

**MONITORING OF BTEX HYDROCARBONS  
IN SOIL ATMOSPHERE  
BY NEW ACTIVATED CARBON CLOTH PASSIVE SAMPLER  
WITHOUT A MEMBRANE**

By Nina Vylkov

A Thesis

Submitted to the Faculty of Graduate Studies  
in Partial Fulfillment of the Requirements  
for the Degree of  
**MASTER OF SCIENCE**

Department of Chemistry  
The University of Manitoba  
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NINA VYLKOV

A Thesis/Practicum submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements for the degree of

MASTER  
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*Is this the region, this the soil, the clime,  
Said then the lost archangel, this the seat  
That we must change for Heav'n, this mournful gloom  
For that celestial light?*

Paradise Lost, bk. I, 1.242

John Milton

1608-1674

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## ABSTRACT

The development and evaluation of a new passive sampler without a membrane and its applicability as an environmental monitor for benzene, toluene, ethylbenzene and xylenes (BTEX) in soil atmosphere is reported. The sampler was deployed at the ground surface and beneath (60 cm) the surface level and measured soil-air fluxes of organic contaminants coming to the surface by the passive sampling element - activated carbon cloth (ACC). The effect of relative humidity on the multicomponent vapour phase adsorption by ACC sampler's performance was determined. Also, a few field demonstrations were conducted at fuel-contaminated sites. The samplers were quantitatively analyzed by liquid extraction and gas chromatography with a flame ionization detector.

It was shown that the ACC passive sampler offers a cost efficient new method of monitoring of organic vapours originating from soil and groundwater contamination. The ACC passive sampler can accurately measure fluxes over both long and short periods. High adsorption capacity and fast adsorption kinetic rate of activated carbon cloth as well as the absence of diffusive membrane in the construction of the sampler allows the cloth to collect sufficient amount of analyte for analysis at very low concentrations (ppb).

The method is inexpensive and practical and can be readily duplicated by others using off-the-shelf equipment and normally available laboratory skills.

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**CHAPTER I**

**INTRODUCTION**

## 1.1. Introduction

Soil contaminants include a very broad spectrum of industrial products released during production, transportation, and storage. Sites of contamination are typically found near some pipelines, chemical plants, gasoline stations, waste disposal sites, and other facilities that are part of modern industrial society. Soil contaminants can cause many problems. For example, contaminants can reduce soil fertility, cause plant damage or death, and become concentrated in the tissues of animals that eat contaminated plants and seeds. Heavy rains can leach these chemicals from the soil and transfer them directly into streams. The migration of contaminants into the water table poses risks to the biosphere, and humans who are exposed through their consumption of contaminated plants, animals and water (1-7). Soil remediation, therefore, is a human health issue as well as an environmental one.

Potential sources of contamination include volatile liquids such as solvents and hydrocarbon fuels originated from chemical spills, leaking underground storage tanks, improper disposal of spent solvents, or contaminated groundwater. Contamination of soils with volatile organic chemicals (VOCs) is widespread in the developed countries of the world (8).

Once these chemicals are introduced into the soil, they will volatilize into the soil gas and can be transported toward building substructures by advection under the pressure gradient that results from temperature differences between indoors and outdoors, wind, and in some instances, the operation of devices

such as furnaces and exhaust fans, or by diffusion if a concentration gradient exists. The VOCs may enter the building through cracks or openings in the substructure, or through building materials (9 - 19).

It is also possible that the VOCs may migrate from the soil first to the groundwater and may be present either as a dissolved constituent or as a part of an immiscible fluid such as gasoline which floats on the top of the water table. Some of these contaminated locations may contain considerable chemical mass which can potentially volatilize for years, contaminating the overlying soil gas with their vapours (20).

Although at one time little concern was raised over volatile emissions of potentially hazardous organic chemicals from the soil, this is no longer the case. Many of the volatile organic compounds found in groundwater and in landfills have been found to have adverse health effects in toxicology studies (21, 22).

The determination of the extent and location of subsurface contamination is generally done by testing samples from monitoring wells or soil bore holes. This process is usually expensive and time-consuming. Recently, soil gas analysis has been used as an alternative method for detecting and mapping the extent of subsurface contamination by VOCs (23-27).

