

Vegetation/soil partitioning of semivolatile organic compounds

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Introduction

Numerous semivolatile organic compounds are released into the environment by their use or by emissions from various sources. Their different physico-chemical properties are responsible for a different behaviour and fate in the environment. These properties are therefore important parameters to be evaluated before a new chemical is put on the market. The present contribution deals with the different partitioning of a number of semivolatile organic compounds between spruce needles and forest soil of remote forest sites and its relation to the different physico-chemical properties of the investigated compounds.

Methods

Spruce needles representing one growing period (1st needle age class taken in October) and the corresponding humus layer were sampled at 25 background forest sites located far away from settlements, factories and public roads. In addition, samples of the underlying mineral soil layers 0-5 cm and 5-10 cm were taken at five of these sites. The samples were investigated for their concentrations of PCDD/F, PCB, PAH, HCB and HCH (analytical methods are given in [1,2]). The ratios between the concentrations in the needles and the concentrations in the humus layer of each site were calculated. This was done for all compounds which showed detectable concentrations for both the needles and the humus layer, and with available data for the chosen physico-chemical parameters, vapour pressure and n-octanol/water partition coefficient. Data for these parameters were taken from [3] (PCDD/F), [4] (PAH) and [5] (α -, γ -HCH, HCB).

Results and Discussion

Nearly all compounds with vapour pressures ($\log p$) higher than about -3 and all compounds with n-octanol/water partition coefficients ($\log K_{ow}$) lower than 5 showed a higher mean concentration in the spruce needles than in the humus layer. This includes the compounds α -, γ -HCH, fluorene, anthracene, phenanthrene (figure 1). The few exceptions to these rules were

HCB with a higher mean concentration in the needles but log Kow of about 6, and fluoranthene as well as pyrene with log p of about 3 and lower mean concentrations in the needles. All other less volatile or more hydrophobic compounds were detected with higher concentrations in the humus layer. The log-transformed mean ratios "concentrations in the needles/concentration in the humus layer" (log cN1/cO) of all compounds show a very good correlation with both physico-chemical parameters. These ratios can be described by equations 1 and 2 with a goodness-of-fit (R²) of 0.69 (figure 1).

$$\log (cN1/cO_x) = 0.740 + 0.272 \cdot \log p_x \quad (1)$$

$$\log (cN1/cO_x) = 1.307 - 0.274 \cdot \log Kow_x \quad (2)$$

cN1/cO_xratio "concentration in spruce needles/concentration in the humus layer" of compound x

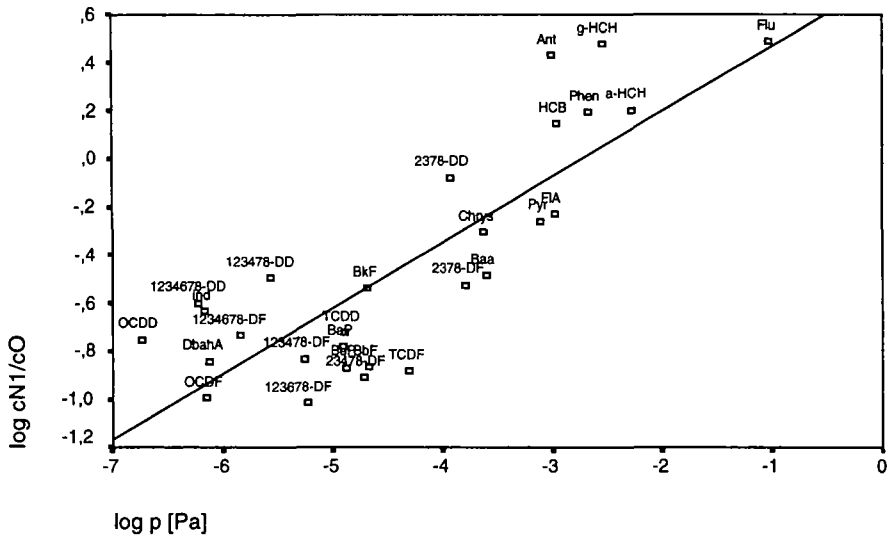
p_x vapour pressure of compound x [Pa]

