# Demonstrating the Utility of Continuous Monitoring to Remedy the Flaws in Spot Sampling of Ground Gas

A dissertation submitted to the University of Manchester for the degree of Master of Science in Environmental Sciences, Policy, and Management (MESPOM) in the Faculty of Engineering and Physical Sciences

2009

Musbau Adeoye Bello

School of Earth, Atmospheric and Environmental Sciences

**Erasmus Mundus Masters Course in Environmental Sciences, Policy and Management** 





This thesis is submitted in fulfilment of the Master of Science degree awarded as a result of successful completion of the Erasmus Mundus Masters course in Environmental Sciences, Policy and Management (MESPOM) jointly operated by the University of the Aegean (Greece), Central European University (Hungary), Lund University (Sweden) and the University of Manchester (United Kingdom).

Supported by the European Commission's Erasmus Mundus Programme



**Erasmus Mundus** 

# Table of Content

Table of Content	
List of Figures	
Abstract	5
Declaration	6
Copyright	7
Acknowledgement	
1.0 Introduction	9
1.1 Justification	
1.2 Sources, Migration and Health Hazards of VOC and Other Gases	10
1.2.1 Sources of VOC, Methane and Carbon Dioxide	10
1.2.2 Migration Processes in the Subsurface	
1.2.2.1 Diffusion	11
1.2.2.2 Advection	12
1.2.2.3 Groundwater Level	
1.2.2.4 Temperature	14
1.2.3 Health Hazards	14
1.3 Existing Monitoring Techniques and their Associated Flaws	15
1.3.1 Sample Collection	
1.3.2. Extraction and Preservation Method	16
1.3.2.1 Purge and Trap	
1.3.2.2 Static Headspace Extraction	18
1.3.3 Analytical Technique	19
1.3.3.1 Gas Chromatography	19
1.3.3.2 Photo-ionisation Detector	20
1.3.3 Associated Flaws	21
1.4 How could Continuous Data allow these to be remedied?	
1.4.1 Gasclam Continuous In-Borehole Gas Monitor (IGM)	
1.4.2 Continuous Data	22
1.5 Aim and Objectives	
1.6 Aim	
1.7 Objectives	

2.0 Methodology	24
2.1 Data Collection	24
2.2 Field data	24
2.3 Laboratory Model	25
2.3.1 Model Set-up	26
2.3.2 Assumption	26
3.0 Result and Discussion	27
3.1 Determining whether PID will work continuously in borehole envir	onment
	27
3.2 Demonstrating Variability of Gas Concentration at different time	scales
	29
3.2.1 Concentration Duration Curve	31
3.3. Inference of gas production / Migration from Concentration through Correla	ation of
Environmental Parameters	33
3.4. Inference of Gas Production / Migration through Pump Test	38
3.4.1 Model Output	38
3.4.2 Pump Test	38
4.0 Conclusion	43
4.1 Further Work	44
References	45

# List of Figures

Figure 1.34 Sample preparation for VOCs: (a) Purge-and-Trap extraction (dynamic headspace), and (b) Static headspace extraction (SHE)
Figure 1.51: Gasclam In-Borehole Gas Monitor. Picture showing both bottom and head view
Figure 3.1: Time series data indicating presence of, and variation in concentrations of VOC in the three boreholes
Figure 3.21: Time series data indicating variation in methane and carbon dioxide concentration during a short time scale
Figure 3.22: Time series data indicating variation in methane and carbon dioxide concentration on a long time scale
Figure 3.23: Concentration Duration Curve resulting from time series data from site B .32
Figure 3.31: Time series data indicating correlation of atmospheric pressure with carbon dioxide
Figure 3.32: Multi-parameter time series data indicating correlation of atmospheric pressure with gas concentration
Figure 3.33: Multi-parameter time series data indicating correlation of atmospheric pressure with ground gases collected during freezing temperature
Figure 3.34: Multi-parameter time series data indicating correlation of atmospheric pressure with ground gases during increased temperature
Figure 3.41: Gas concentration in different borehole across the model after 18.5 hrs with flow rate 9lmin <sup>-1</sup>
Figure 3.42: Recovery Profiles of $CO_2$ after purging for 5 minutes, at flow rate of 9lmin <sup>-1</sup> . Three replicate tests were performed on each of BH 1 and BH 2 and two each on BH 3 and BH 4
Figure 3.43: Recovery Profiles of CO <sub>2</sub> at different flow rates after purging for 5 minutes (laboratory model)
Figure 3.44: Recovery Profiles of $CO_2$ and $CH_4$ at different sites after purging (field data)
- 42

#### Abstract

Ground gas risk assessment is required in order to determine the true subsurface gas concentration and to predict how this concentration might change in the future. These requirements are currently being met by periodic discrete measurement of gases from which gas regime is inferred. Two fundamental flaws have been identified in this approach; i) data insufficiency due to low sampling frequency, resulting in failure to account for variability in gas concentration, ii) the techniques only measure gas concentration and not flux, thereby neglecting the time-dimension in the gas regime. With the combination of field and laboratory work, this study demonstrates the utility of continuous data to remedy these flaws through the use of Gasclam® In-borehole Gas Monitor. The study revealed that the variability in gas concentration is greater than the sampling frequency of spot sampling, and that the frequency of this variation changes at different time scale. Time series data was also shown to allow understanding of processes that control ground gas migration through the correlation of different environmental parameters. However, the study also found that the widely reported relationships between parameters do not always exist, and therefore there is need to characterise migration and /or production rates in each borehole. Model outcome from the laboratory revealed that the use of pump test for characterising gas production and/or migration rate is reproducible thereby allowing inference of gas flux from the resulting recovery profile. As a result, the study recommends that each site and each borehole be characterised on the basis of their gas production and / or migration rates rather than the conventional data extrapolation. Also, the new application in continuous monitor allowed a successful demonstration of PID sensor for continuous measurement in borehole environment thereby providing a novel application in ground VOC monitoring.

**Keywords**: Ground gas, spot sampling, sampling frequency, variability, flux, pump test, continuous monitoring, GasClam<sup>®</sup>.

# Declaration

I hereby declare that the dissertation work entitled '**Demonstrating the Utility of Continuous Monitoring to Remedy the Flaws in Spot Sampling of Ground Gas'** is an original and independent study. Any material that has been obtained from other sources has been duly acknowledged in the report.

I declare that this study has not been accepted for any degree and it is also not currently being submitted in candidature for any other degree in another University.

> Musbau Adeoye Bello 24<sup>th</sup> May, 2009

# Copyright

i) Copyright in text of this dissertation rests with the author. Copies (by any process) either in full, or extracts, may be made only in accordance with instructions by the author. Details may be obtained from the appropriate Graduate Office. This page must form part of any such copies made. Further copies (by any process) of copies made in accordance with such instructions may not be made without the permission (in writing) of the author.

ii) The ownership of any intellectual property rights which may be described in this dissertation is vested in the University of Manchester, subject to any prior agreement to the contrary, and may not be made available for use by third parties without the written permission of the University, which will prescribe the terms and condition of any such agreement.

iii) Further information on the condition under which disclosures and exploitation may take place is available from the head of the School of Earth, Atmospheric and Environmental Sciences.

> Musbau Adeoye Bello 24<sup>th</sup> May, 2009

# Acknowledgement

First, I want to appreciate the guidance and blessings I have been bestowed by the Almighty from cradle till present. He has provided me the wherewithal that have been used to prosecute existence through hard and very difficult times fate has put me through.

My sincerest appreciation goes to the European Commission and the MESPOM consortium for providing the rare opportunity to participate in this wonderful programme, your gesture has been a good pedestal on which my floating dreams have lived. Thank you for the opportunity.

My sincere appreciation goes to my supervisor, Dr. Stephen Boult for his guidance and encouragement throughout the course of this research. My unalloyed gratitude also goes to Dr. Peter Morris whose ever-willing assistance made this thesis an enjoyable one.

And to all my classmates, MESPOMers, the time spent together will never be forgotten.

Finally to my parents and siblings for their love, support and prayers, I pray God's blessing to enable me reciprocate your outstanding attention on me.

