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Application of Passive Dosimetry for Detection of  
Leaking Underground Storage Tanks

by

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## ABSTRACT

Several modifications to conventional uses of passive dosimetry in industrial hygiene were explored to make the method attractive for both long-term monitoring of underground storage tanks and short-term site assessments of ground water contamination. Methods for both vapor and aqueous phase measurements were of interest. In addition, a colorimetric method was tried to eliminate the need for return of the dosimeter to the laboratory for chemical analysis.

The passive dosimeter for aqueous phase sampling incorporated activated carbon for adsorption of hydrocarbons and a Nuclepore filter as the diffusion barrier in order to increase detection sensitivity. Toluene, ethyl benzene, and m-xylene were detected at concentrations of 0.3 mg/L to 10 mg/L in exposure times ranging from 14 to 81 hours. Components of gasoline were measured at aqueous concentrations ranging from 0.3 mg/L to 1.6 mg/L (aqueous concentrations conventionally expressed on mass per volume basis) in an exposure time of 69 hours. A less sensitive dosimeter was needed for vapor phase measurements. Octane at 1 ppm (gas phase concentrations conventionally expressed on volume per volume basis) was detected in 80 min of exposure. Field tests of the two different passive dosimeters at the fire training area of Pope Air Force Base (Fayetteville, NC) were successful in demonstrating detection of jet fuel in both the ground water and vapor phase (i.e., in the partially saturated zone).

A colorimetric dosimeter was developed for detection of vapor phase hydrocarbons. Chromate powder was used to oxidize hydrocarbons, in the process changing from yellow to green as the chromate was reduced from the +VI to the +III oxidation state. The degree of color change from yellow to green was correlated to the mass of hydrocarbon reacted, and could be expressed as the product of average concentration and time in units of ppm-hr. Theoretically, vapor phase concentrations as low as 6 ppm could be detected if a one week sampling period were employed. Field tests of the colorimetric dosimeter showed promise for fast, qualitative assessments of the extent of contamination. The predicted concentrations were within an order of magnitude of those measured by two, more well-tested, field methods.

The results suggest that passive dosimetry can be a useful qualitative tool for the mapping of the sub-surface of a contaminated area. It is recommended that the dosimeter be used for short-term site-assessments, rather than long-term compliance monitoring applications. A more extensive comparison with other methods of leak detection than was possible in this research may be needed before convincing the private sector to develop a product based on commercial use of these prototype dosimetry devices; nevertheless, these data offer encouragement.



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## SUMMARY AND CONCLUSIONS

1. A passive dosimeter design incorporated granular activated carbon (GAC) for adsorption of analytes and a Nuclepore filter as the diffusion barrier in order to increase sensitivity for detection of hydrocarbons in water.. In laboratory tank tests, dosimeters were exposed to toluene, ethyl benzene, and m-xylene at aqueous concentrations of 0.3 mg/L to 10 mg/L.. Sufficient amounts of these analytes were collected by the dosimeter in exposure times ranging from 14 to 81 hours to allow for determination of their concentrations.. The data suggest that the dosimeter technique is reproducible and that the predicted concentrations are within 25% of values measured by conventional solvent extraction (some predictions, however, were low by 75%).
2. The passive dosimeters were also exposed to gasoline in tank tests.. The same target compounds listed above were measured at concentrations ranging from 0.3 mg/L to 1.6 mg/L in an exposure time of 69 hours.
3. Two recovery experiments revealed relatively low extraction efficiencies of carbon disulfide (CS<sub>2</sub>) for removing the target compounds from GAC. Extraction efficiency values ranged from 5.1% to 10.4% with considerable variability in the data.. The low extraction efficiencies could be due to the inability of CS<sub>2</sub> to penetrate entrained water in the internal GAC structure and to insufficient desorption time.
4. A less-sensitive dosimeter design was developed for detection of hydrocarbons typically found in gasoline from

the vapor phase.. Octane at 1 ppm (by volume in the vapor phase) was detected in 80 min of exposure.

5. Field tests of the two different passive dosimeters at the fire training area of Pope Air Force Base (Fayetteville, NC) were successful in demonstrating detection of jet fuel in both the ground water and vapor phase (i.e., in the partially saturated zone).. However, the technique is considered qualitative rather than quantitative without more research to refine field sampling procedures.
6. Passive dosimetry can be a useful qualitative tool for the mapping of the sub-surface of a contaminated area. The dosimeters showed good sensitivity by measuring concentrations as low as 1 ppm in the vapor-phase after only 90 minutes and 0.2 mg/L in the aqueous-phase after 5 hours.. The sensitivity can be increased easily by allowing longer exposure times. Another advantage is monitoring would not disrupt service.
7. Another modification to the passive dosimetry design was developed to eliminate the need for solvent extraction of the activated carbon and subsequent analysis by gas chromatography.. Instead of activated carbon, a chromate powder was used to oxidize hydrocarbons, in the process changing from yellow to green as the chromate was reduced from the +VI to the +III oxidation state.. Reaction rates were faster for higher molecular weight hydrocarbons (i.e. octane), than for lower molecular weight hydrocarbons (i.e. pentane) as predicted by stoichiometry..
8. Laboratory studies showed that the degree of color change from yellow to green for the colorimetric dosimeter was correlated to the mass of hydrocarbon reacted and could be expressed as the product of average concentration and time in units of ppm-hr.. The detectable concentration limit depends upon the length of time the dosimeter is exposed.

For a three hour sampling period, the minimum detection limit is 300 ppm (which would be indicative of a tank leak), and the maximum detection (point at which powder turns green regardless of additional exposure) is 4670 ppm. Theoretically, concentrations as low as 6 ppm could be detected if a one week sampling period were employed, but degradation of the powder may occur in this extended sampling period.

9. Octane was chosen as a standard to measure total hydrocarbons for the colorimetric dosimeter because it is indicative of higher molecular weight (hence, more reactive) hydrocarbons that can be found in the vapor phase. Concentrations expressed as ppm octane can easily be transformed to hydrocarbon specific concentrations if the stoichiometry is known.
10. Field tests of the colorimetric dosimeter at the Pope Air Force Base site showed promise for fast, qualitative assessments of the extent of contamination; predicted concentrations were within an order of magnitude of those measured by two, more well-tested, field methods (Draeger tubes and carbon adsorption followed by extraction).
11. The best application for the colorimetric dosimeter is for initial site assessments.. It provides a simple, inexpensive method of quickly characterizing a site. More complicated and expensive monitoring techniques could then be applied to those areas which an initial assessment indicates are contaminated.. Because of the low cost and versatility of these dosimeters, many samples at various depths could easily be taken at a site in a given day. The user does not need any special training to use the dosimeter or to interpret results, as the procedure is simple: dig a well, insert dosimeter, backfill the well, remove the dosimeter after three hours, and record the color.



## RECOMMENDATIONS

1. Further controlled studies are needed to define the lower limits of detection for aqueous phase sampling with the dosimeter design that incorporates a Nuclepore filter as the diffusion barrier. Increasing dosimeter exposure times from days to weeks will theoretically allow the accumulation of analyte mass sufficient for detection of aqueous phase concentrations from 1-100 ug/L.
2. More time should be allowed for solvent desorption of analytes from granular activated carbon.. Moreover, extraction efficiencies for the target compounds need to be generated over a broader range of hydrocarbon loadings.. These data will facilitate evaluation of the potential effects of HC loading upon observed extraction efficiencies.
3. An improved vapor-phase sampling methodology should be developed for field studies.
4. More laboratory tests need to be conducted to determine how the dosimeter performs in a quiescent atmosphere.
5.  $\text{Cr}^{+3}$  may eventually reduce to  $\text{Cr}^{+2}$  as was suggested by a color change from green to light blue. This degradation of  $\text{Cr}^{+3}$  to  $\text{Cr}^{+2}$  is problematic for longer sampling periods, and it is recommended that the dosimeter be used for short-term site-assessments, rather than long-term compliance monitoring applications.
6. A more extensive comparison with other methods of leak detection than was possible in this research are needed to develop a product based on these modifications of existing dosimetry devices; nevertheless, these data offer encouragement.



## INTRODUCTION

In the United States, there are between three and five million underground storage tanks (USTs) which store regulated substances, of which petroleum products are the most common (USEPA 1988). Many of these tanks were installed with the belief that they would never leak, and thus, the possible deleterious effects of a leak were overlooked. As a result, there were over 100,000 leaking underground storage tanks (LUSTs) in 1985 and more than 300,000 were predicted by EPA to be leaking by 1990.

To deal with this problem, the EPA was required to promulgate underground storage tank standards in accordance with the 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act (Federal Register 1988). In order to be considered an UST by EPA, a tank must have at least ten percent of its volume (including piping) underground and contain a regulated substance (USEPA 1986). Exemptions include residential fuel tanks less than 1100 gallons, septic tanks and heating oil tanks. The Office of Underground Storage Tanks was established by the EPA to administer and create the necessary regulations. At present, all piping is required to be monitored for leaks by December 1990 and all tanks by 1993 (Wilsek 1989).

The financial and environmental consequences of a leaking tank can be very significant. About two million tanks may be affected by EPA rules with compliance costs of \$2.5 billion per year (Bellamy 1989). If ground water or surface water become contaminated, then the costs will escalate greatly. In fact, at present each tank is required to carry one million dollars of insurance per possible occurrence (Northeast Interstate Water Pollution Control Commission 1989).

Small businesses, exemplified by the convenience store with gasoline and diesel fuel service, need an effective and inexpensive UST leak detection system. While many methods are available, most are fairly expensive and/or require technical expertise. The simplest, of course, is inventory control by which routine measurements of fuel volume and sales can determine if large losses are occurring. However, this requires diligence and may not be accurate enough to detect leaks that are environmentally important. At the other extreme is the use of remote laser light to measure gasoline components in the ground water. Regardless of the method used, the processes of determining the existence of a leak, the leak rate and its pathway, are complicated. As a result, there has been no agreement on leak detection systems for widespread use.

Passive dosimetry has been studied extensively in the industrial hygiene field since the early 1970's with an emphasis upon the development and use of personal samplers i.e., badges worn by workers that detect contaminants in the atmosphere (Rose and Perkins 1982). In general, the samplers offer an easy, quick, and reliable means of evaluating airborne exposure to toxic chemicals (Palmer and Gunnison 1973; McCammon and Woodfin 1977; Tompkins and Goldsmith 1977; and Campbell and Konzen 1980). Various studies have shown that passive dosimeters can be used to detect a variety of organic and inorganic compounds.

Little has been reported in the environmental literature concerning the various potential applications of passive dosimetry as a monitoring tool. Recently, investigators began using passive dosimetry to conduct soil-gas surveys in the vicinity of contaminated ground water (Marrin and Kerfoot 1988; Kerfoot and Mayer 1986). Such studies can yield valuable data for use in the planning of monitoring well networks and tracking of contaminant plumes.

## OBJECTIVES

This research dealt with applications of passive dosimetry to leak detection as a simple and expensive alternative to other methods. The specific purpose of this research was to explore several modifications to conventional uses of passive dosimetry in industrial hygiene that would make the method attractive for both long-term monitoring of underground storage tanks and short-term site assessments of ground water contamination. While the usual application of passive dosimetry is for detection of hydrocarbons in the vapor phase, it was adapted to the aqueous phase to include monitoring of the saturated zone in addition to the unsaturated zone. Also, the conventional procedures for obtaining a result require return of the dosimeter to the laboratory for chemical analyses. To overcome this disadvantage, a rapid colorimetric procedure was adapted from existing commercial devices (e.g., Draeger tubes) for use in a passive dosimeter.

The research consisted of both laboratory studies under controlled conditions to develop the dosimeter designs and field tests at Pope Air Force Base (Fayetteville, NC), a site where the subsurface is contaminated with jet fuel. The emphasis was, therefore, on detection of hydrocarbons. This report has three overall objectives:

1. to test the sensitivity of a passive dosimeter based on extraction of analytes from an adsorbent for application to detection of hydrocarbons in ground water;
2. to test (both laboratory and field) sensitivity of a passive dosimeter based on extractions of analytes from an adsorbent for application to detection of soil gas contaminants; and
3. to test (both laboratory and field) the sensitivity of a passive dosimeter based on a colorimetric procedure for application to detection of soil gas contaminants.



In this equation  $J$  is the flux of a contaminant through diffusion channels in the dosimeter ( $\text{mg}/\text{cm}^2/\text{s}$ ),  $D$  is the molecular diffusivity of the contaminant ( $\text{cm}^2/\text{s}$ ), and  $C$  is the concentration of the contaminant ( $\text{mg}/\text{cm}^3$ ) and  $x$  is the thickness of the diffusion barrier (cm).

$$J = -D(dc/dx) \quad (1)$$

Law of Diffusion:

The governing equation for passive dosimetry is Fick's first

of the adsorbent.

This avoids the need for return of the "badge" for extraction

adsorbent so as to have direct read-out of mass collected.

Alternatively, a color sensitive reactant can replace the

to ambient concentration, as will be detailed later.

collected by the adsorbent over time is measured and related

the badge that keeps the concentration at zero. The amount

small badge worn by workers. An adsorbent is contained within

Figure 1. In industrial hygiene practice, the device is a

of the contaminant across a diffusion barrier, as depicted in

The key to dosimetry is to have a device that shows movement

contaminants for as long a sampling time as necessary.

can be left in an environment to collect or react with these

to measure very low concentrations, but the passive dosimeter

low. Other grab-sampling methods may not have the sensitivity

extremely important tool when species concentrations are very

and inexpensive exposure monitoring device. Dosimetry is an

active parts or pumps are required, a dosimeter is a simple

of dosimeter design and contaminant characteristics. Since no

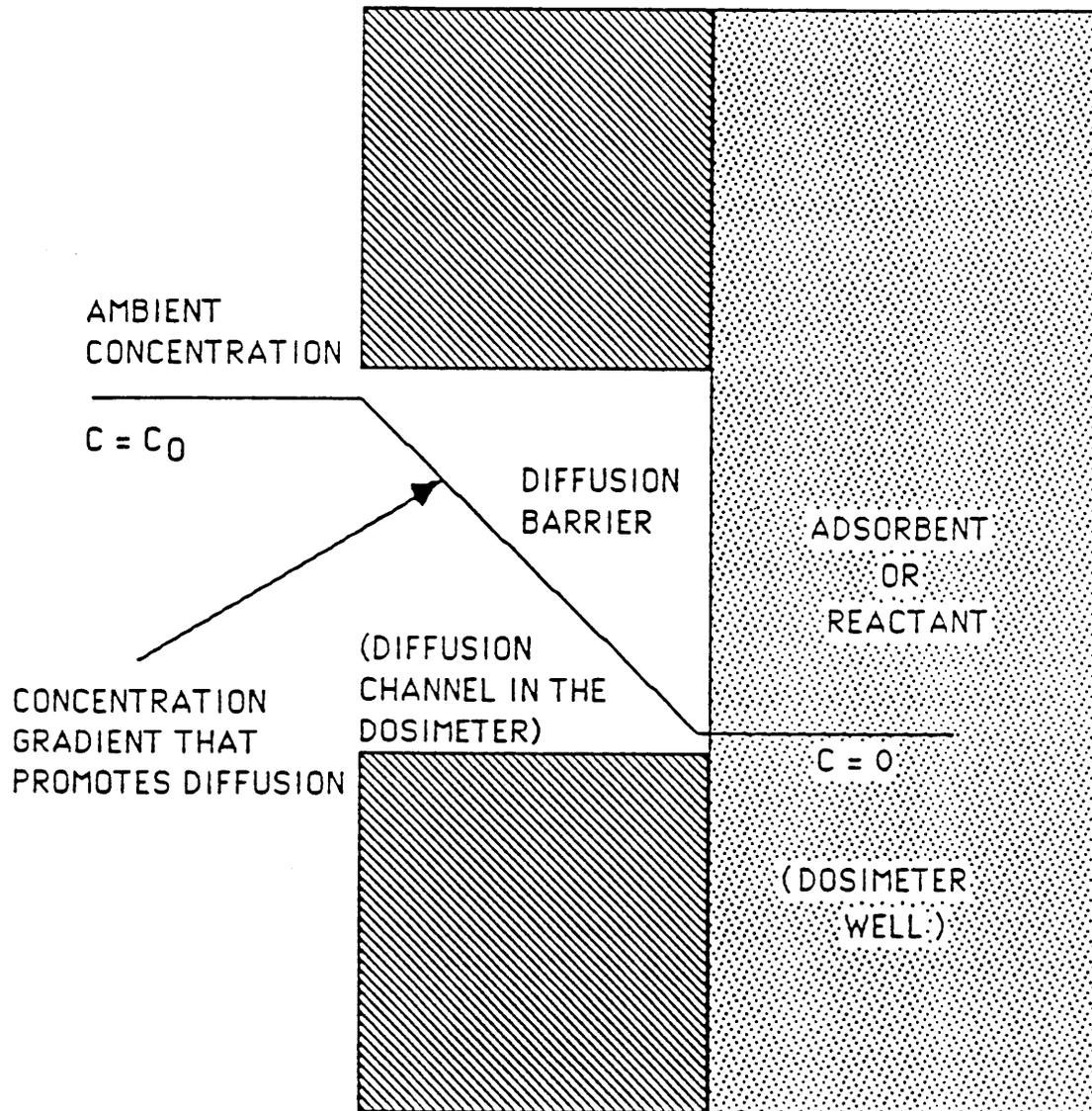
by which contaminants collect in the dosimeter is a function

industrial hygiene field to monitor worker exposure. The rate

contaminant concentration, has been used extensively in the

The principle of passive dosimetry, a time-weighted average of

Figure 1. Description of Concentration Gradient in a Passive Dosimeter



Equation (1) may be readily integrated by assuming that the ambient concentration remains constant (i.e.,  $C(0) = C$ ) and the concentration at the end of the diffusion channel is zero (i.e.  $C(L) = 0$  where  $L$  is the length of a diffusion channel in the dosimeter).

$$J = DC/L \quad (2)$$

where  $L$  is the length of a diffusion channel in the dosimeter. Multiplying both sides by  $A$ , the total area of the dosimeter available for diffusion, and  $t$ , the time of exposure, gives the mass,  $M$ , that is collected by the dosimeter:

$$M = DA t C/L \quad (3)$$

If the dosimeter contains an adsorbent,  $M$  is measured after solvent extraction and detection:

$$M = m/EE \quad (4)$$

where  $m$  is the mass of contaminant detected and  $EE$  is the solvent extraction efficiency.

Equation (3) may then be arranged to yield

$$C = mL/[DA t (EE)] \quad (5)$$

which enables calculation of the concentration.

In determining the average concentration over a sampling period with passive dosimetry, two important rates, sampling and response rates must be considered (Hearl and Manning 1980). The sampling rate predicts the expected volume of contaminant that will diffuse through the dosimetry channels in a specified time. The response rate is the time needed for the dosimeter to integrate changing concentration profiles. A short response rate implies the dosimeter is able to integrate

changing concentration profiles rapidly, which ensures that the sample collected is a true time-weighted average. Equation (3) can be arranged to obtain the sampling rate [M/Ct]:

$$\text{Dosimeter Sampling Rate} = DA/L \text{ (cm}^3\text{/s)} \quad (6)$$

and the response rate is given by:

$$\text{Response Rate} = L^2/[2D] \quad (7)$$

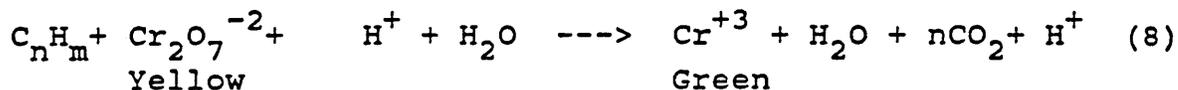
Table 1 lists sampling and response rates for various straight-chained hydrocarbons utilizing a dosimeter proposed by DiGiano, et al. (1988a) in which  $A/L = 1.225$  cm. The diffusivity in air was estimated by procedures given by Lyman, Reehl and Rosenblatt (1982).

