

UPTAKE MECHANISMS OF AIRBORNE PERSISTENT ORGANIC POLLUTANTS IN “PLANTS” – UNDERSTANDING THE BIOLOGICAL INFLUENCE ON THE DEPOSITION OF POPs TO REMOTE TERRESTRIAL ECOSYSTEMS

Kylin H^{1*}, Bouwman H²

¹Department of Water and Environmental Studies, Linköping University, SE-58183 Linköping, Sweden;

²Research Unit: Environmental Sciences and Development, North-West University, Potchefstroom, South Africa

Introduction

“Plants” have gained interest as organisms to monitor airborne hydrophobic persistent organic pollutants (POPs)¹. As they are present in most parts of the world and do not require actively transporting them out to a sampling site, they have been used to study global distillation² or orographic cold trapping³ of POPs. However, to interpret the data in such studies it is essential to understand the uptake process of airborne POPs into “plants”. Without a mechanistic understanding of the deposition and possible revolatilization of POPs it becomes impossible, not only to interpret data from studies of global or orographic processes, but also to understand the role “plants” play for the deposition to and circulation of POPs in terrestrial ecosystems^{4,5}.

To properly interpret “plant” data it is also necessary to understand that “plants” are not a single unified group. In most environmental monitoring studies the term “plants” is used in its Linnaean sense, *i.e.*, with the taxonomic boundaries used by Linnaeus in 1735 for his kingdom “*Vegetabilia*”⁴. The Linnaean classification of “plants” was based on morphological characters only; the concept of phylogeny had not yet been developed in the early 18th century. Thus, the Linnaean “plants” include a wide range of organism groups with widely diverse physiological adaptations, several of which are no longer considered as true plants⁴. Fungi, *e.g.*, including the fungi that constitute the bulk of lichens, are phylogenetically more closely related to animals than to true plants. Thus, using “plant” data to show global or orographic distillation or deposition to remote areas is complex as different “plant” taxa may take up airborne POPs by different mechanisms. In some taxa even different ecotypes may behave differently.

In this text “plants” with citation marks indicates delimitation according to the Linnaean plant kingdom, while plants without citation marks indicate what is regarded as plants with today’s phylogenetic thinking.

In an attempt to clarify how field data of POPs in “plants” can or cannot be used to understand the deposition of POPs to remote areas, we here summarize and compare data from several published and unpublished studies that show the different uptake mechanisms of POPs in vascular plants, mosses, and lichens. We also suggest biologically based explanations for different uptake mechanisms in different “plants” based on their physiological adaptations to different lifestyles: the homoihydric vascular plants and the poikilohydric mosses and lichens.

Materials and methods

The methods have mostly been described previously^{4,7}. Field sampling included long term studies with regular sampling of air and vegetation², and controlled experiments in a laboratory setting¹. Quantifications of contaminants were done with gas chromatography using either an electron capture or a mass selective detector as appropriate. Studies of the diffusion of contaminants through wax were done according to Screiber and Schönherr⁸, but instead of reconstituting the epicuticular wax as extracted from the pine needles, the wax was reconstituted with different amounts using “terpenoids” isolated from the wax as described by Kylin *et al.*⁷

Results and discussion

Based on the experience gained over several years of comparing field measurements^{4,5} with model predictions (*e.g.*⁹) of how airborne POPs are taken up by “plants” the largest difference is seen among the volatile POPs that are mostly in the gas phase. Therefore, we here concentrate on the hexachlorocyclohexanes (HCHs) although similar observations were made for other compounds as well, *e.g.*, hexachlorobenzene. The benefits of using HCHs are 1) they were easily detected in air and vegetation during the experimental period, 2) the air concentrations of the two isomers α -HCH and γ -HCH showed very different seasonal variations during the initial data collection period; since α -HCH was no longer used anywhere in Western Europe the air concentrations in Sweden were more or less constant year round while the air concentrations of γ -HCH had a prominent peak in

