

DETERMINING RISK BASED REMEDIATION REQUIREMENTS USING RAPID FLUX CHAMBER TECHNOLOGY

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ABSTRACT: Risk assessments for industrial facility closures frequently eliminate exposure pathways from further evaluation. However, uncertainties often require confirmatory field analyses to determine air pathway completeness. Available models requiring contaminant concentration, effective diffusivity, biodegradation effect, etc., have high uncertainty and yield unreliable air concentrations. As part of an RCRA Facility Investigation at a former chemical manufacturing facility, surface flux-chambers were used to measure vapor phase fluxes of chemicals associated with subsurface contamination. This approach mitigates uncertainties introduced by existing volatilization models, simplifying and increasing exposure assessment accuracy. Surface fluxes of hexachlorobenzene (C66), hexachlorocyclopentadiene (C56), hexachloro-1,3-butadiene (C46), chloroform, vinyl chloride (VC), and tetrachloroethene (PCE) were measured to evaluate potential risks and hazards associated with the air pathway. Trials show surface fluxes are related to areas of known subsurface impact, demonstrating the utility of this technology for defining risks and remediation requirements for the site. Based upon the success of the trial program, an extensive program consisting of 100 to 150 surface flux measurements will be conducted this summer with EPA approval.

INTRODUCTION

In 1990, the United States Environmental Protection Agency (USEPA) proposed guidelines for corrective action (CA) for solid waste management units (SWMU) at hazardous waste management facilities (USEPA 1990). While the guidelines have yet to be finalized, they have generally provided the basis for ensuring that releases from SWMUs do not result in adverse impacts to human health and the environment. In the published rule, several priorities were established for CA program management. These include, prompt remediation of all significant off-site contamination, streamlined facility investigations, expeditious remedy decisions, and an emphasis in flexibility whenever possible. A fundamental premise of these priorities is that remedial requirements are risk-based and may vary significantly according to differing site settings.

Risk based remediation is predicated on the presence of complete exposure pathways that in-turn require sources, transport mechanisms, exposure points and routes (USEPA 1989). In many instances, potential exposure to soils and groundwater can readily be determined by comparisons to published preliminary remediation goals (PRG) such as those set forth by Region 9 of the USEPA (USEPA 1997). However, estimation of exposures to air secondarily impacted from intermedia transport is complicated not only by lack of specific knowledge of receptor characteristics but also by assumptions required to estimate volatilization to the overlying atmosphere.

Objective. In a 1997 collaborative study (approved by Region 5 of the USEPA), a surface flux chamber was designed and tested with the objective of determining its utility in Phase II investigations, and ultimately for setting remediation requirements for chlorinated hydrocarbons (CHC) at a former chemical manufacturing facility. Prior investigations at the facility delineated subsurface contamination of chlorinated hydrocarbons (hexachlorobenzene (C66), hexachlorocyclopentadiene (C56), hexachloro-1,3-butadiene (C46), chloroform, vinyl chloride (VC), and tetrachloroethene (PCE) in both soils and groundwater, including the presence of free product. While complete characterization of the soil and groundwater pathways continues, the volatility of these chemicals suggested that the upward vapor migration pathway could be substantial. After considering various alternatives to estimate and determine the risk, including the use of volatilization models, it was proposed that direct measurement of surface fluxes at potential source areas would give the most representative values of the upward vapor fluxes, and therefore best define remedial requirements at the site. To test this premise, a trial program consisting of ten (10) flux chamber measurements was conducted in October 1997 at the subject site.

METHODOLOGY

Field Methods: Cylindrical surface flux chambers, were placed at eight locations at the site, including locations with known soil CHC contamination and a background location. The chambers were constructed of galvanized steel, measuring approximately 6 inches (15 cm) in diameter and 6 inches (17.5 cm) high, and equipped with sampling and purge ports. Their simple design resulted in a low per unit cost (<\$10 per unit) which enabled ten to be deployed simultaneously. The deployment of a multitude of chambers allows much greater coverage of the site and yields a much more representative data base, features that are typically cost-prohibitive with more complex and expensive chamber designs.