Table 1. Sampling and response rates of selected hydrocarbons

<u>Hydrocarbon</u>	<u>Diffusivity</u> <u>(cm<sup>2</sup>/sec)</u>	<u>Rates</u>	
		<u>Sampling</u> <u>(cm<sup>3</sup>/hour)</u>	<u>Response</u> <u>seconds</u>
Propane	0.112546	496.3	4.44
Butane	0.095848	422.5	5.22
Pentane	0.084776	374.0	5.90
Octane	0.076772	338.5	6.51
Hexane	0.065764	290.0	7.60

### The Colorimetric Reaction

Instead of using an adsorbent, the dosimeter can also be designed to maintain  $C = 0$  at  $x = L$  by incorporating a chemical reaction to remove the contaminant of interest. The mass (M) of component reacted can be calculated from a colorimetric end-point. Chromic acid is a strong oxidizing agent, and will oxidize any hydrocarbon ( $C_nH_m$ ) by:



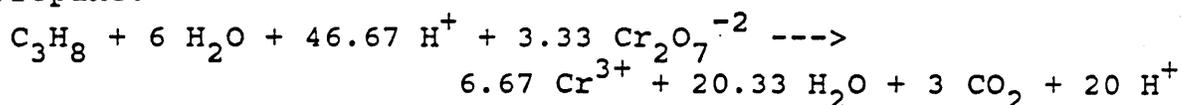
A color change from yellow to green indicates the presence of hydrocarbons, and signifies the reduction of  $Cr^{+6}$  (yellow) to  $Cr^{+3}$  (green). The stoichiometric equations for selected straightchain hydrocarbons are given in Table 2.

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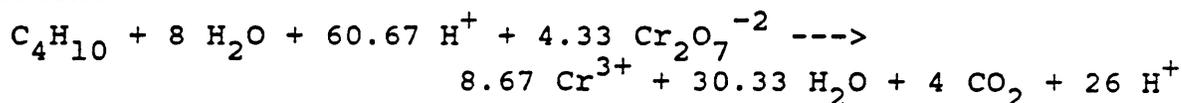
Table 2. Chromate reduction reaction for selected hydrocarbons

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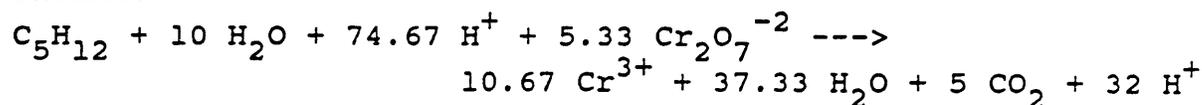
Propane:



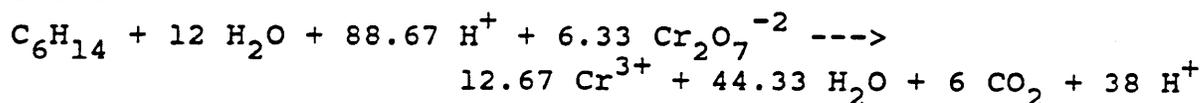
Butane:



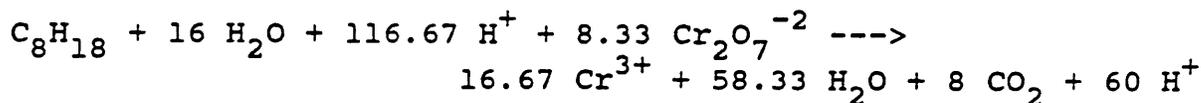
Pentane:



Hexane:



Octane:



The quantity of chromate added to the dosimeter determines, therefore, the quantities of water, acid and hydrocarbon that will react before the color changes from yellow to green. In order for the dosimeter to function properly, the chromate and

acid must be combined with a support medium that is compatible and convenient to use.

Previous Dosimetry Research at UNC-Chapel Hill

DiGiano et al. (1988a) evaluated the feasibility of passive dosimetry to measure two common contaminants, p-xylene (pX) and atrazine, in water. Their work was the forerunner to work presented here. Prototype dosimeters were exposed to concentrations of the target compounds ranging from 0.05 mg/L to 10 mg/L in an exposure tank. The dosimeter-predicted aqueous concentrations closely approximated those obtained by direct solvent extraction of water from the exposure tank as is evident in Table 3.

Table 3. Comparison of dosimeter and extraction techniques for detection of p-xylene and atrazine in water

Analyte	Exposure Time (Days)	Mass Detected (ng/L)	Extraction Efficiency (%)	Concentration of Analyte (in Tank)	
				By Dosimeter	By Solvent <sup>1</sup> Extraction
p-Xylene	20	5.0	40	1.3	1.0
	20	5.0	40	1.3	1.0
	20	5.5	40	1.4	1.0
p-Xylene	5	8.9	40	9.2	10
	5	11.2	40	11.6	10
	5	10.1	40	10.5	10
Atrazine	49	6.1	75	0.091	0.054
	49	3.1	75	0.046	0.054

Source: DiGiano et al. 1988a

<sup>1</sup> Water withdrawn from tank, extracted directly with methylene chloride and analyzed by gas chromatography.

Despite favorable results, greater sensitivity was necessary to allow reduction of exposure time and measurement of lower (1-100 ug/L) analyte concentrations. The design limitation of

the prototype dosimeters was a comparatively long diffusion pathlength of 1 cm.

To improve sensitivity, a second-generation design was developed using a Nuclepore filter as the diffusion barrier. This effectively shortened the diffusion channel length from 1 cm to 10  $\mu\text{m}$ . While further testing with atrazine was limited, detection of 0.054 mg/L concentrations required approximately 7 days. The shortened diffusion pathlength allowed a seven-fold increase in sensitivity.



## APPLICATION OF PASSIVE DOSIMETRY TO DETECTION OF HYDROCARBONS IN WATER

### Objectives

The intent of this portion of the research was to evaluate the ability of passive dosimetry to detect gasoline-derived hydrocarbons (HCs) in the aqueous phase. The specific objectives were:

1. to develop an effective dosimeter design for sampling gasoline HCs found in ground water,
2. to conduct laboratory-scale tests of passive dosimetry for detecting gasoline HCs in water, and
3. to make recommendations upon the scope of field studies designed to evaluate the utility of passive dosimetry in ground water monitoring near a known LUST.

### Reagents and Materials

All chemicals used were certified as A.C.S. reagent grade or better. Toluene (98%), ethyl benzene (99+%), m- xylene (98%), 1-chlorodecane (95%), and carbon disulfide (99.9+%) were all used without purification (Aldrich). The anhydrous sodium sulfate was kept in a dessicator and was used without purification (Fisher A.C.S.).

The granular activated carbon (GAC) was 30 x 40 mesh (U.S. sieve) Filtrasorb 400 (Calgon Corp.) and boiled for 30 minutes prior to use. Boiling the GAC facilitated removal of air bubbles trapped in the tortuous internal structure of the carbon.

### Design of Dosimeter

The dosimeters utilized in this research were second-generation designs based upon previous work reported by DiGiano, et al. (1988a). As shown in Figure 2, the essential components included the base, collection medium, and diffusion barrier.

The dosimeter base was approximately 7.5 cm in diameter and was built from acrylic plastic. A hollowed region in the center of the base contained the GAC collection medium. The barrier was a 10 um thick polycarbonate Nuclepore filter with pores having a nominal diameter of 1 um. The total surface area of the barrier available for diffusion was determined to be 0.635 cm<sup>2</sup> by electron microscopy. A threaded cap secured the diffusion barrier to the dosimeter base.

A small ring on the base allowed attachment of a teflon-coated string for dosimeter placement and retrieval. The dosimeter base was also fitted with a small teflon aperture (Figure 2) to enable replacement of any air bubbles with water using a 10 mL syringe.

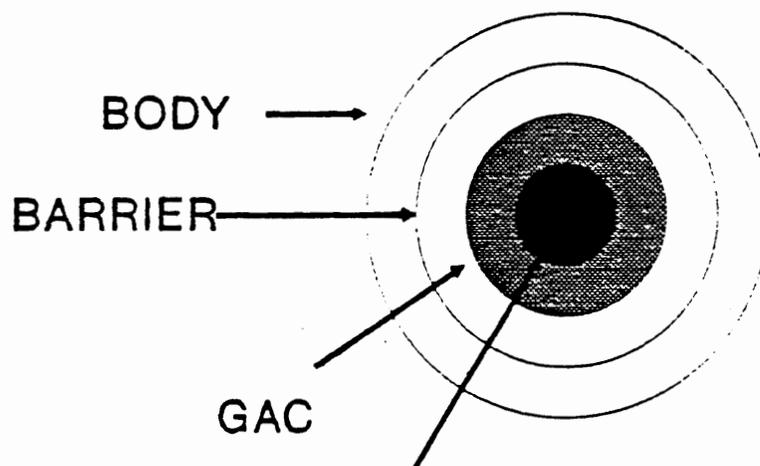
### Selection of Target Compounds

Compound selection was based primarily upon environmental significance to the UST issue. Candidates were required to be major constituents of gasoline, exhibit mobility in the aqueous phase, and be amenable to the experimental method.

The compounds selected were toluene (T), ethyl benzene (EB), and m-xylene (mX). Their aqueous solubilities on the order of 100-500 mg/L make them significantly more mobile in water than most other constituents of gasoline (Koehn and Stanko 1988). The pertinent physical and chemical properties of these compounds are summarized in Table 4.

Figure 2. Components of Passive Dosimeter

## TOP & BOTTOM VIEW



## SEPTUM & CHANNEL

## SIDE VIEW

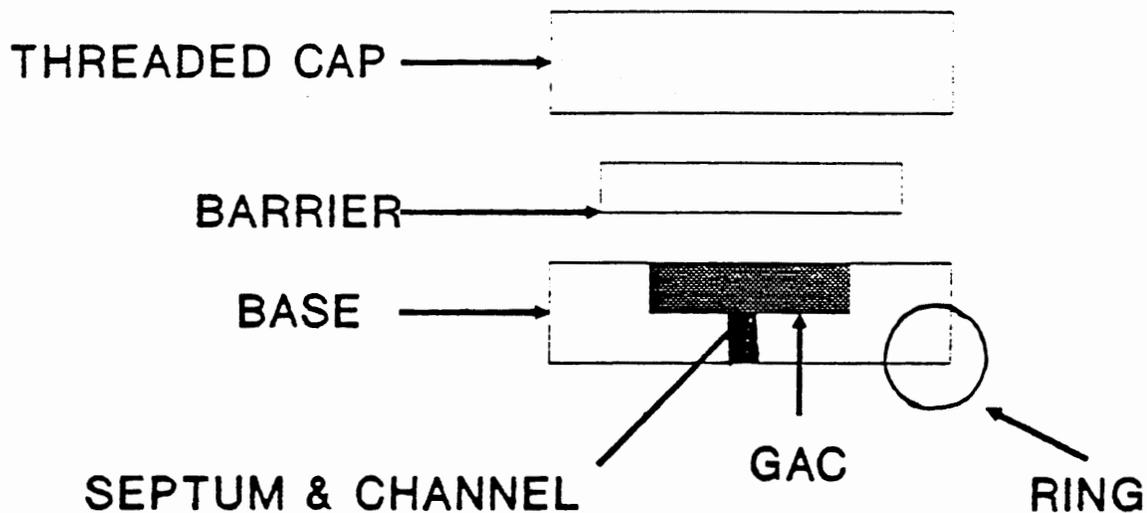


Table 4. Some properties of target compounds

<u>Compound</u>	<u>MW (g/mol)</u>	<u>Aqueous Solubility (mg/L)</u>	<u>Aqueous Molecular<sup>1</sup> Diffusivity<sub>1</sub> (cm<sup>2</sup>/s) x 10<sup>6</sup></u>	<u>Specific Gravity</u>
Toluene	92.14	515	7.9	0.867
Ethyl Benzene	106.20	152	7.1	0.867
m-Xylene	106.20	162	7.1	0.864
Chlorodecane	176.74	0.1	ND	0.868

<sup>1</sup> Determined by Hayduk-Laudie estimation technique (Lyman, Reehl and Rosenblatt 1982; Mailhot and Peters 1988)

ND - Not Determined

#### Recovery Experiments

The recovery experiments provided a quantitative measure of the extraction efficiency (EE) of carbon disulfide (CS<sub>2</sub>) for removing the target compounds from GAC. After boiling for 30 minutes, the GAC was weighed into clean, oven-dried glass bottles fitted with teflon-lined caps and containing 100 mL tap water. Known weights of each target compound were introduced by syringe into the slurries such that resultant loadings (mg target compound/ mg GAC) approximated those expected in the dosimeter exposure studies. Vapor space in the bottles was minimized to discourage volatilization of the analytes.

The slurries were agitated and the GAC subsequently retrieved and placed in clean, oven-dried 12 mL vials (Fisher Scientific) with 10 mL CS<sub>2</sub>. Approximately 1 g anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) was also added to the vials to remove residual water. No attempts were made to separate the GAC and sodium sulfate from the extracts prior to analysis due to potential volatilization losses. The aqueous phase in which

the GAC was suspended was extracted with 10 mL CS<sub>2</sub> in a 125 mL separatory funnel; this was used to calculate the amount of target compound adsorbed by the GAC.

All extracts were spiked with the internal standard, 1-chlorodecane (1-CD), to facilitate quantitation and refrigerated until GC analysis. Holding times for the GAC/CS<sub>2</sub> extract slurries were approximately 24 hours. Injections (1 uL) were generally performed in triplicate.

Two methods of agitation were compared for their rapidity, ease of utility, and effectiveness. The technique used in Recovery Experiment I involved shaking the slurries by hand intermittently for 30 minutes while, in Recovery Experiment II, a Jr. Orbit mechanical agitator operating at 150 rpm for 1 hour was employed.

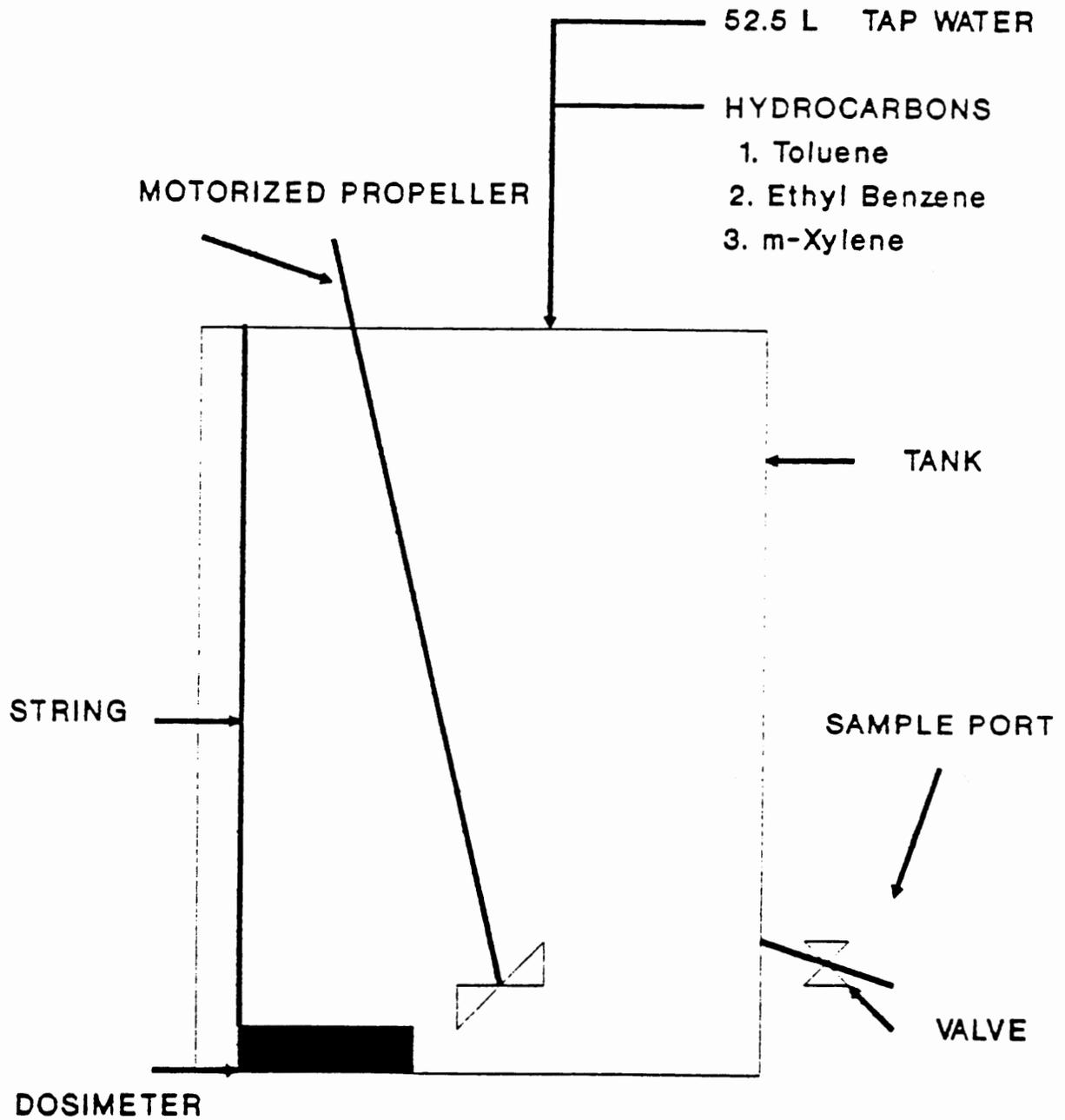
#### Laboratory Exposure Experiments

A series of six laboratory exposure experiments was conducted to evaluate the effectiveness of passive dosimetry in measuring the target compounds in the aqueous phase. A polyethylene tank (Nalge Corp.) was filled with 52.5 L of tap water to serve as the exposure tank as shown in in Figure 3. The target compounds were added with a syringe and the contents of the tank were mixed. Concentrations were approximately 10 percent of solubility. Each passive dosimeter (up to three) was suspended in the tank with a string for a given exposure period.

In a seventh exposure experiment, 3 mL of unleaded gasoline (87 octane) instead of the target compounds was added to 52.5 L tap water. The same three target compounds were measured as in first six exposure experiments.

Tank headspace was minimized to discourage volatilization of the hydrocarbons. The tank was tightly capped and stirred

Figure 3. Exposure Tank for Dosimeter Experiments



vigorously by a motorized stainless steel propeller for 10-15 minutes. The tank water was visually inspected for surface slicks indicating poor mixing and the presence of non-aqueous phase liquids (NAPLs). If NAPLs were detected, an additional 10 minutes of mixing was conducted to insure solubilization.

After boiling the GAC, each loaded dosimeter was placed in a beaker containing 200 mL tap water and approximately 10 mL was drawn through the septum by a syringe (see Figure 2). This facilitated removal of air bubbles trapped in the interstitial spaces between GAC particles in the dosimeter. The dosimeters were then carefully lowered by attached strings through the bulk liquid until resting with diffusion barrier facing upwards into the tank. The tank was then re-capped and the stirring motor turned off for the exposure time.

After exposure, the dosimeters were retrieved and the GAC from each placed in clean, oven-dried 12 mL GC vials with 10 mL CS<sub>2</sub>. Approximately 1 g anhydrous Na<sub>2</sub>SO<sub>4</sub> was also added to remove residual water. No attempts were made to separate the GAC and sodium sulfate from the extracts prior to analysis due to potential volatilization losses. The extracts were agitated, spiked with 1-CD and then refrigerated until GC analysis. Holding times for the extracts varied for the first two experiments but were then standardized to 24 hours in Tank Exposure Experiment III. The initial and final concentrations of target compounds in the tank were determined from 50 mL aliquots obtained from a spigot. The aliquots were extracted with 10 mL CS<sub>2</sub>, worked-up and analyzed in the same manner as extracts from the dosimeters.

#### Gas Chromatographic Analysis of the Extracts

Gas chromatography was used to detect target compounds in both the recovery and tank exposure experiments. The internal standardization technique was employed to facilitate quantitation of analyte concentrations. All raw data from the GC analyses are found elsewhere (Elliott 1990).

A Varian 3700 Aerograph GC equipped with a flame-ionization detector (FID) and a capillary column( 30 m by 0.25 mm i.d.) of borosilicate glass coated with 1.0 um non-polar DB-1 liquid phase (J&W Scientific) was used. Injector and detector temperatures were maintained at 200°C and 280°C, respectively, throughout the analyses. Column temperatures ranged from 60°C to 155°C with a ramp rate of 6°C/min. Helium carrier gas was maintained through the column at a flow rate of 30 mL/min. A Hamilton 10 uL syringe was used for all GC injections. The syringe was rinsed thoroughly with CS<sub>2</sub> between each 1 uL injection. Injections from both the GAC and tank water extracts (1 uL) were generally performed in triplicate.

