

AECOM 500 Enterprise Dr., Suite 1A Rocky Hill, CT 06076 www.aecom.com 860.263.5800 tel 860.263.5888 fax

June 29, 2016

Mr. Jason Metzger Program Manager Response and Remediation Program Environmental Protection Division – Land Protection Division 2 Martin Luther King Jr. Dr., Suite 1054 East Atlanta, GA 30334

### Subject: Semi-Annual Progress Report #02 (January 1, 2016 through June 30, 2016) Former United Technologies Automotive Site, HIS #10543 1884 Warrenton Highway, Thomson, McDuffie County, Georgia Tax Parcel ID # 00200056

### Dear Mr. Metzger,

On behalf of United Technologies Corporation (UTC), AECOM Technical Services, Inc. (AECOM) is submitting this letter as Semi-Annual Progress Report #02 (January1, 2016 through June 30, 2016) for the activities conducted at the former United Technologies Automotive facility located at 1884 Warrenton Highway, Thomson, Georgia (Site). In a letter dated June 30, 2015, the Georgia Environmental Protection Division (EPD) approved the March 12, 2015 Voluntary Remediation Program (VRP) Application submitted by AECOM pursuant to the Georgia Voluntary Remediation Program Act. The initial semi-annual progress report under the VRP was submitted on December 16, 2015 along with the 2015 Annual Groundwater Monitoring Report. EPD reviewed both reports and provided a comment letter dated March 16, 2016. AECOM has prepared a response to those comments in a response to comments (RTC) letter which is presented as **Attachment A** to this progress report.

A summary of activities during the past 6-months are discussed below.

### 1. Actions which have been taken toward achieving compliance during this period:

- A Uniform Environmental Covenant (UEC) was prepared to ensure future control of siterelated exposure pathways. The UEC was prepared with input from UTC and Pelzer. UTC submitted the UEC on May 10, 2016 to EPD via email for review and comment.
- AECOM conducted the annual 2016 groundwater monitoring event in June 2016.

### 2. <u>Results of sampling and tests and all other data received during the reporting period:</u>

 AECOM is currently waiting for the results of the June 2016 sampling event and will subsequently prepare a 2016 Annual Groundwater Monitoring Report for submission to EPD.

### 3. Actions, data, and plans which are scheduled for next semi-annual period:

- AECOM will prepare a 2016 Annual Groundwater Monitoring Report for submission to EPD.
- AECOM will perform soil gas sampling at the site.
- 4. <u>Unresolved or anticipated delays, and efforts made to mitigate those delays or anticipated delays:</u>
  - No delays have been encountered during this reporting period.

### 5. <u>Modifications to the proposed schedule or approach during this reporting period:</u>

• See the RTC letter in Attachment A for AECOM's response to EPD's comments.

Per EPD's VRP approval letter dated June 30, 2015, semi-annual progress reports are due semiannually; the next progress report will be submitted by December 31, 2016. If you have any questions regarding the information provided in this progress report, please do not hesitate to contact Beth Lang at (248) 634-6048 or Matthew A. Panciera at (860) 263-5742.

Sincerely,

Matthew A. Parciera, PE, LEP Project Manager matthew.panciera@aecom.com

cc: Beth Lang (UTC) Bryon Dahlgren (AECOM) Jon Alberg (AECOM) AECOM

Attachment A: Response to EPD's Comments Dated March 16, 2016



AECOM 500 Enterprise Dr., Suite 1A Rocky Hill, CT 06067 www.aecom.com 860.263.5800 tel 860.263.5888 fax

June 29, 2016

Mr. Jason Metzger Program Manager Response and Remediation Program Environmental Protection Division – Land Protection Division 2 Martin Luther King Jr. Dr., Suite 1054 East Atlanta, GA 30334

#### Subject: Attachment A: Response to EPD Comments Letter Dated March 16, 2016 Former United Technologies Automotive Site, HIS #10543

Former United Technologies Automotive Site, HIS #10543 1884 Warrenton Highway, Thomson, McDuffie County, Georgia Tax Parcel ID # 00200056

Dear Mr. Metzger,

AECOM Technical Services (AECOM), on behalf of United Technologies Corporation (UTC), is submitting this letter in response to the Georgia Environmental Protection Division (EPD) letter dated March 16, 2016 for the Former United Technologies Automotive Site located at 1884 Warrenton Highway, Thomson, Georgia (the Site).

The initial semi-annual progress report under the Voluntary Remediation Program (VRP) was submitted on December 16, 2015 along with the 2015 Annual Groundwater Monitoring Report. EPD reviewed both reports and provided a comment letter dated March 16, 2016. AECOM and UTC have reviewed those comments and provide the following responses. GAEPD's comments are in italics.

1. Comment #1 of EPD's June 30, 2015 letter discussed the potential installation of a deeper monitoring well if TCE concentrations continued to be reported above the Risk Reduction Standards (RRS) at M-17. TCE has been reported above the Type 4 RRS for the past four (4) sampling events. In addition, the Mann-Kendall Statistics Summary documented in Appendix E shows TCE as "increasing" in M-17 with a confidence trend of 96.9%. EPD is not requiring that a deeper well be installed at this time; however, if TCE concentrations continue to be reported above the Type 4 RRS at M-17, the installation of a deeper monitoring well will be required. As specified by the Act, vertical delineation is required within 30 months of enrollment.

M-17 will be sampled during each groundwater sampling event in accordance with the VRP. Volatile organic compound (VOC) concentration trends will be evaluated after each sampling event. At 24 months post-VRP enrollment, if vertical delineation is not achieved, AECOM will discuss options with EPD, including the possibility of installing a deeper groundwater monitoring well to achieve vertical delineation.

 TCE also continues to be reported in groundwater above the Type 4 RRS at boundary wells M-07 and M-10. 1,1-DCE was also reported above the Type 4 RRS at boundary well M-09 during the June 2015 sampling event at concentrations two (2) times the level reported during the December 2014 sampling event, 340 µg/L to 698 µg/L, respectively. Please continue to sample and closely



monitor boundary wells M-07, M-09, and M-10 and if concentrations continue to increase, additional wells may be required to the west of these wells. In addition, TCE concentrations at M-14D, located near the suspected release area to the east of M-07, M-09, and M-10, were reported at the highest levels since 2010 at 581 µg/L and is likely contributing to the elevated concentrations of VOCs reported in nearby wells.

Monitoring wells M-07, M-09, M-10, and M-14D will continue to be sampled and closely monitored. Results of the recent June 2016 sampling event will be discussed in the 2016 Annual Report.

3. Comment #2 of EPD's June 30, 2015 letter requested a soil gas sampling plan with proposed locations near the west portion of the main building. AECOM's October 16, 2015 response to EPD's comment stated that the Johnson and Ettinger (J&E) Model proved to be an effective method of demonstrating that vapor intrusion risks do not exist on-site and indication no additional vapor intrusion investigation was necessary. EPD agrees that the J&E Model can be an effective tool for modeling subsurface vapor intrusion; however, because groundwater at M-17 was observed at less than 5 feet-below ground surface (ft-bgs), additional lines of evidence, including soil gas sampling, is warranted. Multiple EPA vapor intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance), state that the use of generic groundwater attenuation factors are inappropriate when groundwater depths are less than 5 ft-bgs. Because groundwater was measured at 0.28 ft-bgs at M-17, please collect sub-slab soil gas samples near the western portion of the main building as initially request in Comment #2 of the EPD's June 30, 2015 letter.

AECOM has prepared a Soil-Gas Sampling Plan as requested in EPD's June 30, 2015 letter. The Sampling Plan is included as a technical memorandum attachment to this letter. It is our intent to implement the plan during the next semi-annual period.

4. Section 2.0 of the December 2015 Annual VRP Progress Report proposes to attempt to locate monitoring wells MW-1R, M-12, and M-12R during the June 2016 sampling event. EPD concurs that these wells should be located and surveyed. If the wells cannot be located, EPD may recommend installing new replacement monitoring wells in the future. Due to the fact that VOC concentrations have never been reported in M-12, EPD agrees M-12 can be abandoned if located.

During the June 2016 groundwater sampling event AECOM again attempted to locate M-1R, M-12, and M-12R. None of the three wells were found. All three wells are suspected to have been destroyed by the current property owner (Pelzer). The 2015 Annual Groundwater Monitoring Report recommended that M-1R and M-12R be rehabilitated if found and added to the annual groundwater monitoring program as these wells are furthest downgradient and separate the source area from the northeast boundary of the Site. Upon further evaluation of the groundwater flow data, it is evident that these wells are not in fact downgradient from the source area, nor do they separate the source area from the northeast boundary of the site. M-1R and M-12R are both side-gradient to the source area; additionally, historic concentrations of VOCs in both wells have been stable and consistently below the Type 4 RRS criteria for all reported compounds. Based on groundwater flow, M-04 is more representative of a downgradient well separating the source area from the eastern side of the Site; furthermore, M-04 is also downgradient from both M-1R and M-12R and 2015 as well as historic concentrations have been non-detect for all reported compounds.

5. The depth to water drawdown was recorded at over 8 feet on the Well Purging and Sample Collection Form for M-18. EPD understands that recovery rates vary at each well, but please make all reasonable attempts to reduce drawdown by adjusting the pump rate of the pump. If



drawdown continues, please "chase" the water column until the well is evacuated. In addition, initial groundwater parameter readings were not included at M-04 and notation began after two (2) gallons had been purged from the well. Please include all data from the beginning of purge to the collection of the sample. Purge volumes on every Well Purging and Sample Collection Form were all noted in 0.25 gallon increments. In the future, please accurately measure and note the actual volume purged and follow SESDPROC-301-R3 to ensure groundwater samples are collected and documented accurately.

Reasonable attempts will be made to reduce well drawdown, initial groundwater parameter readings will be included on data sheets, and purge volumes will be recorded accurately.

6. Comment #5 of EPD's June 30, 2015 letter requested groundwater sampling from the Point of Demonstration (POD) monitoring wells M-3, M-3A, and M-4. Section 4.0 of the December 2015 VRP Annual Progress Report documents M-3 and M-3A as POD wells, but does not include M-4. EPD requests M-4 be added as a POD well because the recorded groundwater flow direction is historically towards the east and the northeast.

M-4 will be documented as a POD well going forward.

7. Section 2.1 of the 2015 Annual VRP Progress Report states that monitoring wells were inspected for missing bolts, o-rings, or damage to the well that might affect its structural integrity. However, during EPD's May 15, 2015 site visit, several bolts were noted as missing on many of the flush mount caps. Please ensure any missing bolts and/or o-rings are replaced during the next sampling event to preserve the integrity of each well.

During the June 2016 groundwater monitoring event the wells were inspected. These findings were documented in the field notes. Where possible, repairs were made during the sampling event; where it was not possible to do so, AECOM is evaluating the need for repairs based on whether the well is sampled, well location, nearby traffic patterns, and the need for the well. AECOM plans to implement select repairs during the next semi-annual period.

We respectfully request that GAEPD review the responses above and provide concurrence with the presented response to comments. If you have any questions regarding the information provided in this response, please do not hesitate to contact Matthew A. Panciera at (860) 263-5742.

Sincerely,

Matthew A. Panciera, PE, LEP Project Manager Matthew.Panciera@aecom.com

cc: Beth Lang (UTC) Bryon Dahlgren (AECOM) Jon Alberg (AECOM)



AECOM 500 Enterprise Drive, Suite 1A Rocky Hill, CT 06067 860.263.5800 tel 860.263.5777 fax

## Memorandum

То	Jason Metzger	Pages	3 w/ attachments
CC	Beth Lang, UTC		
Subject	Soil-Gas Sampling Plan: Former United Techn HIS #10543	ologies Auto	motive Site,
From	Matthew Panciera PE, LEP		
Date	June 27, 2016		

AECOM is submitting this technical memorandum on behalf of United Technologies Corporation (UTC). The purpose of this technical memorandum is to outline a soil-gas sampling plan proposed at the former United Technologies Automotive Site located in Thomson, Georgia (Site). The soil-gas sampling plan was requested by the Georgia Environmental Protection Division (EPD) in a letter of response dated June 30, 2015, to UTCs Voluntary Remediation Program (VRP) Application.

The site was previously managed under the Georgia Hazardous Site Response Act (HSRA) with monitored natural attenuation (MNA) sampling being conducted during semi-annual groundwater sampling events. On March 12, 2015, AECOM submitted an application for the site to be enrolled in the VRP; the application was approved by the EPD on June 30, 2015. The approval letter noted that the Johnson and Ettinger (J&E) vapor intrusion model used in the VRP report was an effective method; however, EPD requested soil-gas sampling as an additional line of evidence. Constituents of interest (COI) from the site, particularly Trichloroethylene (TCE) and Vinyl Chloride (VC) are volatile. The purpose of this sampling plan is to determine if these COIs pose a risk for Vapor Intrusion (VI) into the existing manufacturing facility.

Three wells (M-17, M-14D and M-08R, shown on **Figure 1**) are adjacent to the western edge of the building and are downgradient of a known source area. Groundwater flow is generally to the east. Historically, groundwater in this area has been shallow and wells M-17, M-14D, and M-08R typically have a depth to groundwater of 1 foot below ground surface (ft-bgs) or less. **Table 1** summarizes historical groundwater depths in these three wells.

Wells M-17 and M-14D are both bedrock wells; the depth to bottom is 60 ft-bgs and 25 ft-bgs respectively. Well M-17 has a screened interval of 55-60 ft-bgs and well M-14D has a screened interval of 15-25 ft-bgs. During the most recent sampling event in June 2015, TCE was observed in well M-17 at a concentration of 74 ug/L and in well M-14D at a concentration of 581 ug/L. Well M-08R, which is screened from 5-10 ft-bgs in a weathered bedrock and clay layer; is likely the well with groundwater concentrations most representative of the shallow aquifer under the building. TCE was observed in M-08R at a concentration of 6.7 ug/L during the June 2015 sampling event (the EPD Type 4 RRS criteria is 34.5 ug/L).

Based on COI concentrations in well M-08R, VI is likely not an issue under the active manufacturing facility. Regardless, to satisfy EPD's request, a representative sampling plan is proposed below as an additional line of evidence.

Soil-gas sampling is usually completed at depths of 3 ft-bgs or greater which limits the effects of environmental variables and limits the potential for atmospheric short circuiting. To eliminate these variables and to collect the most representative samples due to the shallow groundwater in this area of the site, we propose to perform surface emission flux monitoring as an alternate to soil-gas sampling.

The surface emission flux monitoring approach was developed by AECOM under contract to the United States Environmental Protection Agency (USEPA) in the 1980's for human health exposure studies at hazardous waste sites. The approach is routinely used at Superfund sites. Emission flux monitoring is an option for VI sites discussed in various guidance documents, which can be provided at EPD's request (e.g., *Vapor Intrusion Pathway: A Practical Guidance* [ITRC], *Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air* [CA Department of Toxic Substances Control], *Vapor Intrusion Technical Guidance* [New Jersey Department of Environmental Protection]). This approach provides a direct measure of mass flux, which in recent years has become a key concept cited by VI researchers for evaluating the VI pathway.

#### **Soil-Gas Emission Monitoring Plan**

Based on the above described emission flux approach, AECOM is proposing that emission flux measurements will be collected outside the western edge of the on-site building to evaluate soil-gas concentrations and VI potential. The building is an active facility which presents both access limitations and potential for background contribution from unrelated industrial activities. Therefore, collection of air data inside the building would neither be practical nor recommended.

