Changes of PCDD/F Homologue Profiles from Forest Canopy to Forest Soil

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Abstract

Nearly all of 25 raw humus samples of background forest sites had lower ratios of PCDD/PCDF and "highly chlorinated/low chlorinated" PCDD/F than the corresponding samples of one year old spruce needles. Within the row 1st - 2nd - 3rd needle age class - raw humus the ratio "highly chlorinated/low chlorinated" PCDD/F shows a tendency to decrease. Because of the known homologue profiles of deposition, gas-phase and particulate matter and the differences of indication between raw humus and spruce needles we assume that the homologue profiles of the total deposition under forest canopy even without litterfall has for unknown reasons higher shares of low chlorinated PCDD/F than the one of uncovered areas. This is an additional reason why forest soils have higher PCDD/F-concentrations in toxic equivalents than agricultural soils.

Introduction

Investigations revealed that the deposition under forest canopy has higher ratios TCDF/OCDD than the one of a clearing (1). In general the PCDD/F deposition under spruce canopy has a higher share of PCDF than the one of a clearing and a beech forest (2). The reasons for that are not completely understood. These results let expect that the ratios PCDD/PCDF and "highly chlorinated/low chlorinated" in forest soils are lower than the ones in adjacent soils of uncovered areas. Soil investigations confirm this (3). In this paper we show the change of relative homologue profiles from the first to the third needle age class and from the raw humus to the soil layer 5-10 cm.

Methods

Raw humus and one year old spruce needles of 25 Austrian background forest sites were taken and investigated for their concentrations of PCDD/F. At five of these sites two and three year old needles and the mineral soil layers 0-5 cm and 5-10 cm were investigated, too. Sampling methods and chemical analysis are described in (4).

Results

The PCDD/F concentrations in the raw humus are about ten times higher than the ones of the one year old spruce needles (4). This is due to the decomposition of organic matter in the humus

layer, a longer exposition period of the raw humus and the decisive additional influence of dry and wet deposition of PCDD/F for the raw humus concentrations in contrast to the spruce needles.

The ratios "highly chlorinated/low chlorinated" and PCDD/PCDF in raw humus are lower than the corresponding ones in the one year old spruce needles of most of the 25 sites (Figure 1, 2, "highly chlorinated" means the sum of hexa- to octachlorinated PCDD/F, "low chlorinated" means the sum of TCDD, TCDF and PeCDF). The same can be calculated from the results of an investigation by (5). These results are remarkable because in view of the homologue profiles for gas-phase, particulate matter, dry and wet deposition of background areas (6, 7, 8) and the assumption of main indication differences of these two compartments one would expect the contrary. The raw humus concentrations should be mainly influenced by deposition, the spruce needle concentrations by the atmosheric concentration (in particular by the gas-phase concentrations) (9, 10).

PCDD/F homologue profiles of the gas-phase of background areas have a dominant share of lower chlorinated furans and have a higher amount of PCDF than PCDD. In contrast the particulate matter of the atmosphere, dry and wet deposition have a dominant share of highly chlorinated dioxins and a higher amount of PCDD than PCDF (6, 7, 8). Litterfall contributes just 30 % of the total PCDD/F deposition under forest canopy (9). Figure 3 indicates that the homologue profiles of the spruce needles are more similar to the one of total atmosphere (gas-phase plus particulate matter) than to the one of the gas-phase. Nevertheless the homologue profiles of raw humus representing an age of several years and being influenced by the homologue profiles of dry and wet deposition should have higher ratios of PCDD/PCDF and "highly chlorinated/low chlorinated" than the corresponding spruce needles. We found the opposite (Figure 1, 2). These results are confirmed by the mean relative PCDD/F homologue profiles of the different needle age classes and the raw humus of 5 thoroughly investigated sites. The share of the low chlorinated homologues increases from the first needle age class to the raw humus and decreases in the mineral soil layers below (Figure 3). PCDD show a tendency to decrease from the one year old needles to the deepest mineral soil layer, PCDF a tendency to increase. The reason for that is the increasing share of low chlorinated homologues with increasing needle age and the increasing share of high chlorinated furans with increasing soil depth (Figure 3).

