benzene, toluene, butyl benzenes.
- ii. Halogenated hydrocarbons, for example, chlorinated ethenes and ethanes (e.g. dry cleaning fluids or degreasers) or chlorofluorocarbons (freons).

<http://www.ejournalofscience.org>

iii. Nitrogen, sulphur and oxygen-containing organic compounds, for example, tetrahydrofuran. VOCs can be derived from natural sources, however; their presence in the environment is mainly due to spillage/leakage of solvents or fuels associated with industrial and commercial activities such as their production, storage, distribution, and use in industrial processing (CIRIA 766). It has been widely observed that volatile organic compounds (VOCs) are often the most frequently detected contaminants in soil and ground water abandoned landfills and Brownfield sites (West et al., 1995). This is largely due to extensive use of solutions of VOCs and products containing some VOCs resulting in accumulation and release of considerable quantities to the environment. In addition, indiscriminate disposal of waste chemicals and accidental discharge from petrol underground storage tank contribute significantly to VOCs released to the environment. The redevelopment of Brownfield and other contaminated sites necessitated by increasing demand for housing in the UK means that the fate, transport and exposure pathways of this contaminant need to be ascertained.

The presence of elevated VOC concentrations in drinking water may be a concern to human health because of their potential as carcinogens (benzene and 1, 3-butadiene) (Rowe et al., 2007). In addition to cancer risk, VOCs may adversely affect the liver, kidneys, spleen, and stomach, as well as the nervous, circulatory, reproductive, immune, cardiovascular, and respiratory systems (Row et al., 2007). There is also an increasing concern about its migration from the subsurface into overlying buildings as important exposure pathways. Given the known or suspected human-health concerns and the increasing demand for contaminated sites, there is therefore need for effective monitoring methodology for its fate and transport from source of discharge in order to determine the true subsurface concentration and the potential for migration.

However, monitoring VOCs is not straightforward. This is because, unlike other ground-gases such as CH₄, CO₂, CO and H₂S; VOCs not only vary in concentration but also in type. Total VOCs is not a good measure for risk assessment since individual VOCs differ in effect (be it health or environmental). There is, therefore, often a requirement to characterize them. This is particularly pertinent due to often close proximity between human population and their potential sources.

2.0 Current VOC monitoring techniques

The monitoring of ground-gas concentrations such as that of VOCs, methane and carbon dioxide, generated by contaminated sites (example, landfills and brownfields) is becoming a more common legislative requirement due to the potential problems these gases pose, such as the risks of explosion, toxicity, carcinogenicity and global warming. Before now, several monitoring techniques have been used for characterisation of contaminated sites and these have helped to shape the policy direction of development of land and remediation strategies. In particular and as detailed before, in-situ monitoring of VOCs can be a complicated task, especially given the fact that they not only vary in concentration but also in type coupled with complex interactions of several factors responsible for generation and migration of VOCs and other ground-gases.

Monitoring of ground-gases including VOCs in contaminated sites can be sub-categorized into **sampling** and **analysis**.

2.1 Sampling – Presently, the majority of contaminated sites gas analysis is achieved either through spot sampling or through the use of large expensive fixed position monitoring stations. Other methods include Purge and trap (also called headspace), solvent extraction (using methanol or hexane), static headspace and

<http://www.ejournalofscience.org>

solid phase micro-extraction (SPME). More recently it has been recognised that gas production and migration responds to environmental factors such as barometric pressure and groundwater movement, with the accompanying realization that these conventional sampling methods will often miss such changes.

For example, using portable gas detection instruments to spot check boreholes from time to time is fraught with potential issues. Considerable published material exists that question whether the traditional method of collecting gas-data from boreholes is at all adequate. The use of the numerous guidance notes (e.g. CIRIA and CL: AIRE) from the legislators and enforcers would seem to indicate they too think the current methods are flawed. To evaluate boreholes effectively detailed and frequent measurements are required, particularly when events occur e.g. such as when the barometric pressure falls. Data collected on in periodic spot check basis does not give a complete picture, so decisions are made reliant on historic set points rather than real trend information on the borehole being monitored.

Investigating VOC contamination in the subsurface involves several components and specific activities are required to assist in the delineating the current nature and extent of contamination and provide appropriate and adequate data to enable site clean-up goals to be established (Siegrist, 2003). Conventionally, risk assessment involves analysis of samples taken from points evenly spaced across a site, as well as sample taken from any area known to be of higher risk due to past land usage or natural patterns.

If an investigation is not designed to assess all aspects and areas of contamination on a site, even if accurate analysis of sample is achieved, result will not present realistic assessment of contamination present (Siegrist, 2003). The conventional methods of monitoring VOCs rely on periodic concentration measurements. They have been proven to be unrepresentative, with significant uncertainties in the prediction of VOC migration in the subsurface.