Kow_x n-octanol/water partition coefficient of compound x

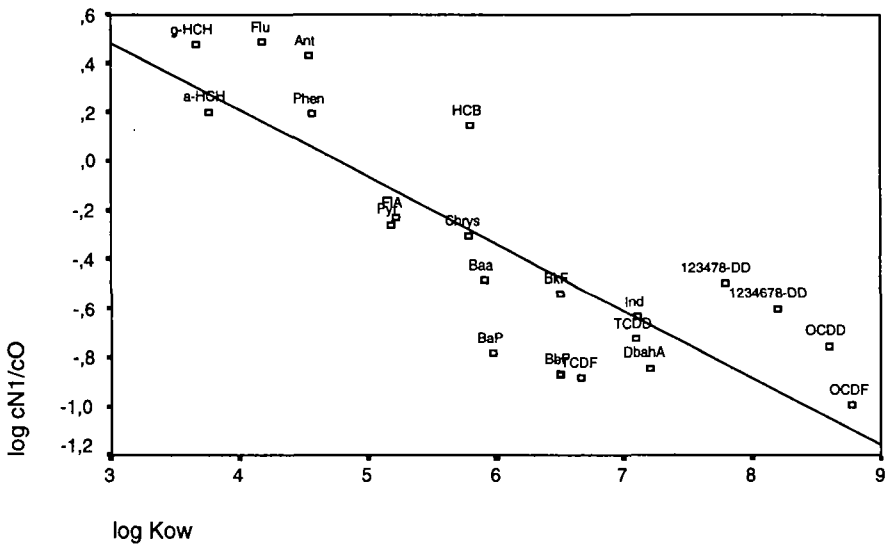
It has to be taken into consideration that these equations are valid for the given basic conditions (range of physico-chemical properties, background sites, site characteristics, 1st needle age class of Norway spruce taken in October, whole humus layer of forest sites stocked to 100 % by Norway spruce, etc.). Furthermore, the concentration ratios represent means of the results for 25 sites. For nearly all of the investigated sites significant correlations between these parameters have been identified, too, but the regression lines differed slightly from each other.

The results indicate that the fate of semivolatile organic compounds released into the terrestrial environment can be divided into two groups by their different properties. More volatile and less hydrophobic compounds are accumulated to a higher extent in half year old needles (being mainly influenced by vapour phase concentrations of the atmosphere during this period [6]) than in forest humus layer (being mainly influenced by litterfall, dry and wet deposition over several years). The reasons for this result might be related to several losses of these compounds in the forest soil, e.g. volatilisation, transfer processes in soil (see further down), and a comparably quicker uptake into the needles compared to the compounds with lower vapour pressure and higher n-octanol/water partition coefficients. Less volatile and more hydrophobic compounds are pronouncedly more accumulated in the humus layer than in the needles, representing one growing period. These differences have major implications for the environmental impact of the individual compounds. For instance, the substitution of a more toxic, less volatile and more hydrophobic semivolatile organic compound by a less toxic, more volatile and less hydrophobic compound might lead to less accumulation in soil, but to a higher uptake of this compound by herbivores.

As can be seen, the calculated ratios for PCDD/F (figure 1 and 2) do not correlate with log p and log Kow. In a previous paper the unexpected higher relative shares of lower chlorinated PCDD/F in the humus layer compared to the needles has been discussed [7]. The reasons for this result are not fully understood. However, this finding is supported by an investigation of the PCDD/F deposition in a forest and an adjacent clearing, which revealed a clearly higher input of lower chlorinated PCDD/F under spruce canopy than on an adjacent clearing, which could be attributed only to a small part to litterfall [8,9]. If just the PAH are taken into consideration, the goodness-of-fit can be improved (compare R² in figure 3 and 1).



$R_{sq} = 0,6850$



$R_{sq} = 0,6915$

Figure 1: Correlation between the mean ratios "concentration in the needles/concentration in the humus layer" (cN1/cO) and vapour pressure (above) and n-octanol/water partition coefficient (below) of several semivolatile organic compounds (PCDD/F: -DD, -DF; PAH: abbreviations in figure 3)

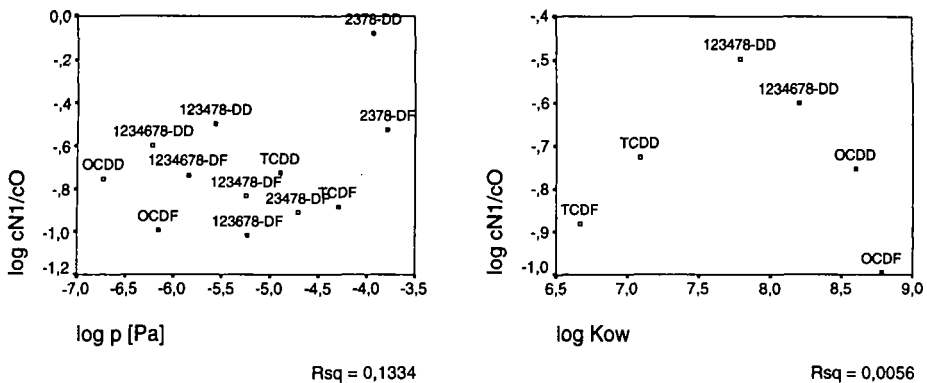


Figure 2: Scatterplots of the mean ratios "concentration in the needles/concentration in the humus layer" (cN1/cO) and vapour pressure (left) and n-octanol/water partition coefficient (right) of several PCDD/F

