

FATE (po)

Volatilisation of polychlorinated biphenyls from sludge-amended soils

Ian T. Cousins, Nicola Hartlieb, Claudia Teichmann and Kevin C. Jones. Environmental Science Division, Institute of Environmental and Biological Sciences, Lancaster University, Lancaster, LA1 4YQ, UK.

1. Introduction

Currently 5.5×10^6 tonnes (dry weight) of sewage sludge are produced within the European Union (EU) each year¹. This amount is expected to double within the next decade, because the volume of wastewater produced is increasing and wastewater treatment processes are improving¹. In the United Kingdom (UK), 47% of the sewage sludge produced is applied to arable/pasture land². Since all marine disposal will be banned as a result of the implementation of the EU Directive in 1998³, the amount applied on land is likely to rise further.

A wide range of organic contaminants are known to be present in sewage sludge⁴ and these include polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs). There are several processes affecting the loss of organic compounds from soils and sludge-amended soils, for example volatilisation, leaching, degradation and plant uptake. Volatilisation may be an important process from soils for many volatile and semi-volatile organic compounds. The objective of this work was to determine the significance of the volatilisation loss process for organic contaminants in sludge-amended soils. Initially, screening experiments were undertaken to determine the relative volatility of PCBs, PAHs and PCDD/Fs. Further experiments were then carried out to quantitatively compare the PCB volatilisation fluxes resulting from the three common methods of sludge application to agricultural land used in the UK, namely: subsurface injection, surface application to grassland and ploughing the sludge into arable land.

2. Materials and methods

2.1 Screening experiments

Portions (100 g) of field contaminated soils and sediments were weighed into glass columns (Omnifit glass chromatography columns with Teflon endpieces, length 250 mm, internal diameter 50 mm), connected to a glass-fibre on-line filter (to remove fine soil particulates) and a Teflon chamber containing pre-cleaned solvent extracted polyurethane foam (PUF) plugs to trap vapour phase organics. Air was circulated around the system by a Teflon-headed pump (i.e. the same air was continually circulated) and gas meters and flow meters were also installed. Teflon tubing with Swagelok[®] fittings were used for all connections.

Separate experiments were carried out for PCBs, PAHs and PCDD/Fs. An agricultural soil (*ca.* 10 mg/kg Σ PAH, 40 ng Σ TEQ/kg of PCDD/Fs) was used for the PAH and PCDD/F screening

experiments and a PCB contaminated marine sediment (*ca.* 50 mg/kg Σ PCB) was used for the PCB screening experiments.

Three columns containing soil or sediment and one empty control column were used in each experiment. Air was circulated through the glass columns for 16 days for the PCB and PAH screening experiments and for 30 days for the PCDD/F screening experiment. Keeping the air flow rate constant through the chambers proved difficult and it varied between 3.5-8 l min⁻¹. At the end of the experiments various samples were prepared for chemical analysis. Triplicate soil samples taken from each column at the beginning and at the end of the experiment were analysed, along with the bulked PUF plugs from each experimental system.

Samples for PCDD/F analysis were soxhlet extracted with toluene for 24 hours, cleaned up, using a combination of alumina and silica column chromatography, and analysed using gas chromatography/high resolution mass spectrometry on an Hewlett Packard (HP) 5890 series II gas chromatograph coupled to a Fisons Autospec Ultima mass spectrometer. Samples for PCB and PAH analysis were soxhlet extracted with hexane for 12 hours, cleaned up using florisil column chromatography and analysed for PCBs, using a HP 5890 gas chromatograph (GC) fitted with an electron capture detector, and PAHs, using a Perkin Elmer liquid chromatograph LC250 fitted with a fluorescence detector.

2.2 Comparison of sludge application methods

An experimental set-up was designed to quantitatively compare the volatilisation fluxes of PCBs that would result from different sludge application techniques. In order to get a meaningful comparison between the different application methods it was necessary to design a set-up in which air-flow, air humidity and soil moisture could be kept relatively constant throughout the experiment. Each set up basically consisted of a glass chamber containing layers of soil and sludge (described below) to simulate different sludge application methods. Humidified air was blown across the surface of the soil/sludge layers and the exhaust air analysed for PCBs.

