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The Importance of Long-Range Transport for the PCDD/F Pollution of High Alpine Areas in Austria

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Abstract

The ratios of highly chlorinated PCDD/F to low chlorinated PCDD/F and PCDD to PCDF of PCDD/F in spruce needles indicated that the PCDD/F pollution of high alpine sites of Austria during the growing period originate from far away sources. The group of these sites had significantly higher PCDD/F concentrations in the needles than the ones being under influence of regional sources, too. We assume that long-range transboundary air pollution can be a main additional reason for these results. The calculations for raw humus showed that emission reducing measures in Austria will be successful in reducing the total PCDD/F input into some of the Austrian background sites. However, the homologue profile of the most polluted raw humus again indicated far away sources of the PCDD/F pollution.

Introduction

An inventory of heavy metals in Austrian forest soils indicated that concentrations of lead and cadmium increase significant with increasing altitude (1). Investigations of the differences of PCDD/F pollution with changing altitude are rare. An investigation of the pollution of forest ecosystems with semi-volatile organic pollutants along an altitude gradient showed that the concentrations of these substances in raw humus and spruce needles were higher at the site in highest altitude. The PCDD/F homologue profiles in the spruce needles of the highest site were different from those of the sites below and indicated long-range transport as source of pollution (2). The investigation of PCDD/F homologue profiles can give good indications for the origins of PCDD/F pollution (3). Therefore we did a statistical examination of PCDD/F homologue profiles and homologue ratios and compared these results with the corresponding concentrations of PCDD/F in the spruce needles and raw humus of (4) to get an idea about the contribution of long range transport for the pollution of Austrian background areas with PCDD/F. In this paper a new method for the assessment of long-range transport by homologue profiles is presented.

Methods

This investigation uses the same PCDD/F values of one year old spruce needles and raw humus of Austrian background forest sites given in (4). Analytical methods and sampling is described there.

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As for the statistical calculations we carried out correlation analyses (Spearman Rank), cluster analyses (Average linkage between groups, Ward), discriminant analyses and non-parametric tests to identify group differences (Mann-Whitney test, Kruskal-Wallis test). For the multivariate calculations the relative homologue profiles were calculated and the percent-values of each homologue of all sites were z-scaled (mean = 0, standard deviation = 1). For the clustering process we used the squared euclidian distance as distance measure. The number of cluster was chosen on account of the results of the dendrograms, the distance values representing the fusion of sites to clusters and the F-values of the clusters. The checking of the resulting cluster solution by discriminant analysis revealed that the homologue profiles of the individual clusters differ significantly.

Results for the spruce needles

Significant positive correlations were found between the concentrations of the higher chlorinated PCDD/F homologues. Weak significant positive correlations were found between TCDD, TCDF and PeCDF. The tetrachlorinated PCDD/F showed significant negative correlations with some highly chlorinated homologues, especially with the hexa- and heptachlorinated homologues. This indicates that the sites with low concentrations of TCDD and TCDF are the ones with comparably higher concentrations of the highly chlorinated homologues. This result is somehow unexpected and surprising and leads to the assumption of a good separation into groups of sites with clearly different homologue profiles. To better illustrate the meaning of this result we did further calculations.

In a first step we added the homologue concentrations of the TCDD, TCDF and PeCDF ("low chlorinated" PCDD/F) of each site and the ones of the hexa- to octachlorinated homologues ("highly chlorinated" PCDD/F). The correlation analysis showed that PeCDD has a position in between these two groups. Therefore it was not included in these calculations. Afterwards we calculated the ratio between "highly chlorinated" and "low chlorinated". Because of the values of these ratios the sites were divided into a group with ratios <10 and a group with ratios >10. This division value separates the sites into a group with relatively high ratios (one third of all sites) and into a group with ratios close to 2 (two thirds of all sites, Figure 1). It was checked if these groups differ in the ratios PCDD to PCDF and in the PCDD/F-concentrations.

