ORGANOCHLORINE CONTAMINANTS IN SOILS COLLECTED FROM REMOTE SITES AROUND THE WORLD

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Introduction

Polychlorinated biphenyls (PCBs), DDT/E, hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB) and dieldrin are global contaminants. They have been detected in air, soil, vegetation, sediment and biota from the equator to the poles at sites that are remote from their use and manufacture. However, in general, individual studies are conducted on relatively small local / regional scales and to get information on global fate of these compounds, results from many studies have to be compared. There are problems in comparison between data sets, however, due to differences in methods that are used in sampling, extraction and analysis of samples. Differences in QA/QC between studies also confound these problems.

In an attempt to start to address these problems, results are reported here from a large-scale global soil survey. Soils were analysed for a range of organochlorine contaminants and the results interpreted with respect to site (latitude, temperature, land-use) and soil (organic matter content, bulk density) parameters. Differences between extraction methods were also investigated.

Materials and Methods

Surface soil samples (0-5 cm, triplicate) were collected from over 100 sites world-wide (selected sites shown in Figure 1). Sites which were chosen were remote from potential sources of analytes – *i.e.* removed from populated / industrialised / agrochemical application areas. Samples were double wrapped in clean foil, sealed in polythene bags and stored frozen until extracted. A separate sample was collected from each site for bulk-density determination. Information from the sample site included latitude & longitude, altitude, land-use, vegetation type, distance from any potential source and mean annual, summer and winter temperatures.

Figure 1: Location of Global Sampling Sites
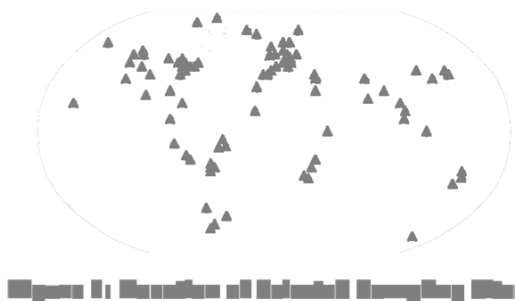
Defrosted samples were mixed with sodium sulphate and extracted for 12 hours in DCM followed by 12 hours in toluene. DCM and toluene extracts were combined for 80 % of samples – they were kept separate for the remaining 20 % to study differences in extraction method. Extracts were cleaned using silica/alumina chromatography followed by size-exclusion chromatography (S-X3 biobeads®). Samples were analysed by GC-MS for 34 PCB congeners, HCB, *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, α-, β- and γ-HCH and dieldrin using a protocol described elsewhere (1).

Results and Discussion

EXTRACTION METHOD: A positive correlation is seen between the amount of compound extracted in the toluene as a percentage of the total amount extracted (DCM plus toluene) and the organic matter content of the soil. For some of the more organic soils, toluene pulls out nearly as much analyte again as the DCM. Most literature data available are for simple DCM, hexane or hexane/acetone extractions. Given that increases in the organic content of a soil increases the amount of analyte not extracted by DCM alone (and presumably therefore also hexane or hexane/acetone), this begs the question "is it justifiable to compare concentrations from these extractions for soils of varying organic matter contents?" We believe that these results are worthy of more study and further work should be carried out to investigate relationships between compound extractability and organic matter type and soil-analyte contact times.

GLOBAL SURVEY: Ranges in analyte concentrations (DCM plus toluene extracts) are given in Table 1. Results are expressed in burden of pollutant per mass dry weight (dwt) of soil, per mass soil organic matter (OM) and per unit area. Clearly the units used to express the results are important in terms of factor differences in concentration ranges. However, what is not obvious from Table 1 is that it also affects the location of the sites at the extremes of the concentration range. Considering PCBs expressed as pg/g dwt, the minimum concentration was observed for a site in Greenland and the maximum for a site in Germany. If PCB concentrations are expressed as pg/g OM, however, the minimum concentration was observed for a site in Arctic Canada and the maximum for a site in Austria. The units used in expressing results could therefore have a large effect on interpretation of results.