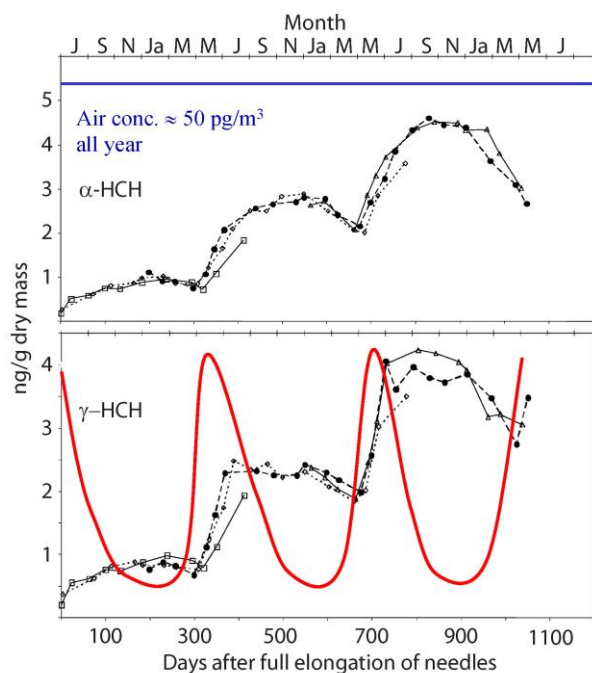


Fig. 1: Accumulation of α - and γ -HCH in Scots Pine needles during a full life cycle. Air concentrations (blue and red) are not quantitative, but illustrate the seasonal variation. Every other month is indicated starting with July. The apparent concentration dip in spring is due to accumulation of starch before it is consumed by growth during summer which affects the dry mass.

terpenoids. To test if the terpenoid concentrations in the pine needles also affected the accumulation rate in the field we performed a yearlong study of the accumulation of HCHs in pine needles in comparison with the amount of endogenous terpenoids. The results show a clear correlation between the amount of terpenoids and the accumulation of HCHs (Fig. 2).

Based on the results from these experiments we suggest that the biology of the pine needles is the governing factor for how much volatile POPs that are accumulated in pine needles. We suggest that the terpenoids act as plasticizers or swelling medium for the wax and cutin components of the cuticle, so that the diffusion rate of the HCHs is higher during summer when the levels of endogenous terpenoids are high than during winter when the terpenoid concentrations are low. Thus, the diffusion through the wax and cuticle would be high during summer and low during winter.

A critical factor here is the total capacity of the pine needles to accumulate volatile POPs. Comparison with other species shows that even in species that retain their foliage longer than Scots Pine (as much as 30 years in *P. balfouriana*, and 50 years in *Cassiope tetragona*), the needles/leaves continue to accumulate HCHs until the onset of senescence (Kylin, unpublished data). Thus, the capacity to accumulate HCHs is not the limiting factor.

spring and early summer due to use in Southern Europe. These seasonal differences helped to elucidate the uptake mechanism into vascular plants.

During a three year long investigation with simultaneous sampling of air (continuous) and pine needles (every two weeks) it was found that both α -HCH and γ -HCH accumulated continuously in the pine needles until the onset of senescence². There were, however, large seasonal differences in the accumulation in the pine needles, with a high accumulation rate during spring and summer while there was very little change of the HCH concentrations during the coldest months (Fig.1). This is opposite of what would have been expected if the deposition was regulated by the vapour pressure of the analytes. The fact that the accumulation in the pine needles of both the HCH isomers was very similar in spite of the radically different seasonal air concentrations also indicated that the air concentration was not the governing factor for the accumulation of HCHs in pine needles. The explanation is likely the much higher levels of endogenous volatile compounds, mostly various terpenoids, that are present in the needles during the warm and dry summer months⁴.

Setting out to test this we investigated desorption of α -HCH from reconstituted wax⁵, isolating wax from pine needles and adding different amounts of terpenoids to the wax. The diffusion rate in the wax was affected substantially by the varying amounts of

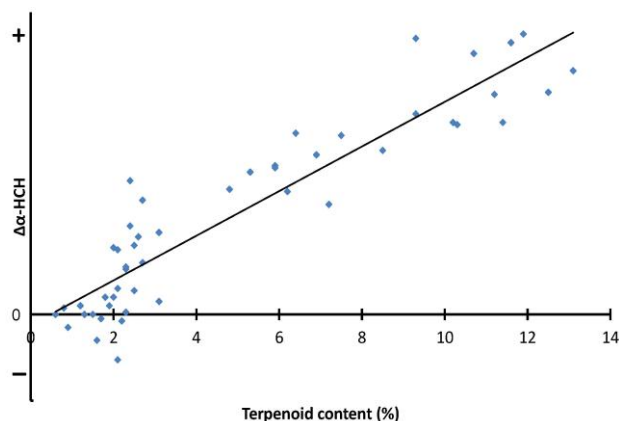


Fig. 2: Weekly relative concentration change of α -HCH ($\Delta\alpha$ -HCH) in Scots Pine needles during a one-year period in relation to the needle content of volatile oils.