The group of sites with a higher "highly chlorinated/low chlorinated" ratio has a significantly higher PCDD/PCDF ratio than the other group (Figure 2). (5) pointed out that the PCDD/PCDF ratios in spruce needles of background areas are higher than the ones in spruce needles of conurbations. Investigations of (6) and (7) found that by the transport of air masses away from PCDD/F sources the ratios PCDD/PCDF and "highly chlorinated/low chlorinated" in the atmosphere increase. The selective washing out of PCDD/F bound to particulate matter by rain leads to a decrease of low chlorinated PCDD/F in atmosphere during the transport of air masses (8). Therefore the results of this investigation indicate that the spruce needles of the group of background sites with ratios >10 were polluted by "older" and therefore longer transported air masses during the growing period.

This assumption is confirmed by the fact that the sites of the group >10 are located significantly higher than the ones of the other group (Figure 3). Nearly all high-alpine sites are within this group. Results of (9) reveal that with decreasing air temperature the share of low chlorinated PCDD/F in the gas-phase of atmosphere decreases while their share in particulate matter

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increases. The highly chlorinated PCDD/F are always - even at higher temperatures - bound in particulate matter of the atmosphere. Spruce needles accumulate lipophilic organic compounds out of the gas-phase (10). Temperature decreasing with increasing altitude could therefore be a reason for the higher "highly chlorinated/low chlorinated" ratios found in spruce needles of elevated alpine sites. Because of the dominant share of highly chlorinated PCDD and low chlorinated PCDF in the atmospheric homologue profile of background sites temperature decreasing with altitude could be a reason for the higher PCDD/PCDF ratios found in spruce needles of the elevated sites, too. Then one should expect the PCDD/F concentrations of the colder high alpine sites to be lower, because there are - compared to lower and therefore warmer sites - more PCDD/F bound to particulate matter and spruce needles accumulate such compounds out of the atmospheric gas-phase. We found the opposite.

The group of high alpine sites had significantly higher PCDD/F concentrations in the needles than the group of the other sites. This is true for the total PCDD/F and the concentrations given in toxic equivalents (Figure 4, 5).

These results could be confirmed by cluster analysis and can be summarized as follows: Concentrations and PCDD/F ratios in spruce needles of Austrian background sites representing the growing period differ because of the altitude of the sites and the distance of transport of air masses which are responsible for the PCDD/F pollution. Spruce needles of high elevated alpine sites which are polluted by air masses from longer range transport and therefore by far away sources show higher ratios of PCDD/PCDF and "highly chlorinated/low chlorinated" PCDD/F than the group of the other sites and have higher concentrations of PCDD/F. These results indicate the importance of long-range transport for the pollution with PCDD/F and the unfavourable conditions of an alpine country as far as the PCDD/F load is concerned. The results for an alpine altitude gradient of an exposed slope in a background area correspond to these results (2).

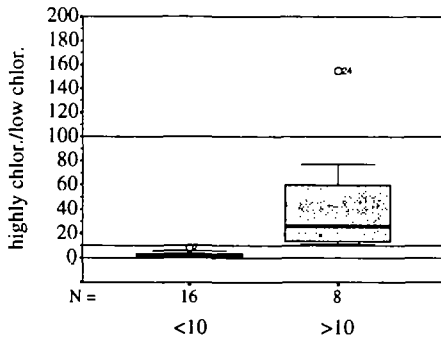
Results for the raw humus

Between all the concentrations of the individual homologues in raw humus there were significant positive correlations. Again the correlations between the highly chlorinated homologues and between the low chlorinated homologues were higher than between these groups. Compared to the mentioned results for atmosphere and spruce needles investigations of PCDD/F in the raw humus or forest soils of sites show that the ratios PCDD/PCDF and "highly chlorinated/low chlorinated" increase with increasing distance from the sources (11, 12). Therefore we did the same calculations for the raw humus as described above.

The results show that the range of ratios "highly chlorinated/low chlorinated" is smaller than the one for the needles. We therefore used the median of the ratios for separating the sites into two groups. Again the group with higher "highly chlorinated/low chlorinated" ratios has significant higher PCDD/PCDF ratios (Figure 6). These two groups do not significantly differ in PCDD/F concentration and represented altitude of the sites, though. We assume that additional regional emission reduction measures in Austria are necessary to reduce the PCDD/F load into Austrian background areas. This is particularly true for sites which are not close to the border but show higher PCDD/F concentrations and low ratios. The most polluted raw humus is within that group of ratios and homologue profiles which indicate very distant sources and is situated close to the border.