Table 1: Ranges in concentrations of Contaminants in Remote Soils

Analyte	Concentration		
	pg/g dwt	pg/g OM	pg/m^2
Σ-PCB[a]	5.6 – 100,000	200 – 360,000	42 – 160,000
Σ-HCH[b]	n.d. – 9,300	n.d. – 22,000	n.d. – 19,000
Σ-DDT[c]	n.d. – 210,000	n.d. – 3,100,000	n.d. – 2,100,000
HCB	n.d. – 5,100	n.d. – 9,200	n.d. – 8,200
Dieldrin	n.d. – 13,000	n.d. – 16,000	n.d. – 7,800

[a]Σ-PCB: sum of concentrations of 34 congeners; [b]Σ-HCH: sum of concentrations of α-, β- and γ-HCH; [c]Σ-DDT: sum of concentrations of DDE, DDD and DDT.
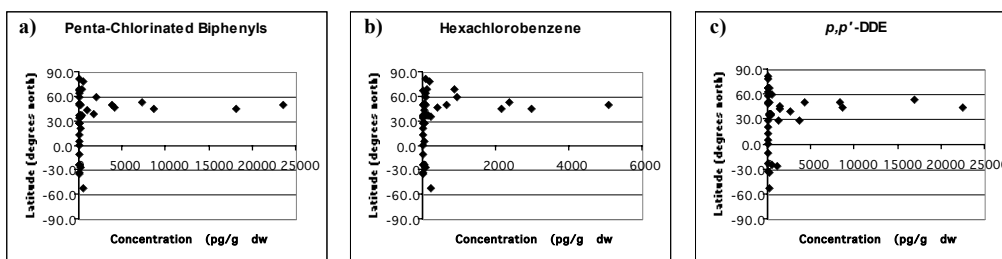

Figure 2: Latitude vs. Concentration for a) Sum penta-chlorinated biphenyls b) HCB c) *p,p'*-DDE.

No correlations are observed between analyte concentration in the soil and soil organic matter content or sample site altitude or temperature (mean annual, summer or winter). Figure 2a-c shows the sample site latitude against concentration (pg/g dwt) for sum penta-chlorinated biphenyls, HCB and p,p'-DDE. A peak in concentrations is clearly seen for samples collected between 30 and 60 ºN. Similarly, a peak in concentrations is seen between these latitudes for all compounds investigated, irrespective of units used for concentration (pg/g dwt; pg/g OM; pg/m^2). This is the major source region of most of the compounds investigated, suggesting that there has been little mass movement of persistent organic compounds away from the regions where they were used.

In order to investigate the effect of land-use on pollutant burdens, at several locations during the survey, woodland and grassland soils were collected from the same sample area. In general, concentrations of analytes are higher in the soils collected from woodland sites than from matching grassland sites if concentrations were expressed as pg/g dwt. This was not always the case if concentrations are expressed as pg/g OM or pg/m^2 (*e.g.* Figure 3a-b). Again, it can be realised that the units used to express results could have a large effect on data interpretation.
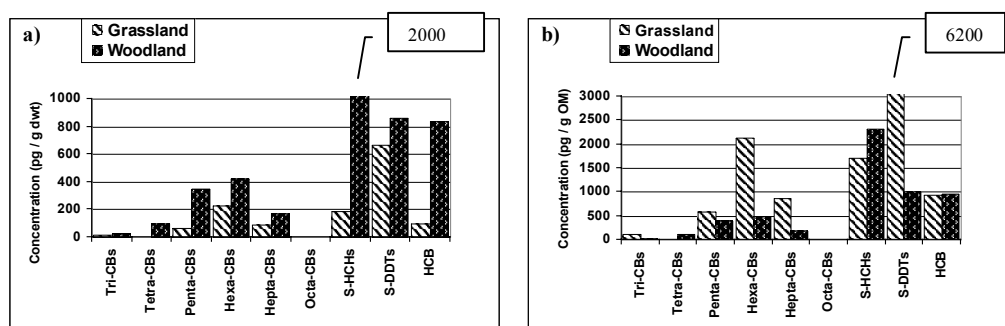

Figure 3: Comparison between soil concentrations for matching grassland and woodland sites a) concentration units pg/g dwt; b) concentration units pg/g OM.