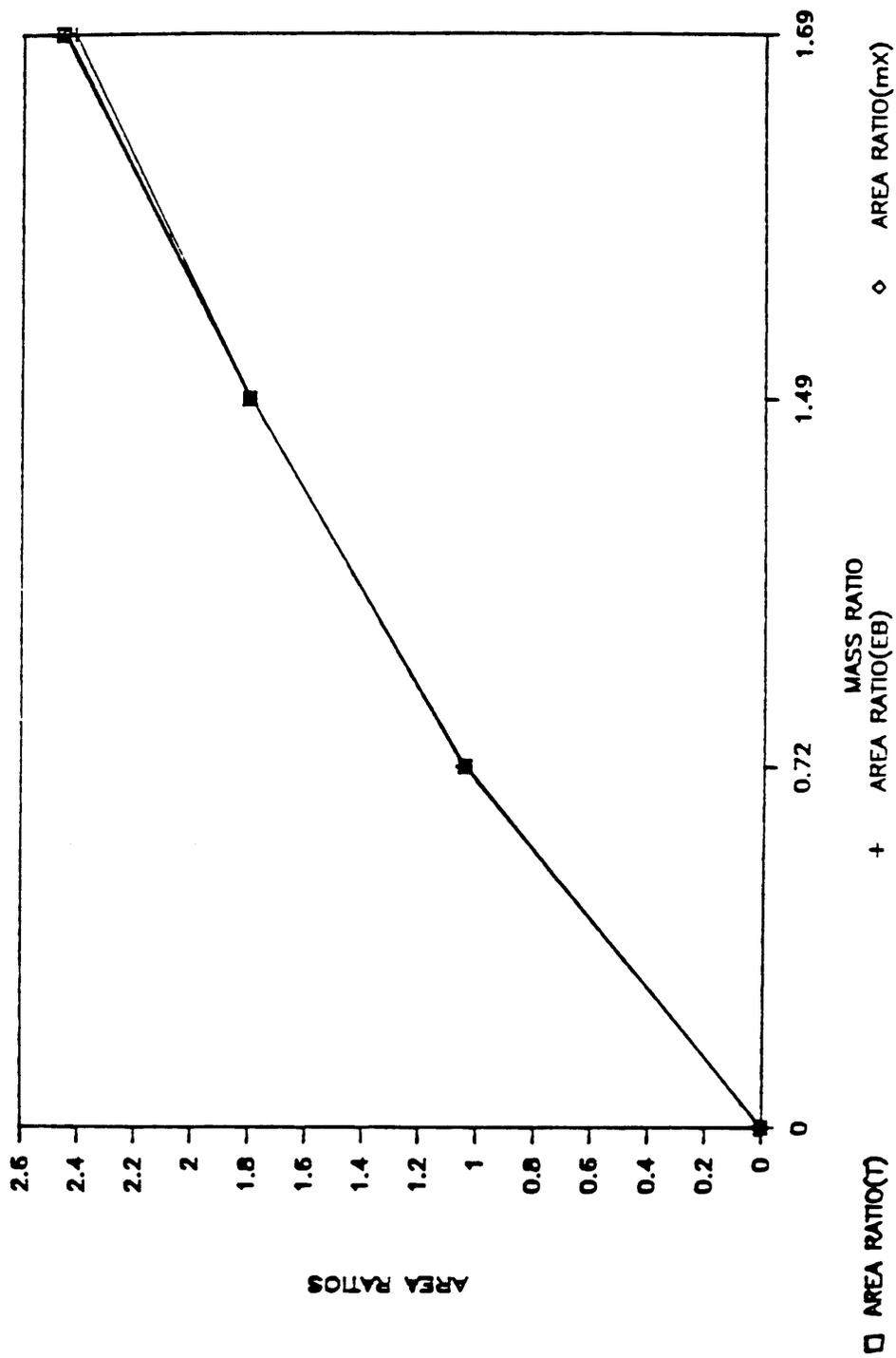
Three standard solutions of the target compounds in CS<sub>2</sub> were prepared to generate a calibration curve and instrumental response factors (RF). The mass of each target compound in each solution was varied while the mass of the internal standard was held constant. Mass and area ratios were determined from the GC results to obtain the calibration curve. Prior to each use of the GC, at least one of the three standards was re-analyzed to ensure that RF values remained constant to within approximately 10 percent.

## Results

Calibration Curve and Response Factors. Area ratios for the three stock solutions are shown in Figure 4 as a function of their respective mass ratios to derive analyte response factors (RF). Response factors for each analyte were given by the slope of line relating their area ratios and mass ratios. The response factors were determined to be 1.35, 1.33, and 1.35 for T, EB, and mX, respectively.

Recovery Experiments. Two recovery experiments (I and II) were performed at different HC loadings to obtain extraction efficiencies of CS<sub>2</sub> for desorption of the target compounds

Figure 4. Calibration Curve for GC Analyses



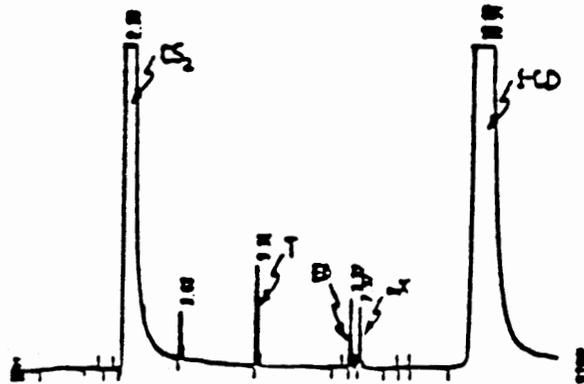
from GAC. The data are summarized in Table 5. The difference between recovery experiments I and II is in the loading of GAC and the method of contacting the GAC and aqueous phase containing the target compounds. In Experiment I, the GAC loadings were about 0.4 mg/g whereas in Experiment II they were about 0.1 mg/g. In Experiment I, the solvent was contacted by intermittent-hand shaking for 30 minutes whereas continuous mechanical shaking for 1 hour was used in Experiment II. Extraction efficiencies did not differ appreciably in these two experiments suggesting that differences in sorbed phase loading, agitation method and agitation time were not significant. In all instances, the extraction efficiencies were less than 10 percent. Such low values could be due to the inability of CS<sub>2</sub> solvent molecules to fully penetrate entrained water in the tortuous internal pore structure of the GAC and/or to the insufficient time (30 min to 1 hour). Poor extraction efficiency of GAC has been cited by others and is a major deterrent to achieving good sensitivity in dosimetry.

Tank Exposure Experiments. The amount of GAC added to each dosimeter, the tank concentration of the target compounds as measured by aqueous phase extraction, and the exposure time to the dosimeters in each experiment are given in Table 6. After GC analysis of the dosimeters, the concentration of the target compounds was calculated using Equation 5. Typical chromatograms obtained after extraction of the GAC in Tank Exposure Experiments 5, 6, and 7 (gasoline) are presented in Figure 5.

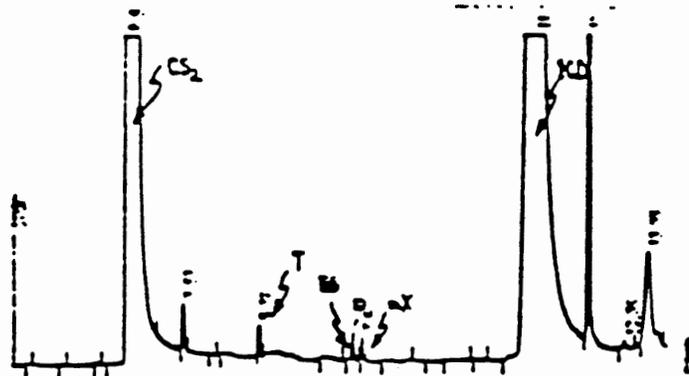
A comparison of the measured (aqueous phase extraction) and predicted (Equation 5) concentrations of each target compound in each exposure experiment is presented in Table 7. Experiments 1 and 2 were conducted using identical initial HC concentrations, agitation procedure, and exposure times. However, the solvent extracts obtained from the dosimeters used in these two experiments were held before analysis for

Figure 5. Representative Chromatograms from Exposure Tank Experiments

TANK EXPOSURE EXPMT. #5, DOSIMETER #3 - INJ. 1



TANK EXPOSURE EXPMT. #6, DOSIMETER #3 - INJ. 2



GASOLINE EXPERIMENT, DOSIMETER #2 - INJ. 1



different times (10 days in Experiment 1 and 3 days in Experiment 2). In all subsequent experiments, the holding time was limited to 24 hours.

Table 5. Data from recovery experiments

1. <u>Experimental Set-Up</u>						
<u>Experiment Number</u>	<u>Run No.</u>	<u>Mass of GAC (g)</u>	<u>Mass of Target Compound Added, mg</u>			
			<u>T</u>	<u>EB</u>	<u>mX</u>	
I	1	2.07835	0.867	0.867	0.864	
II	1	2.12950	0.289	0.289	0.288	
	2	2.25464	0.289	0.288	0.288	
	3	2.13733	0.289	0.289	0.288	

2. <u>Results</u>							
<u>Experiment Number</u>	<u>Run No.</u>	<u>Mass of Target Compound in Extract (mg)</u>			<u>Extraction Efficiency (EE)<sup>a</sup> (%)</u>		
		<u>T</u>	<u>EB</u>	<u>mX</u>	<u>T</u>	<u>EB</u>	<u>mX</u>
I <sup>b</sup>	1	0.067	0.087	0.044	8.5 ±1.4	10.4 ±5.4	5.1 ±0.3
II <sup>c</sup>	1	0.029	0.028	0.025	9.9	9.7	8.8
	2	0.026	0.025	0.020	9.1	8.5	6.8
	3	0.026	0.024	0.019	9.0	8.4	6.5
				Avg.	9.3 ±0.5	8.9 ±2.2	7.4 ±2.8

<sup>a</sup> Mean + One Standard Deviation

<sup>b</sup> GAC extracted by intermittent hand-shaking for 30 min

<sup>c</sup> GAC extracted by Jr. Orbit mechanical agitator operating at 150 rpm for 1 hour

Before analyzing the results of dosimetry, it is important to note that the measured concentrations in the exposure tank

decreased significantly with time, perhaps due to volatilization during the initial mixing of the tank or to sorption onto the tank walls. For example, in Experiment 1, the initial concentrations of toluene, ethyl benzene and m-xylene were 18.2, 18.1 and 16.5 mg/L, respectively (Table 6) while the final values after 14 hours of exposure were 3.07, 6.96 and 6.84 mg/L, respectively (Table 7).

The predicted and measured (final) concentrations (Table 7) were in reasonably good agreement in Experiments 1 and 2, most being within about 25 percent of each other. In Experiments 3 and 4, predicted values were between 25% and 50% of the measured values.. Agreement among replicated dosimeters was only fair. For example, dosimeter numbers 2 and 3 from Experiment 3 significantly over-predicted concentrations while dosimeter number 1 was in close agreement with the measured value. Improper extract work-up or injection may have been responsible for the anomalously high concentrations measured.

In Experiment 4, dosimeter-predicted data were generally reproducible. However, toluene and ethyl benzene concentrations were only 20% to 30% of their respective measured values while m-xylene was nearly 60% of its measured value.

The dosimeters used in Experiments 5 and 6 gave predictions that closely matched the measured values even though concentrations were over an order of magnitude lower than in previous experiments (from 0.5 to 1 mg/L). Moreover, the replicated dosimeters agreed with each other. Predicted concentrations of toluene and m-xylene averaged 92% and 81% of measured values in Experiment 6. Comparisons between predicted and measured concentrations of toluene in Experiment 5 are less credible owing to the fact that the measured toluene concentrations was much higher than expected. However, excellent agreement was obtained for ethyl benzene in Experiment 5.

Table 6. Design of dosimeter exposure experiments

Experiment Number <sup>a</sup>	Number of Dosimeters Used	Mass GAC (g)	Initial Target Compound Concentrations <sup>b</sup> (mg/l)			Exposure Time (hours)
			T	EB	mX	
1	1	1.32640	18.2	18.1	16.5	14
2	1	1.29430	18.2	18.1	16.5	14
	2	1.38990				14
3	1	1.27807	8.3	8.3	8.2	29
	2	1.32605				29
	3	1.39592				29
4	1	1.15115	8.3	8.3	8.2	48
	2	1.16842				48
	3	1.18880				48
5	1	1.27922	0.83	0.83	0.82	81
	2	1.22680				81
	3	1.28779				81
6	1	1.32261	0.83	0.83	0.82	79
	2	1.40793				79
	3	1.33740				79
7	1	1.25720	ND	ND	ND	69
	2	1.24990				69
	3	1.22966				69

<sup>a</sup> Mass of internal standard (1-chlorodecane) for GC analyses was 156.24 mg in Experiment No. 1, 130.20 mg in Experiment No. 2 and 43.4 mg in Experiment Nos. 4-7

<sup>b</sup> Measured by CS<sub>2</sub> extraction of solution added to tank

ND Not determined; only final concentrations measured by liquid-liquid extraction (see Table 7)

The dosimeters were tested using gasoline in Experiment 7. The same target compounds were analyzed as in Experiments 1 to 6 but in this instance, it was necessary to identify these from the many peaks appearing in the chromatogram shown in Figure 5. The GC peaks corresponding to these compounds were

Table 7. Results from tank exposure experiments

Experiment Number	Dosimeter Number	Target Compound Concentrations, (mg/L)							
		Pred <sup>1</sup>		Meas <sup>2</sup>		Pred <sup>1</sup>		Meas <sup>2</sup>	
		T	T	EB	EB	mX	mX		
1 <sup>a,3</sup>	1	4.34	3.07	5.50	6.96	9.95	6.84		
2 <sup>b,3</sup>	1	3.36	4.12	1.04	2.10	2.44	2.01		
	3	4.70		1.35		3.59			
	AVG	4.03		1.20		3.02			
3 <sup>c,3</sup>	1	2.53	5.58	1.69	3.64	2.53	3.04		
	2	11.48		7.68		12.39			
	3	11.04		7.49		11.58			
	AVG	8.35		5.62		8.83			
4 <sup>c,3</sup>	1	1.45	8.00	1.37	4.31	2.39	3.75		
	2	1.29		1.25		2.11			
	3	1.38		1.30		2.29			
	AVG	1.37		1.31		2.26			
5 <sup>c,3</sup>	1	0.58	2.43	0.51	0.59	1.00	0.55		
	2	0.75		0.51		0.92			
	3	0.85		0.61		1.10			
	AVG	0.73		0.54		1.10			
6 <sup>c,4</sup>	1	0.57	0.51	0.67	0.53	0.55	0.39		
	2	0.41		1.08		0.47			
	3	0.44		0.48		0.43			
	AVG	0.47		0.74		0.48			
7 <sup>c,4</sup>	1	1.07	1.66	0.32	0.40	1.00	1.21		
	2	1.61		0.47		1.57			
	3	1.31		0.39		1.27			
	AVG	1.33		0.39		1.28			

- <sup>a</sup> Extracts refrigerated 10 days prior to GC analysis  
<sup>b</sup> Extracts refrigerated 3 days prior to GC analysis  
<sup>c</sup> Extracts refrigerated 24 hours prior to GC analysis  
<sup>1</sup> Predicted by dosimeter  
<sup>2</sup> Measured by CS<sub>2</sub> extraction of solution in tank at end of exposure time  
<sup>3</sup> Agitation Procedure 1 employed for extracts  
<sup>4</sup> Agitation Procedure 2 employed for extracts  
 Recovery Exp I data used for Tank Exps 1-5  
 Recovery Exp II data used for Tank Exps 6-7

identified by assuming that their retention times were as found in known standard solutions. Peak areas for the target compounds were substantial enough to facilitate quantitation using the internal standardization technique employed earlier. However, at gasoline concentrations in the low ug/L range, more sensitive GC/MS techniques may be required. The dosimeters predicted the concentration of target compounds from gasoline to within 75% of measured values. The range of detectable concentrations was from 0.3 mg/L and 1.6 mg/L

#### Factors Contributing to Dosimeter Sensitivity

The second-generation dosimeter design featured use of a Nuclepore filter (L = 10 um) as the diffusion barrier. This design increased the flux of hydrocarbons across the barrier and thus decreased the exposure time required to accumulate a measurable analyte mass. The impact of decreasing the diffusion length on sensitivity can be illustrated by rearranging Equation 5 as follows:

$$t = mL/[CDA(EE)] \quad (9)$$

If some minimum mass, m, is to be collected for analysis, the exposure time, t, is directly proportional to the length, L, of the diffusion barrier and inversely proportional to the concentration, C. For example, in these tank exposure experiments, 81 hours were required to detect 0.3 ppm and 14 hours were needed for 10 ppm. These times are substantially less than needed in the original design of the dosimeter that incorporated a diffusion barrier length of 1 cm (DiGiano et al. 1988a); an exposure time of 5 days (120 hours) was required to detect 10 ppm and 20 days (480 hours) to detect 1 ppm of p-xylene.

The loading of target compounds on GAC in the tank exposure experiments was calculated by knowing the mass of each target compound adsorbed (based on the analysis of the GAC extracts) and the weight of GAC added to the dosimeter as shown below:

$$\text{loading, mg/g} = (m/EE)/(\text{mass GAC}) \quad (10)$$

These loadings ranged from 0.4 mg/g to 1.6 mg/g as shown in Table 8. The loadings are very low given the sorptive capacity (20 to 100 mg/g) of activated carbon for these hydrocarbons (Giusti et al. 1974). Therefore, the assumption of zero concentration near the GAC surface as is needed in the dosimeter calculations (see Figure 1 and Equation 2) is probably very reasonable.

The loadings of target compounds used in the recovery experiments to determine extraction efficiency are also shown in Table 8. These values were from two to ten times lower than obtained in the tank exposure experiments (0.1 mg/g to 0.4 mg/g). Ideally, the loadings in both types of experiments should be similar so as to insure that the extraction efficiency (EE) is applicable.

In general, the GC technique for detection of target compounds extracted from the dosimeters was sensitive enough. As given in Table 9, the range of detection evaluated in the Tank Exposure experiments was between 3 mg/L and 15 mg HC/L. However, the FID occasionally failed to detect the internal standard, 1-CD, in the GAC extracts. The problem occurred periodically in both the Tank Exposure and Recovery experiments. As a result, 1-CD peaks were sometimes omitted from extract chromatograms which consequently voided the data. Temporary lapses in detector sensitivity due to fouling or age may have caused the problem. However, FID detectors are known to occasionally respond erratically to some halocarbons. Use of a more amenable compound class such as alkyl-substituted aromatics as internal standards is recommended. This class is structurally more similar to the analytes and exhibits excellent response to FID detection.

Table 8. Mass loading data: Analytes on GAC in tank exposure and recovery experiments

Tank Exposure (TE) or Recovery (R) Experiment Number	Dosimeter Number	Mass Loading on GAC (mg/g)		
		T	EB	mX
TE 1	1	0.828	0.943	1.897
TE 2	1	0.657	0.186	0.429
	3	0.855	0.221	0.593
TE 3	1	1.035	0.622	0.932
	2	4.535	2.727	4.399
	3	4.142	2.527	3.906
TE 4	1	1.094	0.927	1.618
	2	0.960	0.834	1.414
	3	1.009	0.849	1.501
TE 5	1	0.662	0.526	1.027
	2	0.892	0.549	0.991
	3	0.968	0.620	1.127
TE 6	1	0.610	0.654	0.531
	2	0.420	0.982	0.432
	3	0.466	0.462	0.414
TE 7	1	1.061	0.281	0.917
	2	1.605	0.419	1.444
	3	1.329	0.356	1.186
R I	1	0.378	0.403	0.407
R II	1	0.136	0.136	0.135
	2	0.128	0.128	0.127
	3	0.135	0.135	0.135

The Potential for Applying Passive Dosimetry for Leak Detection and for Ground Water Monitoring

The following discussion pertains only to application of passive dosimetry to measurements of contaminants in the ground water, not to soil gas. Although passive dosimetry

could be utilized as a leak detection system for USTs, operational limitations exist which may limit widespread applicability. The present dosimeter design requires solvent desorption and GC analysis to obtain information regarding the presence of HCs. The time required to obtain data could be quite costly in the event of a major tank failure. Even if field gas chromatographs were used, analyses may take 10 to 20 minutes per injection. This becomes a significant limiting factor if numerous dosimeters must be analyzed simultaneously. In contrast, many remote leak detection systems provide continuous surveillance and rapid response.

