MEASURED AND MODELED AIR EMISSIONS FROM SOILS CONTAMINATED WITH PCBS (Aroclor 1260)

William J. Mills¹, Charles E. Schmidt², Louis Thibodeaux³

1. Mills Consulting Inc., Oak Park, IL, USA

2. Environmental Consultant, Red Bluff, CA, USA

3. Louisiana State University, Baton Rouge, LA, USA

Introduction

Emissions from contaminated soil sites represent a potential major ongoing source of PCB to the environment [1-3]. A Chicago area site which had been the subject of a PCB remediation was alleged to have resulted in residential exposure due to past and current emissions.

A bench-scale study was conducted where an empirical relationship between PCB levels in two soil types (Chicago area top soil and clean, washed sand) and flux were measured using the USEPA surface emission isolation flux chamber (flux chamber)[4, 5]. Soils were tested for background flux using the flux chamber and the USEPA Method TO-10A/1668A high resolution gas chromatography/ high resolution mass spectrometry for all 209 congeners and then again after the standard addition of approx. 5 grams of technical grade Aroclor 1260 resin dissolved in approx. 600 ml acetone added to approximately 45 kg of the soil matrix. At total of three standard additions were performed resulting in a range of PCB soil concentrations from near-method detection to approximately 500 ppm. These empirical data were then used to develop a relationship between PCB soil concentration and surface flux from both soil types. Field data were also collected from the site during February, 2003.

Exposure potential from soils containing polychlorinated biphenyls (PCBs) was also estimated using predictive models [6-8]designed to generate a conservative (upper bound) estimate of mass flux from a given soil source. Estimates of flux using both assessment technologies are provided for comparison.

Methods and Materials

A Quality Assurance Project Plan (QAPP) was prepared prior to undertaking this work. Technical grade Aroclor 1260 was obtained in 5 g vials from a supplier. Reagent grade acetone was used for the bench scale testing. Isopropyl alcohol was commercial grade. Air sampling cartridges were prepared in the laboratory, including spiking with field surrogates. For the bench scale testing soil samples were obtained from the site, packaged in 20 L pails and shipped to the location of the testing (CA). Clean sand was obtained from a commercial hardware store. Field sampling was carried out at the remediated site and a background location in February, 2003.

Flux measurements were made using the USEPA flux chamber and USEPA Method TO-10A utilizing PUF-XAD-2 cartridges for air sampling. Temperatures and flow rates were monitored on a regular basis during the sampling. Soil and air samples were shipped in sealed containers inside coolers to the laboratory for appropriate analysis. PCB analyses were performed by Alta Analytical (El Dorado Hills, CA, USA) using USEPA 1668A with isotope dilution mass spectrometry quantitation. Physical properties were measured by Severn Trent Laboratories (Burlington, VT) using ASTM methods.

Predictive emissions modeling was carried out using procedures outlined in Thibodeaux [6] and Woodrow [7-8]. Equation 1 provides the critical concentration above which the PCB volatilization is essentially constant and based on the vapor pressure.

 $w_{AC} = \frac{p_A^o \kappa_{32}^*}{H_p}$ (1) $p_A^o = pure \text{ component vapor pressure, } \kappa_{32}^* = partition \text{ coefficient,}$ $H_p^o = Henry's Law Constant$

The flux value can then be calculated using equations 2 [7] or 3 [6] below.

$$\ln \eta_{e} = 19.35 + 1.0533 \left[\frac{p_{a}^{0} * AR}{K_{D} * S_{w}} \right]$$
(2)
$$\eta_{e} = {}^{3}k_{A1}^{'} [\Delta C] = {}^{3}k_{A1}^{'} [C_{air} - 0])$$
(3)
$$\eta_{e} = \text{flux} \left(\ln \frac{g}{m^{2}hr} \right), {}^{3}k_{A1}^{'} = \text{mass transfer coefficient, } C_{air} = \text{air concentration (from } p_{a}^{0}, \text{ at } 25 \text{ deg C}).$$

Since the site was surrounded on all sides with a 4 m solid corrugated metal fence, which reduces volatile emissions by an estimated 64% [9] or a multiplier of 0.36 can be applied to the flux.

RESULTS AND DISCUSSION

The results for the physical properties testing for the soil and sand are shown in Table 1. The results for Organic Carbon are in the range of previous measurements at the site. The results from the bench scale test flux test measurements for 0, 1, 2 and 3 aliquot additions of technical grade Aroclor 1260 are summarized in Table 2. The results of the field testing are summarized in Table 3. The range of fluxes measured in the field tests at low temperatures $(0-5^{\circ} \text{ C})$ correspond quite closely to those measured in the bench scale tests, which provides a level of comfort regarding the transferability of the results.