Measurements will be made using surface flux chambers at three (3) locations, SGP-1, SGP-2, and SGP-3, beneath impermeable surfaces, such as asphalt and concrete. Proposed sample locations are presented in **Figure 1** and a summary of sampling methods is presented below.

#### Sampling Method

The proposed sample locations will be installed within 10 feet from the edge of the western edge of the building, downgradient of wells with elevated VOC concentrations. Sampling will be completed using a flux-chamber.

- Prior to sampling, concrete or asphalt will be removed from the sample location (roughly 2 ft. by 2 ft.);
- Measurements will not be collected within 24 hours of a rain event greater than 0.1 inch;
- Sampling will be performed according to the following procedure:
  - Following preparation of the sampling surface, a polished stainless steel or other non-adsorbing material flux chamber will be put atop the soil surface; sweep air will be introduced into the chamber (it will take approximately 30 minutes for the chamber atmosphere to reach steady-state conditions);
  - A grab sample will be collected from the chamber once steady-state conditions have been achieved;
  - Samples will be collected in Summa canisters or Tedlar bags (sampling equipment will be obtained from the laboratory and certified clean at a project-specific level); and

 Samples will be analyzed for VOCs via method EPA TO-15. One duplicate sample will also be collected for QA/QC purposes.

#### Reporting

Following receipt of analytical results, flux chamber concentrations will be used to calculate the emission flux and to estimate resulting indoor air concentrations. The data also can be used to estimate shallow soil-gas concentrations. The following equation will be used to calculate emission flux, where C is the flux chamber concentration, Q is the sweep air flowrate, and A is the surface area sampled.

 $E = \frac{C \cdot Q}{A} \qquad \qquad Equation 1$ 

The emission flux, E, will be multiplied by the square footage of the area of concern to provide a rate (e.g., micrograms per hour) at which vapors are emitting to the ground surface. It is assumed that the calculated emission flux, and by extension the shallow soil-gas concentrations, in this area 10 ft. west of the building are indicative of the sub-slab concentrations within the building. The resulting indoor air concentration will be estimated with calculations that take into account the building dimensions and building ventilation rate, assumed to be one air change per hour (1 ACH).

EPD previously referenced the Vapor Intrusion Screening Level Calculator (VISL) as an acceptable tool to determine potential concern for VI. Therefore, soil-gas and indoor air concentrations calculated from flux measurement sampling will be compared to soil-gas and indoor air screening levels obtained from the VISL. Calculations used to estimate indoor air concentrations would include site-specific risk values; the resulting estimated indoor air concentrations would be compared to inhalation risk levels of concern.

Assuming the above analysis indicates no VI risk; AECOM will prepare a brief summary report summarizing field activities, investigation results, and conclusions. If comparison to VISL screening levels indicates a potential for VI risk, additional site characterization steps will be considered.

Included with this memo we've attached two papers for further reference regarding emission flux monitoring. If you have any questions or wish to discuss the details of the proposed work plan, please feel free to contact me at 860-263-5742 or <u>matthew.panciera@aecom.com</u>.

Yours Sincerely

Matthew Panciera, PE, LEP Project Manager

Table & Figure

## AECOM

### Table 1 Historic Groundwater Depths (feet below ground surface) Former UTA Facility Thomson, Georgia

	Total Well Depth (ft)	Screen Interval (ft)	Average DTW (ft-bgs)	Min DTW (ft-bgs)	Jun-15	Dec-14	Jun-14	Dec-13	Jun-13	Feb-12	Oct-12
M-17	60	55-60	1.13	0.28	0.28	1.6	0.63	0.75	0.3	2.3	2.02
M-14D	25	15-25	0.93	0.41	0.41	1.33	0.61	0.66	0.54	1.7	1.26
M-08R	10	5-10	0.95	0.31	0.72	1.12	0.31	1.04	0.45	1.58	1.42







PROJECT Soil-Gas Plan

FORMER UNITED TECHNOLOGIES AUTOMOTIVE FACILITY THOMSON, GEORGIA

# PREPARED FOR



UNITED TECHNOLOGIES 9 Farm Springs Road Farmington, Connecticut 06032

# PREPARED BY

AECOM One Midtown Plaza 1360 Peachtree Street NE, Suite 500 Atlanta, Georgia 30309 404.965.9600 tel 404.965.9605 fax www.aecom.com

DATE 2015.12.04

**PROJECT NUMBER** 

60432488

FIGURE TITLE Site Layout with Parcel Boundaries

# FIGURE NUMBER

**Reference Papers** 

# Practical Guidance for Flux Chamber Measurements of Fugitive Volatile Organic Emission Rates

Bart Eklund

Radian Corporation Austin, Texas

Hazardous waste sites and industrial facilities contain area sources of fugitive emissions. Emission rate measurements or estimates are necessary for air pathway assessments for these sources. Emission rate data can be useful for the design of emission control and remediation strategies as well as for predictive modeling for population exposure assessments. This paper describes the use of a direct emission measurement approach - the enclosure approach using an emission isolation flux chamber - to measure emission rates of various volatile organic compounds (VOCs) from contaminated soil and water. A variety of flux chamber equipment designs and operating procedures have been employed by various researchers. This paper contains a review of the design and operational variables that affect the accuracy and precision of the method. Guidance is given as to the optimum flux chamber design and operating conditions for various types of emission sources. Also presented is a generic quality control program that gives the minimum number of duplicate, blank, background, and repeat samples that should be performed.

Emission flux measurements provide an estimate of the amount of a single species or multiple species being emitted from a given surface area per unit time. These data can then be used to develop emission rates for a given source for purposes of predictive modeling for population exposure assessments and these data can also be used to develop emission factors for remedial action design. This paper describes the use of a direct emission measurement approach - the enclosure approach using an emission isolation flux chamber - to measure emission rates of various volatile organic compounds (VOCs) from contaminated soil and water.

Flux chamber measurements are now commonly made at Superfund sites as part of the site investigation process. EPA's guidance document on estimating baseline air emissions from Superfund sites<sup>1</sup> identifies the flux chamber as a recommended method. A variety of measurement equipment and operating procedures are employed, and problems have been noted with samplers following a "cookbook" approach to performing these measurements. This paper discusses the theory of the sampling approach and the con-

#### Implications

In air pathway assessments, the greatest uncertainty often is associated with the estimates of emission rates (i.e., source terms), especially for area sources of fugitive emissions such as landfills and lagoons. In general, valid field measurement data are preferable to emission rate estimates based on predictive models. One method that commonly is used to make field measurements of emission rates from area sources is the flux chamber method. The flux chamber measurements, however, are not always performed using the equipment and protocol developed by the U.S. Environmental Protection Agency. Users of flux chambers should be aware of the effect of design variables, operational variables and characteristics of the emission source on the accuracy and precision of the measured emission rates. The effect on the measurement data from any deviations from the standard EPA approach should be determined through rigorous performance tests prior to use of the modified method in the field.

trolling variables that affect the accuracy and precision of the method. Guidance is given related to the optimal size of chamber to use, when opaque vs. transparent construction materials are preferred, techniques to ensure a well-mixed atmosphere within the chamber, special considerations related to various sampling media or instrumentation, etc., for both solid and liquid surfaces. Also presented is a generic quality control program that gives the minimum number of duplicate, blank, background, and repeat samples and discusses why and how these tests should be performed.

#### Theory

The enclosure approach uses an enclosure device, referred to as an emission isolation flux chamber (flux chamber), to sample gaseous emissions from a defined surface area. Clean, dry sweep air is added to the chamber at a fixed, controlled rate (e.g.,  $0.005 \text{ m}^3/\text{min}$ ) that is selected based on site conditions. The volumetric flow rate of sweep air through the chamber is recorded and the concentration of the species of interest is measured at the exit of the chamber. The emission flux is calculated as:

$$EF_1 = \frac{(C_1)(Q)}{A} \tag{1}$$

where:  $EF_i$  = emission rate of species, i (ug/m<sup>2</sup>min)  $C_i$  = measured concentration of species i (ppmv converted to ug/m<sup>3</sup>) Q = sweep air flow rate (m<sup>3</sup>/min) A = exposed surface area (m<sup>2</sup>). All parameters in Equation 1 are measured directly. For the sampling of aerated surface impoundments the addition of sweep air is usually not necessary. In such situations, the rate at which air is entering the chamber from the aeration source is determined (i.e., the off-gas rate) and emission fluxes are calculated using Equation 1.

Copyright 1992-Air & Waste Management Association

**Table I.** Key variables affecting VOC emission process by source type.

	Source type <sup>a</sup>										
Variable	1	2 <sup>b</sup>	3	4 <sup>c</sup>	5						
Contaminant Properties											
Concentration	Х	Х	Х	Х	Х						
Vapor Pressure	Х	Х									
Henry's Law Constant			X	Х	Х						
Molecular Weight of Oil Layer				Х							
Site/Source Properties											
Air-Filed Porosity	Х	х									
Bulk Soil/Water Temperature	х		х		Х						
Surface Temperature		х		х							
Wind Speed			X	х							
Aeration Air Volume					Х						

<sup>a</sup> Key to Source Types: 1 = Subsurface contamination covered by clean soil, 2 = Contaminated surface soils, 3 = Quiescent liquid surface with dissolved contaminants, 4 = Quiescent liquid surface with a floating organic layer, 5 = Aerated liquid surface (subsurface aeration).

<sup>b</sup> Assumes that emissions are diffusion controlled. <sup>c</sup> Assumes that floating layer is oil and not VOCs.

rissumes that hoating layer is on and hot ve

The flux chamber is effectively isolated from most external environmental conditions such as wind speed. Therefore, the measurement data are not strongly dependent on the meteorological conditions present at the site on the days of sampling. The data are thus directly comparable from day to day and site to site.

There is a practical limit as to the size of a flux chamber that is used in the field. Therefore, it is necessary to make a series of flux measurements to assess the spatial variability in emissions for a given source. Repeated measurements at a given location can be performed to assess temporal variability. These data allow estimation of an emission rate with a known confidence limit; i.e., a set of emission flux (mass/ time-area) measurements is necessary to estimate an emission rate (mass/ time) for an entire source.

The nature of the emission source influences the optimal flux chamber design and operation. Five general types of VOC emission sources are:

- 1. Subsurface contamination covered by clean soil
- 2. Contaminated surface soils
- 3. Quiescent liquid surfaces with dissolved contaminants
- 4. Quiescent liquid surfaces with a floating organic layer
- 5. Aerated liquid surfaces

The variables and processes that control the emission rate varies from source type to source type as shown in Table I. An understanding of these variables is necessary since they influence the optimal design and operation of flux chambers for a given application. The goal should always be that the flux chamber measurement process itself have as little impact as possible on the rate controlling factors.

The VOC emission rate from subsur-

face contamination covered by clean soil (Source Type #1) is controlled by the rate at which gas diffuses through the soil pore spaces. Any factors that significantly affect this diffusion rate will significantly affect VOC emission rates. Important chemical processes are the adsorption of gas molecules onto the liquid film surrounding soil particles and subsequent reactions of the adsorbed molecules. The physical transport of vapors through porous media such as soil has been discussed elsewhere.<sup>2-5</sup> In general, physical transport is controlled by the diffusivity in air for the specific compound of interest and the number and type of the air spaces that are present. Macrospaces due to cracks, fissures, spaces between buried drums, etc. will allow for relatively rapid mass transport. The diffusion rate through soil lacking such obvious pathways will be a function of the air-filled porosity (i.e., permeability to air). The permeability of soil to air can vary by up to three orders of magnitude across a typical residential lot.<sup>6</sup> The air-filled porosity will also vary over time. For example, precipitation causes water to fill some of the interstitial spaces in the soil and thereby inhibits diffusion. Similarly, the operation of heavy equipment at a site may lead to compaction of the soil and diminished emissions due to the change in soil porosity. Sites containing municipal wastes may produce significant amounts of methane and the emissions from such sites will not be diffusion-controlled.

The emission processes from contaminated surface soils (Source Type #2) are intermediate in nature between the applicable processes for subsurface contamination and for liquid sources (discussed in the following). Surface contamination due to spills, leaks, or land treatment results in areas of pooled waste both on and below the soil surface. The pooled waste quickly evaporates or percolates down through the soil. The majority of the contamination becomes adsorbed onto the surface of soil particles. The emission rate is usually assumed to be controlled by the diffusion rate in the air pore space when the waste loading and soil particles are both small. In this case, the emission rate is controlled in the same manner as for source type #1 and the same considerations apply. If, however, the surface soils are tilled or otherwise disturbed, large increases in emissions will oc $cur.^7$  This is a result of the contaminants being redistributed so that the depleted near-surface soil layer receives additional waste material. Soil disturbances also expose moist subsurface layers which leads to loss of moisture over time with a resulting increase in the air-filled porosity of the soil.

The rate of VOC emissions from quiescent liquid surfaces (source type #3) will depend on the distribution of the organic species between gas and liquid phases (Henry's Law), the concentration of the organic species in each phase, and the mass transfer characteristics (coefficients) of the species.<sup>2,3</sup> The overall liquid-to-air mass transfer coefficient is the most important term in controlling VOC emissions. The term consists of a resistance to mass transfer in liquid  $(K_l)$  and a resistance to mass transfer in gas  $(K_g)$ . For most VOCs,  $K_g \gg K_l$  and the liquid phase resistance controls the volatilization process. For mass transfer, the chemical and physical properties of the thin film at the liquid-air interface are of more significance than the bulk liquid and bulk gas properties. Any factor that alters the average overall mass transfer coefficient of the

surface impoundment will alter the VOC emission rate from that source. Wind has a major effect because the liquid phase resistance decreases in proportion to the square of the wind velocity. High winds therefore cause low resistance to mass transfer in the liquid phase with resulting high emissions. High winds also cause an increase in wave activity that approximates the activity of an aerator. The emission rate is also sensitive to any factor that increases the mixing of the bulk liquid; e.g., the residence time of liquid in the surface impoundment and the velocity of any influent streams.

The VOC emission rate from quiescent liquid surfaces with a floating organic layer (source type #4) will differ from rates from liquid surfaces without such a layer. If the floating organic is a purely volatile material, then the rate will depend on the vapor pressure of the VOC and the mass transfer coefficient which in turn is dependent on the wind speed and the size of the source. If the floating organic layer is primarily a heavy oil that contains some VOCs, then the VOC emission rate will be lower than that for source type #3. The oil layer adds an additional resistance term to the overall mass transfer coefficient due to mass transfer in the oil phase.

Emissions from aerated liquid surfaces (source type #5) are generally much higher than emissions from nonaerated liquid surfaces. This is due to the increased surface area and the enhancement of the gas film mass transfer coefficient. The aeration air serves to strip out VOCs from the liquid. Flux chambers are only applicable to the measurement of emissions from sites with subsurface aeration. Direct measurement of emissions from surface (mechanical) aerators is not practical.