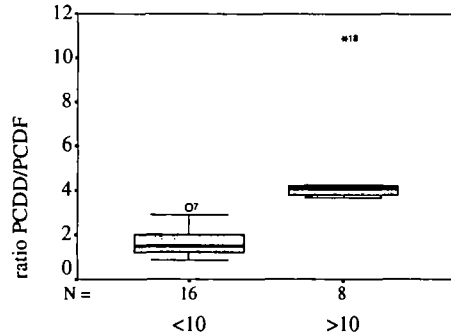
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Sites close to the border showed partly significantly elevated PCDD/F concentrations in raw humus and spruce needles of Austrian regions which are sparsely populated and without big industrial plants. The main wind directions indicate that the main PCDD/F load of these sites results from transboundary air pollution (4). The mass balance of PCDD/F sinks in Austrian forest compartments and annual fluxes and a comparison of these estimates with emission balances reveals that there is much more annual PCDD/F input into the Austrian landscape than the amount of the annual Austrian emissions (13). These results together with the ones presented in this paper clearly point out that long-range transboundary air pollution - in addition to the Austrian PCDD/F emissions - plays an important role for the PCDD/F load of the Austrian landscape and elevated mountainous areas.



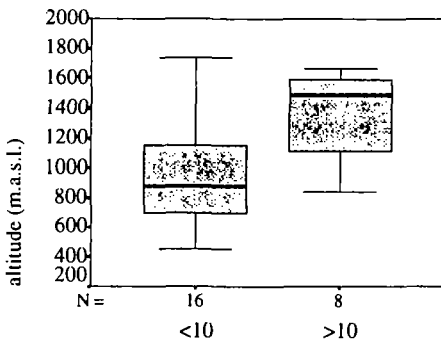
highly chlorinated/low chlorinated

Figure 1) Ratio "highly chlorinated/low chlorinated" PCDD/F in spruce needles of Austrian background sites



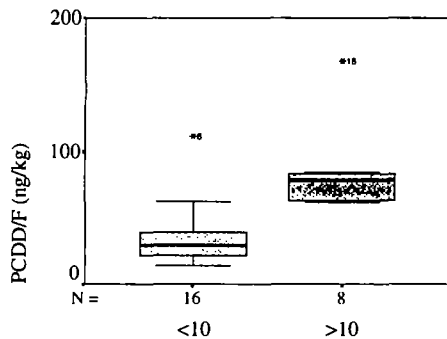
highly chlorinated/low chlorinated

Figure 2) Ratios "highly chlorinated/low chlorinated" PCDD/F and PCDD/PCDF in spruce needles of Austrian background sites



highly chlorinated/low chlorinated

Figure 3) Ratio "highly chlorinated/low chlorinated" PCDD/F in spruce needles and regard to the altitude of Austrian background sites



highly chlorinated/low chlorinated

Figure 4) Ratio "highly chlorinated/low chlorinated" PCDD/F and PCDD/F concentrations in spruce needles of Austrian background sites

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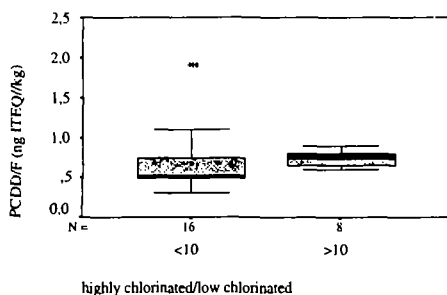


Figure 5) Ratio "highly chlorinated/low chlorinated" PCDD/F and ITEQ in spruce needles of Austrian background sites

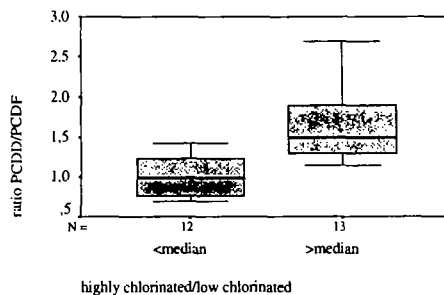


Figure 6) Ratios "highly chlorinated/low chlorinated" PCDD/F and PCDD/PCDF in raw humus of Austrian background sites

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