Table 9. FID detection of the target compounds

<u>Experiment Number</u>	<u>Dosimeter Number</u>	<u>Average Mass Detected in Extract (ng/uL)</u>		
		<u>T</u>	<u>EB</u>	<u>mX</u>
1	1	9.3	13.0	12.8
2	1	7.2	2.5	2.8
	3	10.1	3.2	4.2
	AVG	8.7	2.9	3.5
3	1	11.2	8.3	6.1
4	1	10.7	11.1	9.5
	2	9.5	10.1	8.4
	3	10.2	10.5	9.1
	AVG	10.1	10.6	9.0
5	1	7.2	7.0	6.7
	2	9.3	7.0	6.2
	3	10.6	8.3	7.4
	AVG	9.0	7.4	6.8
6	1	7.5	7.7	5.2
	2	5.5	12.3	4.5
	3	5.8	5.5	4.5
	AVG	6.3	8.5	4.7
7	1	12.4	3.1	8.3
	2	18.7	4.7	13.0
	3	15.2	3.9	10.5
	AVG	15.4	3.9	10.6

While a cost-savings may be realized with dosimetry relative to the remote systems, vital information concerning possible leaks is acquired more slowly. In most applications, the initial economic advantages of passive dosimetry do not adequately outweigh slower detection and response times.

On the other hand, passive dosimetry may be well-suited for ground water monitoring. Dosimeters may readily be lowered into monitoring wells. A series of dosimeters may be nested and retrieved after different exposure times. This would provide a running average concentration of contaminants. Such data would be useful in tracking a contaminant plume from a LUST.

Utilization of passive dosimeters in ground water monitoring draws upon two operational advantages of the technique. The first concerns the fact that passive dosimeters provide time-averaged response. Since ground water flow velocities are typically low and contaminant concentrations are low, dosimeters should provide a reasonable estimate of time averaged concentration and allow for accumulation of sufficient mass to make accurate computations of concentrations.

The target compounds amenable to detection by passive dosimetry could be expanded to include common contaminants such as halogenated aliphatics, alkenes, and aromatics. However, the GC analytical method would require some modification depending upon the analytes under evaluation.

One potential operational difficulty is growth of microorganisms within the GAC reservoir of the dosimeters. Indigenous microbial populations therefore could biodegrade the target compounds. Limiting the the dosimeter exposure times (hour to days) may solve the problem; alternatively, a microbial growth retardant could be added to the dosimeter.

## SOIL GAS AND GROUND WATER MONITORING WITH PASSIVE DOSIMETRY

### Objectives

The objectives of this phase of investigation were as follow:

1. to develop a vapor-phase dosimeter that relies on activated carbon adsorption for monitoring the soil gas in the unsaturated zone at a site contaminated with fuel
2. to conduct field testing of both vapor-phase and aqueous-phase dosimeters at Pope Air Force Base in Fayetteville, North Carolina.

### Laboratory Testing of Vapor-Phase Dosimeter

A laboratory experiment was conducted to determine what concentration the dosimeter would predict in a relatively stagnant situation, which would be analogous to the field condition of vapor-phase measurements in soil gas. The laboratory set-up of the dosimeter test system is given in Figure 6. A prototype dosimeter, similar to that shown in Figure 2, was placed on cardboard stand inside an 8 L desiccator that was sealed with high vacuum grease. This dosimeter was constructed of acrylic polymer, having a diameter of 75 mm and with diffusion channels 1 cm in length and having a total diffusion area of  $3.75 \text{ cm}^2$ .

The desiccator was flooded with 1 ppm octane from a compressed gas cylinder at flow of 1410 L/hr standard for two minutes in order to establish a concentration of one ppm (by volume).<sup>1</sup>

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<sup>1</sup> Vapor phase concentrations are typically expressed in ppm (volume/volume) to indicate volumetric ratio of contaminant to air whereas aqueous phase concentrations are typically expressed in mg/L (mass/volume).

Figure 6. Laboratory Dessicator Set-Up Used to Expose Dosimeter to Octane

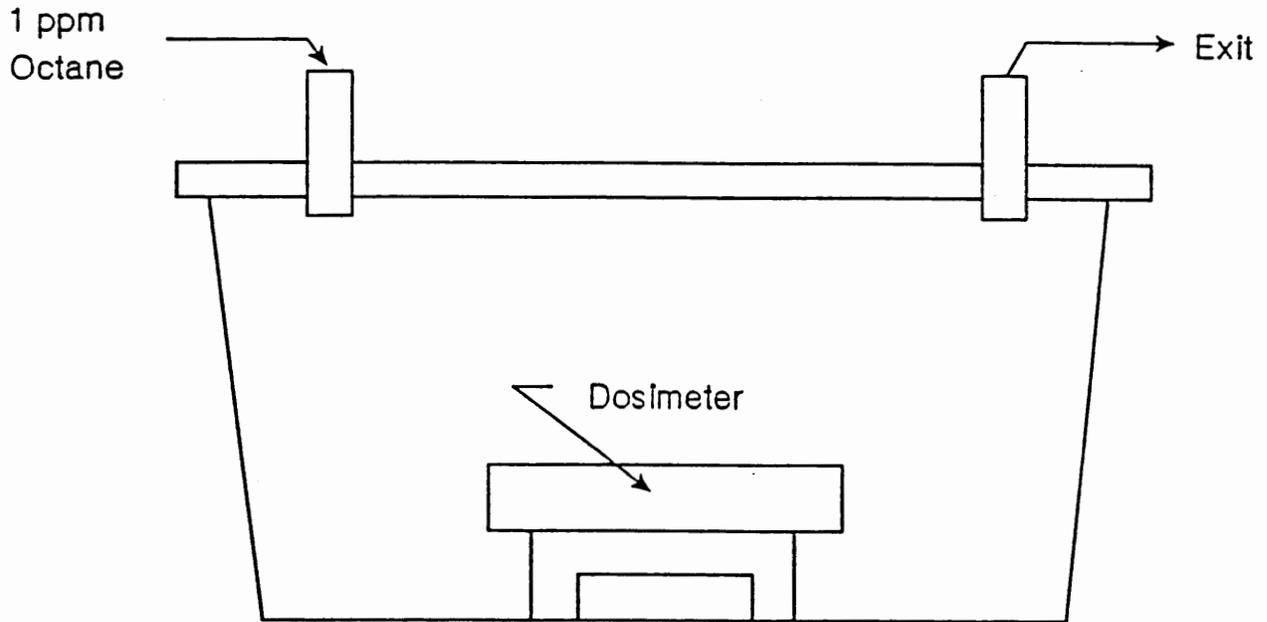
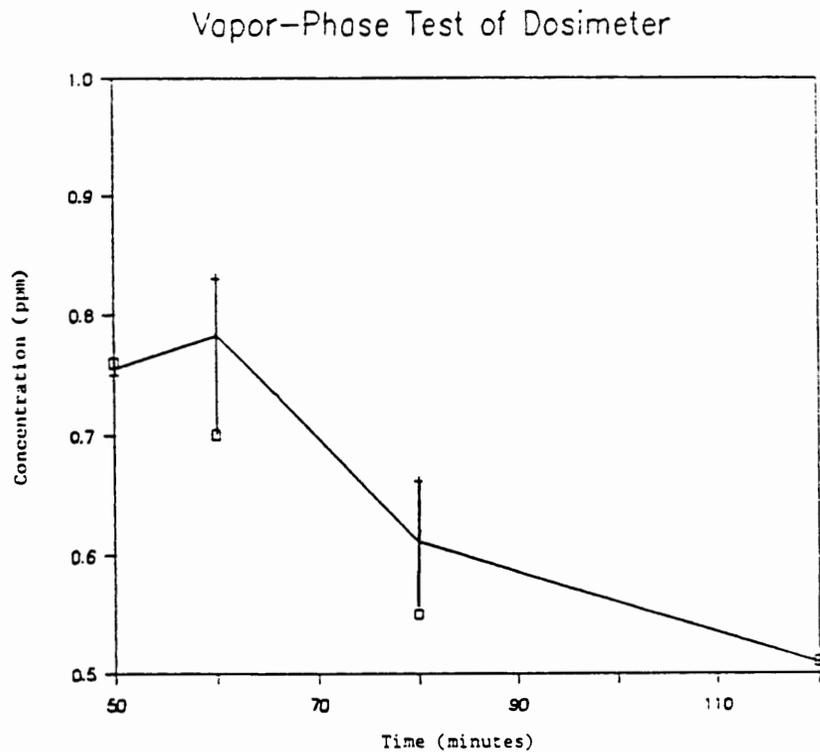


Figure 7. Laboratory Results of Dosimeter Vapor-Phase Sampling of Octane in a Quiescent Atmosphere, with High and Low Values Isolated



In each experiment, the dosimeter was exposed for times ranging from 50 to 120 minutes and then removed for analysis of octane and calculation of the concentration in the desiccator according to Equation 5. The procedures for extracting and analyzing the octane that was adsorbed on the GAC in the dosimeter were the same as described in the previous section except for use of a different internal standard (m-xylene instead of chlorodecane).

The calculated octane concentrations after different exposure times are given in Figure 7. After 50 minutes, the calculated concentration was about 0.75 ppm which agrees fairly well with the expected value of 1.0 ppm. However, lower concentrations were found at longer exposure times. This could be partly due to the fact that in a stagnant space, GAC adsorbs octane thus decreasing the mass in the desiccator volume and thus concentration. After 80 minutes of exposure, the dosimeter adsorbed about 9% of the total initial mass of octane in the desiccator. This loss, however, is not enough to explain the decrease in concentration that was calculated. Octane could have escaped from the desiccator or sorbed onto walls; alternatively, the extraction efficiency of the GAC (EE value in Equation 5) may not be known accurately. Regardless of the reason, the dosimeter was able to measure the octane concentration within a factor of two.

#### Selection of Target Compounds for Field Tests

Three constituents of JP-4 jet fuel were selected: n-octane, m-xylene and o-xylene. These gave peaks well separated on the gas chromatogram, and they represented alkane and aromatic compounds common to the fuel mixture. The physical characteristics of the target compounds are listed in Table 10. Extraction efficiencies and instrument response factors were developed in the laboratory (Pate 1989). The procedure for extraction of GAC in the dosimeter was the same as reported above with the exception of the internal standard which was 1-chloroheptane.

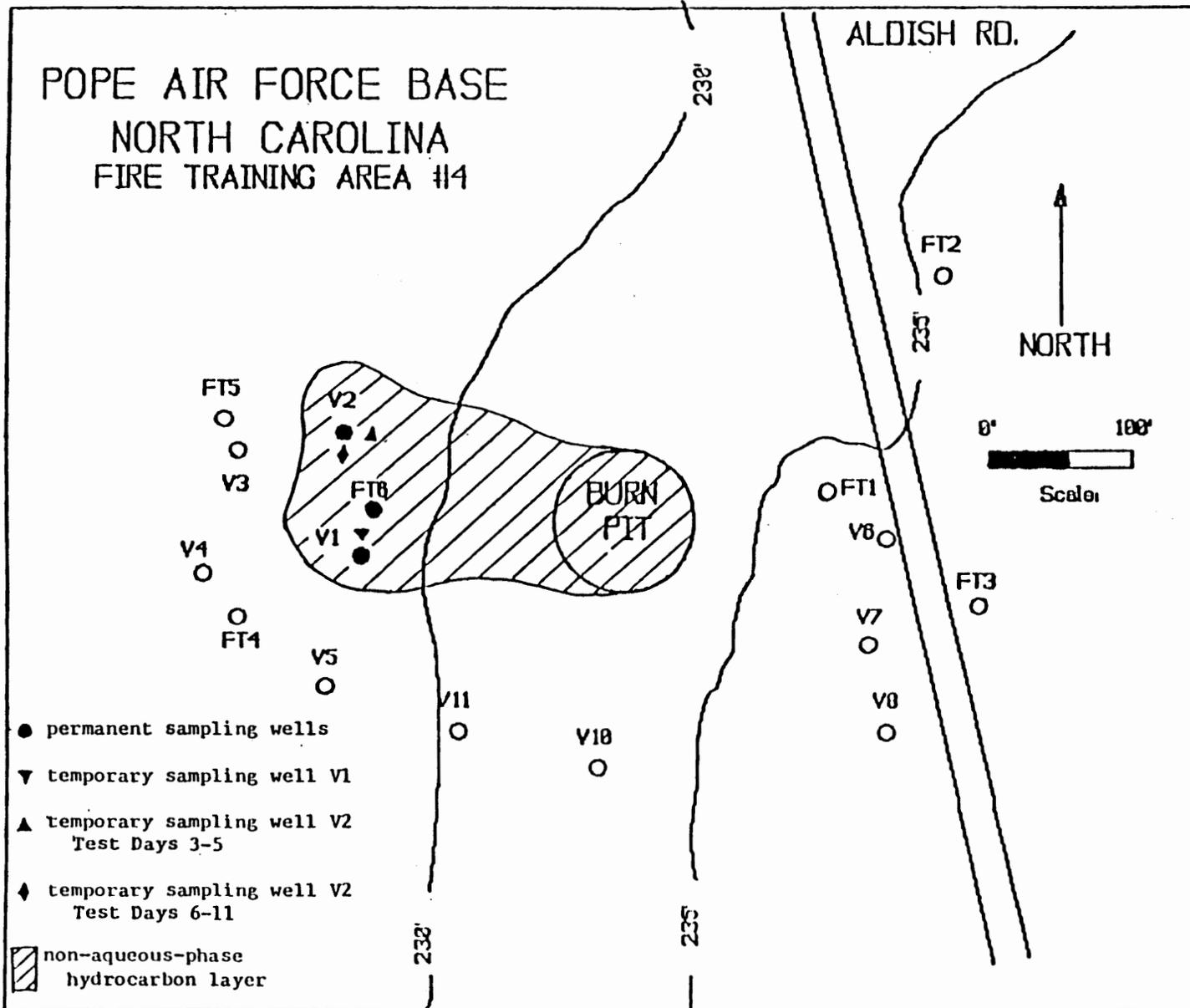
Table 10. Physical properties of the target compounds

<u>Compound</u>	<u>MW</u> (g/mol)	<u>Specific</u> <u>Gravity</u>	<u>Aqueous</u> <u>Solubility</u> (mg/l)	<u>Molecular Diffusivity</u>	
				<u>in Air</u>	(cm <sup>2</sup> /sec) <u>in Water</u>
octane	114	0.703	0.66	0.062	5.63 x 10 <sup>-6</sup>
m-xylene	106	0.868	175	0.069	6.71 x 10 <sup>-6</sup>
o-xylene	106	0.870	175	0.073	6.716 x 10 <sup>-6</sup>

Description of the Field Site

The fire training area at Pope Air Force Base (Pope AFB) near Fayetteville, NC was selected for testing the dosimeters. This site is known to be contaminated with fuel and has been investigated and is well documented by another team from the University of North Carolina (Miller and Staes 1991). A plan view of the site is given in Figure 8. The "burn pit" is about 30 m in diameter and surrounded by a retaining wall of sand about 1 m in height. The burn pit is the middle of a training area that is approximately 170 m long and 135 m wide. Large metal garbage dumpsters and three nozzles are located in the burn pit through which jet fuel (JP-4) can be pumped. During fire training practice, an average of 2200 L of JP-4 is pumped into the pit, the fuel is lit, and the resulting fire is extinguished as a fire-fighting drill (Personal Communication, August 1989, Fire Training and Civil Engineering Personnel at Pope Air Force Base during fire training session). This exercise has taken place three to four times per month for more than twenty years. Because the burn pit is unlined, jet fuel has penetrated into the ground thereby contaminating the soil and ground water.

Figure 8. Field Testing Site, Pope Air Force Base, Fayetteville, North Carolina



Also shown in Figure 8 is the location of sampling wells used for monitoring by other research teams. Permanent wells have been established by the University of North Carolina study team (Miller and Staes 1991) to measure contaminants in both the ground water and soil gas, the latter being referred to as vapor phase samples. The vapor wells, labeled "V" and shown by either open or closed circles, are 3-inch diameter, stainless steel casings which extended down to the ground water. Holes are drilled in the casing at 30 cm intervals beginning 50 cm below the ground surface. Vapor phase samples are then withdrawn from these holes via stainless steel tubes (1/8 inch diameter). Other permanent wells are used for sampling the ground water. These are labeled "FT" (fire training) and consist of 3-inch diameter PVC casings. All sampling in this research was performed from wells located down-gradient from the burn pit.

Soil in the burn pit area is composed of medium sand particles to a depth of 20 to 25 cm, before becoming mixed with a small amount of clay. The soil in the woods nearby contains a much higher organic content in the top layer and hard clay at a depth of about 30 cm. Dosimeter testing was done from March 15, 1989, to June 9, 1989, a period in which rainfall was above normal; a rise in water table of about 60 cm was noted.

The components of jet fuel and their relative amounts (as determined by peak areas of the gas chromatogram) are presented in Table 11 (Bishop et al. 1983). Also shown are the amounts of these same components found typically in gasoline. As noted earlier, the target compounds selected were octane, m-xylene and o-xylene. While these are not the major components (methyl butane, n-pentane and methyl pentane are much more prevalent), they are nevertheless present in detectable amounts.

Table 11. A comparison of components in JP-4 jet fuel and gasoline

<u>Compound</u>	<u>Mol. Wt.</u> <u>(g/mol)</u>	<u>Area %</u> <u>JP-4</u>	<u>Area % Gas</u>
Propane	44.04	1.00	2.10
Isobutane	52.18	2.65	6.00
n-Butane	52.18	5.60	32.50
Methyl butane	72.15	12.25	21.80
n-Pentane	72.15	13.05	10.90
Dimethyl butane	86.18	2.45	1.90
Methyl pentane	86.18	11.30	5.50
n-Hexane	86.18	8.15	2.30
Methyl cyclopentane	84.16	3.45	1.00
Benzene	78.12	1.25	0.50
Cyclohexane	84.16	3.10	0.30
Methyl hexane	100.21	2.70	0.50
Dimethyl pentane	100.21	2.70	0.00
n-Heptane	100.21	4.30	0.40
Methyl cyclohexane	98.19	2.75	0.00
Toluene	92.15	1.15	0.90
Methyl heptane	114.23	1.50	0.00
Dimethyl cyclohexane	112.22	1.50	0.00
n-Octane	114.23	2.00	0.10
Ethyl benzene	106.17	0.18	0.20
Xylenes	106.17	0.68	0.55
Others	-	16.29	12.55

Source: Bishop et al. 1983

#### Design of Dosimeters for Field Test

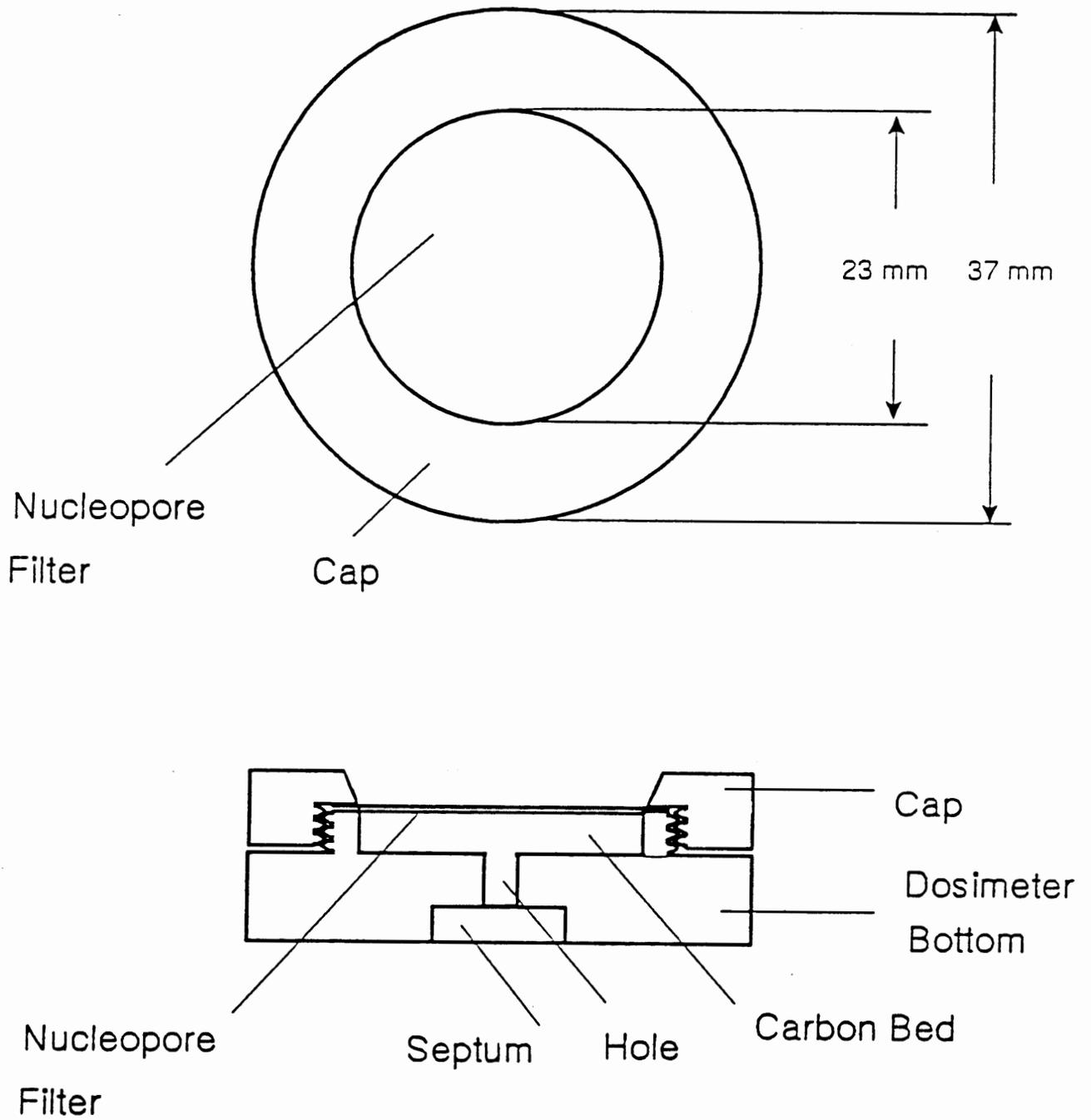
New dosimeters were made from aluminum since the original design used an acrylic polymer that was capable of absorbing hydrocarbons. While absorption was not expected to be a problem for the vapor measurements, there was a thick hydrocarbon layer floating on the aquifer which could irreversibly damage an acrylic dosimeter when used for aqueous-phase sampling. Another modification to the original design was to reduce the diameter of the dosimeter from 75 mm to 37 mm. This allowed the dosimeter to be lowered into the casing of the aqueous-phase sampling wells.

