Alpine PCDD/F contamination along altitudinal gradients

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Abstract

No general altitudinal trend of PCDD/F contamination emerged from the examination of background environmental samples from the Alpine region. Instead, vertical trends did not only diverge between different height profiles, but also between needle and humus samples. However, humus PCDD/F homologue patterns showed rather consistent altitudinal traits like the increase of the less chlorinated PCDD/F fraction and dioxin:furan-ratios with height. Needle homologue patterns had a higher share of tetrachlorinated furans (TCDF) than humus, especially in needles with high PCDD/F content.

Introduction

Emissions of polychlorinated dibenzo(p)dioxins and polychlorinated furans (PCDD/F) are subject to long-range atmospheric transport. Net fluxes of airborne semivolatile organic compounds (SVOCs) to the ground are favoured by the climate at high lati- or altitudes, which renders mountainous regions particularly susceptible to SVOC contamination[1]. Precipitation and temperature, which govern the deposition of SVOCs in mountains, vary with elevation. Accordingly, altitudinal gradients have been described for a number of SVOCs. Not only did the existence of such gradients raise awareness of the role of mountain ranges in global SVOC transport but their formation and variability helps to understand and predict SVOC contamination at high altitudes.

Materials and Methods

In the framework of the international research project MONARPOP[2,3], PCDD/F were measured in environmental samples (six month old Norway spruce needles, humus, mineral soil) from forests of the Alpine region. Sites were generally selected away from any evident sources except one height profile ("Klosters") which ascended from the environs of a small town[a]. In addition to the bulk of sampling sites at a nominal height of 1400 m a. s. l., seven height profiles of 4–5 plots were examined. The height profiles started at 732–1300 m a. s. l. and covered vertical ranges between 400 and 820 m. The concentrations of tetra- to octachlorinated homologues were determined with isotope dilution, using high resolution GC/MS (details of sampling and analysis in[4]).

Results and Discussion

Contamination levels in humus or needles did not follow a consistent trend over all height profiles. Instead, trends, where detectable, could contrast between height profiles: concentrations could increase with elevation at one profile and decrease at the other (compare, e. g., profiles "Klosters" and "Wechsel" in Figure 1). The vertical trends of humus PCDD/F concentrations remained essentially the same, whether related to humus dry

[a]coordinates for 3 D-display of height profiles with Google Earth™ are downloadable at http://www.monarpop.at/downloads/MONARPOP_height_profiles.kml

mass or total organic carbon (TOC) content (Figure 1). Altitudinal variation of PCDD/F levels was thus less consistent across the alpine region than, e. g., concentrations of organochloropesticides [5] or chloroparaffins [6]. The ongoing and unintentional release of PCDD/F as opposed to the long discontinued use of other SVOC might have led to a variety of regional sources whose influence might attenuate climate as the major factor governing background alpine PCDD/F pollution.

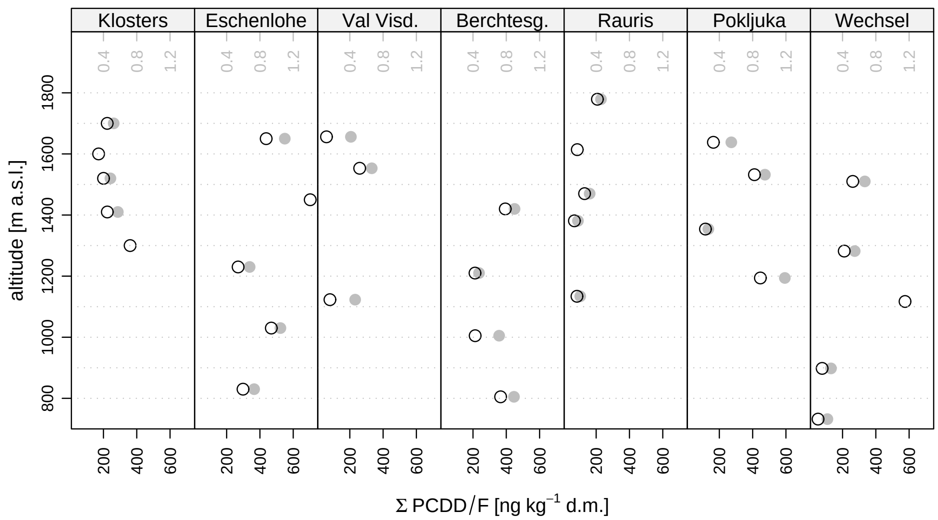

Figure 1: Altitudinal variation of the PCDD/F content of forest humus from background sites. Grey symbols and scales show concentrations in organic carbon content (µg PCDD/F per kg TOC; two values > 1.6 at "Eschenlohe" and "Wechsel" omitted for clarity).