2.2 Analysis - After the in-situ extraction of VOC compound is done, the samples are then taken to the laboratory for analysis with the use of gas chromatographs and/or spectrophotometers (Mercer and Spalding, 1991, 2001). The problem with this approach as noted above is its reliability and representativeness. The off-site laboratory analysis often takes weeks before the result is available. In the best case, in-situ measurement are done with the field portable gas chromatographic system equipped with a variety of detectors including electron capture, photonisation and mass ion detector (Koglin and Einfeld, 2001). The on-site potable analytical techniques can indeed provide a quick-turnaround data in the field which can be used to guide a site investigation in progress which in a way reduces the sampling error resulting from storage and transportation of samples. However, the methodologies, in-situ and ex-situ, require sampling at intervals, thereby missing out the effect the changes in environmental controls (such as temperature and pressure) would have on the migration of the pollutant.

3.0 Major Flaws in current methods

3.1 Sampling – Ground-gas (i.e. products of respiration and VOC) concentration and flow have been recognised to vary with environmental parameters which show high temporal variability. The possibility of getting representative measurement of such parameters requires multiple measurements. In the case of ground-gas risk assessment, flaws in the existing multiple measurement approach to measuring and predicting risk arising from ground-gases such as VOCs have been identified explicitly in the literature (Wilson et al., 2009) and are implicit in the continuous evolution of guidance notes (e.g. CIRIA).

<http://www.ejournalofscience.org>

Boult et al (2011) explained that the two underlying causes of these flaws are that, whilst accurate quantification of risk requires accurate measurement of ground-gas concentration and of ground-gas fluxes,

1. Neither is measured directly :

- concentration of the gas in the ground is inferred from periodic (weekly – monthly) sampling of the gas accumulated within a borehole
- flow of the gas from the ground is inferred from periodic measurement of gasflow from the same borehole.
- The relationships these inferences are based on will be highly site-specific and time dependent.

2. Both are likely to be temporally variable.

3.2 Analysis - There are many different types of VOCs each with differing toxicities and behaviours and therefore, requiring specific identification and quantification. Analysis by typical field instrumentations such as photoionization detector (PID) and flame ionization detector (FID), does not allow this specificity since they give only aggregate VOC concentrations. FID and PID are common tools used for site investigation. PIDs contain a UV lamp of a particular energy (e.g. 10.6 eV or 11.7 eV); any chemical species with an ionization potential at or below this energy will be detected. FIDs require a fuel gas (hydrogen) to burn hydrocarbons in a small flame, ionizing the chemical species which are present; thus any chemical species with a C-H bond (hydrocarbons) will be detected (including lighter end C₁ –C₃ hydrocarbons which may not be considered part of TVOC definition). While each of these instruments responds to a wide range of compounds and yield a “total value”, the detection limits of these instruments are typically in the range of 0.1 – 0.5 ppmv (as isobutylene for PID and as methane for FID), and therefore may not be suitable for the low-level TVOC assessment.

Generally, these approaches are slow, iterative and costly. As observed by West et al (1995), the analysis of each sample can cost as much as 300 dollars. The slow and periodic sampling coupled with the high cost of analysis usually results in inadequate number of samples, and thereby making it absolutely impossible to infer a representative concentration.

“The quantification of risk requires accurate measurement of ground-VOC concentration and fluxes” (Morris, 2008), neither of which can be achieved by the existing technique but by technique that enables collection of time-series data. Time-series data allows temporal variability to be quantified and accounted for and can ultimately improve understanding of processes, thereby reducing uncertainty in risk prediction (Morris, 2008). There is therefore a requirement for a continuous in-situ monitoring methodology which would ensure effective risk assessment and prediction.

Having identified the flaws in the current VOCs monitoring methodology, this paper aims to demonstrate how Gasclam In-Borehole Gas Monitoring technology can be used to obtain an improved VOC risk prediction by remedying the flaws in the current VOC monitoring methodology.

4.0 The solutions to the flaws

<http://www.ejournalofscience.org>

4.1 Solution 1 – In-borehole ground-gas monitor (Gasclam)

The solution will be to increase the sampling frequency of these gases to match the frequency of their environmental controls and also use a device that can measure them directly. Matching the gases with their controls will not only help to derive an optimum methodology for monitoring them, but will also help to predict how the gases will change in future. To do this cost effectively, an in-situ device is needed, and such a device must be secure, able to operate unmanned, and must be certified for explosive environment (ATEX). A recently developed device is the gasclam (Ionscience, UK) (figure 1).



Figure 1: Gasclam

Gasclam In-Borehole Gas Monitor (IGM), developed by Salamander, is the latest gas sensor technology that allows continuous unmanned measurements of ground gas including VOCs. In addition to that, it allows the understanding of spatial and temporal variability in the migration of VOC across a contaminated site. This will allow reduction in the uncertainty in prediction of VOC migration in the subsurface, a more site-specific risk assessment and consequently allows informed decision on remediation and redevelopment strategies for contaminated sites.