The dosimeter was composed of two sections that screwed together. Different designs were used for the aqueous and vapor-phase dosimeters. That of the aqueous phase dosimeter is given in Figure 9. In this design, a Nuclepore filter was needed as the diffusion barrier in order to minimize exposure times needed to collect enough contaminants for measurement (see Section 5 for more details). The bottom-half was aluminum stock out of which a well was drilled to contain 0.9 g of GAC. A Nuclepore filter rests on the bottom-half to provide diffusion channels that are 10  $\mu\text{m}$  in length. A scanning electron microscope was used to estimate the total diffusion area (i.e., the pores in the filter) as being 7.9% of the total filter surface area. Since the diameter of the filters (37 mm) was larger than that of the dosimeter, it was necessary to cut them to a diameter of 32 mm. The top-half of the dosimeter was a screw-on ring (cap) that held the Nuclepore filter in place above the well containing the GAC and provided exposure to the water being sampled.

The vapor-phase dosimeters were similar to the original design used developed by DiGiano et al. (1988a). Because of the relatively high concentrations of contaminants expected in the vapor phase, the diffusion channels did not have to be modified by use of the Nuclepore filter. Instead, into the upper-half section, consisting of aluminum, were drilled 39 diffusion channels, each 1 cm in length and  $0.05 \text{ cm}^2$  in cross-sectional area, giving a total area of  $1.95 \text{ cm}^2$ . The top-half of the dosimeter also contained a 30-mesh (U.S. standard sieve size) screen which prevented loss of GAC from the bottom-half section. The bottom-half was made from aluminum stock from which a space was hollowed-out to make a well to hold 0.8 g of GAC; an O-ring was used to give a tight seal with the top-half.

The GAC used in both dosimeters was Calgon Filtrasorb 400 which was ground to 20 X 30 mesh (U.S. standard sieve size) and washed with distilled water to remove all fine particles.

Figure 9. Design of Dosimeters Used for Aqueous-Phase Sampling



The carbon used in the water analysis was boiled for 30 minutes and stored in water to remove air from the carbon pores.

### Field Measurements

Both the vapor- and aqueous-phase concentrations of target compounds were measured with the appropriate passive dosimeter and a reference procedure. The reference procedure for vapor-phase measurements was use of a Gastec Detector Tube (GDT); that for the aqueous-phase measurements was liquid-liquid extraction (LLE). The GDT method has been used in mapping soil contamination (Crouch 1990). The GDT consists of two sections of activated carbon in series (400 mg followed by 200 mg) contained within a tube (Saalwaechter et al. 1977). A simple hand pump allows 100 cm<sup>3</sup> of air to be pulled through the tube. LLE was performed on aqueous samples (60-70 mL) withdrawn for the aqueous phase sampling wells. The sample was transferred to a separatory funnel and 12-15 mL of unspiked CS<sub>2</sub> was added. The mixture was shaken and allowed to settle before the CS<sub>2</sub> layer was drained into a 15 mL Erlenmeyer flask. The extract was spiked with the 1-chloroheptane as the internal standard and 1 g of sodium sulphate (drying agent) before measurement by gas chromatography. An extraction efficiency of 100% was assumed based on other work by DiGiano et al. (1988b).

While different detection methods (passive dosimetry, GDT or LLE) were used, the final analysis of the CS<sub>2</sub> extracts for the target compounds was made by gas chromatography. Aliquots of 0.9 ul were injected into a Varian 3700 Aerograph gas chromatograph equipped with an FID and an SP-2100 fused silica capillary column. All samples were run with the same temperature program; five minutes at 60°F, then ramped at 4°F/min to an end temperature of 78°F. Although JP-4 is a complex mixture (see Table 11, the vapor-phase chromatogram was made relatively simple by the low vapor pressures of the

heavier organics. The aqueous-phase chromatograms were simplified by the low solubilities of the aliphatic constituents.

The vapor-phase passive dosimeters could not be installed in the permanent wells shown on the site map in Figure 8. Consequently, "temporary wells (TW)" were dug with a post-hole digger within about 2 m of each of two permanent wells (labelled V1 and V2 in Figure 8). These temporary wells were 15 cm in diameter and about 45 cm in depth.

The coding of each type of measurement and in each type of sampling well is given in Table 12. This coding will be used to present the data in both graphical and tabular form.

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Table 12. Coding of field measurements

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<u>Sample</u>	<u>Description</u>
VP/D/TW	Vapor-phase measurements taken with a dosimeter at temporary wells near permanent, vapor-phase wells V1 and V2.
VP/GDT/V	Vapor-Phase measurements taken with Gastec Detector Tube at permanent, vapor-phase wells V1 and V2.
VP/GDT/TW	Vapor-Phase measurements taken with Gastec Detector Tube at temporary wells near permanent, vapor-phase wells V1 and V2.
AP/D	Aqueous-phase measurements taken with a dosimeter at ground water sampling well FT6.
AP/LLE	Aqueous-Phase measurements taken by liquid-liquid extraction at ground water well FT6.

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Testing of the dosimeters was done on nine days in the period March 15 to June 9, 1989. A standard procedure was adopted for

preparing the dosimeters for field measurements. The GAC for each vapor-phase dosimeter was placed in individual vials in preparation for each trip. At the field site, the GAC was discharged into a dosimeter and the dosimeter assembled. The dosimeter was pressed against the side of the temporary well taking care to ensure close contact between the dosimeter face and the soil. The initial protocol did not include covering of the temporary wells to prevent dilution of soil gas with ambient air. However, a cover was used for measurements made on Days 6, 7 and 8. The dosimeters were exposed for 90 minutes near Well V1 and 75 minutes near Well V2. GAC was then removed from the dosimeter and placed into a vial for later analysis.

Dosimeters used for aqueous phase measurements were filled with GAC, covered with a Nuclepore filter, and capped. The dosimeter was submerged in "clean" water and the needle of a syringe was passed through the septum on the bottom of the dosimeter. Water was drawn through the dosimeter and into the syringe to remove the air pockets that formed between the filter and the carbon bed. The dosimeter was then placed in well FT6 for 4.5 to 5 hours. After this time, the dosimeter was removed from the well and the GAC was placed into a vial.

During exposure of the dosimeters, the Gastec Detector Tube was connected to the permanent, vapor-phase well. First, 200 cm<sup>3</sup> of air was pumped from the sampling line of the well. Then the tube containing the activated carbon was attached and 200 cm<sup>3</sup> of sample were drawn slowly through. This procedure was repeated with a second tube. The tubes were placed in a small cooler and returned to the laboratory where they were frozen until analysis, usually 3 to 4 days later.

On Days 7,8 and 9, the Gastec Detector Tube was placed in the temporary wells for a direct comparison with vapor-phase passive dosimeter. A piece of cardboard was used to block air that could enter the sampler from the atmosphere above the temporary well, thus diluting the soil gas concentration. A

two-inch, 19 gauge needle was fastened to a piece of rubber tubing which was connected to the pump. The needle was punched through the cardboard at the bottom of the well. After 200 cm<sup>3</sup> of soil gas was drawn through the sampler, the activated carbon trap was attached and from 800 and 1000 cm<sup>3</sup> of soil gas were drawn through to adsorb the hydrocarbons.

The GAC taken from the vapor phase dosimeters (VP/D/TW) were analyzed in the laboratory within two days after each field test. GAC was extracted by 9 mL CS<sub>2</sub> and spiked with the internal standard. Similarly, the front and backup sections of the activated carbon traps (VP/GDT/V and VP/GDT/TW) were placed in separate vials with 6 mL and 2 mL CS<sub>2</sub> being added, respectively. At least 30 minutes were allowed for extraction prior to GC analysis.

GAC from the aqueous-phase dosimeters (AP/D) was extracted with 8 mL of CS<sub>2</sub> spiked with the internal standard and to which was added 1 g sodium sulphate before allowing to stand (with intermittent shaking) for several hours before analysis.

## Results

Vapor-phase Concentrations. The concentrations (ppm) of octane (OCT), m-xylene (mX) and ortho-xylene (oX) obtained with the vapor-phase dosimeters in the temporary well (VP/D/TW) near V1, and the Gastec Detector Tubes in V1 (VP/GDT/V) or the adjacent temporary well (VP/GDT/TW) are presented in Table 13.

Similarly, those measurements taken at V2 and the temporary well near V2 are presented in Table 14. Multiple measurements with the passive dosimeter are shown on each sampling day. Also included in these tables is the distance of the vapor phase dosimeter above the ground water table. This shows that the water table was rising throughout testing. Samples were taken on nine days from March 15 to June 9, 1989. An additional data point was obtained from the work of Miller and Staes (1991) on March 29. This is labelled as VP/EP/V and

refers to a vapor phase sample drawn by an electric pump (EP) through a GAC trap. The sample volume is larger and known more accurately than that for the Gastec Detector Tube.

The results in Tables 13 and 14 show that the passive dosimeter gave much lower concentrations than the Gastec Detector Tube. Although only one point of comparison is available, the passive dosimeter also gave a lower concentration than obtained by the electric pump/GAC tube system. However, it is necessary to consider that the dosimeter was placed in a temporary well while the other two devices were connected directly to the permanent well. The temporary well was left uncovered during exposure of the dosimeters on all but Days 6,7 and 8. One explanation for low dosimeter measurements, therefore, could be the dilution of soil gas by ambient air. In fact, concentration measured by the Gastec Detector Tube in the temporary well was also low. This problem was not overcome by covering the temporary wells on Test Days 8 through 10; one possible explanation is that dilution air entered during the construction of the temporary well.

A comparison of the passive dosimeter measurements in the temporary well and the Gastec Detector Tube measurements in the adjacent permanent well is given for each target compound in Figures 10-15; these data were taken from Tables 13 and 14. Concentrations obtained with the Gastec Detector Tube were relatively constant over the nine test days and much higher than the passive dosimeter measurements. The relatively high concentration measured by the passive dosimeter on Day 4 may have been caused by pumping of JP-4 fuel into the burn pit in preparation for a fire extinguishing exercise. A large increase in concentration is also suspected from the results of the Gastec Detector Tube. On this sampling day, the back-up section of activated carbon contained a large amount of sorbed contaminants which suggested that not all of the contaminants were captured.

Table 13. Soil gas concentrations in the vicinity of permanent well V1

Day	Date	Sample Code	OCT ppm	mX ppm	oX ppm	Distance from Samples to Ground Water (cm)
1	3/15/89	VP/D/TW	13	6	ND	8.7
		VP/D/TW	16	ND	ND	
2*	3/29/89	VP/D/TW	111	40	6	6.1
		VP/D/TW	86	30	5	
		VP/D/TW	74	24	4	
		VP/EP/V1	247			
3	4/5/89	VP/D/TW	71	29	5	6.3
		VP/GDT/V1	79	10		
		VP/GDT/V1	73	20		
4	4/12/89	VP/D/TW	ND			5.5
		VP/D/TW	34	16	ND	
		VP/D/TW	4	ND	ND	
		VP/D/TW	ND			
		VP/D/TW	40	9	ND	
		VP/GDT/V1	127	40	8	
5	4/19/89	VP/D/TW	2	3	1	4.5
		VP/D/TW	12	12	3	
		VP/D/TW	ND	2	ND	
		VP/D/TW	11	6	2	
		VP/GDT/V1	63	16		
		VP/GDT/V1	88	15		
6	5/2/89	VP/D/TW	ND			4.3
		VP/D/TW	ND			
7	5/12/89	VP/D/TW	ND			1.8
		VP/D/TW	29	15	3	
		VP/D/TW	6	4	1	
		VP/D/TW	1	ND	ND	
8	5/17/89	VP/D/TW	3	3	2	2.0
		VP/D/TW	6	5	2	
		VP/D/TW	4	3	2	
		VP/D/TW	45	18	7	
		VP/GDT/TW	ND			
		VP/GDT/TW	ND	0.2	ND	

Continued

Table 13. Continued

<u>Day</u>	<u>Date</u>	<u>Sample Code</u>	<u>OCT ppm</u>	<u>mX ppm</u>	<u>oX ppm</u>	<u>Distance from Samples to Ground Water (cm)</u>
9	6/9/89	VP/D/TW	ND			4.3
		VP/D/TW	ND	2		
		VP/D/TW	ND			
		VP/D/TW	ND	1	0.8	
		VP/GDT/V1	ND			
		VP/GDT/V1		293	97	7.9
		VP/GDT/V1		307	105	8.3

\* Fire Fighting Test Conducted on Day 2

ND = Not detected

OCT = Octane

mX = m-xylene

oX = o-xylene

VP/EP/V = Vapor phase sample taken with electric pump passed through GAC trap (Miller et al. 1990)

Table 14. Soil gas concentrations in the vicinity of permanent well V2

<u>Day</u>	<u>Date</u>	<u>Sample Code</u>	<u>OCT ppm</u>	<u>mX ppm</u>	<u>oX ppm</u>	<u>Distance from Samples to Ground Water (cm)</u>
1	3/15/89	VP/D/TW VP/D/TW	91 150	32 44	8	3.5
2*	3/29/89	VP/D/TW VP/D/TW VP/D/TW VP/D/TW	202 220 315 360	71 67 106 124	10 16 26 30	1.0
3	4/5/89	VP/D/TW VP/D/TW VP/D/TW VP/D/TW	107 74 91 72	43 38 37 29	11 6 ND ND	0.4
4	4/12/89	VP/D/TW VP/D/TW VP/D/TW VP/D/TW VP/GDT/V2	69 45 75 35 222	41 27 28 18 69	13 4 8 ND 8	4.1 (NEW WELL)
5	4/19/89	VP/D/TW VP/D/TW VP/D/TW VP/CT/V2 VP/CT/V2	98 87 40 294 315			3.3
6	5/2/89	VP/D/TW VP/D/TW VP/D/TW	10 3 25	8 3 9	ND 2 1	1.1
7	5/12/89	VP/D/TW VP/D/TW VP/D/TW VP/D/TW VP/D/TW	13 2 9 7 2	10 1 7 5 3	2 ND 3 ND ND	0.2
8	5/17/89	VP/D/TW VP/D/TW VP/D/TW VP/D/TW VP/D/TW VP/GDT/TW VP/GDT/TW	4 2 4 5 9 0.7 0.9	5 2 3 3 6 0.5 ND	3 1 2 1 1 ND ND	1.0

Continued

Table 14. Continued

<u>Day</u>	<u>Date</u>	<u>Sample Code</u>	<u>OCT ppm</u>	<u>mX ppm</u>	<u>oX ppm</u>	<u>Distance from Samples to Ground Water (cm)</u>
9	6/9/89	VP/D/TW	1	2	ND	2.3
		VP/D/TW	1	1	1	
		VP/D/TW	ND	1	ND	
		VP/GDT/TW	2	0.6	0.4	
		VP/GDT/TW	2	0.7	20	
		VP/GDT/V2	296	119	21	

---

\* Fire Fighting Test Conducted on Day 2  
 ND = Not detected  
 OCT = Octane  
 mX = m-xylene  
 oX = o-xylene

Figure 10. Octane Concentration Measured in Field Soil Gas by Dosimetry (VP/D/TW) and by Gastec Tube (VP/GDT/V1) at Location VI. Vertical Lines Connect High and Low Values.

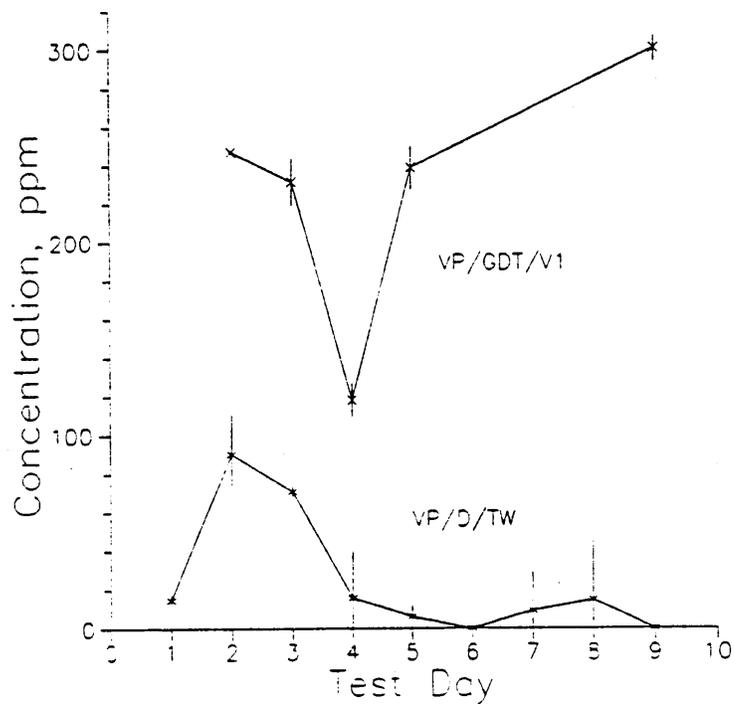


Figure 11. M-xylene Concentration Measured in Field Soil Gas by Dosimetry (VP/D/TW) and by Gastec Tube (VP/GDT/V1) at Location VI. Vertical Lines Connect High and Low Values.

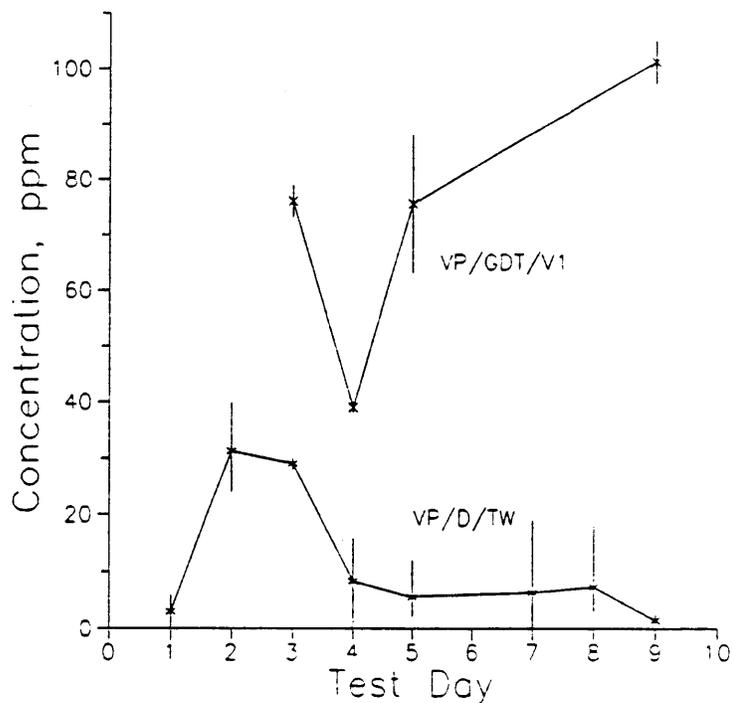


Figure 12. O-xylene Concentration Measured in Field Soil Gas by Dosimetry (VP/D/TW) and by Gastec Tube (VP/GDT/V1) at Location VI. Vertical Lines Connect High and Low Values.