#### Background

Flux chambers have been widely used to measure emission fluxes of volatile organic compounds (VOCs) and inorganic gaseous pollutants from a wide variety of sources. The flux chamber approach was originally developed by soil scientists to measure biogenic emissions of inorganic gases and their use dates back at least two decades.<sup>8,9</sup> In the early 1980's, the U.S. EPA became interested in this technique for estimating emission rates from hazardous wastes and funded a series of projects to develop and evaluate the flux chamber method. The initial work involved the development of a design and approach for measuring VOC fluxes from land surfaces. A test cell was constructed and parametric tests performed to assess chamber design

and operation.<sup>10,11</sup> A series of field tests were performed to evaluate the method under field conditions.<sup>12,13</sup> A user's guide was eventually prepared that summarizes guidance on the design, construction and operation of EPA's recommended flux chamber.<sup>14</sup>

A modified design of the flux chamber has also been developed to measure emission rates during the coring of soil and wastes.<sup>1,15</sup> The downhole flux chamber is placed down the annulus of a hollow-stem auger in the same manner as a core sampler. This allows for the measurement of the approximate emission rates from the soil/ waste were it to be exposed during trenching or excavation activities. A user's guide for downhole flux chambers has also been prepared.<sup>16</sup> Additional developmental work was performed to evaluate the use of flux chambers on liquid surfaces.<sup>17-20</sup> A user's guide for flux chamber sampling of quiescent liquid surfaces was proposed.17

The method has been applied to measuring VOC emission rates from aerated<sup>21</sup> and quiescent surface impoundments,<sup>22</sup> as well as solid emission sources.<sup>22,23</sup> A database of emission flux measurement data is available.<sup>24</sup>

#### Discussion

Practical guidance is presented in the following pages related to the design and construction of flux chambers, optimal sampling strategies, flux chamber operation and sampling QC. The need for such guidance is due to several factors. One, copies of the flux chamber user's guides and development studies cited above are not readily available. Two, the flux chamber design recommended in previous EPAsponsored studies is not available from any vendors for purchase or rental. Three, the recommended design is difficult to fabricate so users have frequently opted for simpler, but unvalidated, system designs. Four, the performance characteristics of a flux chamber are very dependent on the design, so rules-of-thumb applicable to one design may or may not be applicable to an alternate design. The end result of these factors is that widely different design and operating practices are employed, though not always to good effect.

The following discussions of the flux chamber design and operating practices treats the flux chamber validated for land surfaces<sup>14</sup> as the standard approach and discusses other flux chamber designs and operating practices in relation to this standard approach.

#### Flux Chamber Design

The important design factors are chamber size, volume, geometry, construction materials, length of sampling lines, line construction, air delivery system and impeller/mixing system.<sup>25</sup> Each factor is discussed below.

The standard flux chamber used is shown in Figure 1. It is a domed cylinder of 0.41 m (16 in.) diameter that encloses an area of  $0.13 \text{ m}^2$  and has an internal volume of about 0.030  $m^3$  assuming a 2.5 cm depth of penetration. The top of the chamber is a clear acrylic dome with a maximum height of 0.10 m. One 0.6 cm (1/4 inch) port is used to withdraw the off-gas and a second is used to measure the temperature inside the chamber. The chamber includes a 1.8 cm (3/4 in.) opening to maintain atmospheric pressure within the chamber (the chamber atmosphere is assumed to be well-mixed, so any outward leakage is not a concern).

Chamber Size and Volume. The sensitivity of the method is not dependent on the chamber size and volume. The chamber size used is a trade-off between several considerations. The surface area enclosed should be as large as is feasible so that the observed emission flux is not unduly biased by relatively small areas of unrepresentative emissions, so that the areas perturbed by the chamber edge or seal are a small percentage of the total sampling area, and so that wall effects are minimal. Conversely, the chamber should be small enough so that it is lightweight, easy to transport and simple to fabricate.

The chamber volume is directly related to the amount of enclosed area since mixing considerations favor a semi-spherical design. A small chamber volume is advantageous since it minimizes the amount of sweep air used per measurement. The volume should be large enough, however, that the collection of air samples from the exit line does not greatly perturb the chamber atmosphere or pressure. The rate of sample collection can be controlled to minimize this effect. Flux chambers as small as 0.0074 m<sup>3</sup> volume are commercially available, but the use of any chamber smaller than the standard design is strongly discouraged. For aerated surface impoundment applications, the standard size chamber is inadequate and a chamber of at least 0.1 m<sup>3</sup> volume is recommended.

*Chamber Geometry.* The optimal chamber geometry is one that promotes the most complete mixing of the chamber atmosphere in the briefest possible time. When placed on the emitting surface, the flux chamber con-



Figure 1. A cutaway diagram of the emission isolation flux chamber and support equipment.

tains ambient air and it takes some period of time for the concentration within the chamber to reach steadystate conditions. The optimal chamber geometry is closely related to the air delivery system design and rate, as well as to the impeller/mixing system employed (if any).

The standard flux chamber is a dome superimposed on a cylinder. This shape provides efficient mixing since no corners are present and dead spaces are thereby minimized. The use of square or rectangular flux chambers of low height to length ratios is not recommended due to concerns about adequate mixing of the internal chamber atmosphere. The only systematic study of chamber geometry was performed by Adams, et al.<sup>26</sup> Of the eleven chambers tested, the design chosen was a cylinder with a flat top. Vertical and horizontal composition profiles were performed and no stratification was detected. This design was compared to the standard design under field conditions.<sup>13,27</sup> Six measurements were made with each design and no statistically significant effect of chamber geometry on the measured emission flux was detectable.

*Materials of Construction.* The base of the flux chamber is stainless steel and the dome is made of acrylic. All components in contact with the gas are glass, teflon, or stainless steel. The sampling lines used for gas sample collection are typically teflon (FEP or PTFE) with stainless steel fittings. Gas samples for subsequent analysis are typically collected in evacuated, Summa<sup>®</sup>-polished, stainless steel canisters.

Two considerations are important when selecting construction materials for a flux chamber: (1) adsorption or emittance of gas species from the chamber and ancillary equipment; and (2) changes in the net energy flux at the sampling location due to the chamber.<sup>25</sup> The former consideration is addressed in the QC program through blank tests and recovery tests. Emittance of VOCs from the chamber has never proved to be a problem under field conditions (assuming the chamber is cleaned between sampling runs). Absorption of VOCs has also not proved to be a problem, though adsorption onto long teflon lines (e.g., >3m) is a potential concern, as is adsorption of polar VOCs such as methanol and acetone onto chamber surfaces.

Changes in the net energy flux is an important consideration for certain source types. The surface temperature of the emission source will affect the emission rate from source types #2 and #4. As expected, Radian has found in comparisons of clear versus stainless steel/plexiglass flux chambers that there was no significant difference in measured emission rates for diffusion controlled sources,<sup>10</sup> but there was a significant difference when the same tests were performed on a surface spill.<sup>12,13</sup>

The standard flux chamber design permits a portion of the incoming solar radiation to reach the sampling surface. This can lead to an elevation of the internal air temperature (greenhouse effect). The temperature rise may be 10°C in hot weather, when the sun is unobscured and is at a high angle to the horizon. Researchers have used a variety of methods to minimize the greenhouse effect including: circulating cooling water around the chamber, using a high sweep air flow rate, and using an all-metal, insulated chamber.<sup>25</sup> There are advantages to being able to visually observe the inside of the flux chamber during operation for condensation, etc. Therefore, the author recommends that the standard flux chamber be used for emission source types #1, #3 and #5, but that a removable, insulating cover be added when testing emission source types #2and #4.

Line Length and Construction. The standard flux chamber protocol<sup>14</sup> specifies a line length for the inlet and outlet lines of roughly 2 to 3 m of 0.6 cm diameter, clear teflon tubing. This line length is adequate for sampling most solid surfaces and for sampling liquid surfaces from a boat. For sampling surface impoundments remotely from an on-shore location, the sampling lines need to be extended to whatever length is required. Lines of 30m have successfully been tested without adverse effect.<sup>17</sup> Teflon is slightly permeable to non-polar organic compounds, so if long lines are required, adequate quality control checks such as recovery tests should be performed. The long sampling lines

Table II. Recommended design and operating variables for flux chamber sampling.

			Recomm	endation b	y source t	ype <sup>a</sup>
Variable	Units	1	2	3	4	5
Minimum Chamber Di-						
ameter	m	0.4	0.4	0.4	0.4	0.6
Minimum Chamber Vol-						
ume	$m^3$	0.030	0.030	0.030	0.030	0.1
Chamber Geometry		<del>&lt;</del>	not critical			
Insulated, non-transpar-						
ent cover/top needed	—	No	Yes	No	Yes	No
Maximum line length	m	3	3	30	30	30
Sweep air flowrate <sup>b</sup>	m <sup>3</sup> /min	0.005	0.005	0.005	0.005	0
Maximum sampling dura-						
tion	min	N/A	N/A	30	30	30
Maximum depth of pene-						
tration	cm	2.5	2.5	2.5	2.5	N/A
Collar/sealant required		Yes	Yes	No	No	No
Minimum time since last						
rain	days	7	1	N/A	1	<u>N/A</u>

<sup>a</sup> Key to source types: 1 = Subsurface contamination covered by clean soil, 2 = Contaminated surface soils, 3 = Quiescent liquid surface with dissolved contaminants, 4 = Quiescent liquid surface with a floating organic layer, 5 = Aerated liquid surface (subsurface aeration). <sup>b</sup> Recommendation will vary with chamber volume and design.

may also cause a large pressure drop across the line. This may pressurize the chamber if no pressure relief port is present and may make extraction of a sample difficult. Finally, long sampling lines increase the likelihood that the lines will inadvertently come in contact with the emission source. One solution is to encase the sampling lines within a garden hose to minimize contact and make cleaning easier. The use of adhesive tapes on the lines should be avoided as the adhesive may permeate the tubing and contaminate the samples.

Air Delivery System. The air delivery system consists of a source of sweep air, a metering device, and an air delivery system within the chamber. Two sources of clean, dry sweep air are readily available: compressed gas cylinders and clean air generators. Gas cylinders typically have a lower total hydrocarbon (THC) content and one that is less variable. The use of aluminum cylinders is recommended due to their relatively light weight. Assuming a typical sweep air flow rate of 0.005 m<sup>3</sup>/min, a standard 149 ft<sup>3</sup> tank of gas should be sufficient for one flux chamber for two days of noncontinuous sampling. The major drawback of clean air sources are that they require external power and that they must be checked or maintained periodically to ensure proper function. Also, some type of moisture trap may be necessary. For non-standard sampling runs such as 24-hr continuous sampling, it may be advisable to use humidified air to minimize evaporation of water from the emission source (solid or liquid).

The metering system should accurately deliver an air stream at a controlled flow rate. Rotometers are typically accurate to about  $\pm 5$  percent and

reproducible to  $\pm 1$  percent. The accuracy is a function of the care taken to set the rotometer and the frequency of calibrations.

The introduction of sweep air into the flux chamber is the most important design factor. The standard approach is to use a 1.3 m line of 0.6 cm diameter wrapped around the inside of the chamber near the intersection of the cylinder and the dome. The line contains at least four perforations equidistantly spaced around the chamber. The first hole in line is 5/64 in. in diameter and the others are 3/32 in. The air flow is directed towards the center of the chamber and parallel to the emitting surface. This approach has been shown to have adequate mixing based on smoke tests and tests of the time required to reach steady-state conditions.<sup>10</sup> Tests were also conducted using a liquid surface. Flowrates below  $0.013 \text{ m}^3/\text{min}$  did not produce an observable perturbation of the quiescent liquid surface. The effect of sweep air flow rate on measured emission fluxes is discussed later in this paper.

If the sweep air introduction system is not properly designed and tested, then the chamber atmosphere may not be well mixed and the measurement results will be biased. This is a critical consideration and must be addressed if the data are to be valid.

Impeller/Mixing System. Since having a well-mixed chamber atmosphere is such a key concern, numerous researchers have employed an impeller or other device to promote mixing. The use of an impeller does require some type of power source. A number of studies have demonstrated that the use of an impeller had no significant effect on measured emission rates.<sup>11,28,29</sup> It is important to note that the omission of an impeller is only warranted if the chamber atmosphere is already adequately mixed due to the design of the sweep air introduction system.

#### **Flux Chamber Operation**

The important operating factors are sweep air composition, sweep air flow rate, impeller rate, sampling time, placement/seal, and environmental conditions.<sup>25</sup> Each factor is discussed below. The effect of key factors for various emission source types is summarized in Table II.

The standard protocol specifies the following generic sampling procedure:

- Establish a grid system over the area to be sampled
- Randomly select six or more points to be sampled
- Begin sweep air flow
- Record time, met conditions, and temperatures
- Place clean enclosure on emitting surface and insert into ground
- Monitor emissions and note when steady-state concentrations are reached
- Record air and surface temperatures inside the chamber
- Collect samples
- Remove enclosure

The residence time,  $\tau$ , is defined as the chamber volume divided by the sweep air flow rate. It typically takes three to four residence times before steady-state concentrations are reached inside the chamber and sampling can be initiated. For a 0.030 m<sup>3</sup> chamber and a sweep air flow rate of 0.005 m<sup>3</sup>/min, this means that gas sample collection is typically started 24 minutes after the chamber is placed on the surface.

Sweep Air Composition. The standard protocol specifies the use of bot-

tled gas that approximates ambient air except that it should contain only minimal amounts of THC, moisture, and carbon dioxide. Either ultra-high purity (UHP) air or nitrogen is acceptable for most applications. The use of moisture-free sweep air theoretically could cause partial dehydration of the surface layer of the soil surface and thereby alter the mass transfer characteristics of the medium. Tests of humidified versus non-humidified sweep air, however, indicated that there was no effect on measured emission rates for land surfaces.<sup>11,13</sup> The use of heated (29°C) and humidified (60 percent R.H.) air was found to shorten the time required to reach steady-state conditions due to increased mixing due to thermal effects.<sup>11</sup> The use of humidified air is discouraged since its use would increase the likelihood of condensation occurring within the chamber and sampling lines. It would also be difficult to adequately control the temperature and humidity of sweep air under field conditions. The use of humidified sweep air might be warranted for extended test runs of biodegradation processes where the moisture content of the air and soil had a direct effect on biological activity and hence on emission rates. Another modification that might be appropriate under certain conditions is the use of oxygenfree sweep air to limit oxidation reactions and thereby increase the shelflife of collected gas samples.

Sweep Air Flowrate. This is the single most important operating factor. The sweep air flow rate can be varied to achieve the desired analytical sensitivity. The slower the flow rate, the lower the detection limit, but the longer it takes to reach steady-state concentrations within the chamber. A fast sweep air flow rate results in a short residence time within the chamber, thereby limiting the reaction time available. It also lowers the relative humidity within the chamber and minimizes condensation. Finally, a fast sweep air flow rate results in lower concentrations within the chamber and thereby minimizes any depression of emission rate due to the change in concentration gradient (driving force).

Flux chamber measurements are almost always made using a positive pressure sweep air source rather than by inducing a sweep air flow by the use of a vacuum pump (except for the special case of aerated surface impoundments). If an induced sweep air design is used, the air flow characteristics within the chamber are apt to be less uniform and ground-pumping of the emissions becomes a concern. The pressure gradient under positive pressure was found in one study to be only one-eighth of that under suction (and of opposite sign).<sup>30</sup> Although using positive pressure somewhat inhibits the emission flux, it yields data that are closer to the true emission flux than those obtained using induced sweep air.

As the sweep air exits through the ports in the standard design, it creates jets which entrain air and VOCs from the surrounding chamber atmosphere. In the standard design, these jets with their entrained flow impinge on each other at the center axis of the chamber. This creates additional turbulence and mixing. The velocity of the air at the ports is 0.29 m/sec  $(1.5 \text{ mph}).^{25}$ The velocity at the jet dissipation point is 0.055 m/sec. This "windspeed" within the chamber results in air that is considered still, but not stagnant. The mixing, while adequate, is not intense. The ratio of circulation turnover time to residence time is 0.14, suggesting that the average fluid (air) packet circulates seven times through the chamber before exiting. Mixing conditions in terms of Reynold's numbers have not been adequately addressed. Other researchers have calculated wind speeds within flux chambers of  $0.1-0.2 \text{ m/sec}^{26}$  and have measured internal wind speeds of 0.045 m/sec at a height above the ground of 0.0125m.<sup>31</sup> A recent validation study found that the bias in the measured emission rate was a function of the sweep air velocity.<sup>32</sup> The last three studies cited did not employ the standard design and operating conditions described above.