# 1.0 Introduction

## 1.1 Justification

Effective risk assessment and remedial actions of subsurface volatile organic compounds (VOC) and other ground gases such as methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) are one of the major challenges of land contamination management. VOC, methane and carbon dioxide are often the most frequently detected contaminants in groundwater, abandoned landfills and Brownfield sites around the world (West *et al.*, 1995). With continued redevelopment of Brownfield sites and other contaminated sites, necessitated by increasing demand for housing and encouragement by government policies, the need for effective risk assessment has become highly imperative as more and more uncertainty is arising around investigation of ground gases and VOC. The presence of elevated concentration and the inherent chronic and acute risk of these gases require that remedial actions be taken in order to ensure that land is both safe and suitable for its intended use.

Risk assessment involves several activities including site monitoring and characterisation. The primary objectives of ground gas monitoring are to determine the true subsurface gas concentration as this relates directly to explosion hazard and vapour intrusion, and to be able to predict how this might change in the future (Morris et al., 2008; Todman 2008). These requirements are currently being met by 'spot' sampling technique where discrete gas measurements are obtained on weekly or monthly basis and from these measurements, ground gas regime is inferred. Consequently, several guidance documents about risk assessment are often based on arbitrary, prescribed gas concentration (Sladen et al., 2001). In the UK, for example, the use of a threshold or trigger value of 5% v/v of methane and 1% v/v for CO<sub>2</sub> is recommended (Morris et al., 2008; Wilson et al., 2008; Sladen et al., 2001). It requires that the worst case concentration be taking into consideration during site monitoring. This approach to monitoring has been considered by many researchers as misleading and overly-conservative (Wilson et al., 2007, Sladen et al., 2001). Siegrist et al., (2003) and Tillman (2003) have noted that this approach of using gas concentration as significance of contamination have far reaching effect on redevelopment plan and it is therefore essential that they be based on accurate measurement. Sladen et al. (2001) suggests that the presence of measurable concentration of gases in the subsurface does not automatically indicate contamination problem as other processes like generation and

migration are more important indication of level of risk. These processes (generation and migration) are predominantly driven by environmental factors such as diffusion and advection (controlled by atmospheric pressure) thereby causing variation in gas concentration with time (Wilson *et al.*, 2007; Ho and Webb 2006). Accounting for this variation will provide useful insight into the ground gas behaviour.

It is therefore imperative that monitoring technique that allows the understanding of these processes is applied in ground gas risk assessment.

#### 1.2. Sources, Migration and Health Hazards of VOC and Other gases

#### 1.2.1. Sources of VOC, Methane and Carbon dioxide

Methane and  $CO_2$  gas are produced from both natural and anthropogenic sources. Methane is regarded as the second most important "greenhouse gas", after carbon dioxide, resulting from human activities (EA, 2008). They are found in landfill sites as breakdown products of the organic content of waste such as food, garden, wood and paper waste (NHBC, 2007). Around the world, landfill accounts for a significant amount of total methane emission in the past decades. In the UK, for example, landfill accounted for about 46% of the total methane emissions during 1996 (EA, 2008). In addition to landfill sites, methane and  $CO_2$  gas are produced from several other anthropogenic and natural sources containing biodegradable organic materials (Wilson *et al.*, 2008). They can also be trapped in materials such as coal and peat, and be released during activities like mining and piling respectively (Wilson *et al.*, 2008). Over the last two decades, emission from coal mining have reduced considerably, however, it still provides a significant contribution to the total emission (EA, 2008).

On the other hand, VOC prevalence is due to extensive use of solutions of product containing VOC resulting in accumulation and release of considerable quantities to the environment. Compounds such as trichloroethylene (TCE) and toluene are present in diverse products and are commonly among the controlling contaminants in remediation projects (Siegrist *et al.*, 2002). In addition, and in fact most importantly, accidental discharge or leakage from petrol underground storage tank and indiscriminate disposal from dry cleaners and waste chemicals from industrial facilities represent significant sources of VOC released

to the environment (Tillman and Weaver, 2005). A significant level of VOC can also be found at landfill sites.

As noted by Wilson *et al.* (2008), the gas generation and migration patterns of each of these sources differ both in terms of volume and duration and as a consequence vary in their potential risk level.

## 1.2.2. Generation / Migration Processes in the Subsurface

Migration of VOC and ground gases in the subsurface is caused by similar processes that affect contaminants transport in groundwater (Choi *et al.*, 2002). For a gas to migrate from its source there must be driving forces and available pathway. These driving forces include: diffusion, advection (due to atmospheric pressure changes or density gradient), and other environmental parameters such as borehole pressure, groundwater level and temperature (Morris *et al.*, 2008, Tillman and Weaver, 2005).

#### 1.2.2.1. Diffusion

The movement of gas in the subsurface is largely affected by diffusion. Under most environmental condition, gradient in gas concentration will cause gas to flow from locations of higher concentration towards locations of lower concentration (Massman and Farrier, 1992; Tillman, 2005; Ho and Webb 2006). The same is applicable to volatile organic compound as diffusion is regarded as main migration mechanism (Bartelt-Hunt and Smith, 2002). Many studies have confirmed that gas concentration in soil-gas phase in unsaturated media increases with increasing depth creating a concentration profile (Choi et al., 2002; Thornstenson and Pollock, 1989). For a long time, diffusion has been described as a dominant transport process for VOC and ground gases. According to Ho and Webb (2006), diffusion affects the spatial distribution of VOC thereby increasing the probability of detecting the VOC in the subsurface and hence aiding remediation effort. On the other hand, diffusion is also largely responsible for VOC and gas migration in the vadoze zone to the water table causing groundwater contamination (Ho and Webb, 2006; Choi et al., 2002). As a result, most measurements procedures in risk assessment and predictions have focussed on diffusion as the primary transport mechanism (Tillman and Weaver, 2005, Choi et al., 2002; Ho and Webb, 2006). However there are many instances when diffusion is not the principal transport mechanism particularly for volatile organic compounds. Several other factors have been identified some of which are discussed in the sections below.

## **1.2.2.2.** Advection (Atmospheric Pressure - Driven)

In addition to diffusion, advective transport in the soil-gas phase has been identified as an important transport mechanism in the subsurface (Tillman *et al.*, 2003). Apparently, advective flow in the gas phase is mostly driven by changes in atmospheric pressure as it is considered as dominant driving force for gas migration (Morris *et al.*, 2008; Choi *et al.*, 2002). Pressure- driven advection occurs when there is pressure differential in soil-gas, causing gas to flow and carrying any vapours present with it (Tillman and Weaver, 2005). In addition, Speight (2008) reported that the resulting pressure differential between borehole pressure and atmospheric pressure allows gas to move either vertically or laterally depending on whether the atmospheric pressure is higher or lower than the borehole pressure. However as atmospheric pressure increases, gas may be retained temporarily in the subsurface as new pressure balances are established (Speight, 2008).

There is a general assumption that atmospheric pressure changes can induce gas flow in the unsaturated zone to such an extent that the advective flux of organic vapours in unsaturated zone can be significant relative to the gas-phase diffusion flux of these organic vapours (Choi *et al.*, 2002, ). Thornstenson and Pollock (1989) found that a very small pressure gradient can produce advective fluxes of the same magnitude or even greater than diffusive flux in a natural system. On the other hand, diffusive fluxes can also produce pressure gradients of the same magnitude. Wilson *et al.* (2007) also reported that a sharp fall in atmospheric pressure over a small range sometimes has the potential to release a greater concentration of gas than a gradual drop over a greater pressure range

Generally, an inverse relationship between atmospheric pressure and ground gas concentration is widely documented in literature. This may not be true in all situations as there are variations in these parameters and so are their relationships. Modelling experiments by numerous researchers have confirmed that at falling pressures, the ground gas will increase in volume, resulting in increased emission rates as the gases increase in concentration (NHBC, 2007; Choi *et al.*, 2002; Tillman and Weaver, 2005). Conversely, rising atmospheric pressure may cause migration of 'clean' air from land surface into the

subsurface, diluting soil gas concentration (Choi *et al.*, 2002; Tillman and Weaver, 2005; NHBC, 2007). This phenomenon is referred to as barometric pumping, the inward and outward movement of subsurface air in response to cyclical changes in atmospheric pressure (Auer *et al.*, 1996).

In another study, pressure is thought to increase solubility of ground gases resulting in lower concentration within the ground as more gas will be dissolved in water (NHBC, 2007; Mogollon *et al.*, 2009). Conversely, a pressure drop could cause the release of dissolved gas from groundwater into pore spaces and subsequently into atmosphere or along migration routes (NHBC, 2007).