It logs long term, real trend information, allowing informed decision to be made on accurate, reliable data – a revolution in gas management and prediction. The Gasclam gas monitor measures methane, carbon dioxide and oxygen concentrations as well as atmospheric pressure and temperature. Optional CO, H₂S and VOC, plus water depth are available along with a telemetry module for remote, real time data communication. Incorporated into it for VOC measurement is the photoionisation detector (PID). Its sampling frequency can be set and is variable from two minutes, to once daily. Data is downloaded to a PC or viewed remotely using the optional GPRS telemetry system. It is made from stainless steel and therefore intrinsically safe. It is environmentally sealed and has ingress protection rated IP-68. It is battery operated and can be powered for up to three months based on hourly sampling. Target applications for the Gasclam ground gas monitor include landfill for long term profiling, Brownfield for development issues, monitoring for coal mine fires, leakage in crude/petroleum, solvent

<http://www.ejournalofscience.org>

storage and filling stations, refineries for local compliance, and for below ground carbon capture and storage monitoring regimes (www.ionscience.com/products/gasclam). It has the following advantages over the spot sampling:

- The new Gasclam monitor can be installed in a borehole and gas data collected continuously (figure 2).
- Data can be collected for up to 3 months and routine site visits are not necessary, which is always a problem when using portable instruments.
- The savings in time are very significant, but Gasclam doesn't just give a snapshot of gas levels as provided from a portable instrument. It provides continuous and comprehensive information regarding gas conditions.
- Measurements of methane, carbon dioxide, oxygen, hydrogen sulphide, carbon monoxide, VOCs and pressure are logged to memory. Data can be retrieved to a lap-top or can be collected remotely with the telemetry module (figure 2).



Figure 2: Process of Gasclam installation

4.2 Solution 2 - Appropriate sorbent

The solution for identification and quantification of the various VOCs would be to use an appropriate sorbent to collect and transfer the sample of VOCs for analysis (GC-MS). The sorbent must be suitable for the range of VOCs and of sufficient capacity for extended exposure (BS EN ISO 16017-1: 2001). Also, in order to be able to report VOC as concentration, the volume of the gas passed over the sorbent must be recorded. This means that for effective VOC monitoring, dual measurement is required.

5.0 Dual measurement VOC monitoring

Measuring ground VOC can be a difficult task since it would be hard to determine the amount of the soil contributing them. A mixture of VOCs each of unknown mass/volume from the ground is measured by the PID as time resolved aggregate VOC concentration. With the aid of the pump, the mixture is now passed across the sorbent which absorbs them. The sorbent is transferred into the laboratory for their individual identification and quantification as mass using the GC-MS. This mass is now divided with the known volume of the gases gotten 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, the sorbent tackles that of variability of type, hence a dual measurement VOC monitoring (figure 3).

