## Variability In The PCB Concentrations Of Vegetation

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#### Introduction

It is important to know the levels at which semi-volatile organic compounds (e.g. PCBs) are found in vegetation, and the kinetics of their transfer from the air because this will determine: I) the amount which will enter the grass/cow/human food chain<sup>1</sup>; II) processes of air-surface exchange which are of relevance to global cycling and air concentrations<sup>2</sup>; and III) the validity of using vegetation as an indicator of local air concentrations. A number of factors are likely to control PCB concentrations in vegetation, in addition to those which influence air/plant partitioning (i.e. air concentration and temperature). Firstly, there are important biological differences between plant species, such as surface area and cuticle thickness/volume, which will influence the size and nature of the lipophilic compartments where SOCs are stored. Secondly, the habitat in which the plant grows may be important. Thirdly, the 'growth strategy' of the plant is important, i.e. nonevergreen plants produce fresh leaves each spring, which are then shed later the same year, whilst evergreen plants can keep their leaves for more than a year, increasing the amount of long-term accumulation possible. Fourthly, the amount of time and season to which leaves have been exposed to the atmosphere will differ between species/plant types. Finally, some plants produce new leaves quickly, and others such as grasses, have leaves which grow continuously for relatively long periods, at a rate determined by ambient temperatures. In order to assess the variability of plants in the field, a survey of PCB concentrations in a diverse range of plant species was carried out at three different times of the year. The survey included two different habitats: pastureland (grasses, shrubs etc) and woodland (trees, epiphytes, grass and shrubs).

### Method

Vegetation samples were collected from the vicinity of the Hazelrigg field station, a semi-rural site close to Lancaster University, in March, June and October, months corresponding to early spring, early summer and early autumn. The average temperature at each sampling time was 7°C, 14°C and 17°C respectively. The species collected included: Urtica dioica (stinging nettle), Achillea milifolium (millfoil/yarrow), Ranunculus acris (buttercup), Digitalis purpurea (foxglove), Rumex obtusifolius (broad-leaved dock), Rumex acetosum (sorrel), Silene dioica (red campion), Cirsium acaulon (ground thistle); grasses: Festuca ovina (sheep's fescue), Holcus lanatus (yorkshire fog), Poa pratensis (meadow grass), mixed grass sward; climbers: Lonicera periclymenum (honeysuckle), Hedera helix (ivy); trees: Pinus sylvestris (Scots pine), Picea abies (Norwegian spruce), *Quercus robur* (common oak), *Fagus sylvestris* (common/European beech); moss: Homalothecium sericeum and a fungus Auricularia auricula-judae (Jew's ear fungus). Air samples were also taken over 1 week periods throughout the duration of the sample period using 2 polyurethane foam plugs and a glass filter in a 'hi-vol' air sampler, with more frequent (every 1 or 2 days) samples taken in the week prior to vegetation sampling. Prior to extraction, vegetation samples were mixed with 50g of anhydrous sodium sulphate, frozen with liquid nitrogen and blended. Samples were extracted for 16 hours with dichloromethane in a soxhlet apparatus.

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Extracts were cleaned up with dual layer silica/acid silica columns and GPC columns. Air filter and PUF samples were soxhlet extracted for 16 hours with hexane, and then fractionated on a silica column. Analysis was carried out on a Fisons MD800 GC/MS in SIM mode with separation on a CPSil-8 50m column. PCBs quantified were nos. 18, 28, 44, 49, 52, 60, 66, 74, 87, 101, 105, 110, 118, 138, 141, 149, 151, 153, 170, 180, 183 and 187. Analysis of both vegetation and air samples has been described elsewhere <sup>3</sup>. The vegetation surface areas were measured with a leaf area meter, using different sub-samples to those that were used for PCB analysis. These were then subsequently used for dry weight measurement, and estimation of lipid content by 4 hour hexane extraction of the dry, ground samples.