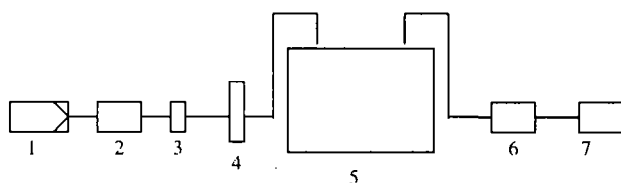


Figure 1 The experimental set up

1 vacuum pump, 2 PUF filter, 3 flow meter, 4 wash bottle, 5 chamber, 6 anhydrous calcium sulphate, 7 PUF plug for air sample

Teflon tubing with Swagelok[®] fittings were used for all connections. The vacuum pump (1) generated the air flow which was then passed through a filter to remove organic contamination from the air. The filter was a pre-extracted PUF plug held within a Teflon cup (2). The incoming flow rate was measured by a flow meter (3) and then passed through a 500 ml wash bottle (4), which was filled with deionised water to humidify the air. The air was humidified to prevent the surface soil/sludge from drying. The air was then led through the chamber (5) over the surface of the soil/sludge. The outflowing air passed through a Teflon cup filled with anhydrous sodium sulphate chips to dry the air before it then passed through the sampling PUF plug, which was held in another Teflon cup (7). The outflow was measured periodically using a flow meter and was kept fairly constant at 4 l/min. Temperature variations during

FATE (po)

the experiment were measured using a max/min thermometer located next to the apparatus (the temperature ranged from 14 to 22°C).

The glass chambers used in both experiments were purchased from Aldrich (25.5 mm height, 26.5 mm length, 70 mm width). A clamping device was used to attach the lids and make them completely air tight. It consisted of a wood and aluminium frame with two screws attached to apply downward pressure to the lids. A Nitrile o-ring between the lid and the top of the chamber served as a seal. All chambers were filled with a 6 cm layer of clay particles soaked in deionised water. Between the clay/water layer and the next layer which consisted of soil, a capillary matting was laid to enable the water to be drawn up by the soil as its water content diminished.

A subsurface sandy soil (97% sand, 2% silt, 1% clay), collected from the field, was used in the experiments. The soil was sieved through a 2 mm sieve prior to the experiment. The water content of the soil used was determined (by drying overnight in an oven at 105°C) to be 13.7% and organic matter content was determined (by loss on ignition) to be 4.7%. A sludge with high PCB concentrations was sought to ensure that volatilisation fluxes could be easily measured with the analytical methodology available. The sludge selected had been contaminated in the past with Aroclors 1242 (90%) and 1260 (10%) and has a total PCB content of *ca.* 33 mg/kg. For the experiment it was centrifuged at 2800 rpm for 50 minutes and the dry weight determined to be 13.7% and the organic matter content determined to be 59%.

Various duplicate experimental set-ups were prepared: (1) soil only, (2) soil with a 1 cm thick surface application of sludge, (3) soil with a 1 cm thick subsurface application of sludge 5 cm below the soil surface and (4) soil and sludge mixed together to a depth of 5 cm. The same mass of sludge (250 g) and approximately the same mass of soil was used for each experimental set-up.

Air samples were taken on day 8, 16 and 32 of the experiments. Soil and sludge samples were also taken at the beginning and end of the experiment. All samples generated by the experiments were Soxhlet extracted with hexane for 12 hours. The extracts were then cleaned up and analysed by a Hewlett Packard 5890 gas chromatograph fitted with an electron capture detector.

3. Results and discussion

3.1 Screening experiments

In the PCB and PAH screening experiments a wide range of PCBs and PAHs were detected in the PUF plugs analysed after pumping for 16 days. However, some of the higher chlorinated PCB congeners (those with 8 or more chlorines) and heavier weight PAHs (heavier than pyrene) were not detected in any of the air samples, although they were present in the soil. Volumes of air sampled over the 16 days of the experiment were of the order of 150 m³. Detection limits for individual PAHs were of the order of 5 ng per PUF plug and for individual PCB congeners they were of the order of 1 ng per PUF plug.

The analytical results from the PCDD/F screening experiment showed that there was no volatilisation of any PCDD/F congener after 30 days. Volumes of air sampled over the 30 days of the experiments varied from *ca.* 170 m³ to *ca.* 250 m³, depending on flow rates through the soil columns. Detection limits for individual PCDD/Fs were of the order of 0.1 pg per PUF plug. If the experiment had been run for longer, and much greater volumes of air had been sampled then it is likely that the PCDD/Fs would have been detected in the air samples. The exchange between soil and air in this experiment can be explained as a simple partitioning phenomenon. The magnitude of the air-soil partitioning coefficient

is dependent on the properties of the chemical and the soil. The octanol-air partitioning coefficient, K_{OA} , is a good descriptor of air-soil partitioning and has been used to give an indication of the volatilisation potential of a compound¹¹. For example, values of $\log K_{OA}$ calculated for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and octachlorodibenzo-*p*-dioxin, using the ratio of the octanol-water partitioning coefficient and the dimensionless Henry's Law constant, are 9.3 and 12.1 respectively. The values of K_{OA} for PCDD/Fs are extremely large and it is therefore expected that the concentrations in the air sampled in this experiment to be very low or undetectable.

