

THE COLD CONDENSATION & GLOBAL FRACTIONATION HYPOTHESES: THE SEARCH FOR SUPPORTING EVIDENCE

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INTRODUCTION

For many years, the Arctic and Antarctic were considered to be pristine environments - too far removed from industrialised regions for pollution to be of any major concern. In the late 1960s and 1970s, however, higher than expected concentrations of several persistent organic pollutants (POPs), including chlorinated pesticides and polychlorinated biphenyls (PCBs), were detected in these remote regions^{1,4}. But how did they get there when there are few localised sources? Several theories have been put forward to attempt to explain these findings, but the one which has, perhaps, been given greatest credibility is that of Wania and Mackay⁵. These workers suggested that semi-volatile organic compounds (SOCs) would volatilise from the warm and temperate areas of their manufacture and use, and would then be subject to long-range atmospheric transport. Such compounds would then recondense when they reached colder circumpolar regions. This has become known as the "cold condensation" theory. It has been further hypothesised that differences in volatility and lability will lead to a latitudinal fractionation of SOCs - this is known as the "global fractionation" hypothesis⁵. As yet, however, there is little evidence available to support these theories. One reason for this is that few studies have attempted to obtain concentrations of a particular compound within the same environmental matrix from polar and temperate regions simultaneously. There are problems associated with collecting samples which are far removed from localised sources and there are uncertainties over the distribution of POPs between terrestrial and aquatic environments. Also, the input for most of these compounds was not limited to a short period, as most models assume, but continued for several decades, and in many cases is still occurring today.

It is envisaged that for a compound to be subject to global fractionation it would 1) be environmentally persistent and stable in the atmosphere and 2) have an 'intermediate' vapour pressure. In this study, we have chosen to focus on PCBs because 1) there are fully validated methods for their analysis; 2) there is literature available for the physico-chemical properties of the 209 possible congeners and 3) they are representative of a broad range of halogenated organics. In addition to this, there are data available which show that concentrations of these compounds in many environmental compartments in temperate areas have declined in recent years, and it is suggested that this is due to volatilisation from compartments where they have previously been deposited⁶⁻¹⁴. There are also some limited data for concentrations in polar regions which provide some evidence for latitudinal fractionation¹³⁻¹⁶. In terms of global fractionation, the physical and chemical properties would indicate that the less chlorinated PCB congeners may move further northwards and be degraded more rapidly than the higher chlorinated congeners, and therefore, they make an ideal group of compounds to study when looking for evidence of this process.

EXPERIMENTAL

Archived (1950-1970) and matching contemporary (1993) soil samples from 46 sites across the UK, contemporary (1990) forest soil samples from 12 Norwegian sites and samples of matching archived (1977 and 1985) and contemporary (1990) epegeic moss (*Hylocomium splendens*) from 46 Norwegian sites¹⁷ have been extracted and analysed for 37 PCB congeners using previously validated methods^{8,17}.

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RESULTS AND DISCUSSION

Temporal changes in PCB content of UK soils

It was found that there was an increase in the total PCB (Σ PCB; sum of the 37 congeners analysed) content of UK soils between 1950 and the late 1960s, after which there was a substantial decline, to a mean contemporary Σ PCB concentration of 4 $\mu\text{g}/\text{kg}$ (Figure 1). This trend was seen for all homologue groups, but the decrease in concentration was more dramatic for the least chlorinated congeners - the mean concentration of tri-CBs fell by a factor of approximately 1000, while that of the hepta- and octa-CBs declined by a factor of 5. A change in the congener profile was therefore seen, such that there was an increase in the relative contribution of the more chlorinated PCBs. This would suggest that since the late 1960s, PCBs have been lost from the soil primarily as a result of volatilisation, rendering them available for long range atmospheric transport.

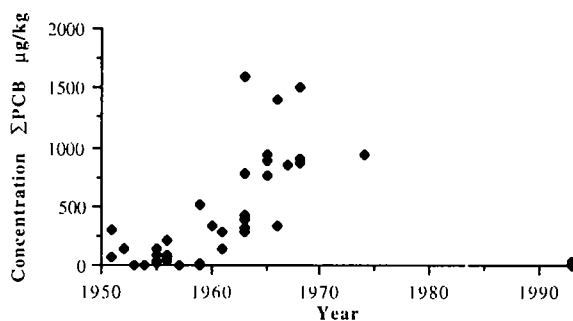


FIGURE 1: Change in UK soil PCB concentration over time. 1993 point represents all 46 sample sites - concentration Σ PCB ranges from ca. 0.5 to 20 $\mu\text{g}/\text{kg}$, with a mean value of 4 $\mu\text{g}/\text{kg}$.

PCB content of contemporary UK and Norwegian soils - spatial differences

The PCB content of soils from southern and northern Norway was significantly higher than that of soils from the UK (99% confidence limit) (Table 1). Principal component analyses were used to investigate this observation further, and these suggested that the difference was primarily caused by a higher proportion of mid-molecular weight congeners in the Norwegian soils. The soils from Norway were all collected from forested areas, whereas those from the UK are predominantly from grassland sites. Therefore, the difference in concentration may be due to landuse not latitudinal differences. There were four woodland soils which were analysed from the UK, and these were found to be evenly distributed in the UK PCA plot, suggesting concentration differences were due to spatial variations in samples. However, if results are expressed on a mass of PCB per unit area basis, rather than per unit dry weight, then the differences in concentration between the UK and Norwegian samples is reduced (Table 1).