The above results seem applicable to all vascular plants with hydrophobic cuticles, i.e., they are adapted to a homoihydric lifestyle where the cuticle serves to retain water. There will be differences between terpenoid rich and terpenoid poor species and species that retain their leaves for different periods of time, but we suggest that these are differences in degree, not in the specific mechanism of uptake. Even so, the accumulation rate of volatile POPs in vascular plants containing different amounts of terpenoids may be an order of magnitude, and due caution should be exercised before comparing data from different species.

If homoihydric vascular plants are at one end of the spectrum, the other end of the spectrum contains mosses and lichens, all of which are adapted to a poikilohydric lifestyle, withstanding total desiccation and with a hydrophilic surface that allows rapid re-hydration upon rain or fog events.

In the 1980s the Swedish Environmental Protection Agency commissioned a feasibility study on the use of moss or lichen to monitor the deposition of POPs as a complement to monitor the deposition of heavy metals¹. This showed an erratic uptake of the HCHs depending on weather conditions. A controlled experiment was therefore performed in a disused pesticides formulation control laboratory heavily contaminated with HCHs¹. This confirmed the assumption that the hydration state of the moss or lichen was critical for how much HCH that

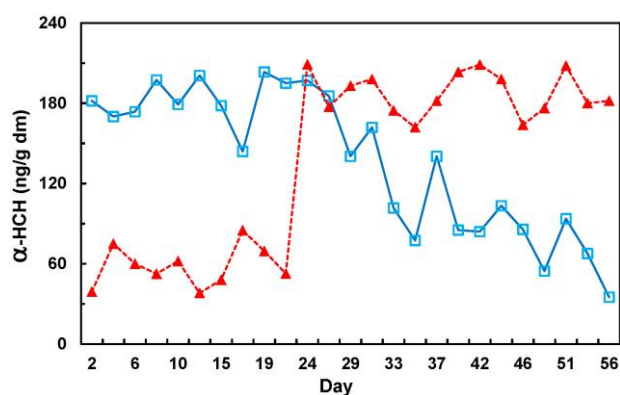


Fig. 3: Dynamics of airborne α -HCH in *Hylocomium splendens* in relation to hydration. Blue: fully hydrated at the start of the exposure then allowed to dry after Day 22. Red: Desiccated at the start and hydrated on Day 22. The air concentration was constant.

was taken up from the air⁴. Fig. 3 shows the results for the moss *Hylocomium splendens*. Obviously, mosses and lichens take up airborne HCHs by a completely different mechanism than vascular plants. Further, similar physiological adaptations are more important than taxonomic proximity (mosses are plants, lichens are not) for the uptake mechanism. We, therefore, question the logic in mixing data from vascular plants, mosses and lichens to assess the deposition of POPs to terrestrial ecosystems in remote areas.

Further, as the uptake of airborne volatile POPs into the green parts of vascular plants is heavily influenced by the amount of endogenous volatile oils, it is reasonable to assume that the same is true for bark; the suberin in bark is essentially a polymeric lipid as is the cutin of the cuticle of the foliage and should undergo swelling in a similar way. Therefore, reporting data on the content of volatile POPs in bark from different parts of the

world² without noting the species makes it essentially impossible to interpret the data. Although it is possible to draw the conclusion that the higher concentrations of HCHs and HCB found in bark at high latitudes is due to cold condensation, an at least equally plausible explanation is that bark samples from high latitudes primarily came from conifers while barks samples from low latitudes came from Angiosperms; conifers, generally, are dominant at high and Angiosperms at low latitudes. However, it would probably not have been necessary to know the species from which the bark was taken. The conclusions drawn by Simoich and Hites² could have been evaluated by noting if the bark was taken from a conifer or an Angiosperm, as the conifers generally contain much more volatile endogenous oils than the Angiosperms. We claim that without this information the data reported by Simonich and Hites² needs further interpretation before any connection between the results and global distillation can be inferred.

