

# Evaluating Vapor Intrusion Risk Using Comparative Dynamic and Passive Flux Chambers at a TCE Impacted Site in Sydney, Australia

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## ABSTRACT

A network of shallow soil vapor bores and vapor profiles from four nested soil bores (1 m, 2 m, 3 m & 4 m) showed high concentrations of TCE and PCE and a potential for unacceptable vapor intrusion into commercial units at a former manufacturing site. Profiles confirmed a significant mass flux of TCE and PCE from groundwater (at 5.5 m below ground level) to the shallow soil horizon (TCE 450,000  $\mu\text{g}/\text{m}^3$  at 4 m to 110,000  $\mu\text{g}/\text{m}^3$  at 1 m). Potential for vapor intrusion was further evaluated by measuring surface mass fluxes of TCE & PCE at two locations adjacent to soil profile bores. Flux measurements were taken using the traditional dynamic flux chamber method and a newly developed passive flux chamber method designed to extend sampling durations to overcome temporal variability in flux rates due to temperature and pressure changes in the soil profile and to provide lower detection limits. The passive flux chamber method is described. Comparative measurements from dynamic and passive flux chambers were taken in the cool month of June and in the warm month of November. Higher flux rates from dynamic and passive flux chambers were measured in the warmer period. Generally good agreement was found between the standard dynamic flux chamber method and the new passive flux chamber method. For comparative pairs of dynamic and passive flux chambers, measured TCE fluxes using the dynamic chambers ranged from 56  $\mu\text{g}/\text{m}^2/\text{h}$  to 132  $\mu\text{g}/\text{m}^2/\text{h}$ , while passive flux chambers recorded values of 41  $\mu\text{g}/\text{m}^2/\text{h}$  to 312  $\mu\text{g}/\text{m}^2/\text{h}$ . Measured flux rates were used in a dilution box model to provide conservative estimates of potential indoor air concentrations of up to 77.6  $\mu\text{g}/\text{m}^3$  for an indoor air space of a commercial unit (assuming no floor attenuation). Results indicated a need for sub-slab and indoor air testing in affected units to confirm health risk levels.

## **INTRODUCTION**

The use of trichloroethene (TCE) and tetrachloroethene (PCE) at a metal products manufacturing plant in Sydney, Australia, caused widespread impact to groundwater at and beyond the site boundaries. At the time of the vapor intrusion investigations discussed herein, the plant had been demolished and the site sold for redevelopment. Earlier attempts to delineate the solvent plumes and to identify all solvent sources by sampling and analysis of groundwater had largely failed and a disperse pattern of TCE and PCE, and daughter compounds, was observed in the 60 pairs of deep and shallow nested monitoring wells installed in a roughly grid pattern across the 2 hectare (5 acre) site and down-gradient off-site. Concentrations of TCE in groundwater were typically 200 µg/L to 500 µg/L with a few wells recording 1,400 µg/L. The concentration ranges of PCE were similar.

As the site was demolished and vacant a vapor intrusion risk for on-site did not currently exist, however, impacted groundwater had extended beyond the site boundaries beneath commercial office and warehousing buildings for which vapor intrusion was considered a potential risk. A critical and immediate need was to determine the potential for health risk to occupiers of commercial warehouses adjacent and down-gradient of the manufacturing plant. However, prior to a consideration of engaging the off-site building occupiers and owners in respect of a potential vapor intrusion risk, the risk was investigated by soil vapor and flux measurements external to the buildings on the boundary of the industrial site.

### **Site Geology**

Site geology was characterised by deep Aeolian sand deposits interbedded with alluvial medium to fine grained sands to a depth of 35 m and underlain by sandstone. Lenses of silty clay and organic rich lenses were also present. An unconfined aquifer with a slight gradient of 1 in 300 was present at a depth of around 6 m below grade.

## **METHODS**

The methods adopted to evaluate the likelihood that a vapor intrusion risk existed at the off-site commercial units immediately adjacent to the former industrial site's southern boundary comprised the sampling of soil vapor at five shallow soil bores to 1 m, the measurement of soil surface vapor flux coincident with the soil vapor bores and the subsequent sampling of soil vapor depth profiles to 4 m. Sampling of the shallow soil bores and surface flux was conducted in the cool month of June 2009 and repeated in warm weather in September and October 2009. Sampling locations are depicted in Figure 1.