Consequently, accounting for diffusion and atmospheric pressure effect is very important in understanding gas migration from the subsurface and an important aspect of conceptual modelling in risk assessment. These processes often make site investigation a complex task. It is therefore expected that monitoring techniques will allow reconciliation of these complex relationships.

#### **1.2.2.3.** Groundwater level

Increase in groundwater level as a result of high levels of precipitation will reduce the available pore space in which VOC, methane and carbon dioxide can exist in a gaseous state (Wilson *et al.*, 2007; NHBC, 2007). The increase in peizometric head will favour a significant increase in concentration and consequently creates upward movement of gases and their release to the atmosphere (Wilson *et al.*, 2007; ATSDR 2001). The change in water table may also be a response to change in barometric pressure. A rise in water table level due to precipitation would increase pressure in soil pore spaces, hence increasing flow of ground gases into service ducts, building voids, etc.

Another effect of precipitation would be a temporary sealing of the ground surface, either trapping ground gases within the ground or causing emissions of ground gases in a different location (Wilson *et al.*, NHBC, 2007). Where the ground gas is trapped, generation is likely to continue at the same rate, which will result in increased gas pressure (NHBC, 2007). Furthermore, if prolonged sealing occurs, aerobic conditions may become anaerobic,

causing increased methane generation. When the surface dries out, release of ground gases may occur at a faster rate until a state closer to equilibrium is reached (NHBC, 2007).

### 1.2.2.4. Temperature

Changes in daily and seasonal temperature will have impact on the rate of biological activities which are considered to influence ground gas production. Studies show that increases in temperature stimulate gas movement while also increase gas diffusion, so that gas might spread faster in warmer condition (ATSDR, 2001; Speight, 2008). However, at freezing temperature, the surface soil may create a barrier to upward gas migration causing the gas to migrate horizontally through soil (ATSDR, 2001; Speight, 2008).

Temperature also affects solubility of gas as decrease in temperature favours increase in solubility and vice versa. In other words, the higher the temperature the more mobile the gas becomes (Wilson *et al.*, 2007; ASTDR, 2001). However there is variation in the response of some compounds, such as benzene, to changes in temperature. The available literatures show that the extent of these influence on gas migration have not been adequately researched suggesting that either the impacts are not significant in ground gas monitoring or that the available monitoring procedures are not adequate for recognising clear trend.

#### 1.2.3. Health Hazards

The health and other hazardous effects of elevated concentration of VOC,  $CH_4$  and  $CO_2$  and their potential migration into buildings have gained significant attention in the UK due to a number of vapour intrusion and explosion incidents that occurred in the past, for example *Loscoe* explosion in March 1986 (EA, 2008). This resulted in a few temporary evacuations of residents in housing estates built on top of old landfill sites where sufficient venting of gases have not occurred (EA, 2008).

Methane is a flammable gas and when mixed with air at a volume between LEL (lower explosive limit) of 5% and UEL (upper explosive limit) of 15% can be highly explosive (ATSDR, 2001). At high concentration, landfill gas also poses an asphyxiation hazard when it collects in an enclosed space such as basement by displacing the existing air and creating an oxygen-deficient environment (ATSDR, 2001).

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).

## 1.3. Existing Monitoring Techniques and Their Associated Flaws

As detailed above, there exist complex interactions of several factors responsible for generation and migration of VOC and other ground gases which in turn makes site monitoring a complex task. In the past years, several monitoring techniques have been used for characterization of contaminated sites and these have helped to shape the policy direction of development of land and remediation strategies.

Monitoring approach for VOC, CH<sub>4</sub>, and CO<sub>2</sub> in contaminated sites can be sub-categorised into sampling, extraction and/or preservation and analytical techniques.

#### **1.3.1.** Sample Collection

Investigating VOC contamination in the subsurface involves several components, and specific activities are required to assist in delineating the current nature and extent of contamination and to 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 samples 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 samples is achieved, results will not present a realistic assessment of contamination present. However, sampling is regarded as one of the most critical components of this exercise. It involves specifying a position in space and time and often followed by collection of soil and/or groundwater sample upon which measurement can be made either on-site or at a remote location (Siegrist 2003). Soil samples are collected at different depth below the ground using; a hydraulic probe sampler (Geoprobe), a JCB to dig a trial pit, or borehole excavation using a window sampler or a cable percussion rig. Samples are contained in headspace glass vials with Teflon lined silicon septum caps, or

brown glass jars sealed to contain the minimum amount of air possible (West et al., 1995). This is to minimise further breakdown and volatilisation of contaminants when in contact with air and sunlight. The subsamples are then sent to off-site laboratory for analysis or in the best case on-site analysis are performed where possible.

#### **1.3.2.** Extraction and Preservation Methods

Before samples are ready for analysis, extraction and preservation of subsamples are performed. Different extraction and preservation techniques are used depending on whether the samples are collected from free phase or solid phase. For free phase samples, analysis are performed directly while for solid phase, VOC and other gases must be separated from the soil subsamples. The available extraction techniques include: purge and trap (also called dynamic headspace), solvent extraction (using methanol or hexane), static headspace, and solid phase micro-extraction (SPME).

### **1.3.2.1.** Purge and Trap (Dynamic Headspace)

Originally developed for water analysis, purge and trap concentration method, also called dynamic headspace, has been widely used for extracting VOCs from various matrices; solid, water, other liquids and air (Lee et al., 2001). Its use for measuring VOC was based on the assumption that soil VOCs equilibrate with soil very rapidly. The process comprises basically three steps: purging, adsorption and desorption-trap baking. See figure 1.34. First, the VOCs in water are purged with clean nitrogen or helium gas to sweep the VOCs out of the water sample; they are adsorbed into the trap (Tenax/charcoal/silica gel) and once the purging is complete, the trap is then quickly heated at high temperature and back-flushed with inert gas to desorbs the component onto a gas chromatographic column for analysis (Lee et al., 2001; Down and Lehr 2004; Askari et al., 1996).

Over the years, the effectiveness of this technique has been strongly criticised by various studies. Studies have shown that purge and trap only measures a small fraction of total soil contaminants since it only measures the readily desorbable organic contaminants from soil pore spaces and external soil surfaces but not contaminant that has diffused into internal micropores of soil matrix (Askari et al., 1996).

Another shortcoming in purge and trap techniques is the excessive preparation time. To efficiently remove the analytes from the trap, carrier gas flow rates greater than 5mLmin<sup>-1</sup> are required (Supelco, 1998). The capillary column that is most compatible with this high flow rate is 60-105 m in length and large bore of 320-750µm and they normally take about 30-50 minutes for analysis (Supelco, 1998).



Figure 1.34 Sample preparation for VOCs: (a) Purge-and-Trap extraction (dynamic headspace), and (b) Static headspace extraction (SHE). Source: (Zhang, 2007)

### **1.3.2.2. Static Headspace Extraction (SHE)**

Static headspace extraction, also known as equilibrium headspace, is normally used for analysis where complex extraction of the analytes is not required (Grob and Barry, 2004). Two phases are in equilibrium in a sealed vial, the gas phase (g) and the sample phase (s), see figure 1.34. Sample preparation for SHE is usually simple and straightforward. Once the sample phase is introduced into the vial and the vial is sealed, volatile components diffuse into the gas phase until the headspace has reached a state of equilibrium while a portion of the headspace is swept into a gas chromatograph. The sample is taken from the headspace either by manual injection or by the use of an auto-sampler. The response of limit of detection of compounds in SHE depends largely on their respective partition coefficient. Compounds with high partition coefficient have relatively low responses and high limits of detection while compounds with low partition coefficient have relatively high responses and low limits of detection (Zhang, 2007; Grob and Barry, 2004).

In comparison with purge-and-trap technique, equipment needed is minimal, but the detection limit is comparable (Zhang, 2007; Grob and Barry, 2004). However, both methods cannot analyse compounds with a very low volatility (Zhang, 2007; Grob and Barry, 2004).

