Factors Affecting The Volatilisation Of PCBs From Soil

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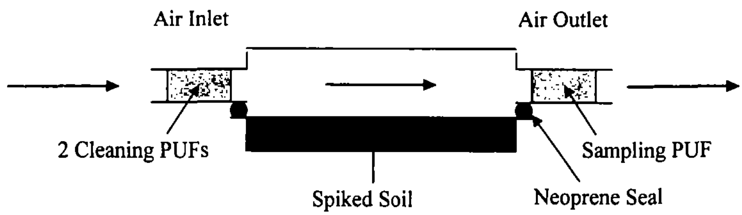
Abstract
A volatilisation chamber has been used to make direct measurements of soil-to-air fluxes of individual PCB congeners. These measurements have facilitated investigation of the factors affecting the magnitude of these volatilisation fluxes. Initial results indicate the following: positive correlations between PCB volatilisation fluxes and soil temperature, soil moisture content and soil PCB concentration. Negative correlations are indicated between PCB volatilisation fluxes and both soil organic carbon content, and K_{OA} for individual congeners.

Introduction
A recent budget and source inventory suggested that volatilisation from topsoil accounts for around 88% - some 40,000 kg yr^{-1} - of ΣPCB currently released to the UK atmosphere[1)]. The volatilisation of PCBs from water has been well studied experimentally in the Great Lakes[2,3)], but despite the evidence of its environmental significance, little direct measurement of PCB volatilisation from topsoil has been conducted. This paper describes a series of laboratory measurements of PCB volatilisation fluxes from soil and discusses the relationships between recorded fluxes and potentially influential properties of both soils and individual PCB congeners.

Experimental Methods
In summary, the experimental approach has been to draw "PCB-free" air over soil contaminated with a known PCB burden, and to measure the quantity of PCB volatilised over the course of the experiment. The chamber design is illustrated in Figure 1. PCBs are removed from incoming air *via* passage through 2 pre-cleaned PUF plugs connected in series, with volatilised PCBs collected using 1 pre-cleaned PUF plug. Soil temperature was held within ±2 °C, using a heater/thermostat below the soil surface, and recorded at 3 hourly intervals throughout the experiment using a platinum film detector connected to a digital voltmeter. Soil moisture content and organic carbon content were measured at the start of each experiment; the latter using a Leco RC-412 multiphase carbon determinator. Soil moisture content was also measured at the end of each experiment and a soil moisture content averaged over the duration of the experiment was calculated. To ensure measurable levels of volatilised PCB, the top 1 cm layer of soil used in each experiment - this was spread over a 7 cm "unspiked" layer of the same soil - was "spiked" at a known level with congeners 28, 52, 101, 138, and 180 (supplied by Promochem UK), in 20 ml of acetone. The "spikes" were applied to the soil using a spray and copious mixing of the soil was conducted to facilitate homogeneous incorporation of the spike into the soil. After a period of 72 h, designed to allow acetone evaporation, and assist incorporation of the "spike", the starting soil PCB burden

was measured by taking ten sub-samples to a 1 cm depth. A similar representative soil sample was taken at the end of the experiment. Each experiment lasted for 24 h, using an accurately determined air sampling flow rate of *ca* 0.75 m3/min, achieved by employing a Graseby-Andersen Hi-Volume sampler.

Figure 1. Schematic Of The Volatilisation Chamber.



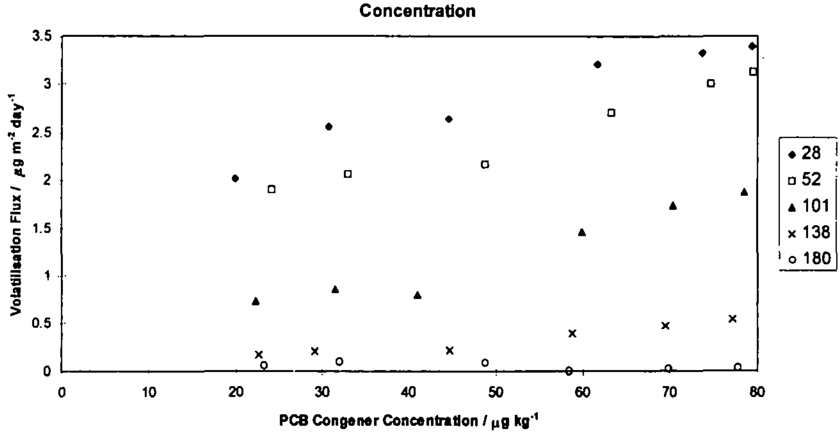
After each experiment, the PCB content of the sampling PUF was determined. All PCB analyses were conducted using well-validated containment-enrichment, GC/MS procedures reported in detail elsewhere[4)]. Chamber blanks - *i.e.* experiments conducted in the absence of soil - were conducted regularly, and results corrected for the average blank concentration. Recoveries of quantitation standards added to check analyte losses during both sampling and analysis ranged between 47 and 90% for all samples.