The concentration within the flux chamber varies with the sweep air flow rate. Ideally, however, the measured emission flux is independent of the sweep air flow rate used. Unfortunately, this does not always prove to be the case. The measured emission rate will vary directly with sweep air flow rate. During the development of the standard approach, it was found that the most accurate emission rate was obtained with a sweep air flow rate of 0.005 m<sup>3</sup>/min for a simulated landfill.<sup>10</sup> The relative bias introduced by altering the flow rate was found to depend on the porosity of the soil. The effect of sweep air flow rate on measured emission rates from surface impoundments has been examined using the standard flux chamber for 0.0014 to  $0.0212 \text{ m}^3/\text{min}^{17}$  and for 0.002 to 0.010 m<sup>3</sup>/min.<sup>20</sup> Both studies found that the measured emission rate increased when the sweep air flow rate was increased from the lowest levels tested. Negative biases of 10 to 50 percent were noted. Both studies recommend the use of a sweep air flow rate of at least 0.005 m<sup>3</sup>/min to avoid any negative bias. Studies using other flux chamber designs have shown variable results: no effect,<sup>33</sup> an increase in emission rate with sweep air flow

rate,<sup>32</sup> and even an increase in emission rate with a lower sweep air flow rate.<sup>29</sup> Reinhardt et al., used a 0.121 m<sup>3</sup> chamber, varied the sweep air flow rate from 0.013 to 0.0185 m<sup>3</sup>/min, and found that the emissions increased with increased flow rate with the most accurate rates at the highest sweep air flow rates.<sup>32</sup>

The bottom line is that the sweep air flow rate affects the flux being measured and the optimal flowrate depends on the design and operating factors of the specific flux chamber used, as well as the strength of the emission source. Again, the need to assess the operating performance of the flux chamber is obvious if any design or operating modifications from the standard approach are made. The sweep air flow rate must be high enough to ensure that good mixing occurs and to promote turbulent reduction of any laminar film boundary above the soil surface.

Impeller Rate/Mixing. As previously discussed, the use of an impeller is not necessary in a well-designed flux chamber system. Therefore, it is not surprising that varying the impeller rate anywhere from 0 to 1000 rpm has been found to have no significant effect on emissions from land surfaces.<sup>11,13</sup> This indicates that the emission process is not limited by gas phase mass transfer. The use of an impeller was found to have a significant effect (increased rate resulted in increased emission fluxes) when testing on liquid surfaces.<sup>18</sup>

Sampling Time. The minimum sampling time necessary is that time required to approach a steady-state concentration within the flux chamber (3-4 residence times). The maximum acceptable sampling time will depend on the nature of the emission source and the objectives of the monitoring program. In general, the longer the flux chamber is in place, the greater the likelihood that the emission process will be perturbed and the results biased. Flux chamber measurements of seven hours in length on a simulated landfill found no significant effect of sampling duration on the measured emission rate.<sup>10</sup> For liquid surfaces, however, this is not the case. Flux chamber measurements of six hours in length on a simulated surface impoundment found the measured emission rate decreased by about 40 percent by the end of the run.<sup>18</sup> It is thought that the chamber isolates a column of water and the contaminants in this water column are depleted (emitted) faster than they are replenished from the bulk liquid. In general, sampling of liquid surfaces has a likelihood that the measurement process will affect the emission process.34 Whenever possible the sampling duration for both soil and liquid surfaces should be held to 30 to 60 minutes, though this will preclude the use of sorbent-based sampling techniques.

Placement/Seal. The standard flux chamber protocol specifies that the chamber be worked in to the surface 2.5 cm (1 in.). This is not always possible and gaps about the chamber base are sometimes present. The influence of surface winds on the concentrations within the chamber in such situations is obvious. The quality of the seal that is achieved measurably affects the emission rate data. Sealing a non-standard chamber to the ground with caulk has been found to improve the standard deviation of the measurements from  $\pm 100$  to  $\pm 30$  percent.<sup>31</sup> Others have observed that surface winds could affect the gas concentration in the chamber even when the chamber is inserted into the soil.<sup>28</sup> The effect was most pronounced for dry soils.

The act of chamber insertion into soil does have a measurable effect on the emission process. The increase in measured emission flux due to the soil disturbance from the insertion of the chamber has been found to be  $80^{32}$ percent, and up to 250 percent.<sup>28</sup> It is recommended that chamber insertion be no more than 2.5 cm and a collar be used to seal the edge of the chamber.

For sampling liquid surfaces, the optimal depth of penetration has not been determined. Variations from 1.3 to 7.6 cm was found to have no effect.<sup>17</sup> The depth should be sufficient so that the chamber edge remains submerged during any wave motion, but not so deep as to isolate a column of liquid within the chamber. A variety of methods have been used to lower the flux chamber onto a liquid surface and control the depth of penetration, including the use of flotation collars, pontoons, and suspension from a cable. Flotation collars are generally the best method. The main consideration is to avoid contaminating the chamber and lines prior to reaching the sampling location of interest. When sampling aerated surface impoundments, air is withdrawn from the chamber at the same rate it enters (this is usually done by balancing the  $\Delta p$  ressure). The pressure within the chamber should be maintained at a slightly positive level or the chamber will tend to become submerged.

*Environmental Conditions.* The standard sampling protocol specifies measuring the initial and final air and surface temperatures, and recording visual observations of meteorological conditions and the emitting surface. Wind speed, wind direction, and air temperature can all affect emission fluxes from some types of emission sources. Changes in barometric pressure can cause ground pumping or inhibition of emissions depending on the pressure gradient between the atmosphere and the soil-gas. The correlation between meteorological conditions and measured emission fluxes has been evaluated.<sup>11,24</sup> In general, the flux chamber isolates the emitting surface from external meteorological conditions and minimizes their impact, though the external wind speed has some effect.<sup>28</sup> An equation is available to correct the measured emission flux for the increased air temperature within the chamber versus the ambient air temperature.<sup>11</sup>

The environmental condition of most importance for emission measurements is precipitation. In tests of a simulated landfill, water was added to dry soil cells to simulate rain events. Trace precipitation (0.01 in.) had no effect on measured emission fluxes. Heavier rains (0.4 in.), however, did have an effect. The emission flux was decreased by 90 to 95 percent and the reduction in emissions lasted for over eight days.<sup>10</sup> These results are consistent with field observations.<sup>12</sup> The effect of rain is to decrease the air-filled porosity of the soil and thereby limit diffusion. There may be a slight, transitory increase in emissions when the rainfall first enters the soil and displaces soil-gas. Precipitation would be expected to have no effect on emissions from emission source types #3 and #5. and little to no effect on emission source types #2 and #4 (unless a water layer formed on top of the waste).

#### **Sampling Strategy**

The optimal sampling strategy will depend on the size and nature of the emission source and the objectives of the measurement program. A statistically based random sampling approach is presented in the flux chamber user's guide<sup>14</sup> and an updated version is contained as Appendix C to Reference 1. The approach allows one to determine an average emission rate for a zone (source) by making a series of emission flux measurements. The approach calls for dividing the total area at a site into zones where heterogeneous chemical distribution is exhibited, i.e., areas expected to exhibit comparable emission rates. Each zone of equivalent emissions is divided into at least 20 grids. The number of grids required varies with the size of the zone and the grid size varies from 25 to a maximum of 200 m<sup>2</sup>. A minimum of six measurements are made at randomly selected gridpoints in each zone. The minimum number of required measurements also varies with the size of the source. The emission measurement data are evaluated and, if the data set exhibits sufficient variability, additional measurements are called for and/or the zone is divided into two or more new zones.

In actual practice, time and resources frequently preclude employing the sampling strategy outlined above. Eight to ten measurements can usually be performed in a day using a single chamber and 2–3 day's data (15–30 measurements) are usually more than adequate to make a preliminary assessment of the average emission rate from a small source. The data quality objectives and the spatial variability in the emissions from the source will dictate the minimum number of data points that are acceptable.

The simplest objective to meet is the measurement of maximum or worstcase emission fluxes. Suitable locations for such measurements can be ascertained from field experience, visual observation of the site, and review of any site records, soil boring data, and soil-gas data. In practice, a common sampling strategy is to evaluate both the worst-case and the average emission rate at a site.

#### Quality Control For Flux Chamber Sampling

A number of quality control tests are specified in the standard protocol<sup>14</sup> and their implementation is recommended. These include tests of the flux chamber, calibration of flow meters and thermocouples, and certification of gases. In addition, standard QC checks of the sample collection and analysis system should be performed.

New or modified flux chamber designs and operating procedures should be evaluated prior to field use. These should include mixing tests, blank tests, precision tests, and recovery efficiency tests. Measurement or calculation of the air velocity within the chamber is also recommended. The tests conditions should mimic the expected field conditions as closely as possible.

Additional QC checks should be performed during each sampling day. Sample blanks should be performed once daily and after any extremely highlevel measurements. The blanks are performed by placing the flux chamber over a teflon-coated surface and operating the chamber in the standard manner. Acceptance criteria are typically <10 ppmv or <10 percent of the field measurements, whichever is more stringent. A field blank or background sample should also be taken daily at a location that approximates the conditions at the field site but that is not contaminated. A minimum of 10 percent of the sampling points should be sampled in duplicate. This can be accomplished by either using adjacent flux chambers or by repeat sampling with a minimal time interval. Information about the sources of variability in

Table III. Accuracy and precision of flux chamber method.

	Accura	асу	Pre	1	
Source Type	Bias	Recovery <sup>c</sup>	<b>Repeatability</b> <sup>d</sup>	Reproducibility <sup>e</sup>	Reference
1—Landfill	$-22 \text{ to } -54\%^{a}$	77-112%	4.4%	6.5%	10
3—Quiescent Liquid	+30% <sup>a</sup>	99–120%	10%	7.5%	17
3—Quiescent Liquid	-41% <sup>b</sup>		8.6%		20

<sup>a</sup> Based on comparison to model predictions and mass balance.

<sup>b</sup> Based on comparison to stack sampling-type approach.

<sup>c</sup> Based on recovery of multicomponent standard gas introduced into flux chamber.

 $^{\rm d}$  Agreement between repeat measurements made with the same flux chamber.

<sup>e</sup> Agreement between measurements made with two different flux chambers.

the data can be obtained by collecting duplicate or triplicate samples from the duplicate chambers and analyzing each sample at least twice. In addition, one sampling location in each emission zone should be used as a control point. Measurements should be made at this location two to three times per day to assess the temporal variability in the emission flux.

#### **Performance Capabilities**

The overall accuracy and precision of flux chamber measurements will depend on the biases and variabilities associated with the emission source, the sampling method, and the analytical method. A variety of sampling and analytical methods have been used with flux chambers. The most common approach is the combined use of a portable total hydrocarbon analyzer (e.g., OVA Model 108) to monitor for steadystate conditions and evacuated, stainless steel canisters to collect samples for the quantification of specific analytes using GC-MD, GC-FID, or GC/ MS. Time-integrated methods such as Tenax, XAD-2, and PUF plugs have also been used, but these methods require relatively long sampling periods to collect adequate samples.

The results of several studies that examined the accuracy and precision of flux chambers are summarized in Table III. The data shown in Table III (with the exception of percent recovery data) are for total hydrocarbon samples collected in glass, gas-tight syringes or canisters and analyzed by GC-FID. In general, it has been found that the spatial and temporal variability in emissions at a given site is a greater source of variability than the sampling and analytical methods.<sup>13,23</sup> The sensitivity of the method using the standard operating conditions of sweep air flowrate is approximately one microgram per square meter per minute.<sup>24</sup>

#### Conclusions

Flux chambers are a valuable tool for measuring emission fluxes from area sources as part of air pathway assessments for Superfund and other types of sites. Their use permits exposures to be assessed and emission rates to be estimated. Standard approaches exist for measuring emission fluxes from a variety of types of emission sources. The standard approaches, however, are not universally used and this has led to the collection of questionable data in some cases. This paper is intended to summarize existing knowledge of the factors that potentially affect emission flux measurements and to explain the underlying assumptions of one standard approach. References

- 1. Radian Corporation. Procedures for Conducting Air Pathway Analyses for Superfund Activities, Interim Final Documents: Volume 2—Estimation of Baseline Air Emissions at Superfund Sites, EPA-450/1-89-002a (NTIS PB90-270588), August 1990. 2. U.S. EPA. Hazardous Waste Treat-
- ment, Storage, and Disposal Facilities (TSDF)—Air Emission Models, EPA-
- (15)r)—Air Emission Models, EPA-450/3-87-026. November 1989. Lyman, W. F.; Reehl, F. W.; Rosen-blatt, D. H. Handbook of Chemical Property Estimation Methods, McGraw-Hill, NY. 1990.
- Devitt, D. A.; Evans, R. B.; Jury, W. A.; Starks, T. H.; Eklund, B.; Gholson, A. 4. Soil Gas Sensing for Detection and Mapping of Volatile Organics, Na-tional Water Well Association, Dublin, OH, 1987.
- Pedersen, T. A.; Curtis, J. T. Handbook of Soil Vapor Extraction (SVE), EPA/ 540/2-91/003.1991.
- 6. Johnson, P. C.; Ettinger, R. A. "Heuristic model for predicting the intrusion
- rate of contaminant vapors into buildings," ES&T 25: 1445 (1991).
  7. Eklund, B. M.; Nelson, T. P.; Wetherold, R. G. Field Assessment of Air Emissions and Their Control at a Refinery Land Treatment Facility, EPA 600/ -86-086 A&B (NTIS PB88-124540 and PB88-124557), September 1986. Aneja, V. P. "Characterization of
- Aneja, V. P. "Characterization of Sources of Biogenic Atmospheric Sul-fur Compounds," M.S. Thesis, North Carolina State University, Raleigh, NC.
- 9. Hill, F. B.; Aneja, V. P.; Felder, R. M. 'A technique for measurements of biogenic sulfur emission fluxes," ' J. Env. Sci. Health AIB **3:** 199 (1978)
- 10. Kienbusch, M.; Ranum, D. Validation of Flux Chamber Emission Measurements On A Soil Surface, Draft Report to EPA-EMSL, Las Vegas, under EPA Contact No. 68-02-3889, Work Assignment 69, June 1986.
- Kienbusch, M., Balfour, W. D.; William-son, S. "The Development of an Opera-tions Protocol for Emission Isolation Flux Chamber Measurements on Soil

Surfaces," Presented at the 79th Annual Meeting of the Air Pollution Control Association (Paper 86-20.1), Minne-

- apolis, MN, June 22–27, 1986. 12. Radian Corporation. Soil Gas Sam-pling Techniques of Chemicals for Ex-
- pling Techniques of Chemicals for Exposure Assessment—Data Volume, Report to EPA-EMSL, Las Vegas under EPA Contact No. 68-02-3513, Work Assignment 32, March 1984.
  13. Balfour, W. D.; Eklund, B. M.; Williamson, S. J. "Measurement of Volatile Organic Emissions from Subsurface Contaminants," in Proceedings of the National Conference on Management of Uncontrolled Hazardous Waste Sites, of Uncontrolled Hazardous Waste Sites, September 1984, pp. 77–81, Hazardous Materials Control Research Institure,
- Silver Springs, MD.
  14. Kienbusch, M. Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux faces Using an Emission Isolation Flux Chamber—User's Guide, EPA 600/8-86-008 (NTIS PB86-223161), February 1986.
- 15. Schmidt, C.; Balfour, W. D. "Direct Gas Emission Measurement Techniques and the Utilization of Emissions Data from Hazardous Waste Sites," in Proceedings of the National Conference on Environmental Engineering, Environmental Engineering Division, ASCE, 1983.
- 16. Eklund, B. User's Guide for the Measurement of Gaseous Emissions From Subsurface Wastes Using a Downhole Flux Chamber. EPA Contract No. 68-CO-0003, WA 0-13, Task 3, May 1, 1991
- 17. Kienbusch, M.; Ranum, D.; Eklund, B. Evaluation of the Flux Chamber Method for Measuring Air Emissions From Surface Impoundments, EPA Contract No. 68-0-3889, Work Assignment 42, January 1988.
- 18. Eklund, B.; Kienbusch, M.; Ranum, D.; Harrison, T. "Development of a Sampling Method for Measuring VOC Emissions from Surface Impoundments," Presented at the EPA/APCA Symposium on Measurement of Toxic and Related Air Pollutants, May 1987
- 19. Gholson, A. R.; Albritton, J. R.; Jay-anty, R. K. Evaluation of the Flux Chamber Method for Measuring Volatile Organic Emissions from Surface Impoundments, EPA/600/S3-89/008 (NTIS PB 89-148 589/AS), September 1989
- 20. Gholson, A. R.; Albritton, J. R.; Jay-anty, R. K. "Evaluation of an Enclosure Method for Measuring Emissions of Volatile Organic Compounds from Quiescent Liquid Surfaces," ES&T 25: **Š**19 (1991).
- Eklund, B.; Green, D.; Blaney, B.; Brown, L. "Assessment of Volatile Organic Air Emissions From an Industrial Aerated Wastewater Treatment Tank," in Proceedings of the 14th Annual EPA Symposium on Land Disposal, Remedial Action, Incineration

and Treatment of Hazardous Waste, pp. 468–475, EPA/600/9-88/021 July 1988.