#### 1.3.2.3. Solid Phase Micro-extraction (SPME)

Solid phase microextraction (SPME) is a relatively new method of sample extraction. Like purge and trap, SPME is a solventless extraction procedure but SPME does not require the complex instrumentation of purge and trap methodology. SPME simply involves immersing a phase-coated fused silica fibre into the liquid sample or the headspace above the sample, to adsorb the analytes of interest. The adsorbed analytes are thermally desorbed in the injection port of the GC and transferred to the capillary column (Supelco, 1998). Similar to purge-and-trap, detection limits differ from compound to compound. In SPME, detection limit depend on the distribution constants and polarity of the analytes. Selectivity can be altered by changing the phase type or thickness (Supelco, 1998). For example, the small distribution constants and low polarity of chlorinated and aromatic VOCs dictate the use of a thick, nonpolar phase for efficient extraction (Supelco, 1998).

Several factors affect the precision of the method: positioning of the fibre in the injector it must be in the hottest part during desorption, "a consistently low cryofocusing temperature, and the time lapse between analyte extraction and desorption, short lapses minimize evaporation of volatile analytes from the fibre" (Supelco, 1998). Precision can be increased by dividing a sample into multiple small aliquots and extracting each aliquot. "A 2mL vial containing analytes with high distribution constants can be depleted after one extraction, and can be exhaustively extracted if required" (Supelco, 1998).

#### 1.3.3. Analytical Techniques

#### 1.3.3.1 Gas chromatography

Gas chromatography (GC) is an analytical technique for separation and analysis of complex mixtures of compounds based primarily on their volatilities. GC provides both qualitative and quantitative information for individual compound present in a sample. Compounds move through a GC column as gases, either because they are normally gases or they can be heated and vaporized into a gaseous state (Welder,?; Gallagher 1997). The separation occurs

through the partitioning of the sample between two phases; a stationary phase which can be either solid or liquid, and a mobile phase (gas) while individual component move through the column at a rate dependent upon its partition coefficient. (Welder,?; Gallagher 1997)

Sample can be injected in two different ways depending on whether the sample is gaseous, liquid, or solid. Liquid samples are generally injected by means of a calibrated hypodermic syringe through a silicon rubber septum into a metal or glass-lined metal injection port, while gaseous samples are introduced by means of a valve and sample looping system (Ho et al., 2006). The injection techniques used for solid is somewhat similar to that of liquid. In order to produce sharp chromatographic peaks, with minimum peak overlap, solid and liquid samples must be vaporized rapidly upon injection by maintaining the injection port at a temperature greater than the components boiling point (Ho et al., 2006). As compounds come off the GC column, they reach a detector. Ideally, components of the mixture will reach the detector at varying times due to difference in the partitioning between mobile and stationary phases.

There are several detectors types that can be used in combination with GC to determine volatile organic compounds depending on the analyte of interest. These include a photo-ionization detector (PID), flame ionization detector (FID), flame photometric detector (FPD), mass spectrometry (MS), ion mobility spectrometer (IMS). The advancement in sensor technology now allows the use of hand held device such as PID and FID for in-situ measurement. The most commonly used are potable GC-MS and handheld PID for gas and vapour respectively.

#### **1.3.3.2 Photo-ionisation Detector**

PID is capable of determining VOCs, gasoline vapours, jet fuel, petroleum gas, benzene, and other organic gases except methane (Wilson et al., 2007). It is highly sensitive, and can detect VOCs at low toxic threshold with over 250 gases and gas mixtures (Wilson et al., 2007). It can be used both separately and in combination with other equipment. Although its readings are sometimes compromised by extreme temperatures, humidity and rain, a quick turnaround data with specific advantage of avoiding analyte loss could still be achieved (Minnich, 1993). However, the gains in time and efficiency still need to be complemented by increased sampling frequency to provide sufficient accurate data (Mitchell et al., 1993).

#### **1.4.** Associated Flaws

In general, the methods suffer from various random and systematic errors which affect the accuracy of the measured analytes. Although, the advancement in sensor technology and the availability of field equipment have significantly reduced the cumbersome nature of the monitoring procedure, however, the measurement is not direct making the inference of gas concentration and flux unrepresentative.

Current studies have identified two major flaws in 'spot' sampling techniques.

i) <u>Insufficient data due to low sampling frequency</u>: It has been recognised that data from spot sampling techniques are insufficient to account for temporal variation in gas concentration. In order words, the temporal variability in gas concentration is greater than the sampling frequency of spot sampling, and therefore not representative of the gas regime (Morris et al., 2008).

ii) <u>Concentration not Flux</u>: Spot sampling only measures gas concentration from the sample taken from the headspace where gas from the surrounding ground accumulates. Inferring flux from this measurement is erroneous since the time dimension in the gas regime is not accounted for. Gas fluxes must be in unit of volume per time and cannot be measured directly without time series data (continuous measurement).

## 1.5. How could Continuous data allow these flaws to be remedied?

#### 1.5.1. Gasclam® Continuous In-Borehole Gas Monitor (IGM)

Continuous monitoring is a new and evolving methodology in ground gas risk assessment. This is made possible by the newly available state of the art In-borehole Gas Monitor (IGM); *Gasclam*®; *see figure*1.51 pictured below. Gasclam® IGM is the latest gas sensor technology that allows continuous unmanned measurements of ground gases such as CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>S, VOC and other environmental parameters that may affect their migrations such as atmospheric pressure, borehole pressure, temperature and peizometric head. Until February this year, it was not possible to measure VOC with the monitor. The latest modification on Gasclam® now have PID sensor attached thereby making it possible to measure continuously VOC in contaminated land. However, the successful use of the sensor in borehole environment is yet to be demonstrated.



Figure 1.51: Gasclam® In-Borehole Gas Monitor. Picture showing both bottom and head view Source: (Morris et al., 2008 ; http://www.gasclam.co.uk/downloads/gasclambrochure.pdf)

Unlike spot sampling techniques where boreholes are sealed before sampling and allowing gas to build up, the IGM fits securely within a borehole while it allows for controlled venting of the borehole. *Gasclam*® has a great ability for intense monitoring at higher temporal resolution for gas concentration and other environmental parameters.

#### 1.5.2. Continuous Data

Continuous data obtained through IGM addresses the identified flaws in the traditional techniques in the following ways:

First, the ability to measure continuously for a long period of time allows temporal variability to be quantified and accounted for, and as a result allows recognition of any discrepancy between sampling frequency and concentration variation (Morris et al., 2008, Todman, 2008). This is achieved by allowing sampling to be performed at higher temporal resolution than the variability of gas concentration thereby allowing optimum sampling frequency to be identified (Morris et al., 2008; Todman, 2008). Temporal variability is addressed in spot sampling techniques by collecting multiple samples from the same sampling point over a long period of time with the aim of providing an improved understanding of average gas concentration over time (McHugh and Nickels, 2007). However, Todman (2008) noted that short period of intense or continuous monitoring may be shown to be better at reducing the uncertainty in risk prediction than long-term periodic

sampling. Accounting for spatial and temporal variability is very important for an efficient and effective investigation program at remediation sites (McHugh and Nickels, 2007). This is because a large number of spatially and temporally separated samples are required to accurately characterize average gas concentration in the sampling media (McHugh and Nickels, 2007). The available guidance documents also recognize the impact of temporal variability in site characterization but provide very little insight on how these should be addressed during site investigation since most of the guidance documents are premised on data from spot sampling techniques.

Also, the collection of multi-parameter time series data will allow any discernible correlation between gas concentration and environmental parameter to be identified. Correlation of multi-parameter time series data will be useful in identifying those parameters with major influence on gas concentration variation and therefore a meaningful inference of production and/or migration through these correlations could be made. Since these parameters also exhibit temporal variation, variability in their correlation will be expected. The analysis of this variability will allow a better understanding of the gas migration and / or production processes which would not have been possible without time series data. Measuring concentration is not enough for effective site characterisation and risk prediction but also quantifying the gas flux. Morris et al., (2008) noted that the quantification of risk requires accurate measurement of concentration and fluxes and these can only be achieved by technique that enables collection of time series data.

Alternatively, IGM allows concentration measurement to be linked directly to gas flux by characterising gas production rates in the sampling boreholes (Morris et al., 2008). By applying pump test method as hydrogeologist do in characterising groundwater production rates, short term time series data for ground gas can be achieved. This is done by purging the boreholes at a constant rate and monitoring response to that perturbation. Inference of gas flux could then be made from the recovery profile generated from this perturbation.