If woodland soils are excluded from the global survey, there is a slight correlation between concentration (pg/g dwt) and soil organic matter content for some of the more volatile compounds, suggesting that these compounds may be well mixed in the environment. No correlations are evident against the other variables investigated. The peak in the region 30 – 60 ºN is still evident for all compounds for the non-woodland sample sites. No correlations can be found for the concentration of analytes in woodland soils against organic matter of the soil or any of the other variables investigated.

Initial results suggest that there may be differences in the contaminant profiles of soils from different regions. Differences are observed in the relative concentrations of penta- and hexa-PCBs, for example, between soils collected in Europe and North America. This could be due to differences in the types of commercial PCB mixtures that were used between these continents. Again this is worthy of more investigation. Figure 4a-c shows the mean profiles of PCB homologue groups in soils collected from southern temperate (30 – 60 ºS), northern temperate (30 – 60 ºN) and northern polar (60 – 90 ºN) regions. There is a significant difference between the profiles of the northern temperate soils and those from southern temperate or northern polar regions. Northern polar and southern temperate profiles are similar, suggesting that we may be

seeing a difference in compound transportability. Alternatively, again, the reason for the difference may be due to differences in PCB use.
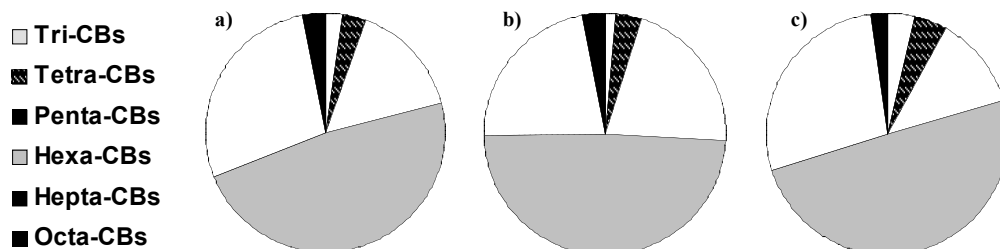
☐ **Tri-CBs**
▨ **Tetra-CBs**
■ **Penta-CBs**
☐ **Hexa-CBs**
■ **Hepta-CBs**
■ **Octa-CBs**

Figure 4: PCB profile comparisons a) 60 – 90 ºN; b) 30 – 60 ºN; c) 30 – 60 ºS.

A recent report suggests that PCBs in the air and soil across the UK and Norway are approaching equilibrium (2). If it is assumed that this is the case across the world, then a simple fugacity based model can be used to calculate air concentrations at the sites where soil samples were collected. Using this approach, a peak in air concentrations is predicted in northern temperate zones. A comparison between the predicted air concentrations and measured air concentrations from literature data gives agreement within a factor of 5 – we feel this to be extremely good given the errors which are encountered in using such a model. We believe that at sites which are removed from local sources of PCBs, the air and soil are very close to equilibrium and that at these sites it will be extremes in temperature which will drive net volatilisation or deposition. This would suggest, therefore, that the global separation of these compounds according to differences in compound volatility (global fractionation/distillation), an hypothesis which has been advocated by Wania and Mackay (3), is still very much in its infancy.

References
1. Ockenden, W.A.; Prest, H.F.; Thomas, G.O.; Sweetman, A.; Jones, K.C. **1998** Passive air sampling of PCBs: Field calculation of atmospheric sampling rates by triolein containing semipermeable membrane devices *Environ. Sci. Technol.* **32:** 1538 – 1543.
2. Ockenden, W.A.; Sweetman, A.J.; Prest, H.F.; Steinnes, E.; Jones, K.C. **1998** Toward an understanding of the global atmospheric distribution of persistent organic pollutants: The use of semipermeable membrane devices as time integrated passive samplers *Environ. Sci. Technol.* **32:** 2795 – 2803.
3. Wania, F.; Mackay, D. **1993** Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions *Ambio* **22:** 10 – 18.