- Eklund, B.; Balfour, W. D.; Schmidt, C.
   "Measurement of fugitive volatile organic compound emission rates with an
- ganic compound emission rates with an emission isolation flux chamber," Environ. Prog. 4: 199 (1985).
  23. Wetherold, R. G.; Eklund, B. M.; Blaney, B. L.; Thornloe, S. A. "Assessment of Volatile Organic Emissions from a Petroleum Refinery Landtreatment Site," in Proceedings of the Hazardous Materials Control Research Inctifuto's 2nd National Conference on the second s stitute's 3rd National Conference on Hazardous Wastes and Hazardous Ma-
- Hazardous Wastes and Hazardous Materials, March 1986, EPA 600/D-86-074 (NTIS WE-RS-00679).
  24. Eklund, B.; Petrinec, C.; Ranum, D.; Howlett, L. Database of Emission Rate Measurement Projects—Draft Technical Note, EPA-450/1-91-003 (NTIS# PB91-222059LDL), May 1991.
  25. Eklund, B. Evaluation of Flux Chamber Design and Operation Factors, Draft Technical Note, EPA Report to EPA-EMB, RTP, NC under EPA Contract No. 68-02-3889, Work Assignment 42, August 1985.
- Adams, D. F.; Farwell, S. O.; Robinson, E.; Pack, M. R. Biogenic Sulfur Emis-sions in the SURE Region, Report No.
- EA-1516, Electric Power Research Institure, Palo Alto, CA, 1980.
  27. Radian Corporation, Soil Gas Sampling Techniques of Chemicals for Exposure Assessment—Tustin Spill Site Det Values, Desert to EDA EMSE Data Volume, Report to EPA-EMSL, Las Vegas under EPA Contact No. 68-02-3513, Work Assignment 32, July 1984 1984.
- 28. Matthias, A. D.; Blackmer, A. M.; Brem-ner, J.M. "A simple chamber technique for field measurement of emissions of nitrous oxide from soils," J. Env. Quality 9: 251 (1980).
- McClenny, W. A.; Shaw, R. W.; Baum-gardner, R. E.; Paur, R.; Coleman, A.; Braman, R. S.; Ammons, J. M. Evaluation of Techniques for Measuring Bio-genic Airborne Sulfur Compounds— Cedar Island Field Study 1977, EPA-
- 600/2-79-004, January 1979.
  30. Kanemasu, E. T.; Powers, W. L.; Sij, J. W. "Field chamber measurements of CO<sub>2</sub> flux from soil surface," Soil Sci-ure 118, 929 (1074). ence **118**: 233 (1974). 31. Pearson, J. E.; Rimbey, D. H.; Jones,

G. E. "A soil-gas emanation measurement system used for radon-222,' J

- Applied Meteorology 4: 349 (1965).
  32. Reinhart, D. R.; Cooper, C. D.; Walker, B.; Rash, F. "Flux chamber design and operation for the measurement of muoperation for the measurement of mu-nicipal solid waste landfill gas emission rates," J. Air Waste Manage. Assoc. 42: 1067 (1992). Ryden, J. C.; Lund, L. J.; Focht, D. D. "Direct in-field measurement of ni-trous oxide flux from soils, Soil Sci-ences of America J. 42: 731 (1978). Hitchcock, D. R. A Problem With Flux Chamber Measurements of Biogenic Sulfur Emissions. EPA-600/3-79-033, April 1979
- 33.
- 34. April 1979.

The author is with Radian Corporation, P.O. 201088, Austin, TX 78720-1088. This manuscript was submitted for peer review on April 14, 1992. This manuscipt was received on August 17, 1992.

Presented and Published in the Proceedings of the Air and Waste Management Association Specialty Conference on Vapor Intrusion Los Angeles, California, September 13-15, 2006

# "Use of Flux Chambers and Indoor Air Measurements to Evaluate Vapor Intrusion"

C. E. Schmidt Environmental Consultant 19200 Live Oak Road Red Bluff, CA 96080

Robert Kick The Forrester Group 605 North Boonville Avenue Springfield, MO 65806

### ABSTRACT

The assessment of potential vapor intrusion (VI) into structures from subsurface vapor sources is a complex and challenging task for scientists, regulators, and site owners/developers. Site assessment for vapor intrusion (VI) into structures as recommended by the USEPA includes using a 'tiered' assessment approach where typically the presence of possible soil gas sources are evaluated by studying site records, then if necessary, the contamination source below the structure is studied (e.g. groundwater collection and analysis, soil sampling and analysis, or soil gas sampling and analysis) and the data are compared with screening levels in look-up tables or a 'source term' is used in a predictive model to estimate the potential exposure.<sup>1</sup> This approach, assuming that the predictive modeling (Johnson & Ettinger equation<sup>2</sup> or other predictive equations) describes the site conditions accurately and the source data are representative, generally results in a conservative assessment of potential exposure to occupants in the subject structure. If the assessment results in an estimate of health risk that is acceptable (e.g., increased cancer risk of less than one in a million and a hazard index of less than one), then the pathway is considered 'incomplete' and no further assessment is recommended. But if the assessment results in an estimate of health risk that is above criteria, then further assessment (Tier 3) is recommended in order to generate a more refined, representative, or less conservative estimate of potential exposure and health risk to occupants. Additional information including more source data, can be collected and the predictive modeling enhanced, or direct measurement technologies can be used in a variety of ways to provide parallel lines of evidence that can be used to demonstrate the intrusion potential or support a refined health risk assessment. Direct

measurement technologies can also be used for different purposes throughout the multi-tiered process of assessing potential vapor intrusion.

There are two main direct measurement approaches available for assessing potential exposure to occupants in structures that are applicable for Tier 3 level assessment other than sub slab soil gas testing and refined predictive modeling, including: 1) the direct measurement of flux using the USEPA surface emission isolation flux chamber; and 2) the measurement of indoor and outdoor ambient air quality at the subject structure<sup>1, 3, 4</sup>. The application of these direct measurement technologies to the 'vapor intrusion site' will be presented as four specific project functions or options, including: 1) initial site survey screening assessment; 2) in-depth site investigation; 3) verification testing; and 4) investigations supporting the future building scenario.

The goal of the paper is to present various technical approaches for VI site assessment that include the measurement of vapor flux using the USEPA flux chamber and the direct measurement of indoor air. Case study information will be provided demonstrating these applications utilizing direct measurement technologies.

### **TECHNICAL APPROACH**

As identified in the federal guidance document for conducting VI assessment, direct measurement technologies provide support to the multi-tiered VI assessment approach, typically as a 'parallel line of evidence', refining potential health risk, discerning the VOC source, or confirming the health risk assessment generated by other technologies. Given the weight of responsibility to perform a representative and defensible VI assessment, conducting assessments using a variety of technologies and methodologies is prudent and provides for thorough site assessment. A VI assessment that relies on predictive modeling can be unnecessarily conservative leading to improper site restoration or site management. Likewise, an assessment without verification testing is less credible. Specific recommendations for using direct measurement technologies, including the USEPA flux chamber technology and/or indoor and outdoor ambient air measurements are provided below:

- 1) Initial Site Survey
- 2) Site Investigation following the APA Approach
- 3) Verification Testing
- 4) Future Building Scenario

### Initial Site Survey

A useful and non-invasive approach for site survey assessment includes using the USEPA flux chamber over a known subsurface source, especially over areas with the highest potential for vapor flux (i.e., high groundwater isocontour zone, points of solvent release) or at locations of particular interest (maximally exposed receptor, sensitive receptor groups). Often in site assessment and for various project reasons, site screening at scientifically selected locations on a limited basis provides for site screening data that: 1) can be used to address immediate issues of potential exposure; 2) can be conducted on public property such as road ways, right-of-ways, property fencelines, public parks, and municipal properties; 3) does not require intrusive work permits and notifications; 4) provides rapid site investigation data that can be used for planning

purposes, and 5) can be used at various times during a site restoration to the chart progress of selected remedial alternatives. With the low level of detection available by USEPA Method TO-14/TO-15, source testing at the land surface using this direct measurement approach provides very useful assessment data that can be correlated with other project data such as groundwater data and site geology/lithology. A case study is presented where a screening activity using the USEPA flux chamber was used to collect information after the installation and operation of a soil vapor extraction system. A limited surface flux data set was collected after soil gas extraction and prior to site redevelopment in order to assess the potential for surface flux prior to constructing structures. A second case study is also presented where open soil flux was collected in a neighborhood with an underlying groundwater contamination as a Tier 3 activity<sup>5</sup>. Open soil flux data were collected on public property over a known groundwater plume along three transects across the plume. These data were collected with the hope that any potential exposure to the public could be detected prior to testing on private property. These data were also used to confirm the expectation of low or non-detected flux that was predicted as determined by a thick clay layer above the groundwater plume; it was expected that the clay layer would prevent the vertical migration of soil gas from the groundwater plume. The open soil flux testing did in fact show that the study compound was not detected in the neighborhood.

Follow-up testing can also be conducted using indoor/outdoor ambient air sampling provided that a building is available for testing, and testing is conducted so that a representative data set is collected<sup>6</sup>. A minimum of one outdoor ambient air sample (positioned upwind of the building) and several indoor ambient air samples (positioned at points in the structure where potential impacts are more likely as related to a subsurface source- crawl spaces, utility vaults, service functions with utility conduits, poorly ventilated rooms) can be used for this purpose. Given that many VOCs can be assessed with method detection limits below regulatory health criteria, direct measurement of indoor air as compared to outdoor air provides very useful and immediate project data that can meet many project data needs.

### Site Investigation

A detailed site investigation using the air pathway approach (APA) as outlined by EPA using direct measurement technologies includes a study of: the surface flux potential of the site (open soil flux chamber testing defining the source potential); the indoor infiltration potential in one or more test structures over the source (flux chamber testing on points of infiltration in the structure assessing the infiltration flux potential); and indoor/outdoor ambient air testing in one or more test structures (assessing the potential effect of infiltration into candidate structures)<sup>7</sup>. When these three procedures are performed on a site, a data set is generated that can be used to: 1) define the subsurface pathway from the receptor to the know subsurface source, 2) develop mass transfer coefficients for a site-specific predictive modeling capability,

3) provide data that can be used to support an additional assessment of exposure generating a comparative health risk assessment, and

4) help to differentiate between different sources of VOCs found in the ambient air of structures.

A site investigation can be performed over a short time frame, depending on the particular site characteristics, with less that 30 flux chamber and ambient air samples collected for the

assessment. This is especially true if representative groundwater and soil gas data are available from prior testing activities. Direct measurement assessments are often correlated with groundwater and soil gas data, providing more in-depth assessment that is a bridge between source potential and actual infiltration. Mass transfer coefficients are often generated which make the existing predictive modeling more effective and representative. Tier 3 requirements can often be realized with a site-specific model that is enhanced with measured mass transfer coefficients. Given that health risk assessment is the decision-making tool for comparing potential exposure to health criteria, these data can also be used as input to a health risk assessment and then compared to health risk developed using for instance soil gas data and predictive modeling. A health risk assessment can be performed using all three data sets (open soil flux, infiltration flux, and indoor air quality) thus benchmarking an existing health risk assessment using direct measured data<sup>8, 9, 10</sup>. These data can also be used conservatively (i.e., maximum flux data or maximum indoor air data) so that issues about representativeness can be addressed without over-extending the measured data. And finally, an APA as described can provide a data set that is useful in differentiating the source of VOCs detected on site. Given that many compounds found in the subsurface source are also found in outdoor air, product usage indoors, and materials off-gassing, open soil flux data and infiltration flux data can be used to identify sources related to the subsurface infiltration pathway versus other unrelated sources. The case study presented demonstrates this with a site that had a groundwater plume containing a chlorinated solvent, and the chlorinated solvent was also common to the urban air shed. A study of the indoor air quality in the absence of a flux chamber assessment would have indicated an infiltration pathway, however, the absence of surface flux over the plume and infiltration flux indicated an ambient source that was later demonstrated by control group testing, to be the source of the study compound in the target area.

A secondary pathway can also be evaluated using the USEPA flux chamber, namely compounds released to the air at the land surface (open soil), traveling to receptors as an atmospheric plume, and resulting in potential exposure to downwind receptors. This ambient pathway is typically not significant give the low level of surface flux typically measured over groundwater plumes and the dilution of soil gas with dispersion on transport. Open soil flux data can, however, be used for this purpose.

### Verification Testing

Direct measurement is most often used to confirm the health risk assessment conducted using soil gas data and predictive modeling. Confirmation is very useful in VI assessments because it provides for an assessment of exposure that is made by an independent approach which does not involve predictive modeling. All technologies have limitations, but different technologies do not typically have the same limitations thus making conformational testing a prudent assessment approach. A case study is presented where a site assessment included thorough soil gas testing and predictive modeling, the health risk assessment using predictive modeling demonstrated acceptable risk levels, and the risk levels were met with regulatory approval. However, additional verification was required for project purposes, and an APA using direct assessment technologies was conducted<sup>7</sup>. Data from the additional studies supported the project health risk assessment in that potential exposure beyond control group data was not found. Verification testing can meet

many project needs including additional assurance to residence and community groups, as well and defense for legal actions.

### Future Building Scenario

A growing concern is related to land redevelopment of industrial properties that have a subsurface source, and there are no buildings where indoor air measurements can be conducted to support predictive exposure assessments. Open soil flux conducted over the known subsurface contamination and in the footprints of future buildings can be used to asses potential vapor intrusion to these future structures. The issue of potential building underpressurization can also be address by operating the USEPA flux chamber in a containment that simulates negative pressure. Although buildings are not designed as such, building underpressurization is a component of predictive modeling (-4 Pa). Since the USEPA dynamic flux chamber is a 'pressure vented' chamber, or a chamber that is designed to communicate the ambient pressure around the chamber, the direct flux chamber measurement technology can be used in a pressure controlled environment for this purpose as well<sup>11</sup>. A case study is presented where the data for the future building scenario can be collected and used for project purposes.