#### Results

The  $\Sigma$ PCBs concentrations detected in the vegetation by dry weight ranged from 738 pg/g in fungus to 8234 pg/g in honeysuckle in the spring ( $\overline{x}$ =3648,  $\sigma$ =247), from 248 pg/g in sheep's fescue to 3474 pg/g in spruce in the summer ( $\overline{x}$ =1513,  $\sigma$ =1032) and from 954 pg/g in sorrel to 7921 pg/g in honeysuckle in the autumn ( $\overline{x}$  =2962,  $\sigma$ =2027). When these were converted to  $\Sigma$ PCB concentrations per ug of extractable lipid, they ranged from 0.095 ug/g in pine to 2.01 ug/g in ivy in the spring ( $\overline{\mathbf{x}}$  =0.735,  $\sigma$ =0.485), from 0.020 µg/g in sheep's fescue to 0.557 µg/g in moss in the summer ( $\overline{x}$ =0.141,  $\sigma$ =0.145) and from 0.0080 µg/g in thistle to 0.921 µg/g in buttercup in the autumn ( $\overline{\mathbf{x}} = 0.235$ ,  $\sigma = 0.259$ ). Finally, as  $\Sigma$ PCB concentrations per surface area, they ranged from 0.86 pg/cm<sup>2</sup> in beech to 15 pg/cm<sup>2</sup> in spruce in the summer ( $\overline{x}$  =5.31,  $\sigma$ =4.77) and from 1.5 pg/cm<sup>2</sup> in thistle to 28 pg/cm<sup>2</sup> in spruce in the autumn ( $\overline{x}$  =9.03,  $\sigma$ =8.43). Clearly there were major differences in concentrations, varying by over 30-fold on a dry weight basis, with the amounts detected varying according to how the results are presented. The physical characteristics of the plants studied varied considerably, with lipid content varying between species by factors of 23 in the spring, 14 in the summer and 50 in the autumn, and surface areas varying between species by factors of 8 in the summer and 6 in the autumn. Furthermore, there was also variation between seasons for individual species, with lipid content varying by up to a factor of 17 ( $\overline{x} = 3.8$ ) and surface area varying by up to a factor of 2.4 ( $\overline{X}$  = 1.5). There was no correlation between either the lipid content or the surface area of plants and the  $\Sigma$ PCB concentration detected. PCA analysis did not show any relationship between PCB concentration and species type or PCB concentration and season, although for one season (spring), it did show a relationship between PCB concentration and location within the sample site, separating plants growing in the middle of the field from plants growing in the woodland area. The PCB congener patterns could be broadly grouped into: I) plants with a long exposure time, i.e. evergreens and mosses (Fig.1); II) plants with leaves with an initial rapid growth which then don't grow after opening, i.e. oak and beech (Fig.2); III) plants with a thin cuticle and fast seasonal growth, i.e. grasses (Fig.3); and IV) other non-evergreens. The beech and oak showed a large increase in leaf PCB burden in autumn, particularly for the heavier PCBs (Fig.2). From this, assuming linear uptake, estimations of average rates of  $\Sigma$ PCB accumulation of 15.1 pg/g day in beech and 19.8 pg/g day in oak have been made. Scavenging plots for the different species all have gradients less than 1, ranging from 0.21 (foxglove, nettle) to 0.85 (oak), with the y intercept also very variable, ranging from -6.7 in oak to -0.29 in Scots pine, similar to those previously found for grasses <sup>4</sup> and a range of smaller plants <sup>5</sup>. Scavenging plots for individual species also varied with season, with both gradient and intercept changing (e.g. honeysuckle, Fig.4).

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Fig.1 PCB congener profile for moss in spring, summer and autumn



Fig.2 PCB congener profiles for beech (summer), beech (autumn), oak (summer) and oak (autumn).



Fig.3 PCB congener profiles for mixed sward in spring, summer and autumn.

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Fig.4 PCB Scavenging plots for honeysuckle for the three different seasons.

#### Discussion

The species survey has shown that the concentration of PCBs found in vegetation is very variable. depending, among other things, on the species/plant type and season. Clearly, numerous factors can contribute to this interspecies variability, such as cuticle thickness and structure, leaf surface area and growth rate. These factors are compounded by interseasonal variability, i.e. a combination of growth dilution, changes in cuticle thickness, cuticle structure and leaf surface area, long-term accumulation, and the effects of temperature on partitioning. The fact that PCA created separate clusters for species in a field to species in a copse 100m away suggests that there may also be variation with location over small distances. The concentration of PAHs found in leaves of oak and maple trees is dependent on the location of the tree within the wood, with highest concentrations being found on the windward <sup>6</sup>. The survey did not show PCB levels to be higher in plants close to the ground, so proximity with the soil *per se* was not seen to have any effect in this study. In summary, these variables make it difficult to use vegetation as a predictor for air concentrations without first defining the relationship between the vegetation and air concentrations for a given species, and the factors controlling that relationship. These need to be established under controlled laboratory conditions which allow examination of the effects of a single variable at a time, in order to improve our understanding of air/plant partitioning of PCBs and other SOCs, and the factors controlling plant concentrations in the field.

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