**Figure 1** Site layout and sampling locations

## Soil Vapor in Shallow Bores

Five 1 m deep soil vapor bores of 65 mm diameter were installed by hand auger in a transect along the site boundary, approximately 2 m from foundation walls of the off-site commercial units. Soil vapor samples were obtained by implanting Teflon tubing with perforated stainless steel end-pieces, to the base of the boreholes. Perforated end pieces were buried with coarse 2 mm – 5 mm washed sand and a concrete plug was placed immediately above the sand pack. The boreholes were thence backfilled with bentonite. Following purging of the sample lines samples were collected directly into solid sorbent “Type 2 Air Toxics” thermal desorption sampling tubes using an SKC constant flow air-sampling pump, low flow adapter and rotameter to measure the flow rate. Isopropanol leak testing was performed to ensure no ambient air was drawn into the samples during sample collection.

Flow rate was set at 0.1 L/min and sampling durations were set based on concentrations anticipated from field screening using a photo-ionisation detector (PID). At each sampling location three sampling runs were conducted to allow collection of three different volumes to ensure analysed concentrations fell within the optimal MS response curve and to achieve practical quantitation limits down to 2 µg/m<sup>3</sup> in soils with low level impact.

Analysis was performed using a Markes International Unity Thermal Desorption Unit coupled with a Hewlett Packard 6890 High Resolution Capillary Gas Chromatograph and HP5973 Mass Spectrometer detector.

## Surface Soil Flux

Flux of volatile organic compounds (VOCs) from the natural ground surface was measured using a newly developed passive flux chamber. As a comparison with the new method, a dynamic flux chamber (US EPA method <sup>1</sup>) was run alongside passive flux chambers at two locations in June 2009 and at one location in October 2009. The chambers, as deployed at SV8, are shown in Photo 1.



**Photo 1. Duplicate pairs of passive flux & head space chambers and a dynamic flux chamber deployed at SV8.**

The passive flux chamber utilized a high uptake rate sorption tube placed directly within a stainless steel headspace chamber located directly on the ground surface. After a deployment period, ranging from several hours to several days, the passive sorption tube was collected for laboratory analysis after desorption, by GC-MS.

During the June 2009 sampling event Radiello thermal desorption tubes <sup>2</sup> (ID code 145 cartridge) were used. The thermal desorption tubes allowed a detection limit of 5 ng/tube and were thus suitable for short term sampling runs of one to several hours – depending on flux strengths. For the subsequent sampling in October and November 2009, Radiello solvent desorption tubes (ID code 130 cartridge) were used, allowing a detection limit of 0.1 µg/tube and suitable for longer deployment periods of 2 to 7 days.

The principal of operation of the passive flux chamber is that the VOC mass absorbed onto the passive tube placed within the chamber void, is a close approximation of the total VOC

mass flux from the surface beneath the chamber. For the mass collected on the sampling sorption tube to be approximately equal to the mass flux into the chamber relies on equilibrium in concentration between the chamber void and the soil pore space immediately beneath the chamber, not being reached. The maintenance of this concentration depression in the passive flux chamber void is achieved through the high VOC uptake rate of the sorption tube. To demonstrate that concentrations in the passive flux chambers, at the conclusion of the flux chamber sampling run, remained below equilibrium concentrations, air samples were analysed (by active sampling) from the void of a passive flux chamber and from the void of a headspace chamber (an identical chamber not fitted with a sorption tube) located directly beside the flux chamber. Where the final VOC concentration in the passive flux chamber void is less than the concentration in the headspace chamber, it can be assumed that flux into the passive chamber has been approximately constant allowing unimpeded flux.

Flux into the passive chamber can thus be expressed as:

$$\text{Flux } (\mu\text{g}/\text{m}^2/\text{h}) = \text{mass on tube } (\mu\text{g}) \times 1/\text{chamber footprint } (\text{m}^2) \times 1/\text{sampling duration } (\text{h})$$

## Soil Vapor Profiles

At four locations where 1 m soil vapor concentrations and surface flux measurements were high deeper soil vapor bores were installed to investigate the vertical gradient of VOC concentrations. Bores were sampled at depths of 1 m, 2 m, 3 m and 4 m. Samples were obtained from implanted Teflon sampling tubing fitted with perforated stainless steel end pieces. Soil vapor bore construction is shown in Figure 2.