Soil gas surveying was originally developed for oil and gas exploration (28). The monitoring and analysis of VOC vapours in soil can be accomplished by several different techniques, which have been recently developed by many workers (29-44) and applied for the detection and measurement of soil and

groundwater contamination. One of these techniques is passive sampling. Since the pore spaces in the soil can form a conduit for the movement of volatile contaminants from the underground spill to the surface, a surface soil gas sample can give information about an underground spill without having to drill down to the actual spill location (45).

Passive samplers, which are also often called diffusive samplers, have been defined by Brown *et al.* (46) as devices which are capable of taking samples of gas or vapour pollutants at a rate controlled by a physical process such as diffusion through the static air or permeation through a membrane, but which do not involve the active movement of the air through the sampler.

A passive sampler usually consists of a diffusion barrier, a collection medium, and a sampler case. Such samplers have become an important tool in air pollution studies, as well as soil atmosphere analysis (47).

Passive sampling utilizes an adsorbent to trap contaminants that diffuse through the soil gases. Passive samplers are buried in the soil and allowed to remain undisturbed for a period of days to weeks and then retrieved for analysis. Both solvent extraction (48) and thermal desorption techniques (49) have been used to desorb soil gas VOCs prior to analysis by gas-chromatography or mass spectrometry (50).

The advantage of passive soil gas sampling is that field operations require minimal training, and the technique averages out concentration fluctuations caused by changes in environmental conditions. It does not require expensive

pumping and use of other geophysical instruments. Multi-point as well as multi-level sampling can be done over a large area at the same period of time (36). Passive sampling, therefore, offers a most attractive alternative to the active sampling technique, and it has been widely used as a method for early detection and long time monitoring of potential leaks from underground storage tanks and associated fuel storage lines (37). The major disadvantage of passive sampling is a relatively low sampling rate due to the permeability of each contaminant through a membrane or diffusion tube. The necessity to collect sufficient analyte for analysis at very low ambient VOC concentrations (ppb or ppt) exacerbates this problem. Additionally, passive sampling may not be appropriate for VOCs that have boiling points below approximately 5°C (36).

Passive monitors rely upon a concentration gradient across a diffusion barrier (membrane or diffusion tubes) to produce a mass transfer of gaseous molecules. The principle of operation is based on Fick's first law of diffusion. This states that the mass transfer rate of gas during diffusion is directly proportional to the diffusivity of the gas in air, the concentration gradient and the diffusion path cross-sectional area (51). According to Fick's law, the contaminant concentration,  $C$  ( $\text{g}/\text{cm}^3$ ), is determined by exposing the monitor for a given time,  $t$  (sec), extracting the adsorbent to measure the mass,  $M$  (g), of the contaminant collected, and can be calculated as follows:

$$C = ML / (DA t) \quad (1)$$

where  $L$  (cm) is the length,  $A$  ( $\text{cm}^2$ ) is the cross-sectional area of the diffusion pathways, and  $D$  ( $\text{cm}^2 \cdot \text{sec}^{-1}$ ) is the molecular diffusivity of the contaminant (52). In equation (1), the expression  $DA / L$ , which has the same units ( $\text{cm}^3 \cdot \text{sec}^{-1}$ ) as the air flow rate in conventional pumped (active) samplers, is defined as diffusive uptake rate  $R$ . This value depends only on the sampler design and diffusivity of the contaminant in the air. Therefore, equation (1) can be rewritten as:

$$C = M / t * R \quad (2)$$

In the case of diffusion samplers with membranes, the uptake rate can only be determined experimentally because the permeation constants for gases through specific membrane materials cannot be calculated from data available in the literature (51).

Recent developments in sorbent technology (e.g., activated carbon fibers, which can be manufactured in the form of cloth, etc.) led to the idea of designing a new generation of passive samplers without a membrane or any other kind of diffusive barrier which offers considerable promise for lowering the limit of detection and reducing the exposure time of the monitor as well as permitting the sampling rate of different vapours to be directly proportional to their concentration.