Similar complications face the interpretations of the data presented by Davidson *et al.*³ The data, interpreted as supporting orographic distillation of POPs, are reported on a lipid mass basis, which is normal when working with animal samples. However, for plants this does not work⁵ as traditional lipid determination methods will miss much of the mass of hydrophobic compounds in the foliage. The volatile compounds, which, as described above, govern the uptake of volatile POPs into the foliage will evaporate if a traditional lipid determination method is used, and the cutin that constitutes the cuticular membrane is a polymeric lipid that will not be dissolved or be accounted for on lipid determination. In many mountainous areas there is also a tendency that taxa or ecotypes that grow at high altitudes also have higher contents of terpenoids than those growing at low altitudes. Taking these facts into account and the uptake mechanisms of volatile POPs into plants, the data presented by Davidson *et al.*³ are inconclusive with respect to orographic cold condensation of POPs.

A further clue to the importance of vascular plants for the deposition to terrestrial ecosystem was obtained in a study of sediment from 100 lakes covering the length of Sweden¹⁰. The concentrations of HCHs (or any other POPs, *i.e.*, DDTs, PCBs, HCB) in the sediment did not correlate with latitude, eutrophication, or other factors that have been suggested to affect the sequestering of POPs in the sediment (Fig. 4). However, there was a striking correlation with the length of the vegetation period, *i.e.*, the period during which volatile, airborne POPs are taken up most efficiently by the vegetation. It would, therefore, seem that plants are a major vector of airborne POPs to terrestrial, including limnic ecosystems in the Nemoral and Boreal zones.

In conclusion, the uptake mechanisms of airborne POPs into “plants” are critical for the deposition of POPs to terrestrial ecosystems, but vary substantially between different “plant” groups. Using the Linnaean definition of “plants” is out of date and does not reflect differences in ecophysiological adaptations between different taxa at the Class or Order level. Even within the same family or genus there may be large differences in adaptations and the amount of endogenous terpenoids (that regulate the rate of uptake) may vary even within the same species depending on edaphic conditions and ecotype. In our view, although plants may be useful to map relative abundances of airborne POPs, it is impossible to use such data to understand the deposition of POPs to terrestrial ecosystems without taking the specific uptake mechanisms of the organisms’ studies into account. We have seen no published work that correctly have used data from plants to explain their role or influence on global or regional processes as the physical chemical models used do not take into account variations in the uptake processes that are of importance for the deposition over several seasons.

References:

1. Eriksson G, Jensen S, Kylin H, Strachan W. (1989); *Nature*. 341:42-4
2. Simonich SL, Hites RA. (1995); *Science*. 269:1851-4
3. Davidson DA, Wilkinson AC, Blais JM, Kimpe LE, McDonald KA, Schindler DW. (2003); *Environ Sci Technol*. 37:209-15
4. Kylin H, Bouwman H. (2012); *Environ Sci Technol*. 46:10982-9
5. Kylin H, Sjödin A. (2003); *Environ Sci Technol*. 37:2350-5
6. Kylin H, Nordstrand E, Sjödin A, Jensen S. (1996); *Fresenius J Anal Chem*. 356:62-9
7. Kylin H, Söderkvist K, Undeman A, Franich R. (2002); *Bull Environ Contam Toxicol*. 68:155-60
8. Schreiber L, Schönherr R. (1993) *Pestic Sci*. 38:353-61
9. Wania F, McLachlan MS. (2001). *Environ Sci Technol*. 35:582-90
10. Söderström M, Asplund L, Kylin H, Sundin P. (2002). In: *Söderström M. Thesis*, Stockholm Univ.

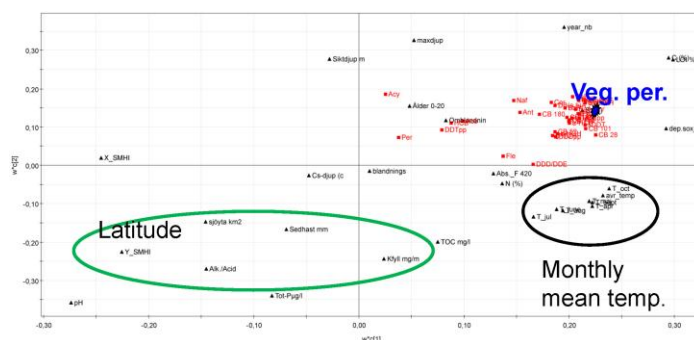


Fig. 4: PLS of data on physical, chemical and biological data from 100 Swedish lakes and concentrations of POPs and PAHs. Red represents the analytes and black edaphic information and water physical/chemical/biological parameters. Green encircles parameters usually used to model the deposition of POPs. The length of the vegetation period is defined as the number of days per year with an average temp. above 5 °C.