### METHODOLOGY

### Direct Flux Measurement

Assessing potential exposure by the air pathway from subsurface contamination can be accomplished using the USEPA surface emission isolation flux chamber.<sup>3</sup> The standard operating procedure using the USEPA flux chamber includes placing the chamber (30-liter, pressure vented mixed tank reactor) approximately 0.25 inch into the emitting surface (e.g., soil), forming an airtight seal, and adding a clean (ultra-high purity air) sweep gas (5.0 liters per minute) until the contents are at equilibrium. This occurs after about four or five residence times, or about 30 minutes (following the USEPA flux chamber user's Guide). Once the sampler has reached equilibrium, the vapors in the chamber are collected in an evacuated stainless-steel canister. Note that the USEPA flux chamber technology as a dynamic chamber is promoted for this application; the use of non-validated static chamber approach is not recommended<sup>12</sup>.

USEPA flux chamber recovery data has been reported that demonstrates the recovery of study compounds to detection limits lower than those used for the original method development and validation work<sup>3</sup>. A multi-component standard was added to the flux chamber in a laboratory at different flow rates generating different standard levels of recovery<sup>7</sup>. The chamber was operated as per standard operating protocols and sampled as in the field using TO-15. Although the limited chamber work was not conducted as a validation study, it is useful in demonstrating the performance of the technology down to current analytical method detection limits (i.e., 0.2-to-0.3 ppbv range). The table below presents the chamber target concentration levels (secondary standard) and actual concentration levels measured in the chamber, along with the percent recovery of standard for benzene and trichloroethene.

Compound Used in the Chamber Recovery Test	Measured Chamber Concentration in the Flux Chamber	Added Secondary Standard Concentration	Percent Recovery of Standard <sup>a</sup>
	(ppbv)	(ppbv)	(%)
Benzene	16	16	100
Benzene	1.4	1.9	74
Benzene	0.25	0.21	120
Trichloroethene	25	24	100
Trichloroethene	2.1	2.8	75
Trichloroethene	0.26	0.30	87

a- Reported to two significant figures

The results of the QC recovery study show compound recovery within method specifications down to a chamber concentration of 0.25 ppbv. The analytical accuracy for USEPA Method TO-15 is roughly  $\pm 30\%$  and the accuracy specifications for the flux chamber technology, considering field and laboratory variability is  $\pm 50\%$ . The recovery data indicate acceptable performance to levels that are applicable to intrusion site assessments. Note that error is incurred in adding low flow rates of a primary standard gas into the flux chamber, or in the preparation of what amounts to a 'secondary calibration standard'. The flux level included in the low-level QC recovery study at 0.21 ppbv for benzene or 0.63 ug/m3, corresponds to a flux rate of 0.024 ug/m2,min<sup>-1</sup>.

The flux chamber technology is an ideal assessment tool for quantitating the flux of subsurface VOCs. The method detection limit (MDL) for USEPA TO-15 is as low as about 0.01 ppbv, which translates to a flux of about 0.002 ug/m<sup>2</sup>, min<sup>-1</sup> for open soil flux.

### Ambient Air Measurements

Indoor and outdoor ambient air measurements are very useful in assessing potential impact to structures under investigation. Indoor and outdoor air measurements are conducted by collecting 8-hr or 24-hr integrated air samples in evacuated canisters using calibrated flow controller devices for metered air collection.<sup>6</sup> Although many current ambient air testing protocols recommend conducting ambient air testing as part of intrusion site assessment after the removal of all products and materials that contain VOCs or may off gas VOCs, and sealing the building for several days prior to testing, these activities are not always practical and are usually not followed. There are three reasons for this: 1) it is typically not possible to remove all products that contain VOCs or remove all materials that might off-gas VOCs from the test structure; 2) it is typically not possible to restrict access to occupied structures by closing the facility prior to and during testing- additionally, this procedure results in conditions that do not represent historic or current exposure to occupants from the potential infiltration source; and 3) when ambient air is measured as part of a VI investigation, especially if flux is measured using the USEPA flux chamber, there is no need to conduct indoor air testing to represent a 'worst-case exposure scenario' given that direct measurement open soil flux and direct measurement infiltration flux data are available for use in evaluating potential intrusion (i.e., direct measurement of infiltration flux isolates the VOC subsurface source from other sources of VOCs found in indoor air).

### Analytical Methodology

Open soil flux, infiltration flux, and ambient air sampling usually includes the assessment of volatile organic compounds (VOCs) using USEPA Method TO-14 or TO-15 for method listed non-methane hydrocarbon compounds.<sup>13,14</sup> VOC samples are collected in stainless steel canisters and analyzed by gas chromatography and mass spectrometry (GC/MS). GC/MS can be operated with large compound lists in the full scan mode, or in the selective ion mode for fewer compounds reported at lower MDLs. This analytical method is ideal for VI assessment providing analytical data of both high quality, low level of detection, and positive compound identification.

### CASE STUDY#1 - INITIAL SITE SURVEY (Muti-Phased Program)

A large groundwater plume with chlorinated solvents was discovered under a residential area located in the mid-West<sup>5</sup>. The soil type was silty clay and groundwater was at a depth of about 21 feet. Site records indicated that TCE was present. Tier 2 assessment further indicated potential unacceptable risk of TCE vapor intrusion given that groundwater TCE concentrations exceed EPA's maximum contaminant levels (MCLs). Subsequently J&E modeling utilizing sitespecific groundwater chemistry and hydrogeology did not indicate an unacceptable intrusion and health risk for occupants in structures located over the plume  $(2.4 \times 10^{-7})$ . However, agency concerns triggered Tier 3 level analysis, which included the use of direct measurement technologies for an in-depth assessment.

Direct measurement was conducted in a two-phase field testing effort. A test approach was developed which included two phases of field investigation in order to demonstrate if the presumed intrusion into structures over the plume was real or an artifact of screening level modeling known to be conservative by design.

Field measurements were conducted in Phase 1 for project-specific volatile organic compounds (VOCs) found in the subsurface groundwater plume and associated with the release. The compound list included: vinyl chloride, 1,1-dichloroethene, t-1,2-dichloroethene, c-1,2-dichloroethene, chloroform, carbon tetrachloride, trichloroethene, bromomethane, and 1,1,2-trichloroethane. These compounds were known to be present in the groundwater on site and were considered to potentially have an effect on the air pathway to receptors in the area. However, trichloroethene (TCE) is the only chemical of concern found at significant levels in groundwater beneath the residential area.

Testing was performed using the USEPA emission flux chamber along three transects that traversed the migrating groundwater plume in the residential neighborhood. A total of 20 open soil flux tests and 12 infiltration flux tests on outdoor surface coverings (sidewalks, gutters, and streets) were performed. Testing was conducted to generally correspond with GeoProbe® direct-push sampling locations above the groundwater plume where vapors from the groundwater could potentially be detected at the land surface. As such, these test locations are representative of potential maximum surface emissions of study VOCs found in groundwater.

Both open soil flux and infiltration flux samples were collected at collocated locations where possible. Quality control testing included media blank samples, flux chamber system field blank samples, replicate samples, and background samples. Flux measurements were performed following the USEPA flux chamber protocol and all surface flux samples were shipped to a California-certified laboratory for detailed analysis following USEPA Method TO-14a gas chromatography/mass spectroscopy (GC/MS) for VOCs operated in the selective ion mode (SIM). Quality control (QC) data indicated acceptable laboratory (lab blank, lab replicate, and matrix recovery data) and field (system blank and field replicate) data.

The Phase 1 measurement program included USEPA emission flux measurements on open soil and points of infiltration on public property (street right-of-ways, parks and city-owned property) throughout the study area. In general, the Phase 1 results of the open soil flux data for the project list of compounds (<0.06 ug/m<sup>2</sup>, min<sup>-1</sup>), like the infiltration flux data (<0.004 ug/ft, min<sup>-1</sup>), showed infrequent detection of the primary study compound TCE in both data sets supporting the J&E modeling result. The maximum levels of study VOCs are summarized below.

COMPOUND	MAXIMUM SOIL FLUX (ug/m <sup>2</sup> ,min <sup>-1</sup> )	MAXIMUM INFLTRATION FLUX
		(ug/ft,min <sup>-1</sup> )
Vinyl Chloride	ND	ND
1,1-Dichloroethene	0.030	0.0039
t-1,2-Dichloroethene	ND	ND
c-1,2-Dichloroethene	ND	ND
Chloroform	0.055	0.00097
Carbon Tetrachloride	0.011	0.0023
Trichloroethene	0.0053	0.0014
Bromomethane	ND	ND
1,1,2-Trichloroethane	ND	ND

TCE was detected at only two of the thirty-two sampling locations including one open soil flux location (geographically) closest to the source and at one location on a crack in a surface covering (concrete). Both "hits" were at low levels just above the detection limit and TCE was not detected at the paired infiltration and soil flux location, respectively. In general, the potential for intrusion was demonstrated with this data set alone since the 'incomplete pathway' was evident.

Soil flux data were used in a simple box model calculation to estimate potential intrusion into residential structures by assuming an emission value equal to 1% of the open soil flux. The structures were represented with a single-compartment 'box' having a surface area of 100 square meters, a volume of 244 cubic meters, and an air exchange rate of 0.5 exchanges per hour. Calculated indoor air concentrations were compared to USEPA Region IX Preliminary Remediation Goals (PRGs) adjusted to a  $1 \times 10^{-5}$  excess lifetime cancer risk (adjusted PRGs).

Infiltration flux was similarly used to estimate indoor air concentrations by assuming a crack length equal to the building perimeter, in this case 40 meters. These concentrations were then used to estimate indoor exposure through comparison with adjusted PRGs.

The results of these estimates of indoor air concentration of study compound TCE (0.0047 ug/m3) and associate risk were well below the indoor air concentration of concern for TCE (PRG 0.17 ug/m3) and indicate no unacceptable health risk. These results, along with infrequent detection of TCE over the area of highest TCE groundwater impact in the neighborhood, indicate the screening risk levels estimated in Tier 2 from look-up tables are conservative estimates of exposure. Results from J&E modeling are consistent with observed results. Conservative J&E screening estimates have been reported previously in the literature.<sup>15, 16</sup>

The results of the Phase 1 testing conducted on public property over the plume indicated that no significant impact was indicated. Although the direct measurement data collected during this initial testing satisfied the project objectives, a second phase of investigation was required by the governing agency. Phase 2 testing on residential property provided a unique opportunity to better quantify potential exposure to occupants, and it also provided very useful confirmation of estimates of exposure collected on public property.

# **CASE STUDY#2 - INITIAL SITE SURVEY (Post Remediation/Pre Construction)**

Soil contaminated with trichloroethene (TCE) was discovered on an industrial site located in a western state. A site investigation identified the level and extent of soils contamination by chlorinated solvents, and a soil gas extraction system was designed, installed and operated for a predetermined length of time satisfying the agreement for site restoration. After removing the target amount of TCE from the contaminated soil on site, open soil flux was measured using the USEPA flux chamber technology. A total of 11 locations were selected for testing based on historic soil contamination data. Many of the test locations where proposed building sites (future building scenario). The objective was to measure flux at key locations to determine the effectiveness of the soil gas extraction remediation, and to measure the potential flux of TCE at planned building site locations. A total of 14 flux measurements were performed in during a one-day testing event, including: system blank, background location test, replicate sample, and 11 site locations. The test data showed that the sensitivity of the approach resulted in method detection limits in flux units (ug/m2,min-1) of about 0.03 ug/m2,min-1. TCE was not detected above method detection limits of about 0.1 ppbv in the system blank (0.07 (U) ug/m2,min-1), the site background test location (0.03 (U) ug/m2,min-1), and in 7 of the 11 on site samples. The average flux for the non-detect samples was about 0.05 (U) ug/m2,min-1. However, four of the 11 on site test locations had measurable levels of TCE flux ranging from 0.06 ug/m2,min-1 to 0.8 ug/m2,min-1 including detections found at some of the future building footprint locations (average flux detection of about 0.4 ug/m2,min-1).

Results of TCE Detailed Screening	TCE Flux (ug/m2,min-1)
Field System Blank	0.065 (U)
Background Sample Location	0.027 (U)
Range of Non-Detect On Site Locations	0.027 (U) to 0.067 (U)
Range of TCE Detected On Site	0.059 to 0.78

This information was very useful because it illustrated the effectiveness of the soil gas extraction system by measuring the levels of TCE flux that were residual from the clean up effort, and it also provided engineering information that was useful for designing the level of vapor barrier protection needed for the future structures. The design engineers used this information to generate a structure design that would prevent the potential infiltration of TCE into the structure. Note that as a general rule of thumb, measured flux levels above data qualifiers (reporting limits and project QC data such as system blank and background flux levels) of around 1 ug/m2,min-1 should be considered, depending on the building slab attenuation and pressure considerations of the structure, that could present a migration pathway into structures. This level of potential vapor intrusion can be a concern, depending on the toxicity of the compound(s) of interest, unless mitigation measures or vapor intrusion barriers are engineered into the building design.

After construction of the structure, conformational indoor air samples were collected and TCE was detected in the structure despite the design considerations for the prevention of vapor intrusion. Additional testing and inspection of the structure was conducted to identify the source of the vapor intrusion, and a large section of open soil in a utility corridor was discovered that had not been poured after all utilities were installed. With the open utility corridor, the facility slab construction was essentially incomplete. The building design was not flawed, the vapor intrusion occurred as a result of a construction oversight in the completion phase of the project. Once the open soil pathway was sealed with the completion of the facility slab as per the structure design, the levels of TCE detected in the structure immediately dropped to ambient outdoor air levels. This case study demonstrates the utility of detailed screening using direct measurement technology, both the USEPA flux chamber on open soil supporting the site remediation effort and building design effort, as well as indoor and outdoor ambient air data that was collected to confirm an incomplete pathway to vapor intrusion.

### **CASE STUDY #3- SITE INVESTIGATION**

At the Case Study #1 site described earlier, direct measurement technologies were later used to study potential vapor intrusion on residential properties in the same area<sup>5</sup>. Locations were selected to represent maximum potential exposure based on dissolved chemical concentrations. A total of five structures over the plume and three structures located in a control area were selected for indoor/outdoor ambient air sampling. Air sampling included 24-hour integrated air sample collection at one outdoor location per property, one crawl space sample per property, and two indoor locations per structure. Flux chamber testing was performed at three of the five study structures over the plume and one control structure on open soil nearest to the foundation stem wall of the structures on all four sides. At one of the properties, one flux sample was collected in the crawl space under the structure on open soil.

Testing focused on a total of five study structures over the plume and three not over the plume (control structures). For this phase of testing, the analyte list was limited to only those compounds detected in groundwater beneath residential structures and potential decay products, including TCE, trans and cis-1,2-dichloroethene and vinyl chloride. TCE was considered to be the primary compound of interest. The results supported the initial site survey in that:

- 1. TCE was not found in any study structure or structure crawl space at levels greater than outdoor air or indoor air in the <u>control structures</u>; and
- 2. Open soil flux data collected on private property was likewise not impacted by TCE from the subsurface source.