Phys Parameters	ASTM Method	Soil	Sand
In-Place Density (g/cm3)	(D2937)	1.08/1.19	1.51/1.52
Specific Gravity	(D854)	2.51/2.47	2.66/2.64
Organic Content (%)	(D854)	10.4/10.7	0.2/0.2
Permeability (cm/sec)	(D2434)	6.2E-04/3.7E-04	3.1E-02/3.7E-2
Porosity (%)	(D2937 + D854)	56.9/51.6	43.4/42.6

Table1: Physical Property Test Results

Table 2: PCB Flux Results-Bench Scale Testing

Std Addition	soil conc. (ppm)	soil flux (ng/ sq. m. hr)	soil temperature (deg. C)	sand conc. (ppm)	sand flux (ng/sq. m hr)	sand temperature (deg. C)
0	0.0000684	4.5	18.9	0.0833	4.6	20.0
1	117	5164.1	13.3	92.3	2943.5	11.7
2	215	13837.1	12.2	248	6271.6	15.6
3	563	18105.4	14.4	431	10488.6	17.2

Field Test	soil conc. (ppm)	soil flux (ng/ sq. m. hr)	soil temperature (deg. C)
S-001	0.035	1.2	2
S-002	0.035	4.3	2
B-001	0.22	1.8	4

The measured flux for the bench scale testing of sand and soil are plotted in Figure 1. As expected, the flux increased as a function of the amount of PCB present in the soil. The flux vs. concentration fitted linearly for sand. However a power function was a better fit for the soil case. The power function fit corresponds with the theory of a critical concentration.



Figure 1: Measured PCB (total) Flux vs. PCB Concentration Bench Scale Testing

The equation 1 calculation indicates w_{ac} =1200 mg/kg, at concentrations above this, the PCB volatilization flux will be independent of concentration. The fluxes predicted by Equations 2 and 3 are shown in Table 4. The predicted fluxes for soil at 25° C are 3-4 times greater than the observed fluxes (Table 2) at 14° C, which indicates the conservative nature of the model.

Table 4: Modeled Flux Results						
Basis of Calculation	Equation 2	Equation 3				
	(> 1200 ppm)	(pure product)				
estimated flux (ng/m ² hr), 25 deg C, no fence effect,	4.01E+05	3.40E+05				
estimated flux (ng/m ² hr), 25 deg C, with fence effect	1.44E+05	1.22E+05				
estimated flux (ng/m ² hr), 25 deg C, with fence effect,	6.77E+04	5.74E+04				
difference in actual concentration vs. calculated						
Ratio Predicted @ 25 deg C vs. Observed @ 14 deg C	3.74	3.2				

Conclusion

The feasibility, applicability and the repeatability of the bench scale testing approach and flux chambers are illustrated by this work. This type of approach should be applicable to other types of chemicals, especially semi-volatile organic compounds (SVOC). The empirical data provided above adds to the database on air emissions of gas-phase PCBs from contaminated soils. This offers the possibility of carrying out some order of magnitude estimates for vapor phase emissions from PCB contaminated soils, provided the site area is known. In the cases where the concentrations are not known the use of the critical concentration provides an upper boundary to the flux estimate.

Additional work is recommended in this area. It is recommended that the additional work address some or all of the following, empirical verification of the critical concentration value of 1200 ppm for Aroclor 1260 contaminated soils, the effect of moisture, effect of temperature, porosity, depth of diffusion. In the absence of more precise empirical data the use of predictive emissions modeling is often useful. However it is important to note that the type of modeling approach followed here provides conservative overestimates of the actual fluxes.

Finally measured or predicted fluxes can be used as input into air dispersion models which can then be used to provide exposure estimates.

References

- 1. Mills, W.J., *Polychlorinated Biphenyls, Dioxins and Furans in Ambient Air During the Smithville PCB Incineration Project*, in *Environmental & Occupational Health Sciences*. 2001, University of Illinois: Chicago, IL. p. 515, lx.
- Green, M.L., et al., Regional Spatial And Temporal Interpolation of Atmospheric PCBs: Interpretation of Lake Michigan Mass Balance Data. Environmental Science & Technology, 2000. 34(9): p. 1833-1841.
- 3. Wania, F., et al., *Temperature Dependence of Atmospheric Concentrations of Semivolatile Organic Compounds*. Environmental Science & Technology, 1998. **32**(8): p. 1013-1021.
- 4. USEPA, Measurement of Gaseous Emission Rates From Land Surfaces Using an Emission Isolation Flux Chamber, Users Guide. 1986, EPA Environmental Monitoring Systems Laboratory,: Las Vegas, Nevada.
- 5. USEPA, *Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS.* 1999, Office of Water: Washington, DC.
- 6. Thibodeaux, L.J., *Environmental Chemodynamics*. 2nd ed. 1996, New York, NY: J. Wiley and Sons Inc.
- Woodrow, J.E., J.N. Seiber, and L.W. Baker, *Correlation Technique for Estimating Pesticide Volatilization Flux and Downwind Concentrations*. Environmental Science & Technology, 1997. 31(2): p. 523-529.
- Woodrow, J.E., J.N. Seiber, and C. Dary, *Predicting Pesticide Emissions and Downwind Concentrations Using Correlations with Estimated Vapor Pressures*. J. Agric. Food Chem., 2001. 49: p. 3841-3846.
- 9. Thibodeaux, L.J., C. Springer, and R.S. Parker, *Design for Control of Volatile Chemicals from Surface Impoundments*. Hazardous Waste and Hazardous Materials, 1985. **2**(1): p. 99-106.