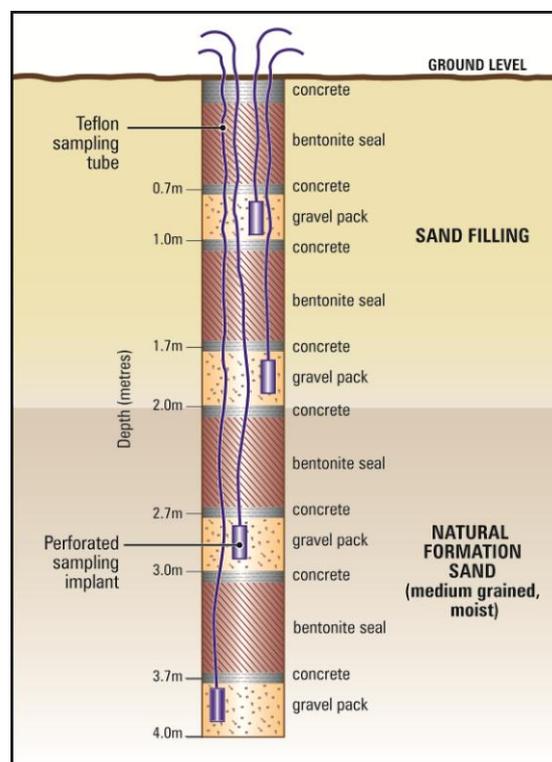


Figure 2 Nested soil vapour bore construction

## RESULTS

### Shallow Soil Vapor Bores

Soil vapor concentrations of TCE were high (33,000  $\mu\text{g}/\text{m}^3$  to 130,000  $\mu\text{g}/\text{m}^3$ ) in three of the five shallow (1 m) soil bores. PCE concentrations were high at two of the five locations (23,000  $\mu\text{g}/\text{m}^3$  and 34,000  $\mu\text{g}/\text{m}^3$ ). Concentration differences between sampling events in the cool month of June and the warm month of November were minor (Table 1).

**Table 1.** Concentrations of TCE and PCE in Shallow Soil Bores (1 m).

Location	Sample date	TCE ( $\mu\text{g}/\text{m}^3$ )	PCE ( $\mu\text{g}/\text{m}^3$ )
SV5	11 June 2009	350	4,200
SV5	4 November 2009	360	5,100
SV6	11 June 2009	44,000	4,000
SV6	4 November 2009	86,000	2,800
SV6 duplicate	4 November 2009	96,000	2,800
SV7	11 June 2009	33,000	24,000
SV7	4 November 2009	40,000	34,000
SV7 duplicate	4 November 2009	34,000	34,000
SV8	11 June 2009	130,000	27,000
SV8	4 November 2009	91,000	23,000
SV9	11 June 2009	660	1,900
SV9	4 November 2009	440	1,500

### Soil Vapor Profiles – Nested Bores

To evaluate whether the high concentrations of TCE and PCE measured in the shallow 1 m bores were a consequence of an upward flux from the groundwater, or whether the contaminant source was surface based, four bores were installed to a depth of 4 m, terminating 1.5 m above the groundwater surface, with soil vapor samples taken at intervals of 1 m. The deeper soil vapor profiling was undertaken six weeks after the second sampling round of the shallow bores.

Depth profiles showed that TCE and PCE concentrations were higher in the deeper samples (3 m and 4 m) than in the shallower samples (1 m and 2 m), though the upward attenuation was not pronounced (Table 2). Nevertheless, as the pattern of contaminant concentrations showed distinctly greater concentrations at depth, a groundwater source was inferred.

**Table 2.** Contaminant Soil Vapor Depth Profiles (units:  $\mu\text{g}/\text{m}^3$ )

Location	Depth	TCE	PCE
SV5a	1 m	170,000	4,000
	2 m	360,000	6,200
	3 m	380,000	8,300
	4 m	330,000	7,200
SV6	1 m	110,000	5,200
	2 m	310,000	16,000
	3 m	530,000	19,000
	4 m	450,000	16,000
SV7	1 m	67,000	65,000
	2 m	78,000	54,000
	3 m	150,000	91,000
	4 m	180,000	130,000
SV7a	1 m	140,000	82,000
	2 m	170,000	71,000
	3 m	330,000	180,000
	4 m	280,000	130,000

### Soil Vapor Flux – Passive Chambers

Surface soil flux was measured, using the passive flux chamber method, adjacent to the five shallow soil vapor bores in June and October 2009. Flux strengths were commensurate with soil vapor concentrations in so much as low flux rates were measured at SV5 and SV9 where soil vapor concentrations were relatively low, while high flux rates were measured at the three bores, SV6, SV7 and SV8 at which soil vapor concentrations were high (Table 3, TCE and Table 4, PCE).