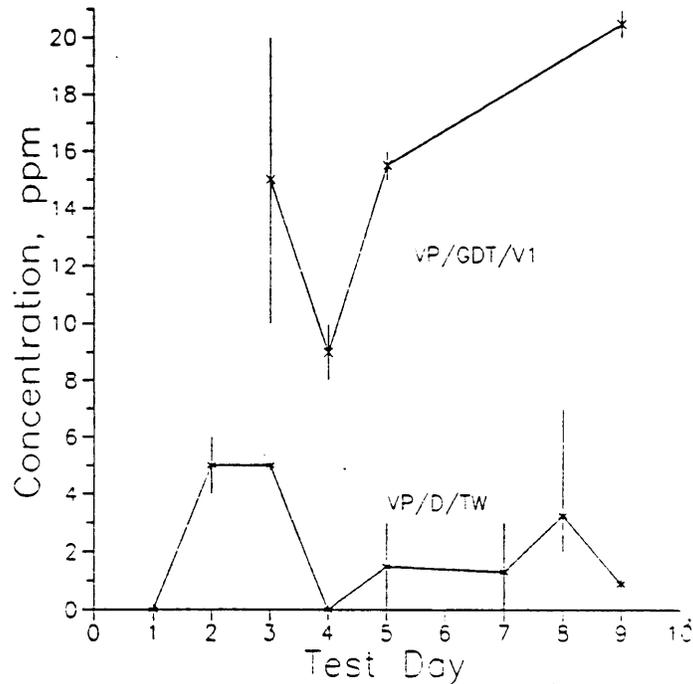


Figure 13. Octane Concentration Measured in Field Soil Gas by Dosimetry (VP/D/TW) and by Gastec Tube (VP/GDT/V2) at Location V2. Vertical Lines Connect High and Low Values.

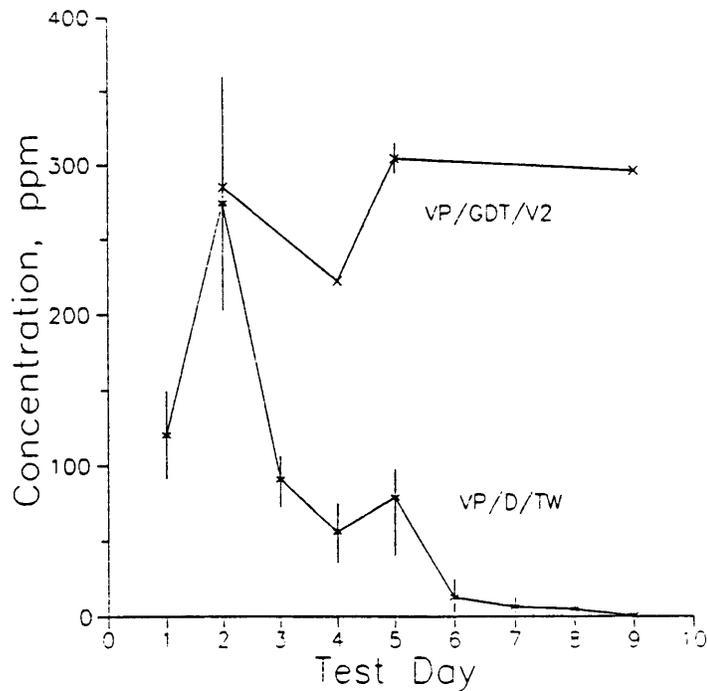


Figure 14. M-xylene Concentration Measured in Field Soil Gas by Dosimetry (VP/D/TW) and by Gastec Tube (VP/GDT/V2) at Location V2. Vertical Lines Connect High and Low Values.

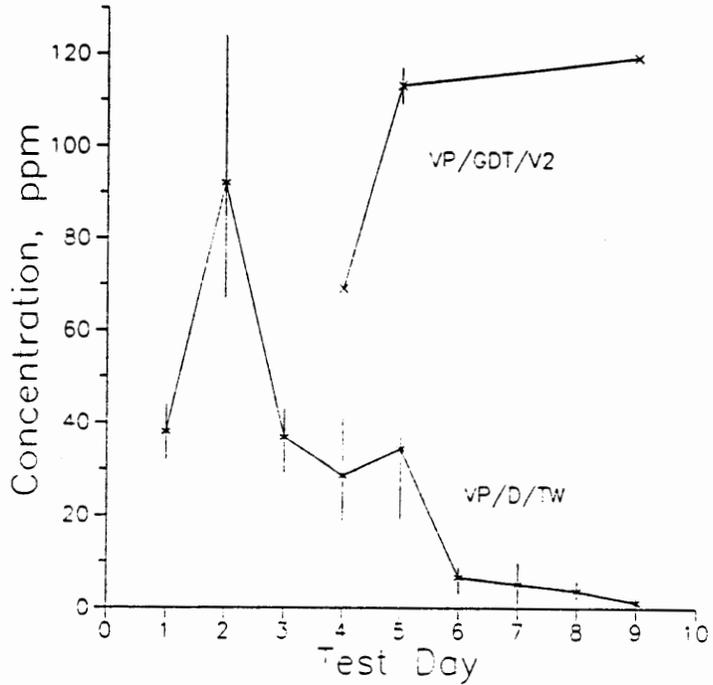
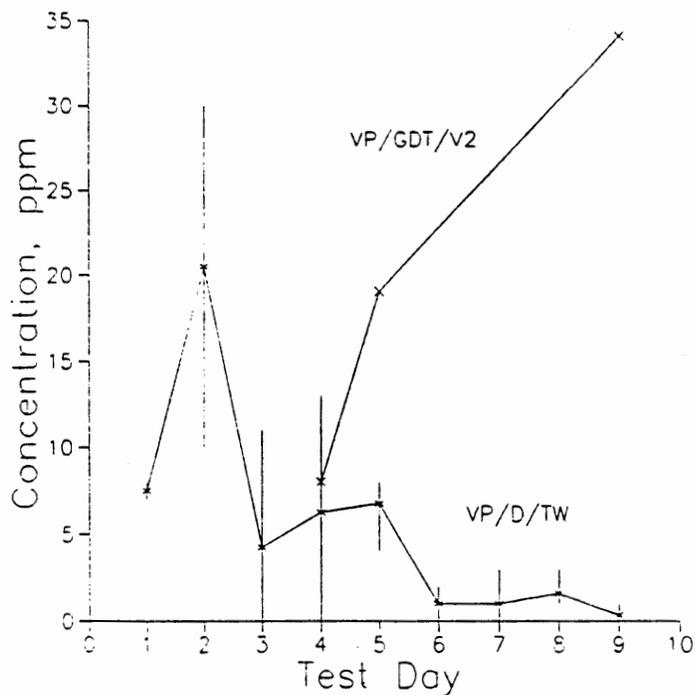


Figure 15. O-xylene Concentration Measured in Field Soil Gas by Dosimetry (VP/D/TW) and by Gastec Tube (VP/GDT/V2) at Location V2. Vertical Lines Connect High and Low Values.



## Ground Water Concentrations

A comparison of passive dosimetry and liquid-liquid extraction measurements on samples taken from the ground water well FT6 is given in Figure 16 for m-xylene and in Figure 17 for o-xylene. All concentrations are expressed in mass per volume units (mg/L). The data confirm that ground water contamination is very significant. Concentrations were on the order of 0.5 to 1 mg/L, or 500 to 1000 ug/L. Agreement between the dosimeter and reference technique was better than found for soil gas measurements. The data used to construct Figures 16 and 17 show that the ratio of passive dosimetry/liquid-liquid extraction measurements varied from 0.18 to 0.99.

A rising and falling limb of concentration with time is indicated in Figures 16 and 17 for both measurement techniques. The rise in concentration may be explained by the fact that on day 4 the fuel pit was filled for a firefighting test. A subsequent decline in concentration may have been due to dilution as the ground water table began to rise following heavy rainfalls. The extent of dilution can be appreciated by the following data recorded for the distance to the ground water table on each of the sampling days: Day 4 (92 cm); Day 6 (873 cm); Day 7 (82 cm); Day 8 (72 cm); and Day 9 (56 cm). A 13-inch rise in ground water table could provide substantial dilution of contaminants.

Figure 16. M-xylene Concentrations Measured in Field Ground Water by Dosimetry (AP/D) and by Liquid-Liquid Extraction (AP/LLE). Vertical Lines Connect High and Low Values.

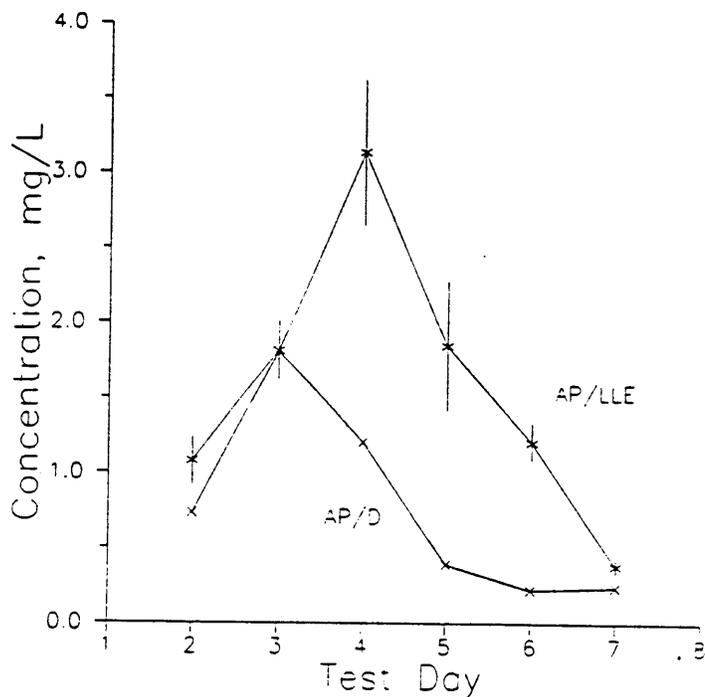
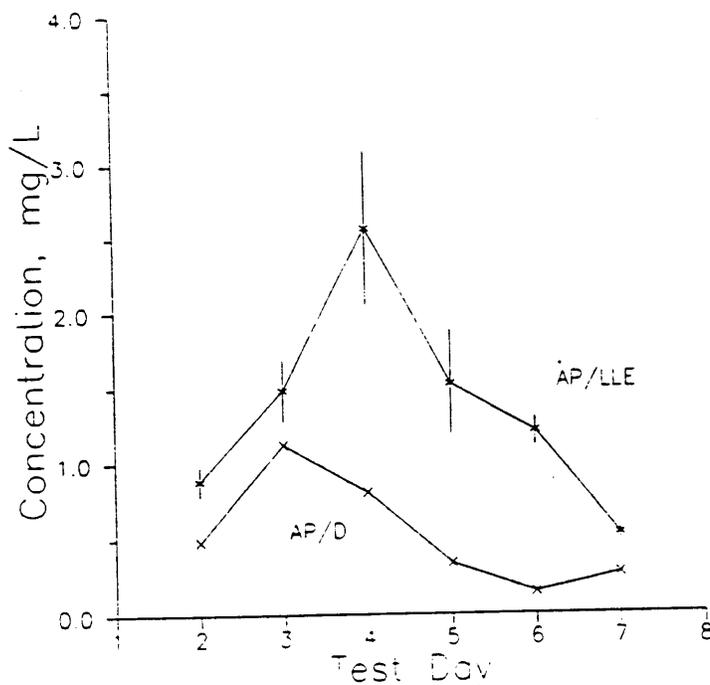


Figure 17. O-xylene Concentrations Measured in Field Ground Water by Dosimetry (AP/D) and by Liquid-Liquid Extraction (AP/LLE). Vertical Lines Connect High and Low Values.





SOIL GAS MONITORING WITH PASSIVE DOSIMETRY  
(COLORIMETRIC TECHNIQUE)

Objectives

The overall goal of this phase of the research was to develop an alternative to the passive dosimeter design with activated carbon as the adsorption media. Replacement of activated carbon with a color sensitive medium provides the advantage of on-site, instantaneous measurement by eliminating the need for laboratory analysis of extracted activated carbon. The specific objectives were:

1. to develop a colorimetric passive dosimeter to detect hydrocarbons in the vapor phase thus enabling monitoring of the soil gas around underground storage tanks, and
2. to test the dosimeter in the field at Pope AFB site.

Development of a Colorimetric Media

The stoichiometry describing the oxidation of hydrocarbons and the reduction of  $\text{Cr}^{+6}$  to  $\text{Cr}^{+3}$  was presented earlier. This was used to calculate the amount of concentrated sulfuric acid (28 N) and water needed per gram of potassium dichromate:

<u>Reagent</u>	<u>Mol. Weight</u>	<u>Moles Acid Required per Mole Chromate</u>	<u>Amount Acid Required</u>
$\text{K}_2\text{Cr}_2\text{O}_7$	216	-	1.00 g
$\text{H}_2\text{SO}_4$ (28 N)	98	13.9	11.7 mL
$\text{H}_2\text{O}$	18	1.9	0.2 mL

A solid medium was needed as an impregnating agent for the chromate solution so that it could be added in convenient form to the well of the dosimeter in a similar fashion as granular activated carbon. Various solid media were tried; among these were silica gel, glass beads and activated alumina. Activated alumina was best suited because swelling did not occur with humidity (silica gel was unacceptable for this reason) and the chromate solution was readily absorbed giving the characteristic yellow/orange color of oxidized chrome ( $\text{Cr}^{+6}$ ).

The oxidizing power of the colorimetric powder is determined by the amount of potassium dichromate added to the impregnating medium, i.e., activated alumina. The greater the amount of chromate per gram of finished colorimetric powder, the more orange is the initial, unreacted powder and the greater the mass of hydrocarbons that will be oxidized before the powder changes to the green color characteristic of  $\text{Cr}^{+3}$ . After some experimentation, the final formula chosen for preparation of the colorimetric powder was: 1 gram potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ); 70 mL of 28 N sulfuric acid; ( $\text{H}_2\text{SO}_4$ ); 10 mL tap water; and 200 grams activated alumina powder (80 x 200 mesh).

Color instability was a problem in both the preparation and storage of the colorimetric powder. Two colorimetric side reactions were noted. Upon addition of sulfuric acid to the chromate/water mixture, a red precipitate sometimes appeared. This could be the acetate of  $\text{Cr}^{+2}$ , one of the most common, stable, and easily prepared chrome compounds (Cotton and Wilkinson 1966). This can be avoided by placing the chromate in an icebath and adding the acid slowly. The other side-reaction produced a sky blue color which possibly could be due to reduction of  $\text{Cr}^{+3}$  to  $\text{Cr}^{+2}$ . The reaction was notably faster if the powder was exposed too long to the air. One explanation is  $\text{Cr}^{+3}$  stripping an electron from molecular oxygen (Cotton and Wilkinson 1966). It was also found that storage of the colorimetric powder for more than four to six

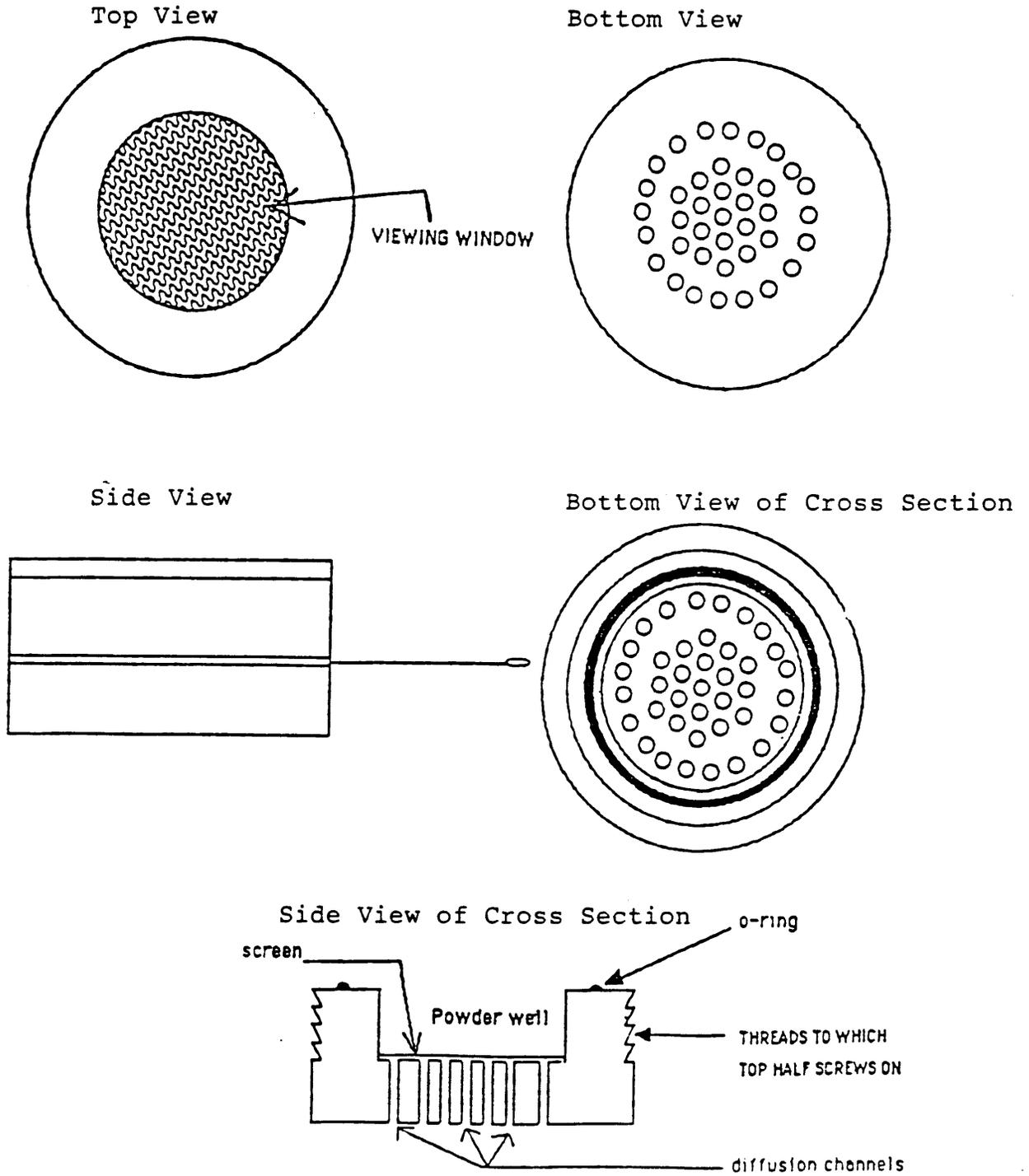
weeks produced a noticeable lessening of sensitivity to color change upon exposure to hydrocarbons.

To minimize color instability and loss of sensitivity, fresh batches of powder were made every two to three weeks. The shelf life could probably be extended if the powder were to be stored under nitrogen rather than ambient air. A loss in sensitivity is indicated when the color of the unreacted powder fades from yellow/orange to white. In addition to minimizing storage, readings of color from exposed dosimeters were made without delay to avoid possible interferences from the side reactions discussed above.

#### Dosimeter Design

The dosimeter used in this research is shown in Figure 18. The construction was similar to that described in Section 6. Aluminum rather than acrylic was used to mill the two sections of the dosimeter, each having a diameter of 3.7 cm. The major difference in design from the previously discussed dosimeter is replacement of granular activated carbon with the colorimetric powder. The bottom section of the dosimeter has 39 diffusion channels, each 1 cm in length and  $0.032 \text{ cm}^2$  in cross-sectional area. These channels enable hydrocarbons to diffuse from the ambient vapor phase to the colorimetric powder (1 gm) that filled the "powder well" shown in Figure 18. A Nuclepore filter (10  $\mu\text{m}$  in thickness) was placed under the powder to prevent loss through the diffusion channels. Given that the length of the diffusion channels was 1 cm, this additional diffusion barrier was insignificant. The top-half of the dosimeter consists of circular window to view the color of the powder in the well below. An O-ring provides a tight seal between the top and bottom sections of the dosimeter when screwed together.

Figure 18. Adaptation of Dosimeter Design for Colorimetric Measurements



### Sensitivity of the Passive Dosimeter: Preliminary Field Test

A preliminary field test was performed at Pope AFB (see Figure 8). To test the dosimeter, a temporary well was dug with a six-inch post-hole digger to a depth of 8 cm. A string was attached to a wire loop on the dosimeter to facilitate retrieval at the end of the exposure time. The dosimeter was lowered into the temporary well with the diffusion channels facing downward so as to rest against the undisturbed soil at the bottom. Layers of soil that were excavated from the hole were replaced in the roughly the same order as taken out. The dosimeter was exposed to the soil gas for 5 hours before observing the color of the chromate powder.