Brown *et al.* (53) observed that the same sampling rates for VOCs studied were obtained for the Perkin-Elmer tubes with and without the diffusion cap. Ballesta *et al.* (54) used a stainless steel mesh as a membrane with open (effective) area of  $8.02 \text{ cm}^2$  which permitted a passive sampling rate of 50

mL/min onto activated carbon. The sampling rate did not change when the sampler changed its orientation relative to the air flow direction.

Several authors (55-57) reported the results of uptake of organic chemicals from biomonitors by the waxy outer surfaces of plants (e.g., the needles of conifers), which showed that the needles could act as passive samplers.

Gesser and Giller (58) have proposed a new passive sampler without a membrane for monitoring VOCs in indoor air. They showed that a membrane was not necessary to control diffusion, and that the sampling rate of uptake of benzene and toluene from air were shown to be 10 times greater than the sampling rate for the commercially available 3M organic vapour monitor, if calculated for the same mass of activated carbon. It was also observed that the absence of a membrane did not affect the linearity of the sampling rate, and that it appeared that ACC sampled various compounds (of widely different molecular weights) at a rate directly proportional to their molar concentration.

The primary goal and the basic idea of this thesis was to design and evaluate a passive soil gas sampler without a membrane for the monitoring of VOCs in the soil atmosphere.

## 1.2. Literature Review

### 1.2.1. Sampling of Soil Atmospheres and Gases

Smith (59) has defined the soil atmosphere as the gaseous phase of that heterogeneous porous material on the surface of the earth - the air that fills the pores between the solid particles which are not occupied by water.

Since the vapour will move up to 50 times more quickly than the migrating liquid, vapour sensing can provide the response time needed to take corrective actions before leaking liquids contaminate groundwater supplies or cause explosions from migrations into homes or office buildings (60).

Soil gas or vapour monitoring techniques utilize an *in situ* gas analysis or sample collecting device that is installed beneath the surface or at the ground surface (61). For soil gas sampling to give an accurate indication of the underground situation, several factors must be taken into consideration. These factors include properties of the contaminant compound and the geology, hydrology, and soil conditions of the site. The compound to be sampled should be volatile enough to be detectable at the surface. It should also be minimally soluble in water to maximize the ratio of the amount of material in the soil gas to the amount of material dissolved in the soil's water. These two criteria are related to Henry's law constant  $K_H$  which reflects the air to water partitioning of a compound. A high Henry's law constant indicates a good candidate for soil gas sampling (36). Table 1.2-1 lists the 10 substances which are amenable to soil



gas surveying and most frequently encountered at Superfund sites and their Henry's law constants.

**Table 1.2-1**

**Most Frequently Identified Substances at 546 Superfund Sites<sup>a</sup>**

Rank	Substance	Henry's Law Constant (ppbv L / $\mu$ g)	Percent of sites
1	Trichloroethylene	72	33
2	Toluene	56	28
3	Benzene	71	26
4	1, 1, 1-Trichloroethane	30	14
5	Chloroform	40	20
6	Tetrachloroethylene	123	16
7	Ethylbenzene	59	13
8	Xylenes	43	13
9	Methylene Chloride	23	12
10	<i>trans</i> -1, 2-Dichloroethylene	580	11

<sup>a</sup> Source: Kerfoot, H.B. and Harrows, I. J., "Soil Gas Measurement for the Detection of Subsurface Organic Contamination," U.S. EPA, Las Vegas, NV, 1986, p. 2

In addition, major components of petroleum products which can leak from underground storage tanks can be detected using this technique (33). The compound of interest should also be fairly inert so that its biological, chemical or

physical changes are minimal as it moves from an underground spill to the surface.

The geology and groundwater position of the site may affect soil gas sampling and sample evaluation (e.g., fissures or impermeable lenses). Water percolating down from the surface or flowing in aquifers can absorb and/or transport contamination from a spill. Soil conditions, such as porosity, may influence the migration of soil gases because large pore size, loosely packed soils (e.g., sand), allow gases to travel through them much more quickly than do small-pored tightly packed soils (e.g., clay).