TCE was detected in all of the study homes, both in the indoor rooms and in the crawl spaces of the study homes indicating initially that there might be a relation between the subsurface source and the TCE measured in the study area. However, the levels of TCE found in the crawl spaces, indoor air and outdoor air in the study area homes were comparable or lower that the crawl space, indoor air and outdoor air levels found in the control area. The diagram below shows the results of the ambient air testing (crawl space, indoor air, and outdoor air TCE concentrations) in collected in the three control structures in the control area (homes 1, 6, and 7) and in the five structures in the study area (homes 2, 3, 4, 5, and 8).

### **Control Area Homes**

**Study Area Homes** 

Given the relatively high concentrations in ambient air, there apparently was an industrial source of TCE upwind and closer to the control area homes that were part of the study, and this upwind source was affecting the air quality in the control area as well as the study area under investigation. (Note that the SIP indicated 296,000 pounds of TCE emissions for the year 2001; relevant TCE emission data for the study year were not available.) Since there was no subsurface source in the control area, and the outdoor air levels of TCE were higher than the indoor air levels, all evidence pointed to an upwind industrial source unrelated to the groundwater contamination. Open soil flux chamber testing in both the control area and the study area around these test structures confirmed that there was no measurable surface flux or subsurface source that could be responsible for the measured crawl space, indoor air, and outdoor air levels of TCE. Calculated concentrations of indoor air TCE in using infiltration flux measurements was approximately an order of magnitude or more higher than from open soil flux measurements. Given that the study structures exhibit a crawl space, rather than slab-on-grade design, the soil flux results are considered more representative of actual conditions.

Predictive modeling using the open soil flux data and outdoor infiltration flux data indicates that estimated indoor TCE levels associated with detection limit levels of flux are well below the adjusted PRG indoor TCE level of 0.17 ug/m3. There is an incomplete pathway for vapor intrusion.



Figure 1 Predicted Indoor Air TCE Concentrations

The used of direct measured surface flux data and indoor/outdoor air data taken in the control area and the study area, provided the parallel lines of evidence that differentiated the source of TCE and demonstrated an incomplete pathway for vapor intrusion. There was no measurable, unacceptable health risk in the neighborhood as related to the TCE groundwater as a potential subsurface source.

### **CASE STUDY #4- VERIFICATION TESTING**

A test approach was designed and conducted in to evaluate vapor intrusion at a large, multistructure facility. A USEPA mathematical model was used to provide a conservative estimate of the amount of soil gas that could potentially migrate into a structure on site. The estimate of carcinogenic risk to occupants in structures (30 year exposure at 24 hours per day) associated with the soil gas source was estimated at  $1 \times 10^{-7}$  chances of increased risk in contracting cancer with a hazard index of 0.038. The local, responsible agency evaluated the air quality on the facility with multiple studies and concluded that the compounds found were below health protective standards established by the state. Despite the agreement of acceptable risk and documented acceptable air quality in structures on the facility, additional scientific assessment or Tier 3 assessment was performed in order to confirm the site classification of 'incomplete pathway' for vapor intrusion.

A detailed and robust field program was conducted and flux measurements were made using the USEPA recommended surface flux chamber<sup>3</sup> and standard ambient air monitoring sampling techniques<sup>5</sup>. The USEPA flux chamber testing was conducted on open soil in the upper open soil

area where subsurface soil gas was detected, across the facility at numerous locations, and off site on the neighboring property that was used as the control study area. In addition, the flux chamber testing was conducted on seams and cracks in portions of three different buildings on site (Buildings A, B, and C) assessing direct infiltration through the building slabs, and in the basement of the off site structure (control study area). Background open soil flux data were also collected off site.<sup>17</sup> Outdoor ambient air was tested at multiple locations outside of the three test structures on site, and indoor ambient air was tested at multiple locations inside the three test structures. Outdoor and indoor air was also tested at the control study area (structure) at multiple locations. Where possible, open soil surface flux measurements were performed at or near locations where soil gas testing was conducted and at all locations where elevated levels of compounds in soil gas were found. An evaluation of these data indicate that measurable levels of 13 study compounds and were found above reporting limits and QC qualifying limits relative to the subsurface soil gas source, including: methane, carbonyl sulfide, carbonyl disulfide, odor, acetone, cis-1,2-dichloroethene, 1,1,1-trichloroethane, methyl isobutyl ketone, toluene, tetrachloroethene, ethylbenzene, m/p-xylene, o-xylene, and 1,2,4-trimethylbenzene. Benzene was not detected in on site open soil flux above the reporting limit. The open soil flux levels for these compounds can be used in a calculation to estimate exposure to receptors outdoors on open soil and in structures on site.

Open soil flux data collected on site are reported in Table 1 and are expressed as median and maximum values. The detections of these compounds from open soil flux measurements at locations in the known soil gas source area (12 locations) were summarized and were compared to open soil flux measurements at locations over the balance of the site (12 locations). Some of the study compounds were found slightly higher in the soil gas source study area as compared to the other on site test locations, and some were found at lower levels. There did not appear to be a significant difference in these two data sets indicating that the soil gas detected in the soil gas source area was not well correlated with the surface flux, or the effect from the soil gas source at the surface was not discernible. Methane was found at the highest flux level and at only about twice the QC criteria level. The compounds found in soil gas data were used as a 'fingerprint' of soil gas including methane, carbon disulfide, benzene, toluene, ethylbenzene, and xylenes (BTEX) as indicated by the summary of soil gas collected on site from the historic soil gas assessment. Some of these compounds were detected above reporting limits, but at higher levels away from the soil gas source area. Benzene was also found on site at levels higher than the control site or the off site study area (see Table 3). The conclusion from these data suggest that benzene was detected at low levels and less than reporting levels, but at levels higher than the control area indicating some possible relation to the soil gas source in the soil gas source area or other sources including benzene found in ambient air.

This is the case for other study compounds including methane, which is the study compound found at the highest level in the soil gas in the soil gas source area. The mean flux and maximum flux for methane in the soil gas source area on site is less than the mean and maximum flux from the other locations studied on site and is about the same as the methane flux measured in the control area.

Infiltration flux measurements were performed in order to study the direct migration of soil gas through the slabs in test structures located on site. A testing strategy was developed where areas in three structures were tested that were in the closest proximity to the known subsurface soil gas located in the source area. Three structures were selected for testing so that infiltration flux data could be collected from structures on the three different elevations on the site. A total of eight measurements were made on uncracked and cracked or seamed locations in these areas searching for infiltration through the slabs. All seams and cracks in a test area were screened using a FID/PID analyzer capable of detecting soil gas infiltration at low concentration levels (i.e., approx. 10 ppbv sensitivity). No detections of soil gas by field inspection were found on any seam or crack in structures A, B, or C. Specific test locations were selected to represent the study areas geographically. Infiltration data are reported in Table 2 and are reported as flux per foot of seam or crack. All infiltration flux data were compared to project QC data (lab blanks and field blanks) and background open soil flux data (away from the known soil gas source). Data collected on site above the QC data set is taken to be related to the subsurface soil gas source. These comparisons do not indicate intrusion of study compounds (Table 1) in the test structures by infiltration through the slab and demonstrate an 'incomplete pathway' for soil gas intrusion through the building slabs.

The indoor/outdoor air testing in the test structures served two purposes: 1) the ambient air data provided a direct measured data set that can be used as representative input to a health risk assessment useful in evaluating the effect of compounds found in indoor ambient air; and 2) the indoor air quality data, when compared to outdoor air quality data, support the infiltration flux data set or the 'pathway analysis' portion of the three-part APA.

A summary of indoor and outdoor ambient air concentration data are provided in Table 4. An evaluation of these data indicate that measurable levels of 13 study compounds were found in either outdoor air or indoor air samples, including: methane, chloromethane, acetone, carbon disulfide, 2-butanone, benzene, trichloroethene, methyl isobutyl ketone, toluene, octane, tetrachloroethene, ethylbenzene, and m/p-xylene. Compounds reported in the open soil flux or soil gas source assessment (Table 1; c-1,2-dichloroethene, 1,1,1-trichloroethene, o-xylene, and 1,2,4-trimethylbenzene) were also reported in Table 4 for comparison purposes. The median and maximum concentration of study compounds found in the indoor air in all three study structures were compared to the corresponding outdoor air quality, the QC criteria, and to the indoor/outdoor air quality in the control structure off site. The indoor/outdoor air quality in all three structures is similar, and similar to the control structure air quality. Several compounds, typically associated with other non-methane VOCs are detected in the indoor air quality in the study and control structures.

For a compound to be found in indoor air as a result of infiltration, it is most likely that the compound will be found in the associated infiltration flux data set at significant levels, and certainly the open soil flux data set at even higher flux levels. The evaluation of all three data sets (open soil flux, infiltration flux, and ambient air) in support of identifying the presence and the source of

compounds found in the indoor air, suggest that that the compounds found in the indoor air of all three study areas are not related to VOCs found in the soil gas on the facility.

The source area assessment using the USEPA flux chamber directly over the known subsurface soil gas source on site indicted low but measurable levels of study compounds emitted at the surface. However, these flux levels, when compared to other on site locations removed from the source area were not significantly different (similar median and maximum values). The open soil flux measured was low in comparison to background levels (neighborhood flux levels), literature background flux levels, and flux levels found off site in the control study area. These data indicate that, although there may be low-level flux associated with the subsurface soil gas source in the known soil gas source area as anticipated, these levels are low and are not likely to be related to indoor infiltration, especially at the levels measured and at the distances that exist between the known source area and the nearest structures on site (150' away or more). The first of three steps of the APA found low or indeterminate levels of surface flux in the soil gas source area.

The assessment of infiltration in the three nearest structures showed 'no significant infiltration flux' as defined by measured infiltration flux levels above reporting limits. Flux levels above analytical method detection limits (trend analysis) but below reporting limits showed a low level of methane flux in only one of the three structures at levels close to background and control structure flux levels, indicating an insignificant exposure potential or incomplete pathway. The infiltration of non-methane VOCs was not indicated by the data.

The final step in the analysis included the assessment of indoor air quality, which indicated no significant difference in outdoor air quality for study compounds as compared to indoor air quality. The presence and levels of compounds found in outdoor air and indoor air are typical of outdoor and indoor air quality in this region. Some compounds were found at higher levels than outdoor air levels, which are commonly detected compounds that are related to other sources of indoor air pollution, including off-gassing from construction materials, off-gassing from indoor furnishings, VOCs released from products used indoors, and VOCs released from activities involving products that contain VOCs. Study compounds identified in the soil gas source assessment (Table 1) were shown in subsequent data tables to demonstrate that the expected type and levels of petroleum compounds identified in the soil gas in the known soil gas source area are not found in the indoor air quality at levels that indicate intrusion.

Data from the APA of vapor intrusion indicate an incomplete pathway.

# CASE STUDY#5 - NO BUILDING SCENARIO AND PROPERTY TRANSACIONS

The development of defunct industrial properties including building renovation and new building construction on property that has been affected by industrial activity has potential for vapor migration. Many properties show some level of environmental contamination, often at low levels of soil and groundwater impact, but still require assessment demonstrating an incomplete pathway for future building occupants. Indoor air measurement can be conducted in existing structures as part of the site assessment, provided that a building exists on site suitable for

testing. Often such properties are in an industrial area and compounds found in ambient air from an unrelated source (i.e., upwind point or area source off site) are attributed to a subsurface migration source. Compound identification and association with the site contamination or site history can help differentiate these unrelated sources. In addition, a limited amount of direct flux chamber testing can also be used to identify potential sources of vapor migration.

One such site investigation involved a retail warehouse located in Northern California, where bulk quantities of herbicides and pesticides were sold for many decades<sup>18</sup>. Staining of the brick walls and cement slab floor from the repackaging and distribution of bulk liquid chemicals raised the concern regarding the off gassing of chemicals. After steam cleaning/pressure washing, a limited flux chamber testing program was conducted where off gassing of herbicides, pesticides, and volatile carrier agents or VOCs were measured using the flux chamber. Flux chamber testing was conducted on a number of wall and floor stains where semi-volatile (SVOC) and VOC testing was performed under ambient temperatures and artificially elevated surface temperatures (over 120° F) simulating high summer temperatures. Infrared heat lamps positioned above the flux chamber were used to generate high surface temperatures in order to promote the volatilization of VOC and SVOC compounds. Data was collected that demonstrated the detection of herbicide and pesticide 'carrier' compounds such as hexane and other organic compounds, which increased at higher temperatures but were, even at higher temperatures, being emitted at relatively low levels. These data indicated that there was an insignificant pathway of exposure from the building materials contacted with herbicides and pesticides.

### **CASE STUDY#6 - NO BUILDING SCENARIO**

Undeveloped properties, typically the outlying areas on large industrial facilities, are becoming available for development. Often, these outlying properties have not historically been used for industrial activities, but are near solvent use areas or are underlain with low levels of groundwater contamination. This site assessment challenge can be satisfied with detailed screening using the USEPA flux chamber on affected areas or on areas where future building sites are proposed. Although a building may not be available for indoor air testing, the exposure potential to future structures can be assessed by measuring the flux in an array of test locations on open soil. These data can be used to estimate potential exposure, but for sites with adequate distance to groundwater or with low-level groundwater contamination, open soil flux measurement can be performed over the areas of interest and compared to background areas in order to determine if the potential for surface flux is detected. The application of the flux chamber technology here is similar to Case Study #1.

In addition, open soil flux measurements can also be performed under negative pressure, simulating the condition of a building under the influence of negative pressure<sup>11</sup>. This can be accomplished by placing a containment around the flux chamber and creating a negative pressure inside the containment which affects the operation of the pressure-vented dynamic chamber. Two projects were conducted using the negative pressure enclosure around the flux chamber; one study was over cracks and seams in a slab over an area of the building with both soil and groundwater contamination, and a second study conducted on open soil over a low-level groundwater plume. The data from the site where infiltration flux was measured over a crack in

a cement slab with measurable flux showed a dramatic increase in flux at a -6 Pa pressure. The flux of study compound TCE increased from 0.47 ug/ft,min-1 to 27 ug/ft,min-1 (56 fold increase). On the other hand, open soil flux testing on the other over a groundwater plume showed little difference in the measured flux, with or without the negative pressure enclosure operated at -4Pa (0.0072 ug/m2,min-1 to 0.0066 ug/m2,min-1, respectively). Additional testing using the negative pressure enclosure approach for collecting site assessment data that addresses the future building scenario is needed. However, flux data collected in a negative pressure environment can be used to satisfy project needs for estimating exposure representing a range of future building scenarios. The direct measurement of flux on open soil or on cracks and seams in outdoor slabs or existing structure slabs for redevelopment sites, presents a viable alternative for vapor intrusion assessment using direct measurement technologies.

### CONCLUSIONS

The technical approach presented in support of vapor intrusion assessment, affords the unique opportunity to compare the results from applicable, direct assessment technologies used to study intrusion and potential exposure to occupants in structures near or over a subsurface soil gas source. For many sites, the assessment of intrusion ends with the determination of predicted exposure as determined from the robust soil gas assessment and conservative predictive modeling. The use of exposure as determined by directly measuring the flux of vapors at the ground surface or on points of infiltration into structures, provides for 'parallel lines of evidence'. These measurement approaches can be used in screening level assessment of exposure that can be used in site assessment or in health risk assessment. These measurement approaches generate exposure assessment data at low levels of detection, and the data can be used to define the components of vapor intrusion: source potential, migration potential, and exposure to compounds found in indoor air

The USEPA flux chamber, used along with the direct measurement of indoor air quality, is a useful approach for assessing the intrusion of soil gas into structures and supporting exposure and health risk assessments.