In summary, time-series data allows temporal variability to be quantified and accounted for and can ultimately improve understanding of processes of gas migration. Its great potential of reducing errors arising from both the indirect nature and temporal variability of the measurement will significantly reduce uncertainty in risk prediction (Morris et al., 2008). Continuous measurements will prove highly essential for site characterisation with respect to gas production as this will allow a monitoring programme that not only attempts to resolve sampling frequency and gas variability problems in the existing techniques, but also provide data feedback for development of conceptual model and scientific basis for overall risk prediction. An improved conceptual model will provide a better understanding of the complex interactions between environmental parameters and gas regime which hitherto could not be achieved by the traditional monitoring techniques

There is therefore a requirement to demonstrate the utility of continuous monitoring as an improved way of monitoring ground gases in contaminated land.

#### 1.6. Aim

This research work therefore aim to demonstrate the utility of continuous monitoring to remedy the flaws in the current monitoring ('spot' sampling) of ground gases.

## 1.7. Objectives

The following objectives are considered during the course of this research:

- To determine whether PID will work continuously in borehole environment. This is to show that PID can continuously detect VOC in borehole environment, and if it does, whether variations are accounted for.
- ii) To demonstrate variability of gas concentration at different time scales and therefore the inefficiency of periodic sampling. This is to show that the frequency of variability in gas concentration at different time scale (short time and long time) is greater than the sampling frequency in spot sampling.
- iii) To demonstrate the inference of gas production / migration from concentration by improved conceptual model through correlation of environmental parameters. This is to identify any correlation between parameters, and as a result determine which environmental factors play dominant role in gas production and/or migration, and also determine whether these relationships are consistent or not.
- iv) To demonstrate inference of gas production / migration through pump test. This is to determine whether the use of pump test for characterising gas production rates in borehole is practical, and to determine under what condition the pump test data are predominantly a function of gas flow rates than of the borehole.

# 2.0 Methodology

## 2.1. Data Collection

This research has at its very core the understanding of processes of ground gas migration and how the new methodology compares with the existing techniques for ground gas measurement. Field measurements were conducted where IGM were deployed to various sites for monitoring exercise. In addition to the field measurement, laboratory experiment in the form of a physical model was set up to simulate gas migration in the subsurface as a way of understanding the processes that govern subsurface transport. The results from the model will also be compared with the field measurement and, when possible, correlations will be drawn to validate the methodology.

## 2.2. Field Data

Field measurement of VOC, methane, carbon dioxide, barometric pressure, borehole pressure, oxygen, temperature, and groundwater level were conducted using Gasclam® In-Borehole Gas Monitor. Comparison was drawn with data that would have resulted from spot technique (GC-MS etc.). The data used is a combination of data from current and previous investigations. Various sites with different contamination history were considered in order to have a comprehensive overview of time series data resulting from the IGM. The sites sampled include former landfill sites and former industrial plant contaminated with VOC. In each case, the equipment was calibrated with gas (methane and carbon dioxide) while VOC was calibrated with 100ppm VOC. Calibration of atmospheric pressure was performed at each site. Gasclam allows measurement to be made both in venting and non-venting mode. Its ability for unmanned measurement meant that data are downloaded through a data logging system simultaneously without tampering with sampling. The device was left on site for a minimum of two weeks and more in some cases. Gasclam can be left on site for three months without power interruption after which the battery will be replaced.

The reproducibility of the data collected, gas production rate and the relationship between flux and concentration were determined by conducting pump test on the sampling boreholes. This involves pumping out the gas at a constant rate and measuring how long it will take the gas to recover i.e. return curve or recovery profile. The result obtained will be compared with that from the laboratory model.

## 2.3. Laboratory Model – Sand *Box* Gas Migration Simulator

The use of laboratory model is based on the understanding that boreholes may not be representative sampling points for gas measurement as these may be affected by prevailing driving forces such as advection, buoyancy and diffusion (Morris et al., 2008). In order to allow a close investigation of gas migration processes under these conditions, both field and laboratory data were used to assess the utility of boreholes as representative sampling points for subsurface gas concentration and gas fluxes (Morris et al., 2008).

By varying the sampling height, concentration data from both field and laboratory boreholes are compared. Pump tests were also performed on the laboratory borehole and gas flux quantified. The result will allow any discernible trend between pump test and gas flow rates to be recognised. Also, it will be possible to determine under what conditions the pump test data are predominantly a function of gas flow rates than of the borehole.

#### 2.3.1. Model Set-up

The main structure of the model is a cuboids' tank with a sealing door on one end; internal dimensions  $200 \ l \ x \ 100 \ d \ x \ 100 \ h \ (cm)$ . The model was filled with porous material (5-micron grain size quartz sand) considered representative of the subsurface. A sub-frame was constructed to support the sand and serve as delivery chamber. The delivery chamber is required for two reasons i) to be able to monitor the concentration and pressure of gas entering the model and ii) to deliver the gas over a larger area to promote dispersion of the gas throughout the model allowing a steady state to be achieved faster (Morris et al., 2008).

For health and safety reasons,  $CO_2$  was used while the behaviour of methane and VOC concentration is inferred. The model contained four vertical cavities (at different sampling height), representative of the boreholes, to which the IGM is attached. Also, there are four miniature gas sensor buried throughout the model and attached to the data logging system that is used in the IGM.

The modelling experiment was divided into two parts. The initial stage involved filling the model with  $CO_2$  gas until saturation is reached. With approximately 17,000 litres of gas delivered at a flow rate of 9lmin<sup>-1</sup>, the model was left running overnight until the concentration in the boreholes attained a steady state (c.a.100% v/v). The second part of the experiment involves carrying out pump tests at different flow rate. Pump test were

conducted by purging the borehole with atmospheric air using an electric pump (Cadet Pump) at constant flow rates of  $9\text{lmin}^{-1}$  for the duration of 5 minutes on each of the boreholes. The air was directed down the borehole using a 5m pipe to promote displacement as this was sufficient to purge the CO<sub>2</sub> concentration in all cases. After purging, the gas sensors were inserted into the boreholes making a gas-tight seal. Sampling was initiated immediately with five seconds sampling frequency and the change in CO<sub>2</sub> concentration (C/C<sub>o</sub>) with time was then recorded. Multiple pump tests at the same flow rate were later carried out on each borehole to quantify the reproducibility of this method for characterising ground-gas recharge. The flow rates were later varied as follows:  $18\text{lmin}^{-1}$ ,  $31.5\text{lmin}^{-1}$ ,  $9\text{lmin}^{-1}$ ,  $6\text{lmin}^{-1}$ , and zero flow, to quantify the effect of different flow rates on ground gas recharge. The data obtained from the test (recovery profiles) will also be used to explain field observation.

The result obtained will help to determine the practicality of pump tests for characterising gas production, particularly in relation to the development of conceptual model. The data obtained will also provide an opportunity to make some observations about the processes of ground gas migration while allowing the dominant control on gas concentration to be recognised. Consequently, it is hoped that the overall results will allow reduction in the uncertainty in prediction of VOC and gas migration in the subsurface, a more site-specific risk assessment and more importantly informed decision on remediation and redevelopment strategies for contaminated sites.

#### 2.3.2. Assumptions and Limitation

For the model experiment, it was assumed that the behaviour of  $CO_2$  in homogeneous porous media is similar to that of methane and VOC. While this may be true for methane, it is difficult at this stage to confirm VOC given that volatility effect are not accounted for. Time was a huge limitation for this research. Given the time frame, available units of IGM, and bureaucracies in sites permission, it was impossible to collect data from different sites with varying land use history.

# **Result and Discussion**

### 3.1. Determining whether PID will work continuously in borehole environment

As observed in literature, the accurate measurement of volatile organic compound in the subsurface is difficult to achieve due to errors relating to sampling, storage and analytical techniques. In response to these uncertainties, field monitoring device such as handheld PID has provided the impetus for improved efficiency in monitoring particularly for short term environmental project (Minnich, 1993). The opportunity offered by Gasclam monitor allowed this to be demonstrated. Like methane and carbon dioxide, time series data of VOC provides an opportunity for obtaining the true vapour concentration in the surface which hitherto could not be obtained. Since the conventional use of PID is for discrete measurement, then the question is; can PID be used continuously to monitor VOC in borehole environment?