Three temporary wells were used, all being located 30-40 m west (down gradient) of the edge of the fuel pit. After the 5 hours of exposure, dosimeters in two of the three wells had turned green, and a distinct color change toward green was evident in the third. This suggested that the dosimeter design was sufficiently sensitive to allow fairly short exposure times, i.e., less than 5 hours given the extent of contamination at this field site.

### Calibration of the Colorimetric Dosimeter

Color Development. The development of color in the dosimeter is expected to be proportional to the ratio of unreacted (yellow) to reacted (green) chromate. At any instant in exposure time prior to exhaustion of the chromate capacity to oxidize hydrocarbons, a fraction of the chromate has reacted with some mass,  $M$ , of hydrocarbon. According to dosimeter principles discussed earlier rearranging Equation (3) gives:

$$C_t = ML/DA \quad (11)$$

That is, for any given mass of hydrocarbon oxidized, and a corresponding color development between yellow and green, the

product of hydrocarbon concentration, C, and dosimeter exposure time, t, is a constant. The objective of the laboratory experimentation was to verify this concept. If the concept was proven valid, the dosimeter could be used to obtain the concentration of hydrocarbon by reading the color after exposure time, t, and then using a calibration chart to obtain the corresponding Ct value from which C is calculated.

Laboratory Apparatus. Colorimetric dosimeters were exposed to known concentrations of target compounds in 5.5 L desiccator in experiments similar to those described in the previous section (see Figure 6 for description of experimental set-up). A known volume of hydrocarbon was injected into the desiccator and allowed to evaporate to attain the desired concentration (volume/volume basis as microliters hydrocarbon per liter air) according to:

$$V = \frac{C P (5.5) MW}{d R T 10^3} \quad (12)$$

Where: V = Liquid hydrocarbon volume, (uL)  
 C = Concentration of hydrocarbon, (mg/L)  
 P/RT = 1/Molar volume of gas (24.45 at STP)  
 5.5 = Volume of desiccator (L)  
 MW = Molecular weight of liquid (g)  
 d = Density of liquid (g/cm<sup>3</sup>)

The vapor pressures of the hydrocarbons were high enough to ensure that all of the liquid would volatilize within a few minutes. The desiccator injection ports were sealed immediately after the injection, and the dosimeter was exposed to the hydrocarbon vapor for a predetermined length of time. Prior to removal of the dosimeter at the end of the sampling time, fresh air was blown into the desiccator so that the hydrocarbon-containing air was forced into a hood.

Description of Colors Produced. Crayola crayons were used as a simple way to standardize the color produced by the dosimeter. The initial powder is a lemon yellow color which turns green when reduced by hydrocarbons. Colors between yellow and green are caused by some granules of chromate powder being in the oxidized state (yellow) while others are in the reduced state (green). These end-point colors were given numerical values of 0 and 4, respectively. Three mixtures of yellow and green were assigned values of 1, 2 and 3 as shown in Table 15. Two Crayola crayons were used to produce each color, the first listed being the base color and the second, the top color. All color combinations were covered with white to blend the colors and to give a powder-like appearance similar to that of the chromate powder.

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Table 15. Description of colors produced by reduction of  $\text{Cr}^{+6}$

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<u>Color Number</u>	<u>Description</u>	<u>Crayola Crayon Combination</u>
0:	Unreacted yellow powder	Yellow, Maize
1:	Yellow with a hint of green	Maize, Olive Green
2:	Half green, half yellow	Olive Green, Maize
3:	Mostly green with only a hint of yellow	Sea Green, Spring Green
4:	All green, fully reacted	Sea Green

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Note: All colors covered with white to evenly blend colors.

Exposure to Pentane and Octane. The concentration (ppm by volume) of octane used in the first series of dosimeter exposures was 7,120 ppm; that of pentane was 10,030 ppm. Color was recorded after six different exposure times as is shown in Figure 19. Octane caused a more rapid change in color from yellow to green. Thus, octane reacts faster than

the pentane even though the concentration of octane was lower than that of pentane. A faster reaction may be inferred from the stoichiometry presented in Table 2. Hydrocarbons with more carbon atoms require a greater amount of  $\text{Cr}^{+6}$  (mole per mole basis) for oxidation. Thus, octane having more carbon atoms per mole will require more  $\text{Cr}^{+6}$ , and this means a faster rate of color change.

Selection of a Standard Hydrocarbon. The above experiments showed that the color change after a fixed time of exposure is not the same for different hydrocarbons. Thus, octane was selected as a reference hydrocarbon. The criteria used were its presence in fuels, relatively high volatility that insures its presence in soil gas and relatively high number of carbon atoms per mole to maximize the amount of  $\text{Cr}^{+6}$ . An even higher molecular weight hydrocarbon ( $\text{C}>8$ ) was not chosen because the literature suggests these species are more likely to be adsorbed into the soil or to be transported in ground water due to their lower vapor pressures and would therefore not be expected to be found in the soil gas. Even though lower molecular weight hydrocarbons have higher volatilities, these hydrocarbons do not reduce the chromate as effectively on a per mole basis as does octane. If the soil contaminant is gasoline (average molecular weight  $\sim 70$  g/mole, similar to pentane), octane will cause the color change to be indicative of a concentration higher than the actual concentration. A conservative approach is desirable in determination of environmental contamination assessments.

A calibration experiment was designed in which three different concentrations of octane (3,560, 7,210 and 14,240 ppm) were generated in the desiccator and the dosimeters exposed for times ranging from 2 to 6 hours. Thus a range of Ct values was sought to verify the proportionality with color that is expected according to Equation 11.

To obtain C for use in the Ct expression, it is first necessary to calculate the average concentration to which the dosimeter is exposed in the desiccator. The volumetric sampling rate of the dosimeter was presented earlier as Equation 6:

$$\text{Dosimeter Sampling Rate} = DA/L \quad (6)$$

Representing the dosimeter sampling rate as R (cm<sup>3</sup>/hr), the mass balance on octane in the desiccator is:

$$v (dC/dt) = - RC \quad (13)$$

where v is the volume of the desiccator and C is the concentration at any time t and R is the dosimeter sampling rate. In this equation, volume is assumed constant although the dosimeter is removing volume; the amount removed, however, is very small. Integrating over the sampling time gives:

$$\ln (C_t / C_o) = -(R/v)t \quad (14)$$

where C<sub>o</sub> is the initial concentration and C<sub>t</sub> is the concentration at the end of the exposure period. The linearly averaged concentration is:

$$C_a = [C_o + C_t]/2 \quad (15)$$

The value of R is assumed as 290 cm<sup>3</sup>/hr based on the dimensions of the dosimeter (A/L = 1.23 cm) and the diffusivity of octane in air (D = 0.066 cm<sup>2</sup>/s). The desiccator volume is 5,500 cm<sup>3</sup>. Therefore, if the sampling time is 3 hours and the initial concentration of octane is 7,000 ppm, the concentration remaining is:

$$C_t = 5,976 \text{ ppm} \quad (16)$$

and thus the average concentration is:

$$C_a = [7,000 + 5976]/2 = 6,488 \text{ ppm} \quad (17)$$

The results of exposing the colorimetric dosimeters to three different concentrations of octane for various amounts of time are given in Figure 20. The data for these experiments are listed in Table 16. It must be noted that interpolation of color development was done on the scale of 0 to 4 as presented in Table 15 to plot these data. The data indicate that a good correlation exists between color and Ct thereby insuring that the dosimeter can be used in the field to obtain a measurement of concentration by observing the color, finding the corresponding value of Ct and calculating C by knowing the exposure time.

Table 16. Data to obtain Ct calibration curve for dosimeter using octane

<u>Average.</u> <u>Conc. (ppm)</u>	<u>Exposure</u> <u>Time (hrs)</u>	<u>Ct Value</u> <u>(ppm-hr)</u>	<u>Color</u> <u>Number</u>
144	3	432	0.5
433	2	866	0.3
405	4	1620	1.0
561	3	1683	0.5
433	4	1732	0.5
1587	2	3173	1.0
1122	3	3366	0.9
1823	2	3464	1.0
1117	4	4467	1.2
2784	2	5568	1.5
1586	4	6344	1.7
2244	3	6732	1.8
2396	3	7188	1.8
4467	2	8934	2.4
2227	5	11135	2.9
3172	4	12688	3.4
4467	3	13401	2.5

Figure 19. Development of Color in Dosimeter Caused by Reduction of  $\text{Cr}^{6+}$  in Presence of Octane and Pentane

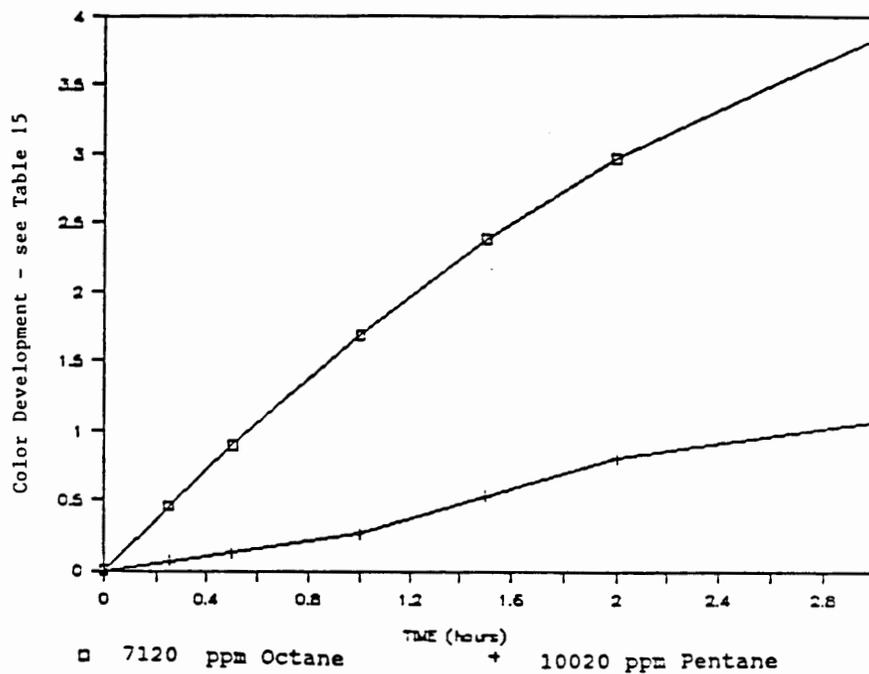
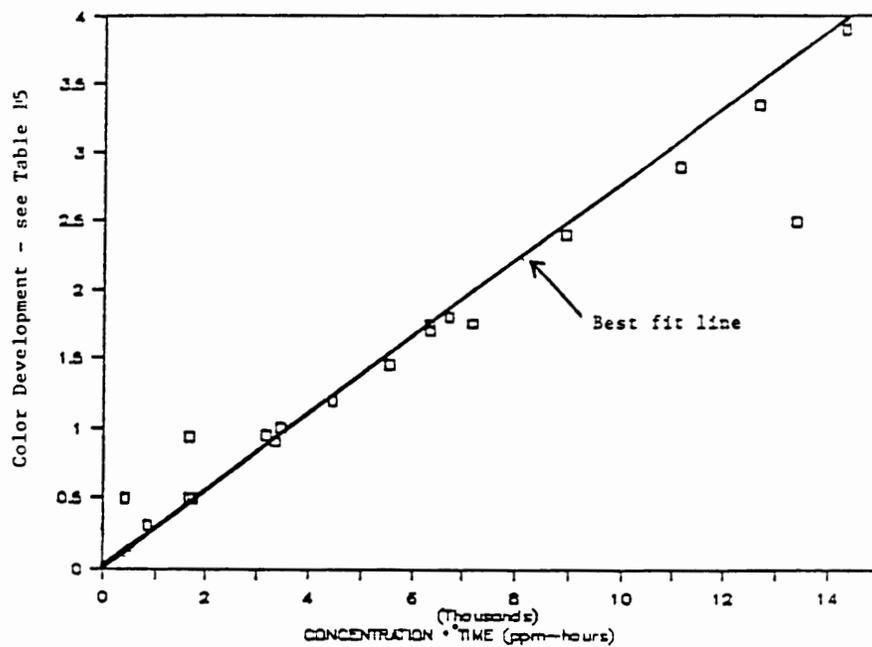


Figure 20. Development of Color Calibration Curve for Dosimeter Using Exposure to Octane



The above calibration procedure expresses the concentration of hydrocarbons as octane (in ppm by volume). The concentration can also be expressed in terms of other hydrocarbons should, for example, the fuel be known to be better characterized in this manner. The procedure needed for conversion is based on the stoichiometry of hydrocarbon oxidation as presented in Table 2. If gasoline is the leaking fuel, its average molecular weight (70 g/mole) is close enough to that of pentane (72.15 g/mole) to use pentane for expressing concentration. The moles of chromate needed per mole of pentane is 5.33 compared to 8.33 for octane. Therefore, if the concentration is 100 ppm as octane, it is  $(5.33/8.33) \times 100$  or 64 ppm as pentane.

Stoichiometric Validity of Dosimeter Response. The ordinate of the calibration relationship presented in Figure 20 is subjective because it is an arbitrarily chosen scale that was obtained by grading colors from yellow to green. The next objective was to determine if the color could be related stoichiometrically to the amount of octane oxidized. This was tested by completely reacting a few grams of powder (with octane) to achieve the green color and then mixing with unreacted powder (yellow) in the following proportions: 20% reacted:80% unreacted; 40% reacted:60% unreacted; 60% reacted:40% unreacted; and 80% reacted:20% unreacted. The Crayola colors used to represent the extent of  $\text{Cr}^{+6}$  reduction are given in Table 17. These colors represent the amount of  $\text{Cr}^{+6}$  reacted and therefore can be used to construct a quantitative-color scale. That is, if the total amount of  $\text{Cr}^{+6}$  added to the dosimeter is known, then the amount reacted can be calculated from the color scale in Table 17. Further, if the stoichiometry of Table 2 holds, it should be possible to then obtain the amount of hydrocarbon oxidized.

Table 17. Crayola crayons (By Name) used to develop stoichiometric calibration of dosimeter based on percent of chromate powder reacted (reduced)

<u>Percent Reacted</u>	<u>Crayola Crayon Combination</u>
0	Orange-Yellow
20	Maize
40	Spring Green, Maize
60	Sea Green
80	Spring Green, Sea Green
100	Sea Green with hint of Sea Green

Note. All colors were covered with white to evenly blend colors, so as to better represent actual powder color.

Another series of dosimeter exposure experiments was conducted to test the validity of a stoichiometric relationship. In each experiment, the dosimeter was exposed to a given octane concentration for 3 hours to generate a relationship between percent  $\text{Cr}^{+6}$  reacted and Ct. The percent  $\text{Cr}^{+6}$  reacted was obtained by noting the color development and using the calibration given by Table 17. The effect of chromate powder storage time on color development was also measured by comparing results using powder that was stored less than 2 days with results using powder stored for 10 days.

The relationships between percent reacted and Ct (ppm-hr) for the two series of experiments (fresh and old chromate powder) are given in Figure 21. This shows that the fresh powder is considerably more reactive than the 10-day old powder. However, more important is the observation that neither produces the linear relationship expected if the reaction is stoichiometric. Further investigation revealed a large discrepancy with stoichiometry as illustrated by the computations provided in Table 18.

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Table 18. Comparison of stoichiometric amount of octane reduced with actual amount sampled by dosimeter for exposure to 356 ppm of octane for three hours

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Calculation of Stoichiometric Amount

Amount of  $K_2Cr_2O_7$  per g of colorimetric powder = 0.0029 g

Moles of  $Cr^{+6}$  present =  $0.0029 / 104 \text{ g } Cr^{+6} / \text{mole } K_2Cr_2O_7$   
 $= 2.8 \times 10^{-5} \text{ moles}$

Moles of octane capable of oxidation =  $2.8 \times 10^{-5} / 8.33$   
 $= 3.3 \times 10^{-6} \text{ moles}$

Fraction of  $Cr^{+6}$  reacted based on Ct value:  
 $Ct = 356 \times 3 = 1068 \text{ ppm-hr}$   
 From Figure 21, percent reacted = 60%

Moles of Octane reacted =  $0.6 \times 3.3 \times 10^{-6} = 2 \times 10^{-6}$

Calculated Amount of Octane Sampled by Dosimeter

Exposure rate of dosimeter (DA/L) =  $290 \text{ cm}^3 / \text{hr}$

13 uL of octane added to exposure chamber to give 356 ppm

Volume of octane sampled by dosimeter:

$$\frac{13 \text{ uL octane}}{5500 \text{ cm}^3} \left| \frac{290 \text{ cm}^3}{\text{hrs}} \right| \frac{3 \text{ hours}}{1} = 2.056 \text{ uL}$$

Moles of octane sampled by dosimeter:

$$= 2.056 \text{ uL} / 11.422 \text{ g/mole} / 704 \text{ uL/g}$$

$$= 25 \times 10^{-6} \text{ moles}$$

Ratio of Moles Octane Reacted to Moles Octane Sampled

$$= 2 \times 10^{-6} / 25 \times 10^{-6} \text{ moles} = 0.08$$


---

These calculations show that the powder reacts with eight percent of the octane diffusing into the dosimeter. The validity of these calculations, however, is premised on the theoretical dosimeter sampling rate which determines the mass of octane diffusing into the dosimeter. A slower sampling rate is possible for either of two reasons. First, if chromate oxidation is slower than expected it will cause a build-up of octane within the dosimeter and make the diffusive driving force less than assumed with octane concentration being zero inside the dosimeter. Second, if stagnant regions exist within the unstirred exposure chamber (the 5.5 L desiccator) it may also lower the dosimeter sampling rate.

The results above indicate a lack of conformity to a stoichiometric relationship that would allow calculation of concentration simply by knowing the amount of  $\text{Cr}^{+6}$  added to the dosimeter and the amount reacted. Further research is needed to understand why the discrepancy exists and to modify the dosimeter design accordingly. It is very likely that the chromate powder is simply not made reactive enough through the impregnation procedure used. Nevertheless, the present design is still useful with the calibration procedure presented in Figure 20. Concentration can be calculated if the color of the dosimeter is recorded and the exposure time is known.

#### Field Testing of Colorimetric Dosimeter

Description of Sampling. Field testing of the colorimetric dosimeter was conducted at the fire training area at Pope AFB near Fayetteville, NC. This same site was also used to field test the dosimeter using granular activated carbon (GAC) as the adsorbent material (see previous section). As was done with the adsorbent passive dosimeter, concentrations were compared to those obtained by other sampling methods. Miller and Staes (1991) had performed a series of soil gas measurements from January to March 1989 by pumping vapor through a tube of activated carbon trap and then extracting to

measure hydrocarbons. While measurements with the colorimetric dosimeter were made several months later (July and August 1989), comparisons of concentrations were still considered important. In addition, a Draeger tube was used simultaneously with the colorimetric dosimeter for another comparison.

Draeger tubes operate on the same principle as the colorimetric dosimeter. These small tubes (7 mm in diameter) contain a solid material impregnated with chromate. A pump is used to pass a known volume of air through the tube. Reduction of  $\text{Cr}^{+6}$  causes the color to change from yellow to green. The position along the length of the tube at which the color is determined to change from green (reacted) to yellow (unreacted) corresponds to a scale of hydrocarbon concentration as is shown in Figure 22. The distance between divisions varied, being largest on the low (30-300 ppm) end of the scale and smallest on the high end. Divisions between 400 and 1000 ppm are so close together as to cause a reading error of +/- 100 ppm.

A series of temporary sampling wells was constructed using a 6-inch diameter, post-hole digger. These were each 50 cm deep. These wells were spaced at 15 m intervals away from the center of the fuel pit in each of the following compass directions: north (N); northeast (NE); east (E); south (S); southeast (SE); west (W); southwest (SW); west (W) and northwest (NW). A total of 34 wells was sampled. Detailed field notes for each sampling day are provided by Napfel (1989).