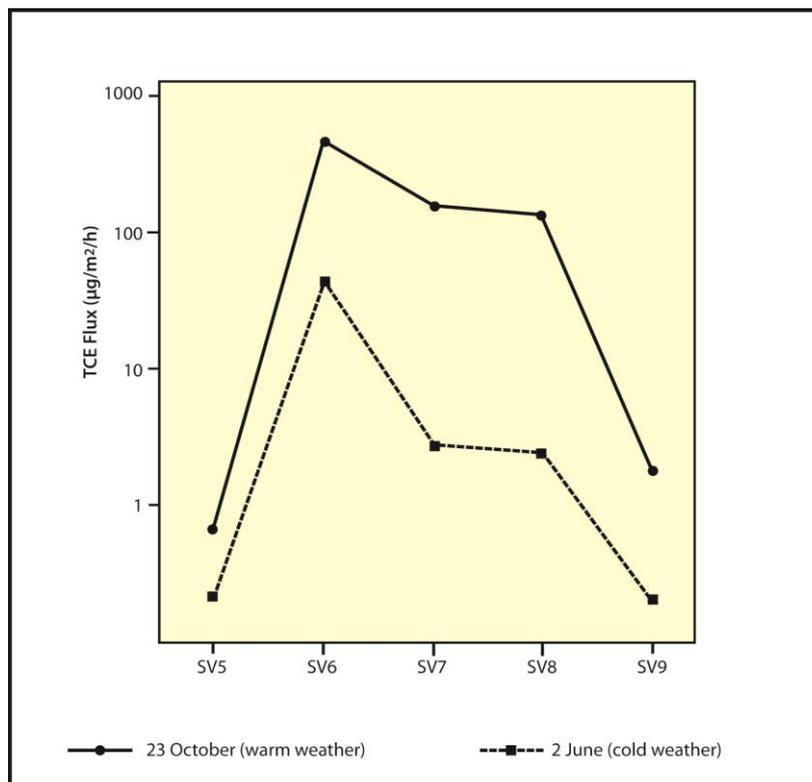
**Table 3.** Comparison of Soil Vapor Concentrations and Surface Flux Strengths (TCE)

Location	Soil Vapor ( $\mu\text{g}/\text{m}^3$ )	Flux ( $\mu\text{g}/\text{m}^2/\text{h}$ )	Soil Vapor ( $\mu\text{g}/\text{m}^3$ )	Flux ( $\mu\text{g}/\text{m}^2/\text{h}$ )
	11 June 2009	11 June 2009	4 Nov 2009	23 Oct 2009
SV5	350	0.2	360	0.6
SV6	44,000	41	86,000	466
SV7	33,000	28	34,000	167
SV8	130,000	21	91,000	128
SV9	660	0.2	440	1.7

**Table 4.** Comparison of Soil Vapor Concentrations and Surface Flux Strengths (PCE)

Location	Soil Vapor ( $\mu\text{g}/\text{m}^3$ )	Flux ( $\mu\text{g}/\text{m}^2/\text{h}$ )	Soil Vapor ( $\mu\text{g}/\text{m}^3$ )	Flux ( $\mu\text{g}/\text{m}^2/\text{h}$ )
	11 June 2009	11 June 2009	4 Nov 2009	23 Oct 2009
SV5	4,200	1.7	5,100	8
SV6	4,000	8	2,800	26
SV7	24,000	21	34,000	182
SV8	27,000	7	23,000	34
SV9	1,900	0.5	1,500	7

Although soil bore vapor concentrations showed minimal differences between measurements taken in the cooler and warmer months, flux rates were substantially greater in the second sampling event in the warmer month of October by factors of 3 to 10. Daily ambient air temperatures ranged from 5 to 16 deg C for the June sampling and from 18 to 26 deg C for the October sampling event. The greater flux rates in October may be attributed to the higher surface soil temperatures. Warm and cool season flux comparisons are shown for TCE in Figure 3.



**Figure 3** Comparative flux rates for TCE during warm weather and cool weather sampling

## Passive and Dynamic Flux Chamber Data Comparison

Flux measurements determined by the recently developed passive flux chamber method were compared with measurements taken by the traditional dynamic flux chamber method. Parallel measurements from the two methods were taken at locations SV6 and SV8 on 11 June and a further comparative test was run on 4 November at SV6.