For this demonstration, the new Gasclam instruments were deployed to a known VOC contaminated site. Gasclams were installed in two boreholes (BH 01 and BH 02) in venting mode and with a sampling frequency of one hour. After two weeks of monitoring, the equipment (one unit) was pulled out from BH 02 and installed in BH 03, another neighbouring borehole to BH 01, for one month of monitoring. BH 01 is the closest to the source of contamination while BH 02 and BH 03 are neighbouring boreholes. The time series data obtained from the monitoring is shown in Figure 3.1.

As expected, the concentration of VOC in BH 01 is significantly high compare to borehole BH 02 during the monitoring period given the proximity of BH 01 to the identified source. The value ranges from 89 ppm to 239 ppm for BH 01, and -10 ppm to 23 ppm in BH 02. Decrease in concentration over time is observed in BH 01 while the neighbouring BH 02 is slightly increasing suggesting that VOC is migrating from BH 01 to BH 02. The previous investigation at the site was conducted using headspace GC-MS and the result obtained confirmed high and low concentration of VOC in BH 01 and BH 02 respectively. The result also showed that no VOC was found in BH 03. Gasclam was moved from BH 02 to BH 03 to confirm this and to improve the confidence of the demonstration. The time series data shown in Figure 3.1 confirm no VOC was detected in the borehole. The initial concentration

value on the 17<sup>th</sup> May (BH 03) was the effect of the previous reading from BH 02, and within a very short period of time the concentration went back to zero. The zero measurement in Gasclam was set to between 0 and -15.



Figure 3.1. Time series data indicating presence of, and variation in concentrations of VOC in the three boreholes. The sudden increase in VOC concentration in BH 01 was a result of pump test performed on the borehole which indicates VOC was mobilised from the surrounding as a result of pump test.

The detection of VOC in the two boreholes, as shown in the figure, shows that PID can be successfully used to obtain time series data in borehole environment. Unlike the handheld one whose readings are affected by extreme temperature, humidity and rain, Gasclam PID sensor is protected against such disturbances. Although the trend observed depends on a number of environmental factors which therefore make this conclusion difficult to suggest, its observation would not have been possible if spot sampling techniques were used. The detail of these factors is provided in the subsequent section. The data also captured the variability in concentration change further confirming the potential for continuous monitoring in ground VOC risk assessment.

This demonstration indicates that PID could be made more effective through continuous monitoring. Although the measurement from handheld device is usually considered reliable, the inference of gas regime from their periodic use is not since variability in concentration could not be accounted for. Therefore, adapting PID to work in borehole environment provides a novel application for continuous monitoring of VOC.

# **3.2.** Demonstrating variability of gas concentration at different time scales and therefore the inefficiency of periodic sampling

Gas concentration can vary on a range of different timescales. If this is the case, what about the frequency of that variation? The ability to capture short term and long term gas concentration variation during monitoring will provide meaningful summary of concentration measurement.

Figure 3.21 shows the time series data from a gassing landfill site indicating variations in gas concentration from site A. Although the concentration range is not very high, the variability within the short time is significantly high. Figure 3.22 (site B) on the other hand indicates high concentration range but relatively low frequency of concentration variability.



Figure 3.21: Time series data from Site A indicating variation in methane and carbon dioxide concentration during a short time scale. The gridlines indicate random samples selected from the continuous data to represent spot sampling data.



Figure 3.22: Time series data from Site B indicating variation in methane and carbon dioxide concentration on a long time scale.

In both cases, the minimum and maximum concentrations were recorded several times. When compared with data that would have resulted from spot sampling, it can be observed that between relatively small sampling frequencies a significant difference in concentration does exist. This can result in uncertainty if the spot sample measurement is used in risk assessment.

Accounting for temporal variation in ground gas concentration is an important aspect of risk assessment as this does not only reduce evaluation errors in risk prediction but also offers insight into different other factors that affect gas regime. To be able to do this, high frequency data is required. The concentration variations normally experienced during spot sampling are difficult to explain due to very low sampling frequency, and are often referred to as errors or anomalies. Sampling at high frequency for extended period of time will make observations more meaningful and therefore provide basis for additional information before any inference on gas regime and risk potential could be made.

By identifying variations in concentration we can begin to ask questions about factors responsible for these fluctuations thereby improving our understanding of the processes controlling ground gas movement and also improving our judgement on risk potential.

#### **3.2.1.** Concentration Duration Curve

With time-series data, a meaningful summary of concentration measurement can be generated. At present the only meaningful summary is whether a borehole ever had a concentration measurement greater than 5% methane and 1%  $CO_2$  (Morris et al., 2008; Sladen et al., 2001). In these cases (sites A and B), the use of spot sampling to identify the worst case will be misleading. By applying the concept of hydrological flow duration curve, we can generate concentration duration curve which tells us what the worst case concentration is. Figure 3.23 shows the concentration duration curve that resulted from time series data from site B (i.e. figure 3.22). It summarises the concentration measured into percentage time and compare it with random samples from the continuous data to represent spot sampling.



Figure 3.23: Concentration Duration Curve ( $CH_4$  and  $CO_2$ ) resulting from time series data from site B. The grey and dotted are random samples from continuous data to represent spot sample

As shown in the figure, the continuous data concentration duration curve (CDC) indicates that the concentration of  $CH_4$  during the monitoring period is above 50% 20% of the time and below 30% 25% of the time and for  $CO_2$ , above 20% 70% of the time and below 20% 30% of the time. The same could not be said of the 'spot' sampling data as there is disparity between the two sampling regimes. Consequently the apparent risk from the two regimes is very different. The time series data gives greater confidence that the 'worst case' concentration has been observed and also tells us more about the temporal dynamics of the system. As the confidence increases with increasing representative data, CDC can become a useful tool in risk assessment.

# **3.3.** Inference of gas production / migration from concentration by improved conceptual model through correlation of environmental parameters

In order to understand the variations observed in gas concentration, it is important to monitor also the changes that occur in measurements of environmental parameters that play significant role in gas migration. So, when faced with multi-parameter time series data, the first thing to look for is if any discernible trend can be identified. The correlations to look for include correlation between; atmospheric pressure and gas concentration, borehole pressure and gas concentration, and temperature and gas concentration. It is generally assumed that concentrations are higher when pressure is low and vice versa. Current guidance (e.g CIRIA) recommends collecting at least one spot sample below 1000mbar in falling pressure. However we should bear in mind that identifying trends in parameters is not enough but the inference that could be drawn about the gas production and/or migration processes from that relationship. Different scenarios from three sites (A, B, and C) were considered to give a comprehensive understanding of different relationship that could be experienced when dealing with time-series data.

Figure 3.31 shows the continuous data from site A. The widely reported inverse relationship between concentration and pressure is observed. As pressure increases, concentration of  $CO_2$  decreases and vice versa. In addition, the concentration continues to vary in response to changes in atmospheric pressure and not absolute pressure as recommended in the guidance document. However for this site, we can conclude that atmospheric pressure plays the dominant role in gas migration and/or production.



Figure 3.31: Time series data, site A, indicating correlation of atmospheric pressure with carbon dioxide. The expected inverse relationship is observed



Figure 3.32: Multi-parameter time series data from Site B indicating correlation of atmospheric pressure with gas concentration. No correlation with temperature.

Figure 3.32 shows the time series data from a gassing landfill in site B. As observed, changes in atmospheric pressure result in changes in borehole pressure. This indicates that there is potential for gas migration as the borehole can draw gas in due to atmospheric oxygen introduced into the surface soil. The change in atmospheric pressure also correlates with change in gas concentration. However the correlation is not as expected. Unlike site A, the drop in pressure results in decrease in gas concentration and vice versa. This is in contrast with the widely reported inverse relationship as experienced in site A. As there is no differential pressure, it is more likely that atmospheric pressure alone is responsible and not gas generation, and therefore more likely to be the dominant control. On the other hand no correlation is observed between gas concentration and temperature. While the data illustrates a potential for gas migration, it is uncertain whether there is potential for gas generation or not.

Figure 3.33 shows multi-parameter time series data from a borehole adjacent to a landfill in site C. The figure shows a decrease in atmospheric pressure resulting in a continuous lag between change in borehole pressure and atmospheric pressure throughout the monitoring period.



Figure 3.33: Multi-parameter time series data from Site C indicating correlation of atmospheric pressure with ground gases during collected during freezing temperature.