Despite the difficulties mentioned previously, soil gas sampling has been used in the environmental field for many years. A site survey with passive samplers usually results in the collection of a series of contaminant masses at various locations. If sampler response (mass adsorbed) as a function of exposure is known, contaminant concentrations can be calculated for all of the measurement sites. Many different techniques have been developed for soil gas sampling (61). While some methods of sampling utilize active removal of a soil gas sample by syringe or pump, others use an adsorbent to passively collect the contaminant vapours present in the soil.

### **1.2.2. Passive Vapour Sampling: diffusive and permeation sampling techniques**

Both the diffusion sampling technique and the permeation sampling technique offer a unique set of advantages as well as limitations for environmental sampling (63). Generally, diffusion samplers are amenable to thermal desorption into a gas chromatograph, they can be mass produced cheaply enough for one-time, throw-away use and they do not require calibration. However, they may be subject to errors caused by variation in air face velocity and also by fluctuations in temperature. Moreover, the trapping media that are suitable for use in diffusion samplers are confined primarily to adsorptive or reactive solids (as opposed to liquids, which are useful in permeation devices). These solids, in turn, are more susceptible than liquids to the effects of atmospheric humidity.

Permeation samplers, on the other hand, are free from humidity effects (especially when a liquid analyte-trapping medium is employed); they can make use of almost any analyte-trapping medium, liquid or solid; they are not especially susceptible to errors caused either by variations in wind velocity or, if a silicone membrane is used, by variations in temperature; and they generally can be used repeatedly. However, permeation samplers also tend to be costly, and they typically require calibration. Even when calibrated, permeation samplers may exhibit a variable working concentration range (and variable detection limits)

because of the variation in membrane permeabilities from one sampler to the next.

The most often employed commercially available passive monitors are SKC passive samplers (64), 3M (charcoal-based badge-type) Organic Vapour Monitor (65), or Perkin-Elmer stainless steel diffusion tubes (66), which have been used to analyze volatile organic hydrocarbons in air.

One study (67) looked at 3M and two other commercialized badges, but found that generally high blanks and poor sensitivity limited their usefulness for ambient air monitoring. Another study (68) found that interlaboratory reproducibility of 3M monitors was poor (about 13% on average).

The Perkin-Elmer tube has been used in air monitoring of VOCs with different thermally desorbable sorbents (e.g. Tenax TM, Chromosorb 106, Chrompack) (68-71). It was found that with Tenax sorbent, for instance, that the more volatile fraction is sampled with low efficiency because of back diffusion over the long sampling times (53).

Passive samplers were initially developed for the measurement of personal exposures in workplace environments where the concentrations of contaminants are relatively high. One of the key factors limiting the use of passive sampling techniques for the determination of low pollutant concentrations is the build-up of artifacts on the adsorbent and the resultant blank signal (72). This may render some adsorbents unsuitable for use at low concentrations, as well as for thermal desorption methods.

### **1.2.3. Application of Passive Dosimetry to the Monitoring of Volatile Organic Compounds in Soil Atmosphere**

Passive dosimetry has long been used in the industrial hygiene field, and it has recently been applied to soil gas analysis to provide the information about soil and groundwater pollution. The aerial distribution of contaminants in shallow soil gas has been shown to correspond to contaminant distributions in the ground water (61).

The widely used 3M Organic Vapour Monitor, originally designed for use as industrial hygiene personal sampler, has recently been evaluated as a passive soil gas monitor (62). The samplers, constructed of a plastic holder containing an activated charcoal adsorbent and diffusion membrane, were buried in the soil. All samplers showed possible saturation effect at exposures above 2500 ppm \* days for hexane and 7000 ppm \* days for toluene. All of the 3M badges showed much lower contaminant adsorption than was predicted by theoretical calculation. 3M badge samplers exposed under low soil moisture conditions adsorbed 1.5 - 3 times more hexane or toluene than badges exposed at higher soil moistures. All blank samplers were free from contamination. The percent differences between duplicate samplers ranged from 2.1% to 29.4% for hexane and from 0% to 47.2% for toluene.