Results and Discussion

The influence of soil PCB burden

Figure 2 shows volatilisation flux (µg m^{-2} day^{-1}) plotted against soil PCB concentration (µg kg^{-1}) for individual PCB congeners. Each experiment was conducted on the same soil (F_{OC} = 3%), soil temperature was held at 13°C and average soil moisture content during each experiment was in the range 27-40% .

Figure 2. PCB Volatilisation Fluxes Observed With Variation In Soil PCB Concentration



For congeners 28, 52, 101, and 138, a positive linear relationship clearly exists between flux and soil PCB burden. Unfortunately, measured fluxes for congener 180 during these experiments were close to those recorded for chamber blanks, thus masking any similar relationship for this congener.

The influence of soil temperature
Measured volatilisation fluxes are plotted against soil temperature in Figure 3. The soil used in each experiment was identical - F_{OC} = 3% - soil PCB concentration was held at *ca* 35 µg kg^{-1} (accurately measured), and the average soil moisture content during the experiment was in the range 20-40%.

Figure 3. PCB Volatilisation Fluxes Observed With Variation In Soil Temperature

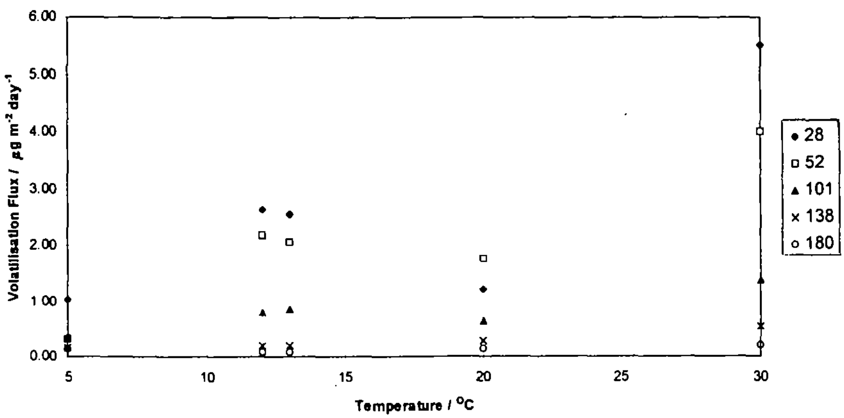


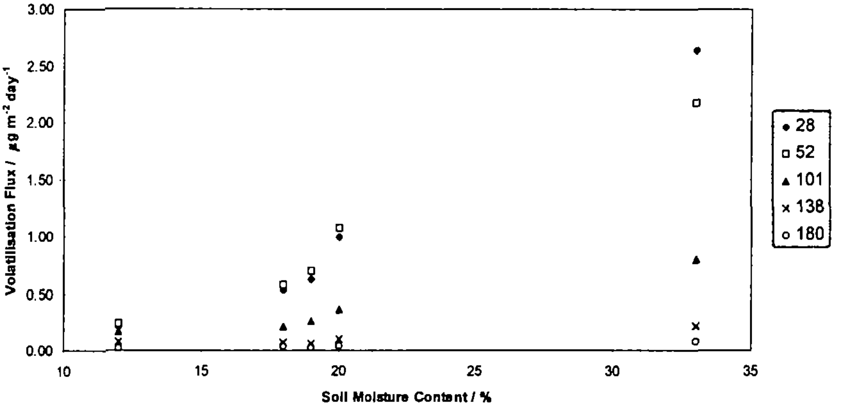
Figure 3 illustrates the basically positive linear correlation between flux and soil temperature. It is interesting to note the anomalously low fluxes observed for all congeners in the experiment conducted at 20°C. As discussed later, this is most likely due to the fact that the average soil moisture content of this experiment was much lower than in the other experiments. Similarly, in contrast to all the other experiments in this series, the volatilisation flux recorded in this experiment for congener 52 was greater than that for congener 28. This is probably due to the fact that the starting soil burden of congener 52 was greater than that of congener 28 in this experiment.

The influence of average soil moisture content
In Figure 4, PCB volatilisation fluxes are plotted against average soil moisture content. The soil used in each of these experiments was identical - F_{OC} = 3% - soil PCB concentration was held at *ca* 23 µg kg^{-1} (accurately measured), and the soil temperature maintained at 13°C. As can be seen from Figure 4, a positive linear relationship appears to exist between flux and starting soil moisture content. As discussed above, the volatilisation fluxes recorded for PCB 52 were greater than those for congener 28 in the majority of these experiments. Where this occurred, it is probably due to the fact that the starting soil burden of congener 52 was greater than that of PCB 28.