The resulting negative borehole pressure indicates that there is potential for gas migration as borehole could suck in air. Therefore increase in gas concentration would be expected. However, no change in concentration, and no correlation between atmospheric pressure and concentration is observed. During the monitoring period, low temperature was observed indicative of a frozen ground condition. This suggests that the frozen ground creates a disconnection or physical barrier between the subsurface and the atmosphere thereby preventing pressure from equilibrating. This may also mean that gas is trapped in the subsurface. As this is not quite apparent, it may be risky to say that the worst case has been observed.

However the same borehole (site C) was monitored three months after the previous investigation. The multi-parameter time series data obtained is shown in Figure 3.34. As shown in the figure, temperature has increased significantly, and the ground defrosted thereby allowing gas to migrate. This is in agreement with Wilson et al. (2007) and Speight (2008) that the higher the temperature the more mobile the gas becomes. As a result the relationship between concentration and atmospheric pressure becomes apparent. The expected inverse relationship between methane concentration and atmospheric pressure is observed as decrease in barometric pressure corresponds to increase in gas (methane and carbon dioxide) concentration. Again as there is no differential pressure, it is more likely that atmospheric pressure alone is responsible for this not gas generation. The dominant control on gas migration in this case is temperature and not atmospheric pressure alone.



Figure 3.34: Multi-parameter time series data site C indicating correlation of atmospheric pressure with ground gases during increased temperature. Data was collected 3 months after the previous investigation.

These examples illustrate that there are correlations between environmental parameters and gas concentration but also that the generally assumed relationships do not always exist. Relationships are different from site to site and from borehole to borehole and these relationships are not absolute, they do change. However, where correlations do exist, they could give confidence in the prediction of concentration from other parameters. When these correlations are drawn, the inefficiencies in spot sampling techniques become even more apparent. Without high frequency data inferring gas regime is dangerous as important

processes would have been missed during spot sampling. Continuous data therefore offers high confidence for data quality through which an improved conceptual model could be achieved. An improved conceptual model will recognise that the widely reported relationships between environmental parameters and concentration do not always exist, and therefore prediction of gas regime or inferences about processes based on these relationships may be risky. Therefore, in order to quantify risk, it is important that risk assessments are designed in such a way that each site and each borehole is characterised rather than extrapolating result from one site to another as it is currently practiced.

# 3.4. Inference of gas production / migration through pump test

To corroborate the correlation between environmental parameters, inference of gas production / migration (i.e. gas flux) can be drawn from short term monitoring by performing pump test on boreholes. The use of pump test for characterising gas production rates in borehole stem from hydrological studies. Hydrogeologists rely on pump test to characterise production rates of water from boreholes. With times series gas concentration data, similar approach was adopted. By performing pump test, recharge characteristics of individual borehole can be identified from which production and/or migration rate can be quantified. In doing this, we can determine if the use of pump test for characterising borehole is practical (reproducible), and hence, determine under what condition the pump test data are predominantly a function of gas flow rates than of the borehole.

## 3.4.1 Model Output

Prior to the tests,  $CO_2$  gas was delivered into the model until saturation is reached. Figure 3.41 shows the gas concentration in the model. Initially the gas was delivered at a flow rate of 9lmin<sup>-1</sup>. At this flow rate, the gas supply lasted for approximately 30hrs. The gas reaches the borehole in the expected order, the entry chamber filling up in less than an hour, and then BH 1, followed by BH 2, BH 3 and BH 4 respectively. The model became saturated in about 19hrs after which the pump test was commenced.



Figure 3.41: Gas concentration in different borehole across the model after 18.5 hrs with flow rate 9lmin<sup>-1</sup>.

#### 3.4.2. Pump Test

Multiple pump tests were then performed on all the channels (boreholes) in the laboratory model at constant flow rate of 9lmin<sup>-1</sup> to establish the reproducibility of the experiment. The results of the tests and their corresponding recovery profiles are as shown in Figure 3.42.



Figure 3.42: Recovery Profiles of  $CO_2$  after purging for 5 minutes, at flow rate of (9lmin<sup>-1</sup>). Three replicate tests were performed on each of BH 1 and BH 2 and two each on BH 3 and BH 4.

The gradient of the recovery profiles, Figure 3.42, for BH 1, BH 2 and BH 3 after three replicate each are identical and similar for BH 4, indicating that the experiment is reproducible for the same borehole under similar conditions. This confirms that the use of borehole for characterising gas production rate is practical.

Having established the reproducibility of the experiment, pump tests were conducted at different flow rate and the resulting recovery profiles are compared, see Figure 3.43. No flow condition was introduced to monitor the effect of diffusion on ground gas migration.



Figure 3.43. Recovery Profiles of CO<sub>2</sub> at different flow rates after purging for 5 minutes (laboratory model)

The volumetric flow rates at which the gas was delivered can be converted to velocity (or volumetric flux). Assuming that the model is 50% sand and 50% pores, with 1m x 1m dimension, the surface area through which the gas flows is 0.5 m<sup>2</sup> i.e. (1m x 1m) x 0.5. Therefore the velocities for the flow rates 18 lmin<sup>-1</sup>, 13.5lmin<sup>-1</sup>, 9lmin<sup>-1</sup> and 6lmin<sup>-1</sup> are calculated as 0.6mms<sup>-1</sup>, 0.45mms<sup>-1</sup>, 0.3mms<sup>-1</sup>, and 0.2mms<sup>-1</sup> respectively. These represent the gas flow rates through the porous media. In spot sampling gas flow rates are measured using flow meter and this is used to predict surface emission from which the potential for gas ingress into building is deduced (Wilson et al., 2008). They are either measured in litre

per seconds or meter per second. As noted by Wilson et al., (2008), little guidance exists to suggest which of the flow rates should be used in risk assessment (Wilson et al., 2008). The use of such value is undermined by a number of assumptions and limitation that were considered which could have significant implication for risk prediction. Pump test data provides more practical information about the recharge potential and therefore more insight into the ground gas regime.

The result shows that for each borehole, the gradient of the recovery profile at different flow rate differs as expected, the higher the flow rate, the quicker the gas recharge. This indicates that the way gas concentration recovers in borehole after a pump test is different despite same absolute concentration. However for no flow condition, the profile indicates that the gas diffuses along the concentration gradient. The pump test results therefore allow a direct link between concentration measurement and gas flux. As shown, the rate of recovery depends largely on production and/or migration rates.

The same method was applied on the field at different sites and the results of pump tests conducted are as shown in figure 3.44 (a-c).



Figure 3.44c: Recovery Profiles of CO<sub>2</sub> and CH<sub>4</sub> at site 3 after purging.

As can be seen, the recharge characteristics of the boreholes also differ from each other. Pump 1 took approximately 20 hours to recover to original concentration while pump 2 recovered after 35 hours.



Figure 3.44c: Recovery Profiles of CO<sub>2</sub> and CH<sub>4</sub> at site 3 after purging.



Figure 3.44c: Recovery Profiles of CO<sub>2</sub> and CH<sub>4</sub> at site 3 after purging.

Pump 3 on the other hand took approximately 1.8 hours. The difference in recharge characteristics could also be a function of the borehole geology. However, the field data agree with the model result therefore reinforcing the need to characterise individual borehole to allow for more reasonable inter-comparison. The recovery profile following the pump test is a function of the gas flux and can therefore be used in comparison with other boreholes to quantify gas production rate.

# 4.0. Conclusion

This research work has demonstrated how continuous monitoring technique could remedy the identified flaws in the existing monitoring methodologies.

The study revealed that the measured gas concentrations are significantly influenced by the sampling frequency. As observed, the frequency of variation in concentration is greater than the sampling frequency of spot sampling method. In addition, variations in ground gas concentration at different timescale was revealed thereby highlighting the inefficiency of spot sampling techniques as these variations would have been missed during spot sampling, or reported as errors or anomalies. As shown in the examples, these variations can be experienced between relatively small sampling frequencies. So if spot sampling data are used for risk assessment, important information about the ground gas behaviour would have been missed which may lead to over conservative risk protection design. The application of concentration duration curve for summarising concentration measurement also revealed the uncertainty in the threshold or trigger value presently employed. The result also nullified the general assumption that the quality of data in relation to a contaminated site is primarily determined by the nature of analytical techniques used to collect information as previously suggested. Time series data can improve our confidence on whether a worst case concentration has been observed or not.