Another commercially available SKC Anasorb-CA monitor has been used as a passive sampling element in a new device for measuring soil-air fluxes of

organic contaminants (34). The sampler was deployed at ground surface and measured fluxes coming to the surface. Measurements were obtained for fuel-contaminated soils near a leaking underground storage tank and at a land treatment unit for refinery wastes. The results, compared to conventional (active) sampling, showed good agreement for benzene. Toluene and ethylbenzene showed a large degree of variability. Four-day average fluxes of benzene and toluene matched very closely with passive/active sampling ratios of 1.00 and 1.10, respectively. Agreement was poor for ethylbenzene, with passive/active ratios of only 0.58. This compound was not detected using the passive sampler on 2 of the 4 days studied. The authors mentioned that possibly the largest source of error was the difficulty of sealing the bottom of the sampler in the rough soil surface.

Malley *et al.* (73) described a measurement method that uses a thin ferromagnetic wire coated with activated charcoal to collect organic vapours. The sample is analyzed in the laboratory by Curie point mass spectrometry and results are reported as relative ion counts; however, the relative ion counts are not directly related to soil gas concentrations. Collection efficiency and the volume of gas sampled by this technique have not been determined.

Kerfoot and Mayers (74) describe a quantitative method that uses a passive sampler that is buried inside an open, inverted 1.14-litre metal can at 0.30 m below the ground level. At the conclusion of the exposure period, the sampler is desorbed by solvent extraction and analyzed by gas chromatography.

A diffusive sampler developed by Karp (37) was constructed of a sorbent tube that fits inside a specially designed sampling chamber equipped with a porous polyethylene membrane. The sorbent tube filled at one end with Carbotrap -™ sorbent (Supelco, Inc.) to retain organic molecules. The other end of the tube is left open to the atmosphere inside the sampling chamber allowing a transfer of organic vapours through the tube by diffusive flux. The results indicate that the passive sampling approach is viable for detecting relatively low concentrations (ppb and ppm) of organic vapours in the vadose zone ("vadose zone" is the geological profile from the ground surface to the upper surface of water table) over a one-day sampling period, as well as providing relatively long-term monitoring periods of up to 58 days. A field test found the sampling approach successful in identifying an area where the vadose zone was contaminated by leaking petroleum underground storage tanks.

#### **1.2.4. Activated Carbon Fibers**

Activated carbon is a typical solid adsorbent used to collect volatile organic compounds. However, for many adsorption applications, activated carbon fibers (ACF) provide greater ease of use than granular activated carbon (GAC) because ACF can be manufactured in the form of cloth (75). Moreover, ACF typically exhibit higher adsorption capacities and faster adsorption kinetics than granulated activated carbons (76).

Activated carbon fibers have additional advantages: the surfaces of ACF can be regenerated in situ with electrical resistance heating, their surfaces can be chemically tailored to allow preferential adsorption of certain compounds, and the pore sizes of ACF typically lie over a narrow range in the micropore region (pore width  $<2$  nm) (76). The narrow pore size allows use of ACF as a molecular sieve in some applications. ACF is widely used for adsorption and filtration of different organic compounds. It is manufactured by the oxygen-free carbonization of a viscose rayon or phenolic fabric followed by activation. This yields a tough, porous, flexible material composed of a network of fibre bundles (20  $\mu\text{m}$  in diameter). It has a surface area comparable with other activated carbons (1300  $\text{m}^2/\text{g}$ ) with a mean pore radius of 0.7 nm (77).

Cal *et al.* (78) used ACF to adsorb ppmv concentrations of VOCs from laboratory generated gas streams. Adsorption isotherms were measured for ACF with three different degrees of activation ( three different BET surface areas) using two individual adsorbates: acetone and benzene at concentrations between 10 ppmv and 1000 ppmv in air. The results indicate that ACF have the potential as an adsorbate to effectively remove volatile organics. The authors noticed that ACF with smaller mean pore size (related to lower BET surface areas) are more effective adsorbents at low adsorbate concentrations than are ACF with larger mean pore sizes (higher BET surface areas) due to the overlap of adsorption potentials in the smaller pores (78). It is believed that as the ACF are activated for longer time periods the micropores widen (79). Greg and Sing