The colorimetric dosimeter was placed in each temporary well according to the same procedures described earlier (see Sensitivity of the Passive Dosimeter: Preliminary Field Test). The dosimeters were exposed for three hours. Color was recorded immediately using crayon swatches and the numerical (0 to 4) classification system (Table 15) to determine the

Figure 21. Test of Stoichiometric Relationship Between Color Development and Mass of Octane Oxidized (ordinate scale is percent of chromate reduced based on Table 17)

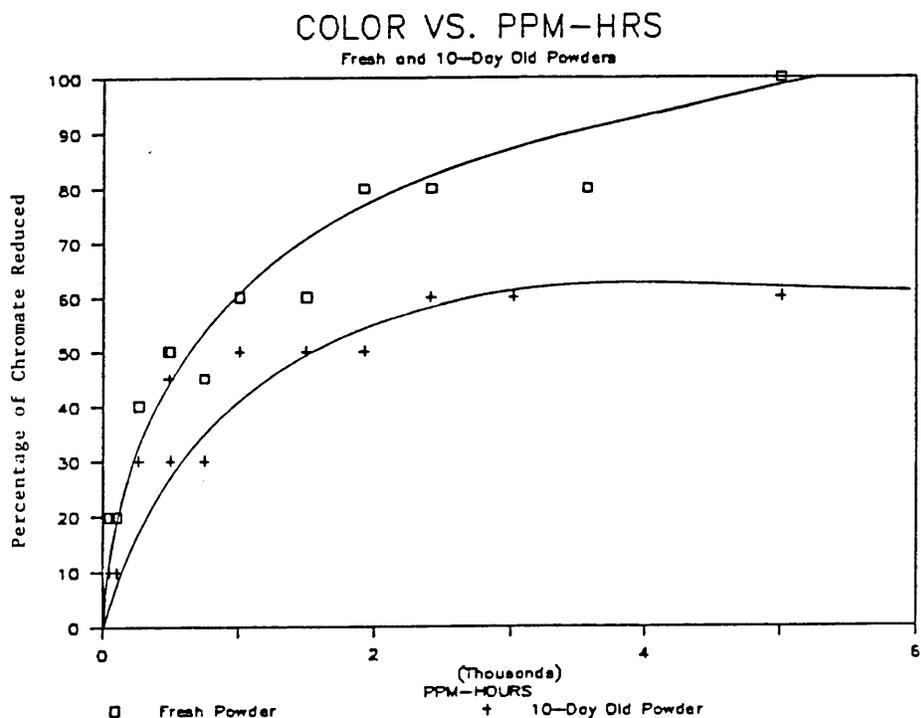
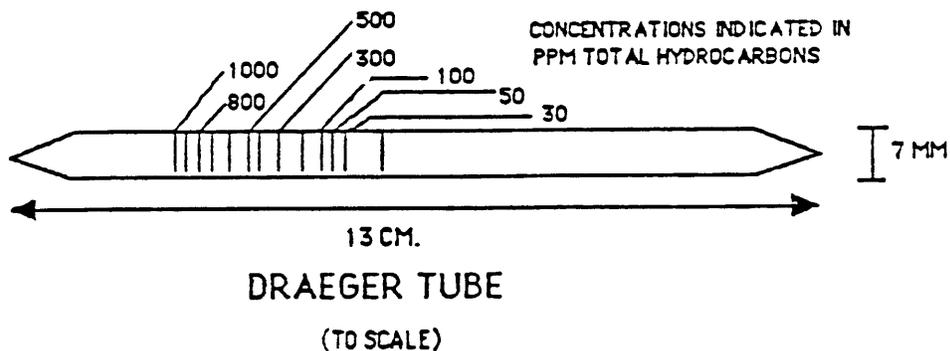


Figure 22. Concentration Scale of the Draeger Tube (to scale); Position on Tube Where Color Changes from Yellow to Green Determines Hydrocarbon Concentration



concentration as octane. Because only three prototype dosimeters were available, it was necessary to remove the exposed chromate powder, replace it with a fresh batch and then place the dosimeter into another temporary sampling well. This allowed each dosimeter to be used for three exposures per day of sampling thus making possible a total of nine measurements.

The Draeger tubes were used in each of eight permanent wells (V1, V2, V4, V5, V6, V8, V10 and V11) at the site (see Figure 8). This allowed for plotting of contour lines of soil gas concentration in the same vicinity as the series of temporary wells.

Results of Sampling with Colorimetric Dosimeter. The concentrations of soil gas, expressed as ppm of octane, at each of temporary wells (located by compass direction and distance away from the fuel pit) and sampling date(s) are given in Table 19. These concentrations were measured over a two-month period and thus do not reflect concentration at one instant in time. It should be noted from the calibration relationship presented in Figure 20 that the maximum concentration measurable by the colorimetric dosimeter is 4670 ppm given an exposure period of 3 hours i.e., at this Ct the color of the dosimeter is green. A kriging and plotting program (Surfer, Golden Software) was used to obtain the contour map of soil gas concentration shown in Figure 23.

For comparison, the contour map of soil gas concentration generated by Miller and Staes (1991) using the pump and activated carbon trap is presented in Figure 24. Both sampling methods show a similar pattern of concentration, the maximum value in each instance being located west of the burn pit; this is also consistent with the general direction of ground water flow at the site. The absolute values of concentration shown on these contour maps are not directly comparable because ppm by volume was used for the colorimetric dosimeter whereas mg octane /m<sup>3</sup> of soil gas was used for the

Table 19. Results of colorimetric dosimeter measurements at Pope AFB (All three hours exposure except where noted)

<u>Location*</u>	<u>Date</u>	<u>Concentration (as octane)</u> <u>(ppm)</u>	
N50	7/28/89	4100	
N100	7/20/89	4670	
N150	7/28/89	2330	
N200	7/28/89	< 585	(2.5 hours Exposure)
NW100	7/14/89	>4670	(5 hours Exposure)
	7/28/89	4095	
NW150	7/14/89	3500	(5 hours Exposure)
NW250	7/28/89	-	
	8/18/89	>4670	
NW300	8/18/89	< 585	
NW350	8/18/89	< 585	
NW300S50**	8/19/89	< 585	
NW300N25**	8/19/89	1170	
NW300N25W25**	8/19/89	1170	
W150	7/14/89	>4670	(5 hours Exposure)
W150	7/20/89	>4670	
W200	7/20/89	>4670	
W250	7/20/89	3500	
W350	7/20/89	>4670	
SW25	8/18/89	>4670	
SW50	7/28/89	< 585	
SW100	7/20/89	NCC	
SW150**	8/19/89	3500	
SW100W100N25**	8/19/89	2330	
SW100W100**	8/19/89	4095	
SW100W150**	8/19/89	>4670	
SW100W50**	8/19/89	1175	
S50	8/18/89	<585	
S100	7/20/89	2330	
SE25	8/18/89	< 585	
SE50	8/18/89	< 585	
E25	8/18/89	< 585	
E50	7/28/89	< 585	
E100	7/20/89	Below detection	
NE25	8/18/89	2330	(15 min Exposure)
NE50	7/28/89	< 585	
W150	8/19/89	1000	(Ambient air)

\* Location: Measured as distance from edge of pit in feet in compass direction indicated.

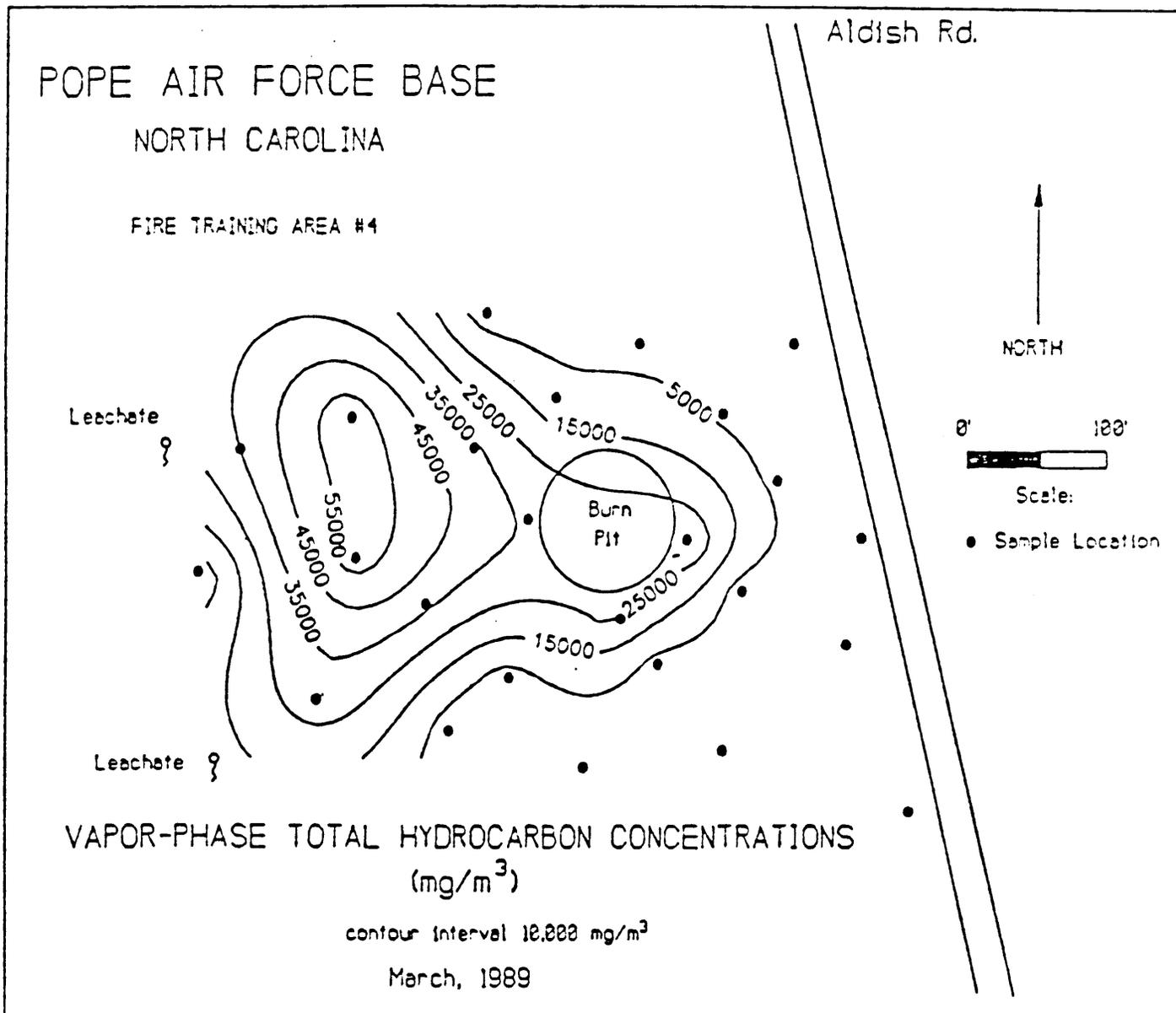
\*\* All concentrations on August 19th were relatively high, probably due to fire training and filling of the fire pit the previous day. Ambient air was also measured and noted to contain 1,000 ppm of octane. Strong fuel odor at site.



Figure 24. Contour Map of Soil Gas Octane Concentration at Pope AFB Field Site as Determined by Miller and Staes (1991) Using Pump and Activated Carbon Adsorption Trap

(IN  $\text{mg}/\text{M}^3$  AS TOTAL HYDROCARBONS)

● INDICATES SAMPLE LOCATION SITE



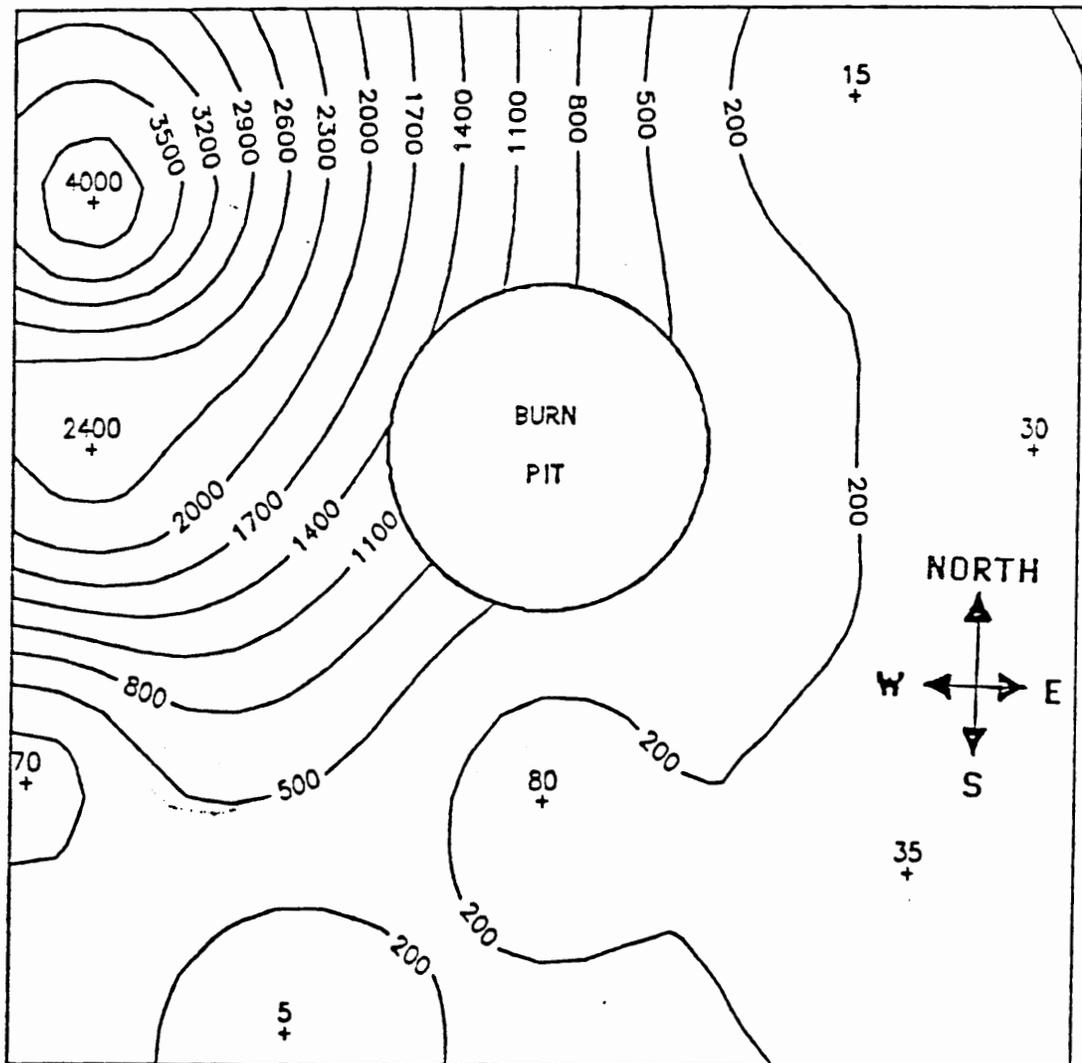
pump and activated carbon trap. The conversion factor is given by  $1 \text{ ppm} = 4.23 \text{ mg/m}^3$ . Accordingly, Miller and Staes (1991) measured a maximum concentration of  $55,000 \text{ mg/M}^3$  which converts to  $11,790 \text{ ppm}$  by volume. The maximum concentration measured by colorimetric dosimetry, however, was about  $4,000 \text{ ppm}$  although several of the measurements listed in Table 19 were recorded as being in excess of the maximum value ( $4,670 \text{ ppm}$ ) read by the dosimeter.

Several factors may explain the lower concentrations obtained by the colorimetric dosimeter. First, the measurements of Miller and Staes (1991) were made in the winter and early spring whereas the dosimeter measurements were made in summer. Changes in the ground water table through the year can affect the soil gas concentration. Additionally, the dosimeter measurements were made in open, temporary wells while the pump and activated carbon trap was connected directly to sampling ports in the permanent wells. As was found in evaluation of the dosimeter using activated carbon as the adsorbent (see Soil Gas and Ground Water Monitoring with Passive Dosimeter section), there is some concern that soil gas in the temporary wells was diluted by ambient air. Finally, the maximum concentration detectable by the dosimeter was  $4,670 \text{ ppm}$  and thus lower than the maximum measured by the pump and activated carbon trap.

The contour map of soil gas concentration generated by the Draeger tube is given in Figure 25. This measurement device also shows a region of high concentration to the west of the burn pit. In this application, the Draeger tube was actually too sensitive. With soil gas concentrations exceeding  $1,000 \text{ ppm}$ , almost the entire length of tube turned from yellow to green. Error is also introduced in the Draeger tube method by failure to maintain a constant pump rate (manual strokes). Concentration obtained by the Draeger tube compared fairly well to those from the colorimetric dosimeter. Both of these devices were used over the same sampling period. This

Figure 25. Contour Map of Soil Gas Hydrocarbon Concentration at Pope AFB Field Site as Determined by Colorimetric Draeger Tubes at Locations Designated by (+)

'+' INDICATES SAMPLING LOCATION AT A PERMANENT WELL



SCALE 1 inch = 50 Feet

suggests that the higher concentrations obtained by Miller and Staes (1991) with the pump and activated carbon trap may have been due to the time of sampling rather than to methodological differences.

#### Assessment of the Colorimetric Dosimeter

This field test showed that the colorimetric dosimeter was responsive to the presence of hydrocarbons and gave concentration measurements that agreed in general with those of the Draeger tube. Although both of these devices gave lower readings than the pump and activated carbon trap, the results may not be directly comparable owing to the difference in time of year when the sampling was done. The dosimeter offers the advantages of being rapid, inexpensive and simple to use. It could serve an important function in initial site investigations to map the contours of soil gas concentrations. In addition, dosimetry could be useful for routine monitoring of underground storage tanks. For example, based on the calibration relationship in Figure 20, it should be possible to measure a Ct value of 4,000 ppm-hr. Thus, if the exposure time is one week, a concentration of about 24 ppm could be detected. However, more study is needed at a field site where such low concentrations may be found. Deterioration of the chromate powder sensitivity needs further investigation if long-term monitoring is of interest.

The desired sensitivity of a leak detection device is open to question. For example, a decision-making procedure is in use in the San Francisco Bay area, which states that if total hydrocarbon analyses indicate that concentrations greater than 100 ppm are present, the case is classified as a "Fuel Leak Site" (Eisenberg et al. 1987). This concentration is determined by selecting certain constituents of fuel using available EPA protocol and then extrapolating to a total hydrocarbon concentration. Alternatively, McNerney (1989) uses 500 ppm total hydrocarbons as an alarm trigger point.

The suggestion is that common background levels are often a few hundred ppm without any leaks and with leaks, concentrations can easily exceed 10,000 ppm.

The design of the colorimetric dosimeter could be modified to improve sensitivity if this was desired. Increasing A/L (either by increasing the diffusional area, decreasing the channel length, or both) increases the sampling rate and thus lessens the time needed to react a given mass of hydrocarbon with the chromate. A medium other than activated alumina may also prove to be more advantageous. Using activated alumina limits the range of chromate/powder combinations that will be both sensitive enough to indicate low concentrations (low chromate:powder ratio) and strong enough to produce a distinct color change. Another medium may allow for a lowering of the chromate:powder ratio while still exhibiting distinct colors.



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## LIST OF ABBREVIATIONS AND SYMBOLS

1-CD	chlorodecane
A	cross-sectional area for diffusion (length <sup>2</sup> )
AFB	Air Force Base
AP	aqueous phase concentration
AP/D	aqueous phase concentration/dosimeter
AP/D/TW	aqueous phase concentration/dosimeter/temporary well
AP/LLE	aqueous phase concentration/liquid-liquid extraction
cm	centimeters
C	concentration
Cr	chrome
CS <sub>2</sub>	carbon disulfide
d	density of liquid (g/cm <sup>3</sup> )
D	molecular diffusivity (length <sup>2</sup> per time)
EB	ethyl benzene
EE	extraction efficiency
EP	electric pump
Exp	experiment
FID	flame ionization detector
FT	fire training permanent vapor phase well
gm	grams
GAC	granular activated carbon
GC	Gas chromatograph
GDT	Gastec Detector Tube
HC	hydrocarbon
J	flux (mass per area per time)

L	length of diffusion path in dosimeter (length)
m	actual mass extracted (mass)
mg/L	milligrams per liter (aqueous phase concentration)
min	minutes
mX	methyl xylene
M	theoretical mass extracted (mass)
MW	molecular weight
NAPL	non-aqueous phase liquid
ND	not detected
oX	o-xylene
OCT	octane
ppm	parts per million by volume (vapor phase concentration)
ppm-hr	parts per million - hours (concentration -time)
pX	p-xylene
rpm	revolutions per minute
R	rate of sample withdrawal
R	recovery experiment
RF	response factor
sec	seconds
STP	standard temperature and pressure
t	time
T	toluene
TE	tank exposure experiment
TW	temporary well
ug/L	microgram per liter (aqueous phase concentration)
uL	microliters
um	micrometers
USEPA	United States Environmental Protection Agency

UST	underground storage tank
v	volume of dessicator
V	liquid hydrocarbon volume (uL)
V1 to V11	permanent vapor phase wells
VP/GDT/V	vapor phase concentration/Gastec Detector Tube/permanent vapor phase well
x	diffusion distance (length)