For the passive versus dynamic flux chamber comparison runs, chambers were placed immediately adjacent – thus the passive and dynamic chambers did not occupy the same footprint. Sampling durations for the passive and dynamic flux chambers also varied. Whereas deployment times for the dynamic chambers were 45 minutes in duration, passive chamber deployment times were 4 hours in the June sampling event and 30 hours in the November event. Notwithstanding the non-overlapping footprints and the much longer sampling duration for the passive chamber runs, comparative results from the two methods were considered consistent and comparable. There was no systematic difference in magnitude between the two methods and most paired measurements were within a factor of 2.

Differences between methods (i.e. adjacently placed passive and dynamic chambers) and within methods (i.e. the primary sample compared to its duplicate), were quantified using Relative Per cent Differences (RPDs) i.e. the absolute difference between the values divided by the average value, expressed as a percentage. In calculating RPDs for passive and dynamic flux chamber results, means of the duplicate pairs were used. Method differences are shown in Table 5 while differences in duplicate pairs within methods are shown in Table 6.

**Table 5.** Relative Percent Differences between Passive and Dynamic Flux Chambers

		Measured Flux ( $\mu\text{g}/\text{m}^2/\text{h}$ )		Relative Percent Difference
		[mean values of primary and duplicate]		
		Passive chamber	Dynamic Chamber	
11 June 2009	SV6 TCE	41.0	58.0	34.4
	SV6 PCE	8.0	4.0	66.6
	SV8 TCE	23.0	36.5	45.4
	SV8 PCE	5.0	8.0	46.2
4 Nov 2009	SV6 TCE	259.5	102.0	87.1
	SV6 PCE	13.5	8.5	45.5

**Table 6** Relative Percent Differences Within Method Duplicates – Passive and Dynamic Flux Chambers

Sampling date	Sampling location	Passive Flux Chamber			Dynamic Flux Chamber		
		Flux ( $\mu\text{g}/\text{m}^2/\text{h}$ )		Relative Percent Difference	Flux ( $\mu\text{g}/\text{m}^2/\text{h}$ )		Relative Percent Difference
		Primary	Duplicate		Primary	Duplicate	
11 Jun 2009	SV6 TCE	41	-	-	60	56	6.9
	SV6 PCE	8	-	-	4	4	0.0
	SV8 TCE	21	25	17.4	40	33	19.2
	SV8 PCE	7	3	80.0	9	7	25.0
4 Nov 2009	SV6 TCE	207	312	40.5	72	132	58.8
	SV6 PCE	11	16	37.0	6	11	58.8

Differences between methods were, overall, larger than differences within methods, though there was no consistent bias towards higher readings from either method. The overall mean RPD for passive to dynamic flux chambers was 54.2%, while the mean RPDs between duplicate passive flux chamber runs was 43.7% and the difference between dynamic flux chamber duplicates was 28.1%.

Considered in the context of the range of flux rates measured, the differences in deployment times between methods and the non-overlapping footprints, the consistency of results between the passive and dynamic flux chamber methods was considered strong.

The variance for the passive chambers could be due to the non-common footprints of the duplicate pairs, while dynamic flux chamber duplicate runs were on a common footprint and sequential in time, and over a short duration of 45 minutes each.

### Testing validity of passive flux assumptions

As the validity of the measured mass flux from the passive chambers depends on the maintenance of sub-equilibrium vapor concentrations in the chamber void (with respect to surficial soil pore space void concentrations beneath the chamber), at the completion of the passive flux chamber runs TCE and PCE concentrations were measured within a flux chamber and within an adjacent equivalent chamber not fitted with a sorption tube (designated a head space chamber). Chamber vapor samples were obtained by collecting 1 L of air on Air Toxics thermal desorption tubes with analysis by TO-17. The test was run in duplicate on 4 November. Results are shown in Table 7.

**Table 7.** Concentrations in the Passive Flux Chambers and Co-located Head Space Chambers (Demonstration of Concentration Depressions in Passive Flux Chambers).  
Units:  $\mu\text{g}/\text{m}^3$

	Head space chamber 1	Head space chamber 2	Passive flux chamber 1	Passive flux chamber 2
TCE	4,100	3,300	2,400	1,900
PCE	300	200	120	78
Dichlorodifluoromethane	5.2	5.1	4.4	3.1

Results showed lower concentrations in the chambers fitted with passive sorption tubes. TCE and PCE were the only soil contaminants detected above the laboratory reporting limit of  $1.9 \mu\text{g}/\text{m}^3$ . However, the widely present atmospheric chlorofluorocarbon, dichlorodifluoromethane (Freon 12), was detected and it also showed depressions in concentrations in the passive flux chamber. Due to the interchange between the atmosphere and the pore space in the shallow soil profile, Freon 12 will be measured as a soil flux. The results are thus interpreted as confirming that the passive sorption tubes fitted to the flux chamber voids were effective in maintaining a concentration depression in the chambers – preventing equilibrium concentrations from being reached. A continuing net flux into the chamber would therefore be maintained throughout the sampling period.