Chambers were buried approximately 1 inch into the ground leaving an inner chamber height of approximately 5 inches (12 cm). A solar shade was placed over the chamber to reduce radiant heat effects. The chambers were left in-place for 10 to 11 days.

At the end of the deployment period, a gas tight syringe was inserted into the sampling port of the chamber and approximately 20 cc of air was withdrawn and immediately analyzed on-site by gas chromatography using a certified mobile laboratory. The on-site analysis was a unique feature of this program. Equipped with an Excel spreadsheet custom designed to calculate the fluxes from the measured data, samples were collected, measured for all the compounds of concern, and the upward vapor risk determined within one-hour of sample collection. This capability enabled real-time decisions regarding the need to leave the chambers in place for additional periods and the need to deploy additional chambers. In addition, the on-site analysis eliminated potential complications and errors introduced when larger volume samples are collected and analyzed off-site.

Determination of Flux-Based Remediation Goals

Published preliminary remediation goals (PRG) such as those set forth by Region 9 of the USEPA (USEPA 1997) are in terms of concentration units. In order to use flux chamber data, it is necessary to relate the concentrations measured in a flux chamber to the published concentrations.

The flux of a compound into an enclosed space (flux chamber or room) is defined as:

$$\text{Flux (mass/area*time)} = (\Delta C * V) / (\text{Area} * \Delta T) = \Delta C * H / \Delta T \quad (1)$$

Where ΔC is the change in concentration in the enclosed space over time
 V is the volume of the enclosed space
 Area is the contact area with the ground surface
 ΔT is the deployment time.
 H is the inner height of the enclosed space.

Using the preceding expression, the flux of a compound into a surface flux chamber (F_c) and an overlying room (F_r) is given by:

$$\text{Flux chamber:} \quad \text{Flux}_c = \Delta C_c * H_c / \Delta T \quad (2)$$

$$\text{Overlying Room:} \quad \text{Flux}_r = \Delta C_r * H_r / \Delta T \quad (3)$$

Because flux is in terms of unit area, the fluxes into a surface chamber or room will be identical at the same location, so that:

$$\text{Flux}_c = \text{Flux}_r - \Delta C_c * H_c / \Delta T = \Delta C_r * H_r / \Delta T \quad (4)$$

ΔT divides out, leaving:

$$\Delta C_c = \Delta C_r * H_r / H_c \quad (5)$$

Equation (5) indicates that although the flux into different-sized enclosed spaces are the same, the resulting concentration in the space depends upon the ratio of the volume to area. For a room 8 feet high, and a flux chamber 5" high, $H_r/H_c = (8/0.4) = 20$ and:

$$\Delta C_c = \Delta C_r * 20 \quad (6)$$

In other words, for the same flux, the concentration in a 5 inch high chamber will build up twenty times faster than the concentration in an 8 foot high room. If the allowable concentration in the room (PRG_r) is set to the EPA Region 9 residential remediation goals in ambient air, then the acceptable concentration for the chamber will be:

$$\text{PRG}_c = \text{PRG}_r * 20 \quad (7)$$

Finally, a correction needs to be made for the fact that room air exchanges during the course of a day, but the air in these chambers did not. If room air only flushed once per day, then the allowable concentration buildup in the chamber each day would be equal to the value in equation (7). However, air exchanges much more rapidly in residential and industrial buildings, typically on the order of a complete room volume every 1 to 2 hours. Thus, the allowable concentration buildup rate in the chamber is equal to:

$$\Delta C_c / \Delta T = \text{PRG}_c / E = \text{PRG}_r * 20 / E \quad (8)$$

Where E is the air exchange rate in the room (exchanges/hr)
 And ΔT is in hours.

For this study, a conservative value of one exchange every 2 hours ($E=0.5$), or 12 exchanges per day was used.

Equation 8 facilitates the interpretation of surface chamber data because it enables the measured concentration change in the chamber to be directly compared to published PRG values for overlying rooms.

Chamber Deployment Times: Once the required chamber concentrations are known as described in the preceding section, the required deployment time for the chambers can be calculated as the analytical detection limit divided by the amount of concentration buildup per hour. For the compounds of concern at this site, minimum deployment times ranging from 3 to 11 days were required depending upon the volume of vapor injected into the instrument. The longer deployment time was chosen since it was considered to yield a more representative flux, because it allowed short term fluctuations on the vapor flux, for example due to barometric pressure changes, to be averaged out.