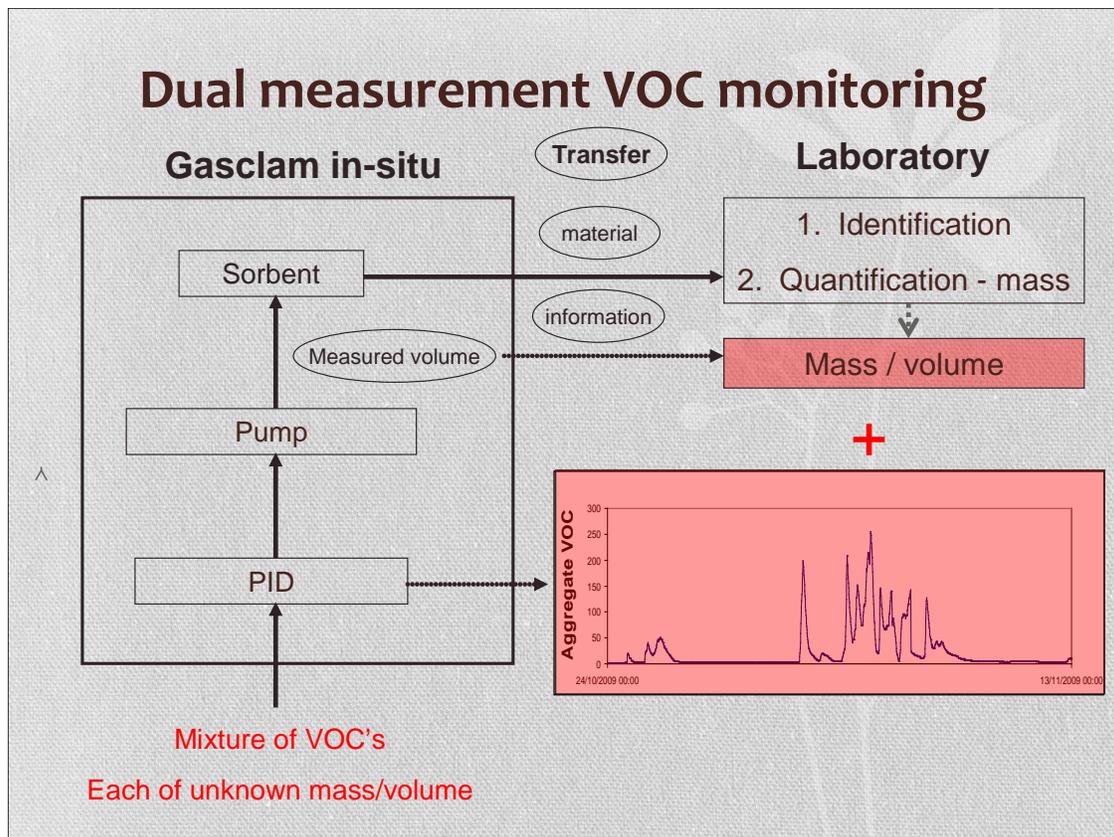


Figure 3: VOC monitoring methodology

6.0 Conclusion

This research demonstrates the utility of Gasclam In-borehole gas monitor, the effectiveness of which depends on the incorporated devices. They are the photoionisation detector (PID) and the adsorbent tube. With the aid of the gasclam PID, it is now possible to collect **Time resolved aggregate VOC's concentration**, whilst with the aid of the sorption material incorporated into the gasclam, VOCs sample can be adsorbed and subsequently desorbed by means of thermal desorption/ Gas Chromatography (TD/GC-MS). The result is a gas chromatogram which gives

<http://www.ejournalofscience.org>

Time averaged individual VOC's concentration. This means that for improved risk prediction from ground VOCs, dual monitoring VOCs measurement is required.

References:

- Barbara, L., Rowe, Patricia L. Toccalino, Michael J. Moran, John S. Zogorski, and Curtis V. Price., (2007). Occurrence and Potential Human-Health Relevance of Volatile Organic Compounds in Drinking Water from Domestic Wells in the United States. *Environmental Health Perspectives* 115:1539–1546.
- Boult, S., Morris, P., & Talbot, S., (2011). Contaminated land application in real environment (CL: AIRE) bulletin, RB 13. [Available online] URL: <http://www.ground-gassolutions.co.uk>
- BS EN ISO 16017-1 :(2001). Indoor, ambient and workplace air. Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography. Pumped sampling
- Harold, J. R., (1998). *Odor and VOC Handbook*. McGraw-Hill publishing Companies, USA.
- IARC, (2004). International Agency for Research on Cancer (IARC), overall evaluation of carcinogenicity to humans, IARC monographs vol. 1-88.
- Katy, B., Helen, H., Lara, P., Don, B., and Cecilia, M., (2009). *The VOCs Handbook: Investigation, assessing, and managing risks from inhalation of VOCs at land affected by contamination*. CIRIA Report 766.
- Koglin, E., and Einfeld, W., (2001). Site characterization and monitoring technologies, technology profile: On-site analysis of VOCs in water. U.S. Environmental Protection Agency.
- Mercer, J.W., and Spalding, C.P., (1991). Characterization of the vadose zone *In Site Characterization for Subsurface Remediation*. U.S. Environmental Protection Agency.
- Morris, P., (2008). How to deal with time series ground-gas data, using analytical

<http://www.ejournalofscience.org>

techniques from other disciplines. (Online) Available:

www.gasclam.co.uk/downloads/Peter%20Morris.ppt. Assessed 11th December, 2008.

Rowe, B.L., Toccalino, P.L., Moran, M.J., Zogorski, J.S., and Price, C.V., (2007).

Occurrence and potential human-health relevance of volatile organic compounds in drinking water from domestic wells in the United States. *Environmental Health Perspective* 115:1539–1546 (2007). Available Online: <http://dx.doi.org/>

Siegrist, R. L., (2003). Sampling technologies for site characterization and long-term monitoring in evaluation of demonstrated and emerging technologies for the treatment and clean up of contaminated land and groundwater (Phase III).

NATO/CCMS Pilot Study, USEPA 542-R-02-011. Accessed 22nd March, 2009.

URL://http://www.epa.gov/swertio1/download/partner/2002_special_session.pdf.

West, O. R., Siegrist, R.L., Mitchell, T.J., and Jenkins, R.A., (1995). Measurement error and spatial variability effects on characterization of volatile organics in the subsurface. *Environmental science and technology*, 1995, 29 (3), 647-656

(Online) Available: <http://pubs.acs.org> Assessed 15th January, 2009.

Wilson, S., Card, G., and Haines, S., (2008). The local authority guide to ground-gas. The Chartered Institute of Environmental Health: London.