Two processes are likely to play a rôle in this positive correlation between volatilisation flux and soil moisture content. One is that the increase in volatilisation is a consequence of the increased competition between water and PCB molecules for soil binding sites as soil moisture increases.

The other process - known as "wicking" - refers to co-evaporation of PCBs with water, a process that is enhanced as the discrepancy between the moisture content of the soil and the air above increases, providing that the relative humidity of the air is less than 100%. If the relative humidity of the air pumped over the soil in the chamber could be maintained at 100% throughout the experiment, then "wicking" should theoretically be minimised, and it should be possible to assess the relative influence of these two processes on volatilisation flux. Unfortunately, practical constraints have prevented the conduct of such experiments to date, and this is an area for future investigation.

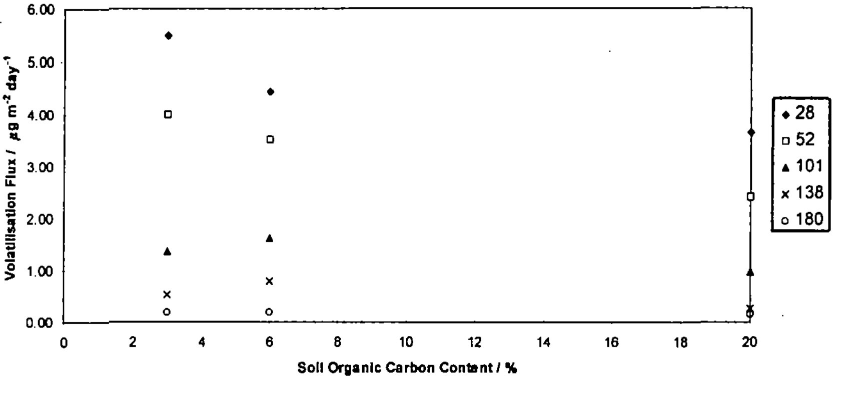
Figure 4. PCB Volatilisation Fluxes Observed With Soil Moisture Variation



The influence of soil organic carbon content

Figure 5 plots volatilisation flux against soil organic carbon content. In each of these experiments, soil PCB concentration was held at *ca* 38 mg m^{-3} (accurately measured), average soil moisture content during the experiment was in the range 26-63% and the soil temperature maintained at 30°C. Whilst based on an extremely limited database, Figure 5 clearly suggests a negative linear correlation between volatilisation flux and soil organic content.

Figure 5. PCB Volatilisation Fluxes Observed With Variation In Soil Organic Carbon Content



The influence of K_{OA}

The natural logarithm of volatilisation flux for individual congeners during a typical experiment, is plotted against the natural logarithm of K_{OA} for the same congeners in Figure 6. Volatilisation fluxes are those measured under the following conditions: F_{OC} = 3%; soil temperature = 13°C; soil PCB burden = 31 μg kg^{-1}, and an average soil moisture content of 20%. K_{OA} values were calculated for 13°C, using previously published algorithms[5].

Figure 6. Fitting PCB Volatilisation Fluxes To K_{OA}

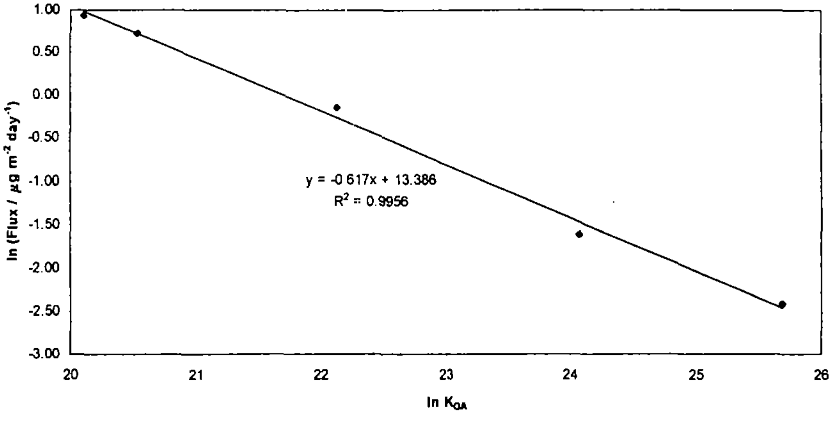


Figure 6 shows there to be a good negative linear correlation between Ln (flux) and Ln K_{OA}, and supports the assertion that K_{OA} is the physicochemical parameter that best describes soil-air exchange of semivolatile organic compounds (SOCs)[6].

Summary

Clear relationships have been elucidated between soil-air fluxes of five individual PCB congeners, and a number of edaphic and congener-specific properties. Upon completion of experimental work, a multiple linear regression analysis of the data will be conducted. It is hoped that this will yield an algorithm that will predict soil-air fluxes of a given SOC, given known values of soil Foc, moisture content, temperature, and SOC burden.

Acknowledgments

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