

A Long Term Study of the Uptake of DDT and HCHs in Pine Needles

Henrik Kylin^{*}, Andreas Sjödin[†]

^{*}Environ. Assess., Swed. Univ. Agric. Sci., P.O. Box 7050, SE-750 07 Uppsala, Sweden.

[†]Environ. Chem., Stockholm Univ., SE-106 91 Stockholm, Sweden.

Introduction

The hydrophobic surface of higher plants will sorb persistent organic pollutants (POPs) from the surrounding air (Kylin 1994). This has been used to map the distribution of airborne POPs, and it has been suggested that the forests of the northern hemisphere plays an important role in the long range transport of POPs, acting as a filter especially for compounds in the gas MacLachlan & Horstmann 1998)).

Coniferous forests should in this context be of special importance, since they cover a large part of the northern temperate zone, the needles are kept on the trees for multiple years and the surface area is high. The intention of the study presented here, is to obtain field measurements of the accumulation of some organochlorines in pine needles, while simultaneously measuring the concentrations in the air, to obtain a greater understanding of the importance of pine needles in long-range transport phenomena and for the deposition of POPs to terrestrial ecosystems.

Materials and Methods

Pine needle samples were taken from 15-20 years old trees in the vicinity of the Stockholm University campus. Samples were collected every 4-8 weeks. Air samples were obtained with low volume air samplers on the roof of a nearby building. The air samplers were operated so as to integrate the air concentrations in the interval between pine needle sampling. Sampling commenced in January 1994 and continued till June 1996.

Analysis of the organochlorines in the pine needles was done according to the method described by Kylin et al (1994). In short the epicuticular wax of the needles is extracted by submersing the fresh needles in dichloromethane for 48 hours. The samples were then treated with konc. sulphuric acid and fractionated on a nitrophenyl silica column to obtain two fractions, one fraction containing the polychlorinated biphenyls (PCB) and 1,1-bis(4-chlorophenyl)-2,2-dichloroethene (DDE) and the other fraction containing the other organochlorine pesticides such as the hexachlorocyclohexanes (HCHs) and 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT). After extracting the epicuticular wax the needles are cut into pieces and the interior lipids are extracted with dichloromethane and the extracts fractionated in the same way as the epicuticular wax. Quantitation was performed on a gas chromatograph equipped with an electron capture detector.

To date the fraction containing the HCHs and DDT of the pine needle samples collected from June 1994 to October 1995 have been analysed.

Results and discussion

Wax

For α -HCHs there is a clear accumulation with time. The accumulation is highest during the warm summer season and then levels off during winter. In early spring there is a decrease in the concentrations as calculated on a dry weight basis. After the spring decrease, the accumulation continues the next summer. The needles grow 3 years old and in the last year-class the spring decrease is followed by senescence. The same general trend can be seen for γ -HCH (Lindane). However there is a prominent extra accumulation during the early summer, more or less coinciding with the spraying season.

For DDT the pattern is completely different. Instead of the highest accumulation in the summer, there is a very high accumulation during winter that is replaced by an almost as prominent decrease in concentrations in spring more or less coinciding with the spring decrease of the HCH concentrations. There is a general trend of increasing concentrations between the year-classes though .

If the dry weight is corrected for the estimated amount of carbohydrates, especially starch, in the needles (Ericsson 1979) a slightly different picture emerges. The rationale for doing this correction is that the carbohydrates will be the only major component of the dry weight that will vary throughout the year. Thus the basis for calculating concentrations if the long term behavior of the contaminants in the air-needle system is to be understood, probably should be the dry weight excluding the carbohydrates,

There is an large increase of the starch content in the needles at the same time of year and of the same magnitude as we the decrease of the HCHs in early spring. Consequently, the concentrations of the HCHs based on the corrected dry weight show no spring decrease during spring. The general seasonal pattern of accumulation of DDT is retained, but the slope of the underlying accumulation is increased.

Internal lipids

The internal lipids also show a general increase of both the HCHs and DDT. The levels are generally an order of magnitude lower than in the wax. When concentrations are based on the carbohydrate corrected dry weights, there is a more or less linear increase of all of the contaminants in the internal lipids.

The fact that the HCHs accumulates faster in the wax during the warm spring and summer than during the winter is surprising. While it to a certain extent could be explained for γ -HCH by increased air levels cause by spraying this pesticide in other European countries, it is very surprising for α -HCH, since this compounds show very little variation in air concentrations during the year (Haugen et al. 1998)). Another interesting observation is that equilibrium is never reached for these compounds in the air-pine needles system; a continuous increase of concentrations is observed until the needles start to undergo senescence. This is contradictory to what has been reported for other conifer species (MacLachlan & Horstmann 1998)).

The seasonal pattern for DDT accumulation in the wax might be explained by the higher tendency to particle association of this compound, and that the concentrations of particles in the air is very much higher during winter than summer. The decrease in spring could then be explained by washoff of the particles. The underlying general concentration increase is interpreted as the sorption of DDT from the gas phase.

The more or less linear concentration increase of the contaminants in the internal lipids is interpreted as caused by a continuous diffusion of these compounds to the internal tissues. This

is indicative that there is very little transference of these compounds from the air via the stomata to the internal tissues. The stomata are generally more open during the summer season and this should be reflected in higher accumulation rates in the internal tissues during the summer if the stomatal conductance is of importance.

The higher accumulation rates of gaseous organochlorines in the wax observed here during the warm season are difficult to explain from a fugacity point of view (Frank Wania, pers. comm.). One explanation would be that the properties of the epicuticular wax changes during the warm season e.g. by the presence of high amounts of monoterpenes. We know from other investigations that the levels of terpenoids in the needles can be several times higher during the warm season than during the winter. However, the terpenoids will not affect the dry weight determinations substantially, since they will evaporate during the drying process. It is possible that high amounts of terpenoids in the needles will alter the wax in such a way as to increase the sorption and/or diffusion rates in the cuticle to cause the observed uptake phenomena.

References

Ericsson A (1979). *Phys Plant* 45:270-280

Haugen J-E, Wania F, Ritter N, Schlabach M (1998) *Environ Sci Technol* 32:217-224

Kylin H (1994) (Thesis) *Airborne Lipophilic Pollutants in Pine Needles*. Stockholm Univ. ISBN 91-7153-197-1

MachLachlan M, Horstmann M (1998) *Environ Sci Technol* 32:413-420