### Estimation of Indoor Air Concentrations from Flux Measurements

The buildings for which vapor intrusion was a possible risk were constructed on structural floor slabs supporting the walls. Thus, with no design joints and no breaks in the flooring, advective flow from sub-slab to indoor air was considered to be an insignificant contributor to indoor air contaminants which would be instead dominated by diffusive floor flux.

TCE and PCE flux rates, measured on natural surfaces adjacent and within 2 m of occupied commercial units, were used to predict indoor air concentrations inside the units and resulting potential risks to occupants. As the retarding influence on flux from concrete flooring was not known, a conservative estimate of indoor air concentrations was calculated assuming no flooring attenuation. To calculate predicted indoor air concentrations from surface flux a simple box dilution model was used. In the case of commercial units ventilation rates are regulated by Australian building codes and set at 2 exchanges per hour by means of forced ventilation. A commercial office with ceiling (mixing height) of 3 m was assumed. Thus, indoor air contaminant concentration derived from surface flux can be calculated as:

$$\text{Air Concentration } (\mu\text{g}/\text{m}^3) = \frac{\text{Flux } (\mu\text{g}/\text{m}^2/\text{h}) \times \text{Floor Area } (\text{m}^2)}{\text{Floor Area } (\text{m}^2) \times \text{Mixing Height } (\text{m}) \times \text{Air Exchange Rate}}$$

Using the highest measured TCE surface flux of 466  $\mu\text{g}/\text{m}^2/\text{h}$  (SV6 on 23 October) the calculated indoor air concentration of TCE in a theoretical building over the measuring location and assuming no floor attenuation would be 77.6  $\mu\text{g}/\text{m}^3$ . On the basis of a unit risk value for TCE of  $4.3 \times 10^{-7}$  (WHO 2000<sup>3</sup>), whereby an ambient air concentration of 2.3  $\mu\text{g}/\text{m}^3$  would indicate a risk of one excess cancer at the  $10^{-6}$  risk level, the theoretical indoor air concentration of 77.6  $\mu\text{g}/\text{m}^3$  was sufficiently high to indicate a need to conduct an investigation of actual vapor concentrations with the industrial units. Such an investigation would likely include sub-slab vapor measurements, indoor and outdoor ambient air and floor surface flux measurements.

## **SUMMARY AND CONCLUSIONS**

A plume of TCE and PCE originating from a former manufacturing plant was shown to present a potential health risk to workers at commercial units adjoining the plant. Soil vapor profiles measured at a distance of 2 m from the foundations of the commercial units showed a strong flux of TCE and PCE vapors at the surface originating from a groundwater solvent plume. Vapor concentration profiles showed minor attenuation in the transect towards the surface and vapor concentrations were typically 2 to 4 times lower at a depth of 1 m compared to the deeper samples from 3 m and 4 m below ground level. Lower concentrations in the shallowest (1 m) depths were attributed to dilution due to exchange across the soil to atmosphere interface. Soil vapor concentrations of TCE at depths of 1 m, up to 130,000  $\mu\text{g}/\text{m}^3$  indicated a potential vapor intrusion risk for neighboring properties.

Surface soil flux strengths were consistent with the vapor concentrations within the soil profile at 1 m, to the extent that measured low surface flux corresponded with low soil vapor measurements (SV5 and SV9) on the plume periphery (Table 3), and high surface flux coincided with high soil vapor (SV6, SV7 and SV8). Notwithstanding the general agreement between soil vapor and surface flux strengths, while soil vapor concentrations showed good consistency between the cool season measurements (11 June 2009) and the warm season measurements (4 November 2009), surface flux strengths were 3 to 10 times greater in the warmer season.

A comparison of a newly developed passive surface flux chamber method with the traditional dynamic chamber method showed good consistency between methods. The passive flux chamber provides a less complex and inexpensive alternative to the established dynamic chamber method and avoids perceived disadvantages attributed to the dynamic method associated with short sampling durations. Passive chambers can provide mean flux values over several days duration integrating over possible fluctuations in flux due to temperature and pressure variability.

Supporting lines of evidence from deep soil vapor profiles, near surface soil vapor concentrations and surface flux showed that a possible hazard from vapor intrusion existed within the industrial units.

## REFERENCES

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