It is also shown that by sampling at higher temporal resolution, continuous monitoring helps improve our understanding of different processes that affect the variation observed through the correlation of environmental parameters. Although the widely reported relationship between gas concentration and atmospheric pressure was observed, variation in the relationship was apparent in the three sites considered. Other factors such as temperature were also found to influence ground gas regime. We can infer from this study that the behaviour of ground gas is very complex and so is the relationship between processes that drive them. This provides another line of evidence that could help to improve our conceptual risk assessment model. However, the current regulatory position on gas concentration as indication of risk could be a gross over-reaction to a perceived problem. There is therefore a need to revise these documents so as to accommodate the new line of evidence. In addition the new PID application in continuous monitor, Gasclam®, has been shown to continuously detect VOC in borehole environment without compromising the accuracy of the measurement. This successful demonstration therefore provides a novel application in ground VOC monitoring thereby creating a platform for research and development.

Pump test data from both laboratory and field experiment confirmed that there is need to characterise each borehole on the basis of their production rate as recharge characteristics vary from site to site and from borehole to borehole. While this is important on a short time, it provides data feedback into the known science of ground gas behaviour and provides an insight into site specific risk assessment.

Although it will be correct to say that the temporal dynamics of gas flux and the factors controlling these dynamics have been fairly studied as this is evident in literature, the application of research findings in site monitoring process has been generally ignored partly due to unavailability of adequate technology. However, given that failure to account for true concentration of the contaminant will directly affect the accuracy of risk prediction and ultimately result in ill-informed decision making, it is therefore hope that the new paradigm to site monitoring will help in this reconciliation.

#### 4.1 Further Work

As this is the first time PID is used for continuous monitoring in borehole environment, it will be interesting to see more research work conducted on VOC monitoring. Also more work should be done to monitor the response of VOC to pump test. The initial result suggests that pump test mobilizes VOC in borehole as against evacuation observed in methane and carbon dioxide.

# 5.0 References

Askari M. D. F., Maskarinec M. P., Smith S. M., Beam P. M, and Travis C. C. (1996). Effectiveness of Purge-and-Trap for measurement of volatile organic compounds in aged soils. [Available online] <u>http://pubs.acs.org/doi/pdf/10.1021/ac960009c</u> Accessed 5<sup>th</sup> April, 2009

- Auer, L. H., Rosenberg, N. D., Birdsell, E. M., and Whitney, E. M. (1996). The effects of barometric pumping on contaminant transport. *Contaminant Hydrology* 24: 145 – 166
- Agency for Toxic Substances Disease Registry (ATSDR) (2001). Landfill Gas Primer -An Overview for Environmental Health Professionals. [Available online] <u>URL://http://www.atsdr.cdc.gov/HAC/landfill/html/intro.html</u> Accessed 7<sup>th</sup> May, 2009
- Bartelt-Hunt S. L. and Smith J. A. (2002). Measurement of effective air diffusion coefficients for trichloroethene in undisturbed soil cores. *Contaminant Hydrology* 56 (2002) 193-198

Choi J., Tillman F. D., and Smith J. A. (2002). Relative importance of gas-phase diffusive and advective trichloroethene (TCE) fluxes in the unsaturated zone under natural conditions. *Environmental Science Technology* 36 (14): 3157-3164

- Down R. D., and Lehr J. H., (2004). Environmental instrumentation and analysis handbook. Wiley-Interscience, a Jon Wiley and Sons Inc. pg 177
- Environmental Agency, (2008). Methane http://www.environment-agency.gov.uk/business/topics/pollution/185.aspx
- Grob R. L. and Barry E. F. (2004). Modern practice of gas chromatography (4<sup>th</sup> ed.). Wiley Interscience, A John Wiley and Sons, Inc. Publication.
- Ho C. K., Kelly M., and Itamura M. T. 2006. Measurement of vapour concentrations pg.303-318 In Gas transport in porous media
- Ho C. K., Webb S. W. (2006). Theory and application of transport in porous media In Gas transport in porous media
- 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.
- Lee K. J., Pyo H., Park S., Yoo E., and Lee D., (2001). A study on purge efficiency in Purge and Trap analysis of VOC in water. *Bulletin of Korean Chemical Society* 22(2)
- Mackay D. M. (1998). Is cleanup of VOC-contaminated groundwater feasible? Geological Society, London, Engineering Geology Special Publications 1998;

v.14; p. 3-11. [Available Online] <u>http://egsp.lyellcollection.org/cgi/reprint/14/1/3</u> Accessed 12<sup>th</sup> March, 2009

- Mercer J.W. and Spalding C.P. (1991). Characterization of the vadoze zone *In* Site Characterization for Subsurface Remediation. U.S. Environmental Protection Agency. [Available Online] URL:// <u>http://www.epa.gov/OUST/cat/sitchasu.pdf</u> Accessed 12<sup>th</sup> Feb., 2009
- McHugh T. E. and Nickels T. N., (2007). Evaluation of spatial and temporal variability in VOC concentrations at vapour intrusion investigation sites. [Available Online] URL://<u>http://www.gsi-net.com/Publications/McHugh\_AWMA\_07\_Paper.pdf</u> Accessed 11<sup>th</sup> Feb., 2009
- Minnich M., (1993). Behaviour and determination of volatile organic compounds in soil: a literature review. USEPA Las Vegas Nevada. Available Online <u>http://www.epa.gov/esd/cmb/pdf/voclr.pdf</u> Accessed 15<sup>th</sup> May, 2009
- Morris P. (2008). How to deal with time series ground-gas data, using analytical techniques from other disciplines. [Available Online] www.gasclam.co.uk/downloads/Peter%20Morris.ppt Accessed 11<sup>th</sup> Dec., 2008
- Mogollon J., Dale A., Heureux I. L., and Regnier P. (2009). Seasonal controls of methane gas solubility and transport on anaerobic oxidation of methane in shallow water marine sediments. Geophysical Research Abstracts, vol. 11
- NHBC, (2007). Guidance on evaluation of development proposals on sites where methane and carbon dioxide are present
- 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 Untied 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. Accesses 22<sup>nd</sup> March, 2009. URL//http://www.epa.gov/swertio1/download/partner/2002\_special\_session.pdf
- Speight G. L., (2008). Synthetic fuels handbook: properties, process and performance. McGraw-Hill Education – Europe

Supelco (1998). Fast Analysis of Volatile Organic Compounds by Solid Phase Micro-extraction/Capillary GC. Sigma-Aldrich Co. Available Online URL://http://www.sigmaaldrich.com/etc/medialib/docs/Supelco/Application\_Notes/4602.Pa r.0001.File.tmp/4602.pdf Accessed 3<sup>rd</sup> May, 2009 Thorstenson D. C. and Pollock D. W. (1989). Gas transport in unsaturated zones:

multicomponent systems and adequacy of Fick's laws. Water Resources Research, Vol. 25 (3), pg. 477-507

- Tillman F. D. and Weaver J. W. 2005. Review of recent research on vapour intrusion. U.S. Environmental Protection Agency, Office of Research and development, Washington, DC 20460
- Todman M., (2008). Ground-gas monitoring: the way forward Urban Vision Partnership Ltd.
- USEPA (2004). Monitored natural attenuation *In* How to evaluate alternative cleanup technologies for underground storage tank sites: A guide for corrective action plan reviewers [Available Online]: <u>http://www.epa.gov/OUST/pubs/tums\_ch9.pdf</u> Accessed 5<sup>th</sup> May, 2009
- Welder Cathy (?). Gas chromatography. Course materials and computing resources, Wake Forest University. [Available Online] <u>http://www.wfu.edu/academics/chemistry/courses/GC/index.html</u> Accessed 7<sup>th</sup> May, 2009
- Gallagher D. (1997). Environmental sampling and monitoring primer. [Available Online] ://http://www.cee.vt.edu/ewr/environmental/teach/smprimer/gc/gc.html#theory Accessed 23<sup>rd</sup> March, 2009
- 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 (Available Online) URL: http://pubs.acs.org Accessed 15<sup>th</sup> January, 2009
- Wilson S., Oliver S., Mallet H., Hutchings H. and Card G. (2007). Assessing risks posed by hazardous ground gases to buildings. CIRIA C665, London
- Wilson S., Card G., and Haines S. (2008) The local authority guide to ground gas. The Chartered Institute of Environmental Health: London
- Zhang C. (2007) Fundamentals of environmental sampling and analysis. Wiley-Interscience, a Jon Wiley and Sons Inc. pg. 183-184