TABLE 1: Mean Σ PCB concentration expressed per unit dry weight and per unit area in UK and Norwegian soils. ^aAssumes all PCBs are present in top 5 cm of soil; ^bAssumes bulk density of grassland soils to be 1000 kg/m^3 ; ^cAssumes bulk density of forest soils to be 250 kg/m^3 .

Region	Σ PCB Concentration ($\mu\text{g}/\text{kg}$)	Σ PCB Concentration ($\mu\text{g}/\text{m}^2$) ^a
UK	4	200 ^b
Southern Norway	17.5	220 ^c
Northern Norway	9.5	120 ^c

The ratio of tri-CB : hexa-CB is slightly higher in the soil samples from the north of Norway than in the southern most Norwegian samples. This observation, together with the relative enrichment of the mid-molecular weight congeners in the Norwegian samples over the UK samples, would suggest that

latitudinal fractionation is occurring. For the less chlorinated, more volatile congeners, it would appear that temperatures are high enough, even in the north of Norway for re-volatilisation to occur, suggesting that these compounds are being transported to still colder environments.

Temporal Changes in PCB content of Norwegian moss¹⁷

The Σ PCB content of *Hylocomium splendens* decreased in all samples from all locations between 1977 and 1990. This reflects the global decline in the manufacture and use of these compounds. The scale of the decrease was region dependent. For example, in coastal areas of northern Norway, mean Σ PCB decreased from 21.2 $\mu\text{g}/\text{kg}$ in 1977 to 6.9 $\mu\text{g}/\text{kg}$ in 1990; in northern inland areas, concentrations fell from 27.7 $\mu\text{g}/\text{kg}$ to 7.9 $\mu\text{g}/\text{kg}$ and in southern Norway the concentration decreased from 52.1 $\mu\text{g}/\text{kg}$ to 9.5 $\mu\text{g}/\text{kg}$. This decrease in the PCB content of moss is indicative of a corresponding decrease in atmospheric PCB concentrations.

Over this time period, a latitudinally dependent change in the congener profile was observed. The relative proportion of the more chlorinated PCBs increased at all sites, but it did so most in samples from the north of Norway (Figure 2). As with the contemporary soil data, these findings suggest a difference in congener cycling in the environment which is largely driven by differences in volatility and ambient temperatures.

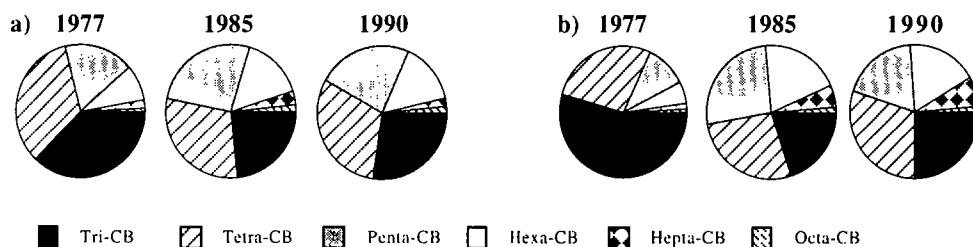


FIGURE 2: Temporal changes in the relative contribution of homologue groups to Σ PCB for samples collected from a) the south of Norway and b) the north of Norway.

GENERAL COMMENTS & CONCLUSIONS

In summary, this study has found a temporal change in PCB concentrations and congener patterns in UK soils between the 1950s and 1990s and in Norwegian mosses between the late 1970s and 1990s. Spatial differences in congener profiles in soils and vegetation between the south of the UK and the north of Norway were also noted. It is tentatively suggested that these observations are consistent with the global fractionation hypothesis: PCBs are being lost from the soils and vegetation of temperate areas, apparently as a result of volatilisation. They are then subject to long range atmospheric transport and there is a subsequent accumulation of the heavier congeners in colder regions. For the less chlorinated groups, however, it would appear that temperatures, even in the north of Norway, are high enough for re-volatilisation to occur. A latitudinal fractionation influenced by generally lower summer temperatures, particularly in the circumpolar regions of Norway, is thus thought to be occurring.

However, it must be stressed that these interpretations are only tentative. The conclusions of this study and of others purporting to support the global fractionation hypothesis must be viewed with caution. There are many confounding factors, such as localised pollutant sources, meteorological patterns, relative pollutant susceptibility to mineralisation and ageing of pollutant residues, which must be considered before firm conclusions can be drawn. PCBs weren't just released into the environment as one pulse, they were released over a time period in excess of 50 years and point sources are still being realised today. Much more data is required before we can really support or disprove the cold condensation and global fractionation hypotheses. In addition to this, there is still confusion as to what exactly meant by ideas such as the "cold condensation" and "global fractionation" hypotheses - these and other terms are frequently, but mistakenly, interchanged, and this problem needs to be addressed.

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Finally, projects need to be specifically designed to attain evidence to support or disprove these theories. This will require simultaneous long-term data from different latitudes/climatic conditions for specific environmental compartments.

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