3.2 Comparison of sludge application methods

PCBs were not detected in the PUF plugs from the experimental treatments containing only soil and thus PCBs detected in the other treatments are due to volatilisation resulting from sludge-amendment. Volatilisation was shown to occur for a wide range of PCB congeners in the surface application. A smaller number were present in detectable concentrations in the air samples from the subsurface application, 12 of which were selected as target compounds, because they were shown to be relatively abundant in the sludge, and are (IUPAC nomenclature): 18, 28, 31, 33, 37, 47, 52, 60, 66, 81/87, 101 and 110/77. Hence the target congeners represent trichlorobiphenyls (congeners 18, 28, 31, 33 and 37), tetrachlorobiphenyls (congeners 47, 52, 60, 66 and 77) and pentachlorobiphenyls (congeners 87, 101 and 110).

Volatilisation fluxes were calculated and, as expected, the highest volatilisation flux resulted from the surface application, followed by the ploughed layer application, with the subsurface injection application yielding the lowest fluxes. Figure 2 shows the mean volatilisation flux for all three application methods. Error bars were calculated from the coefficient of variation between the results of the duplicate chambers.

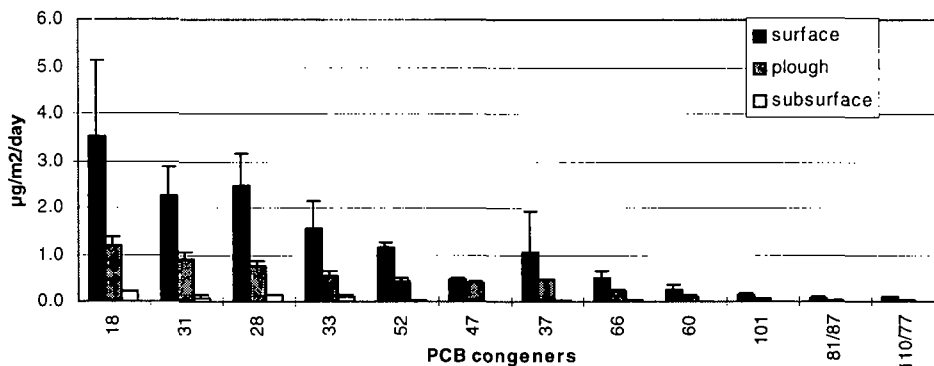


Figure 2 Volatilisation flux during the experiments, PCBs in GC elution order (\pm one standard deviation)

The volatilisation flux from the surface layer application was one order of magnitude higher than that from the subsurface injection application. A marked decrease in volatilisation with increasing chlorination for different congeners was observed. The differences between the duplicates might be due to experimental irregularities and inequalities such as different air flows and air humidities which were

FATE (po)

inevitable in the simple experimental set-up used. The relatively high coefficients of variation also result from the low number of replicates (only two).

As there seems to be an obvious decrease in volatilisation flux with increasing chlorination for the PCBs in this study, an attempt was made to find a correlation between PCB physicochemical properties and volatilisation flux. A good correlation was shown to exist between calculated values of $\log K_{OA}$ (using the ratio of the octanol-water partitioning coefficient and the dimensionless Henry's Law constant) and volatilisation flux for all three application methods (see Figure 3). Since PCBs are known to be transported through soil primarily in the soil-air rather than soil-water,⁵¹ it is not surprising that $\log K_{OA}$, which describes partitioning between an organic phase and the vapour phase, is a good descriptor of PCB volatilisation potential.