It is not clear which processes are reponsible for these results. Different conditions of uptake, sorption, transfer and turn-over in both compartments could play a role. An important explanation can be the particular conditions for deposition under forest canopy. The PCDD/F homologue profile of deposition under canopy clearly differs from the one of adjacent clearings. The deposition under spruce canopy has a higher share of PCDF than the one of adjacent clearings and under beech canopy. Litterfall alone cannot explain this discrepancy between these homologue profiles (2). The change of homologue profiles from one year old needles to the raw humus in this paper indicates as well that dry and wet deposition under canopy without litterfall has a higher share of low chlorinated PCDD/F than the one of uncovered areas. The reasons for this are not clear. Erosion of cuticular waxes of needles in the canopy and the additional deposition of PCDD/F with this erosion are seen as a possible explanation (2). This assumption is confirmed by the fact that the PCDD/F concentrations in spruce needles do not increase with needle age at all of the five sites of this investigation, which is in contrast to results from (11) but corresponds to results from (12, 13). Indeed erosions of cuticular waxes could therefore be an

explanation that PCDD/F concentrations in needles decrease with increasing exposure of spruce needles represented by different needle age classes and that the homologue profiles of deposition under canopy is influenced by this erosion, too. The different polarity of the atmosphere in forests as compared to the one of unstocked areas which is due to the emission of volatile organic compounds by the trees could be another factor accounting for the differences of the deposition homologue profiles. A lot of research still needs to be done in order to answer all these questions. These results are particularly important since they show that the already comparably higher PCDD/F deposition in forest soil caused by the pollutant filtering by crown canopy in addition shows a higher share of more toxic low chlorinated PCDD/F than the deposition in uncovered areas. This is an additional reason why forest soils have higher PCDD/F concentrations in toxic equivalents than agricultural soils.

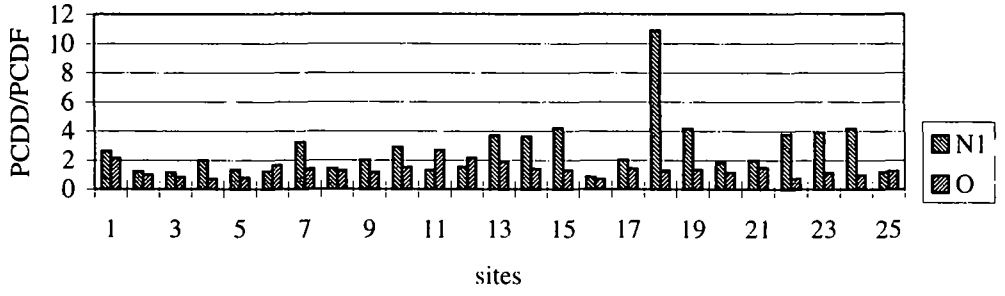

Figure 1) PCDD/PCDF ratios in one year old spruce needles (N1) and in the humus layer (O) of Austrian background forest sites

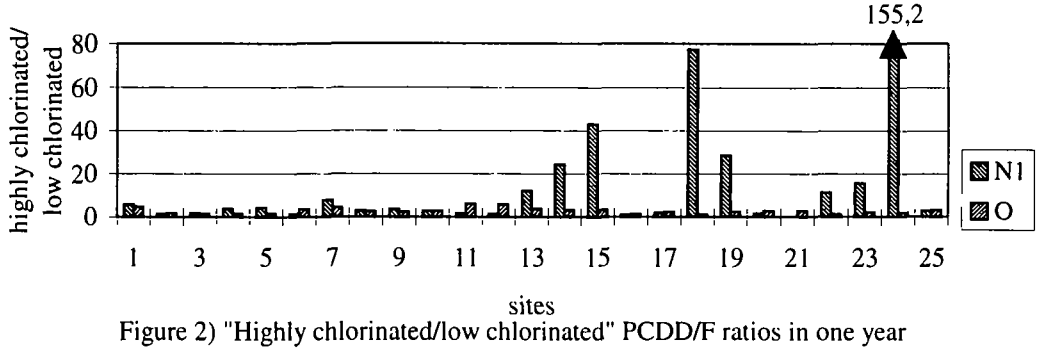

Figure 2) "Highly chlorinated/low chlorinated" PCDD/F ratios in one year old spruce needes (N1) and in the humus layer (O) of Austrian background forest sites

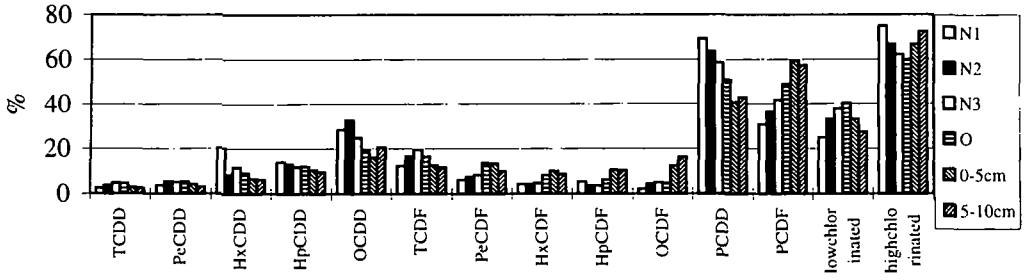

Figure 3) Mean relative PCDD/F homologue profiles of several spruce needle ages (N1-N3), the humus layer (O) and the mineral soil of Austrian background forest sites (n=5)

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