RESULTS AND DISCUSSION

Table 1 shows results for the trial flux chamber measurements compared to permissible fluxes based upon ambient air concentrations protective of residential receptors established by USEPA Region 9 (USEPA 1997).

TABLE 1. Preliminary Flux Chamber Measurement Results (ug/L-h) for Selected Chlorinated Hydrocarbons at a RCRA Site.

Compound ^a	Area	PRG _r ^b	PRG _c ^c	$\Delta C/\Delta T_{PRG}^d$	$\Delta C/\Delta T_m^e$
C66	Impacted	4.2E-06	8.4E-05	4.2E-05	ND
	Background	--	--	--	ND
C56	Impacted	7.3E-05	1.5E-03	0.74E-03	5.6E-02
	Background	--	--	--	ND
C46	Impacted	8.7E-05	1.8E-03	0.88E-03	ND
	Background	--	--	--	ND
CHCl ₃	Impacted	8.4E-05	1.7E-03	0.85E-03	ND
	Background	--	--	--	ND
VC	Impacted	2.2E-05	4.4E-04	2.2E-04	ND
	Background	--	--	--	ND
PCE	Impacted	3.3E-03	6.6E-02	3.3E-02	3.7E-02
	Background	--	--	--	ND

a-see text for definition.

b-in ug/L (USEPA 1997).

c-PRG_r x 20 (in ug/L).

d-from Equation 8.

e-measured chamber concentration divided by deployment time (~260 hr).

Fluxes of two compounds, hexachlorocyclopentadiene (C56), and tetrachloroethylene (PCE), were detected. The measured C56 flux at Site 6 was nearly 80 times above the acceptable limit, strongly indicating that upward vapor migration is a risk pathway of concern at this location. The measured PCE flux at Site 5 was within 10% of the acceptable limit, indicating a possible risk at this location.

Fluxes of the other volatile CHCs were below detection from both impacted and background areas, and did not indicate a potential upward risk of these contaminants at the 8 locations tested. To illustrate the effectiveness of the direct flux measurements versus results obtained from volatilization models, the upward flux and associated risk was calculated from the model described in the ASTM RBCA guide, assuming free product of hexachlorobenzene (C66) at 20 feet bgs. The following default values were used in the model calculation:

Vapor pressure of C66: 1.1 E-05 mm Hg
Total soil porosity: 0.3
Total air filled porosity: 0.15
Slab attenuation factor: 1 (no slab)
Room air exchange rate: 0.5 per hour (12 per day)

The computed flux would have been 0.1 ug/hr-cm² equivalent to a chamber concentration build-up of 0.8 ug/l-hr, which would have failed the risk analysis by 4 times.

The use of flux methodology to determine vapor emissions in general is not particularly new. For instance, trichloroethene fluxes from the unsaturated zone have been made to compare removal effectiveness to that of pump and treat systems at the Picatinny Arsenal (Smith et. al. 1996). Batterman et. al. (1992) used flux measurements to determine petroleum hydrocarbon emissions at waste sites endorsing the use of passive sampling as a means to conserve costs and improve logistics. Kim and Lindberg (1995) demonstrated the use of dynamic enclosure chambers to measure fluxes of mercury vapors from soils. However, all of the flux determinations discussed above depended on the collection of chemical vapors using adsorbents that somewhat complicate handling and may introduce analytical error into the flux measurement.

The methodology used in this preliminary study was unique for several reasons:

1. The number of chambers deployed.
2. The addition of on-site analysis without preconcentration on adsorbants.
3. The on-site determination of risk.
4. The lengthy deployment time.

The preliminary results cannot be used to conclusively determine if risk to receptors is likely without consideration of additional factors, such as mixing or dilution from ambient air. Several such factors are being evaluated for incorporation into a much larger program consisting of 100 to 150 flux chambers, planned for the summer of 1998. Overall, however, the results of this trial program indicate that the methodology has significant potential to help determine investigation and remediation requirements at sites contaminated with volatile CHC, and has distinct advantages over using volatilization models.

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