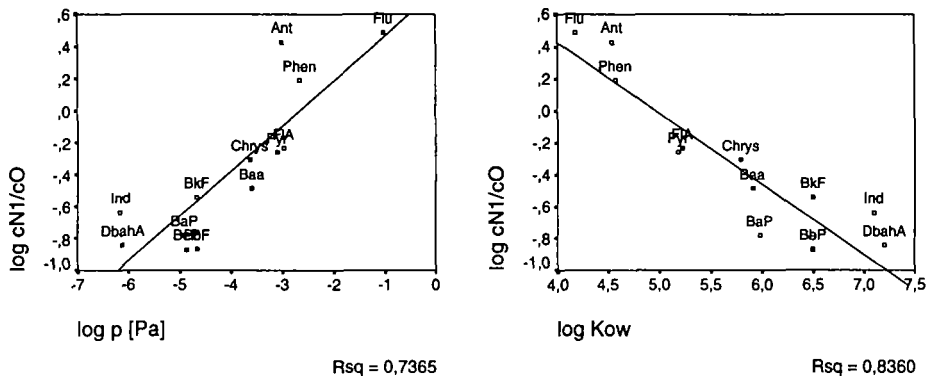


Figure 3: Correlation between the mean ratios "concentration in the needles/concentration in the humus layer" (cN1/cO) and vapour pressure (left) and n-octanol/water partition coefficient (right) of several PAH (Flu: fluorene, Ant: anthracene, Phen: phenanthrene, FIA: fluoranthene, Pyr: pyrene, Chrys: chrysene, Baa: benzo(a)anthracene, BbF: benzo(b)fluoranthene, BkF: benzo(k)fluoranthene, BaP: benzo(a)pyrene, BeP: benzo(e)pyrene, Ind: indeno(1,2,3-c,d)pyrene, DbahA: dibenzo(a,h)anthracene)

Indications for further behaviour in soil:

The mean relative PCB and PAH patterns of the five thoroughly investigated sites clearly show the importance of different properties of the compounds for transfer in soil. The higher shares of the less chlorinated PCB 28 and PCB 52 in the mineral soil layers compared to the humus layer indicate a better transfer of these compounds in soil compared to the highly chlorinated PCB 153 and PCB 180, which show comparably low shares in the mineral soil layer 5-10 cm (figure 4). These findings are supported by a previous investigation of soil profiles [10]. A similar result has been shown for PAH: The share of PAH with three rings is higher in the layer 5-10 cm than in the soil layers above. The result for PAH with five rings is the other way round. However, it is remarkable that PAH with six rings show about the same shares in

all three layers (figure 4). Together with similar findings of [4,11] this result might be explained by a better soil transfer of these PAH by dissolved organic matter.

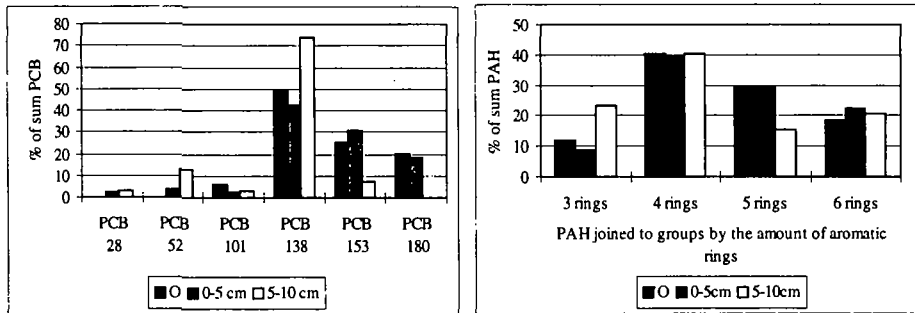


Figure 4: Mean relative PCB and PAH patterns in the humus layer (O) and in the mineral soil layers 0-5 cm and 5-10 cm

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