### REFERENCES

- 1. USEPA. Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance). November 2002.
- Johnson, P.C., and R.A. Ettinger. "Heuristic Model for Predicting the Intrusion Rate of Contaminated Vapors Into Buildings," *Environmental Science and Technology*, 1991; #25, 1445-1452.
- USEPA. Measurement of Gaseous Emission Rates From Land Surfaces Using an Emission Isolation Flux Chamber, Users Guide; EPA Environmental Monitoring Systems Laboratory: Las Vegas, Nevada, EPA Contract No. 68-02-3889, Radian Corporation, Work Assignment No. 18, February 1986.

- 4. USEPA. Office of Air Quality Planning and Standards, Air Superfund National Technical Guidance Study Series, Volume 2: Estimation of Baseline Air Emissions at Superfund Sites; Interim Final, EPA-450/1-89/002, 1989.
- 5. Kick, R.M., C.E. Schmidt, J.D. McDermott, "Case Study- Assessing Potential Air Pathway Exposure to Occupants in Structures Over Groundwater Impacted by Volatile Organic Compounds Using Environmental Data Collected on Public and Private Property", Proceedings of the Air and Waste Management Association Annual Meeting held in Indianapolis, Indiana, June 22-25, 2004
- Schmidt, CE. E. Winegar, S. Hoyt, "A Practical Guide for the Measurement of Indoor Air Impacts from Subsurface Contamination," Paper No. 278, Proceedings of the Air and Waste Management Association, Indianapolis, Indiana, June, 2004.
- Schmidt, C.E., "Evaluating Direct Measurement Approaches Used for Assessing Potential Air Pathway Impacts to Occupants in Structures Over Subsurface Sources", Proceedings of the Symposium on Air Quality Measurement Methods and Technology San Francisco, California, April 19-21, 2005
- 8. Copeland, Teri, C.E. Schmidt, Jim Van de Water, Michael Manning, "Predicting Potential Exposure from the Occupants in Future Buildings Using Direct Measurement and Predictive Modeling Techniques," Paper No. 43141, Proceedings of the Air and Waste Management Association, Baltimore, MD, June, 2002.
- Richter, Rich, Schmidt, C.E., "Assessing Realistic Risk to Indoor Occupants from Subsurface VOC Contamination," Paper No. 69, Proceedings of the Air and Waste Management Association Symposium on Air Quality Measurement Methods and Technology, San Francisco, California, November 13-15, 2002.
- Robles, Heriberto, C.E. Schmidt, Teri Copeland, Jim Van de Water, Michael Manning, "Measured Infiltration Flux as the Preferred Input to Indoor Exposure Assessment," Paper No. 70, Proceedings of the Air and Waste Management Association Symposium on Air Quality Measurement Methods and Technology, San Francisco, California, November 13-15, 2002.
- 11. Sheldon, Andrew, C.E. Schmidt, "USEPA Flux Chamber Technology and the Negative Pressure Enclosure for Assessing Potential Impacts to Occupants in Future Structures Over Contaminated Soil and Groundwater", Proceedings of the Air and Waste Management Association National Conference, Indianapolis, Indiana, June 2004.
- 12. Schmidt, C.E., A. Babyak, John Menatti, "Comparison of Static Chamber and Dynamic Chamber Technology for Assessing Infiltration of Soil Gas into Structures", Proceedings

of the Air and Waste Management Association Annual Meeting held in Indianapolis, Indiana, June 2004

- USEPA. Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air, EPA-600/4-83-027; Environmental Monitoring Systems Laboratory: Research Triangle Park, NC, 1983.
- 14. Hoyt, S.D., and V. Longacre. "Analysis of Selected VOCs at the Low PPTV Level for Risk Assessment: Vinyl Chloride"; Proceedings of the 4th Annual West Coast Regional Air & Waste Management Association Conference, Current Issues in Air Toxics, November 1993; pp 70-90.
- 15. Schmidt, C.E.; Teri L. Copeland; Rich Pesin. "Comparison of Measured and Modeled Emissions from Subsurface Contamination at an Industrial Site in a Residential Neighborhood"; Proceedings of the Annual 1998 AWMA Conference, 98-TA9C.01; San Diego, California, June 1998.
- 16. Schmidt, C.E., et.al., "Comparison of Measured Versus Modeled Surface Flux of VOCs from Contaminated Groundwater", Paper No. 447, Proceedings of the Annual Meeting of the Air and Waste Management Association, Salt Lake City, Utah, June, 2000.
- DeVaull, G.E., J.B. Gustafson, and C.E. Schmidt. "Surface Emission Flux Measurements: Background Levels"; Proceedings of the 5th Annual West Coast Regional Air & Waste Management Association Conference, Current Issues in Air Toxics, November, 1994.
- 18. Dwyer, Scott, C.E. Schmidt, "Indoor Air Health Risk Assessment of Organic Chemicals Adsorbed to Interior Building Surfaces", Submitted for Publication to *Environment International*, March 2006.

### Keywords

Flux chamber, direct measurement, area source assessment, ambient air measurement, vapor intrusion, and health risk assessment.

COMPOUNDS	SURF FLUX		MEDIAN		MAXIMUM		MEDIAN		MAXIMUM	
	QC CRITERIA		SOURCE		SOURCE		SITE- OTHER		SITE- OTHER	
	ug/m2,min-1		ug/m2,min-1		ug/m2,min-1		ug/m2,min-1		ug/m2,min-1	
Methane	24		10		43		23		47	
Carbonyl Sulfide	0.44	J	0.36	J	0.52	J	0.45	J	0.78	
Carbon Disulfide	0.54	J	0.48	J	1.1		0.93		1.4	
Odor ((D/T)/m2,min-1)	0.54		0.89		1.3		0.52		0.62	
Acetone	1.0		0.25		1.6		0.53		1.7	
c-1,2-Dichloroethene	0.0085	J	0.043	J	0.27		0.012	J	0.022	J
1,1,1-Trichloroethane	0.028	J	0.049	J	0.65		0.014	J	0.076	J
Benzene	0.015	J	0.011	J	0.062	J	0.011	J	0.080	J
Methyl Isobutyl Ketone	0.40		0.033	J	0.32	J	0.029	J	0.65	
Toluene	0.060	J	0.030	J	0.16		0.081	J	0.30	
Tetrachloroethene	0.20	J	0.020	J	1.9		0.076	J	0.47	В
Ethylbenzene	0.058	J	0.011	J	0.046	J	0.035		0.13	
m/p-Xylene	0.15		0.040		0.26	J	0.19		0.65	
o-Xylene	0.059	J	0.018		0.11		0.079	J	0.30	
1,2,4-Trimethylbenzene	0.11	J	0.075	J	0.075	J	0.10	J	0.48	

 Table 1. Summary of Open Soil Flux Direct Measurement- Source Assessment Component of APA

Source- open soil flux in soil gas source area; Site Other- open soil flux across facility, non-source area ug/m2,min-1- Micrograms per Square Meter per Minute (flux)

J- Less than Reporting Limit

B (as qualifier)- Compound found in laboratory blanks

QC Criteria- Highest Response for the Compound from the Media Blank QC Data

Compounds and data shown in **bold** are above Reporting Limit and QC Criteria (without B flag)

COMPOUNDS	<b>INFILTR FLUX QC</b>		MEDIAN	I	MAXIMUM		MEDIAN		MAXIMUM		MEDIAN		MAXIMUM	
	CRITERIA		INFIL AREA A	I	INFIL AREA A		INFIL AREA B		INFIL AREA B		INFIL AREA C		INFIL AREA C	
	ug/ft,min-1		ug/ft,min-1	ι	ug/ft,min-1									
Methane	2.3		1.2		1.4		ND		ND		ND		ND	
Carbonyl Sulfide	0.043	J	ND	1	ND									
Carbon Disulfide	0.053	J	ND	1	ND									
Odor ((D/T)/m2,min-1)	0.053		0.041		0.045		0.040		0.041		0.041		0.041	1
Acetone	0.098		0.0078		0.016		0.012		0.082		0.014		0.16	
c-1,2-Dichloroethene	0.00083	J	ND	1	ND									
1,1,1-Trichloroethane	0.0027	J	ND	١	ND									
Benzene	0.0015	J	0.00039 J		0.00068	J	0.00068	J	0.0027	J	0.00059	J	0.0024	J
Methyl Isobutyl Ketone	0.039		ND	1	ND		0.0017	J	0.0017	J	0.0020	J	0.0020	J
Toluene	0.0059	J	0.0037 J		0.0055	J	0.0030	J	0.0085	J	0.0033	J	0.0061	J
Tetrachloroethene	0.020	J	0.0018 J		0.0098	J	0.0024	J	0.0044	J	0.0021	J	0.0022	J
Ethylbenzene	0.0057	J	0.0013 J		0.0030	J	0.0013	J	0.0023	J	0.0013	J	0.0017	J
m/p-Xylene	0.015	J	0.0040 J		0.010	J	0.0039	J	0.0063	J	0.0043	J	0.0056	J
o-Xylene	0.0058	J	0.0016 J		0.0036	J	0.0018	J	0.0029	J	0.0018	J	0.0020	J
1,2,4-Trimethylbenzene	0.011	J	ND	1	ND									
ND Not detected above	I a la a constance a sur a star a star a		La cal Rosa M				_				-			_

ND- Not detected above laboratory method detection limit

ug/ft,min-1- micrograms per foot per minute (infiltration flux)

Infiltration QC Criteria- Highest Response for the Compound from the Media Blank QC Data

Infiltration QC Criteria- Highest Response from Blank (Method, Media, System) and BKGD Data for Infiltration Flux

Shaded (green) Compounds were detected

A- Area A

B- Area B

C- Area C

Sample ID References Sample Type or Function: e.g. SFI- Surface Infiltration Flux Compounds and data shown in **bold** are above Reporting Limit and QC Criteria (without B flag)

COMPOUNDS	SURF FLUX QC		Control Site		Control Site		INFILTR FLUX QC		Control Site		Control Site	_
	CRITERIA		OS- Median		OS- Maximum		CRITERIA		INF- Median		INF- Maximum	
	ug/m2,min-1		ug/m2,min-1		ug/m2,min-1		ug/ft,min-1		ug/ft,min-1		ug/ft,min-1	
Methane	24		12		21		2.3		0.55		0.91	
Carbonyl Sulfide	0.44	J	0.20	J	0.38	J	0.043	J	0.032	J	0.032 J	J
Carbon Disulfide	0.54	J	0.63		0.74		0.053	J	0.043	J	0.043 J	J
Odor ((D/T)/m2,min-1)	0.54		0.39		0.42		0.053		0.049		0.057	
Acetone	1.0		0.18		0.46		0.098		0.0094		0.032	
c-1,2-Dichloroethene	0.0085	J	ND		ND		0.00083	J	ND		ND	
1,1,1-Trichloroethane	0.028	J	ND		ND		0.0027	J	ND		ND	
Benzene	0.015	J	0.006	J	0.008	J	0.0015	J	0.00059	J	0.00078 J	J
Methyl Isobutyl Ketone	0.40		ND		ND		0.039		0.0013	J	0.0013 J	J
Toluene	0.060	J	0.037	J	0.061	J	0.0059	J	0.0023	J	0.0035 J	J
Tetrachloroethene	0.20	J	0.042	J	0.060	J	0.020	J	0.0029	J	0.0035 J	J
Ethylbenzene	0.058	J	0.013	J	0.035	J	0.0057	J	0.0010	J	0.0018 J	J
m/p-Xylene	0.15	J	0.079	J	0.17	J	0.015	J	0.0034	J	0.0054 J	J
o-Xylene	0.059	J	0.029	J	0.064	J	0.0058	J	0.0016	J	0.0024 J	J
1,2,4-Trimethylbenzene	0.11	J	0.072	J	0.087	J	0.011	J	ND		ND	

Table 3. Summary of Open Soil Flux and Infiltration Flux- Control Site and Structure

ug/m2,min-1- Micrograms per Square Meter per Minute (flux) ug/ft,min-1- Micrograms per Foot per Minute (flux)

J- Less than Reporting Limit

B (as qualifier)- Compound found in laboratory blanks QC Criteria- Highest Response for the Compound from the Media Blank QC Data Compounds and data shown in **bold** are above Reporting Limit and QC Criteria (without B flag)

COMPOUNDS	AA QC		MEDIAN	MEDIAN		MEDI	AN		MEDIAN		MEDIAN		MEDIAN		MEDIAN		MEDIAN	
	CRITERIA		OUTDOOR A	INDOOR A		OUT	DOOR B		INDOOR B		OUTDOOR C		INDOOR C		CONTR OUT		CONTROL IN	
	ppbv		ppbv	ppbv		ppbv			ppbv		ppbv		ppbv		ppbv		ppbv	
Methane	<50	U	2,300	2,300			2,100		2,100		2,300		2,400		2,700		2,900	j –
Chloromethane	0.06	J	1.2 J	0.18	J		0.12	J	0.15	J	0.12	J	0.15	J	0.11	J	0.14	, J
Acetone	0.35	J	2.1	6.2			2.1		5.2		2.7		2.9		1.8		3.6	<b>i</b>
Carbon Disulfide	0.10	J	1.4	0.24	J		1.1		ND		0.11	J	0.18	J	0.28	J	0.33	, J
2-Butanone	0.12	J	0.40 J	0.39	J		0.21	J	0.95		0.66		0.40	J	0.24	J	0.25	, J
c-1,2-Dichloroethene	0.23	U	0.10 J	0.10	J	ND			ND		ND		ND		ND		ND	
1,1,1-Trichloroethane	0.03	U	ND	ND		ND			ND		ND		ND		ND		0.09	, J
Benzene	0.03	J	0.38 J	0.38	J		0.30	J	0.21	J	0.17	J	0.30	J	0.22	J	0.29	, J
Trichloroethene	<0.03	U	2.2	0.35	J		0.93		0.04	J	ND		0.22	J	0.45	J	0.19	, J
Methyl Isobutyl Ketone	<0.07	U	0.11 J	0.16	J		0.11	J	0.16	J	ND		0.13	J	0.10	J	0.10	J
Toluene	0.10	J	1.4	3.1			0.71	J	1.2		0.52	J	1.2		0.89	J	2.4	ł
Octane	<0.09	U	0.51 J	0.49	J		0.37	J	0.51	J	0.84		0.45	J	0.3	J	0.50	J
Tetrachloroethene	0.08	J	0.36 J	0.24	J		0.10	J	0.09	J	0.10	J	0.12	J	0.22	J	0.65	, J
Ethylbenzene	0.11	J	0.41 J	0.35	J		0.21	J	0.32	J	0.18	J	0.27	J	0.20	J	0.26	, J
m/p-Xylene	0.22	J	1.6 J	1.3	J		0.92	J	1.6	J	0.63	J	0.95	J	0.82	J	1.2	: J
o-Xylene	0.11	J	0.54 J	0.54	J		0.33	J	0.53	J	0.23	J	0.35	J	0.31	J	0.42	: J
1,2,4-Trimethylbenzene	0.34	J	0.11 J	0.11	J	ND			ND		ND		0.32	J	ND		ND	

Table 4. Summary of Outdoor and Indoor Ambient Air Quality for Three Study Areas and the Control Area (ppbv).

ND- Not detected above Method Detection Limits

ppbv- Parts per Billion, Volume

J- Less than Reporting Limit

B (as qualifier)- Compound found in laboratory blanks

QC Criteria- Highest Response for the Compound from the Media Blank QC Data Compounds and data shown in **bold** are above Reporting Limit and QC Criteria (without B flag)

Shaded (green) Compounds were detected above Reporting Limit and QC Criteria

A- Area A; B- Área B; C- Area C; Contr- Offsite Control Structure