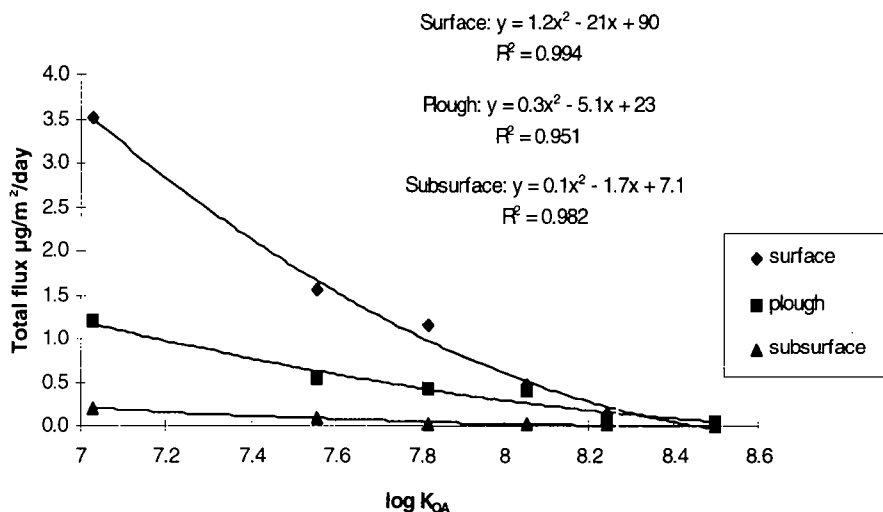


Figure 3 Correlations between $\log K_{OA}$ and volatilisation flux

Total losses of individual target congeners from the sludge layer were calculated and shown to range from 0.1% to 1.6% for target congeners in the surface application and from <0.01% to 0.07% for target congeners in the subsurface application. This equates to experimental volatilisation half-lives of *ca.* 3 to 40 years for target congeners in the surface application and *ca.* 60 to >400 years for target congeners in the subsurface layer. There is an uncertainty over the magnitude of biodegradation half-lives of PCBs in sludge-amended soils, but volatilisation is likely to be an important loss process from sludge-amended soils for surface applications of sludge. However, biodegradation may become the dominant loss process for subsurface applications.

4. Conclusions and ongoing work

The results from this work suggest that volatilisation losses of PCBs can occur from sludge-amended soils in spite of the high organic matter content of the sludge matrix. However, the matrix probably

greatly retards volatilisation through stronger sorption of PCBs⁶⁾. The screening experiments indicate, and we believe, that the soil is a sink for PCDD/Fs and the heavier molecular weight PAHs (i.e. those heavier than pyrene). By comparing the three common sewage sludge application methods, it was shown that the highest PCB volatilisation flux results from a surface applied sewage sludge layer and that the lowest volatilisation flux results from a subsurface injected layer of sludge. Volatilisation from the surface applied sludge layer was measured to be one order of magnitude higher than that of the subsurface layer. It is postulated that volatilisation is still a very important loss process for the lower chlorinated PCBs (the monochlorinated to pentachlorinated biphenyls) in surface applied sludge, but biodegradation may become the dominant loss process for PCBs in subsurface injected sludge. A correlation between volatilisation potential and physicochemical properties of organic compounds has been suggested previously in the literature⁷⁾ and could be confirmed by the strong correlation which was shown to exist between the measured PCB fluxes and $\log K_{OA}$.

The sandy soil used in the experiments to compare sludge application methods is likely to have a high porosity and low adsorption potential for non-ionic organic compounds and may yield a volatilisation flux which is not typical of agricultural soils. In order to gain a better understanding of the effects of soil properties on PCB volatilisation from sludge-amended soils, experiments are currently being carried out to compare the sandy soil with a silt/loam of higher organic matter content. In this work it was assumed that volatilisation is the dominant loss process for PCBs. This hypothesis will be tested in further work with laboratory microcosms in which we will quantify other possible loss processes using carbon-14 labelling techniques.

Acknowledgments

This work was funded by the UK Ministry of Agriculture, Fisheries and Food. Thanks to Dr Michael McLachlan of the University of Bayreuth, Germany for arranging for the PCDD/F analysis to be carried out in their laboratories.

References

- 1) Wild, S.R., Jones, K.C. (1992) Organic contaminants entering agricultural soils in sewage sludges: screening for their potential transfer to crop plants and livestock. *Science of the Total Environment*, 119, 85-119.
- 2) DoE. (1989) Code of practice for agricultural use of sewage sludge. Department of the Environment. UK.
- 3) Commission of the European Communities (1991) Council Directive concerning urban waste water treatment. EC Directive 91/271/EEC. Official Journal of the European Communities, No. L 135/40.
- 4) Duarte-Davidson, R., Wilson, S.C., Alcock, R.E., Jones, K.C. (1995) Identification of priority organic contaminants in sewage sludge. UK Water Industry Research Limited.
- 5) Eduljee, G.H. (1987) Volatility of TCDD and PCB from soil. *Chemosphere*, 16, 4, 907-920.
- 6) Fairbanks, B.C., O'Connor, G.A., Smith, S.E. (1987) Mineralisation and volatilisation of polychlorinated biphenyls in sludge-amended soils. *Journal of Environmental Quality*, 16, 1, 18-24.
- 7) Harner, T., Mackay, D. (1995) Measurement of octanol-air partition coefficients for chlorobenzenes, PCBs, and DDT. *Environmental Science & Technology*, 29, 6, 1599-1606.