Qualitatively, however, the different height profiles shared some common traits. For example, the furan:dioxin ratio in humus usually increased with height (Figure 2), regardless of absolute PCDD/F levels. With increasing elevation, the humus PCDD/F pattern also shifted towards the lighter (4–5 chlorines) homologues (Figure 3). Both phenomena agree with a presumed cold induced atmospheric transition of the more volatile compounds (furans vs. dioxins, lighter vs. heavier homologues) into the particulate phase which is deposited more efficiently. The two height profiles which deviated from this trend ("Val Visdende" and "Pokljuka") had an altogether peculiar PCDD/F pattern (see below).

Grouping the plots of all height profiles by humus PCDD/F pattern into three clusters A–C showed that some of the profiles maintained a similar homologue profile across all height levels. Other profiles, in turn, were less homogeneous: some of their plots were (by homologue pattern) more similar to another height profile than to their neighbouring plots (Figure 4). Sites of cluster A had the highest share of dioxins. Cluster C was characterised by unusually high furan contents (Σ PCDF > Σ PCDD) and, among these, a notable contribution of the heavy furans. Cluster A plots were found at lower elevations, B plots at increased altitudes. The southern height profiles (Val Visdende and Pokljuka) with their higher average temperature consisted of C plots (Figure 4). Remarkably, the humus PCDD/F patterns allowed no conclusions on the contamination level, i. e., there were no significant clusterwise differences of total PCDD/F content.

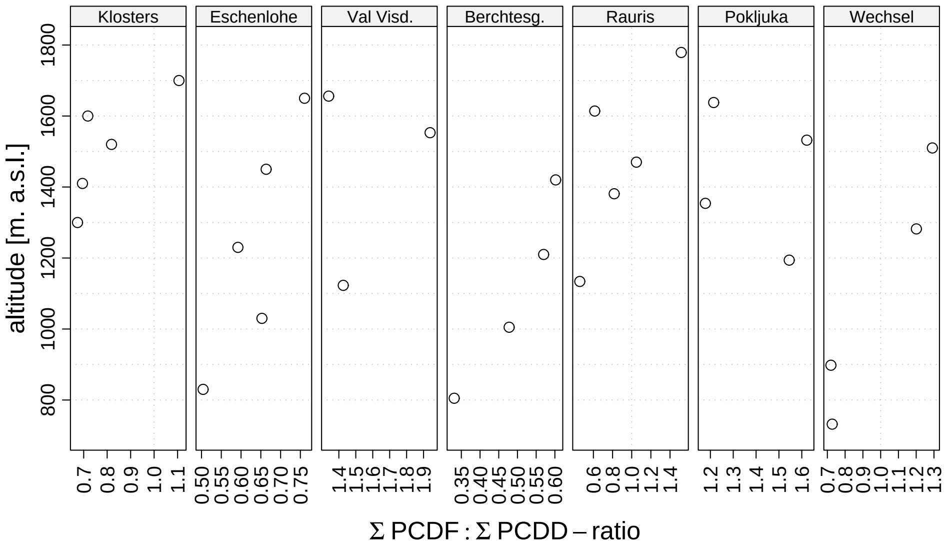

Figure 2: Altitudinal variation of the furan:dioxin-ratio in forest humus from background sites (one plot of profile “Wechsel” at 1117 m a. s. l. with extreme PeCDF content omitted).

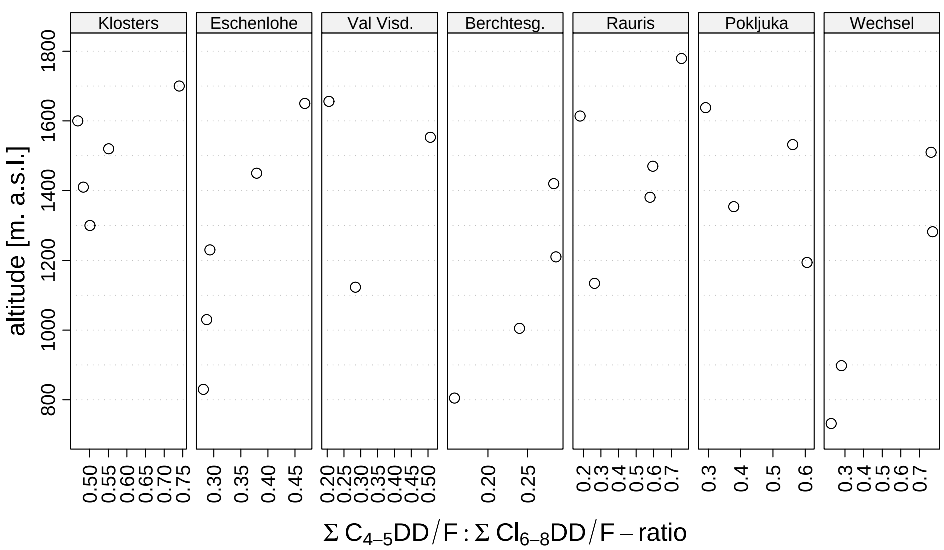

Figure 3: Altitudinal variation of light vs. heavy PCDD/F homologues in forest humus from background sites

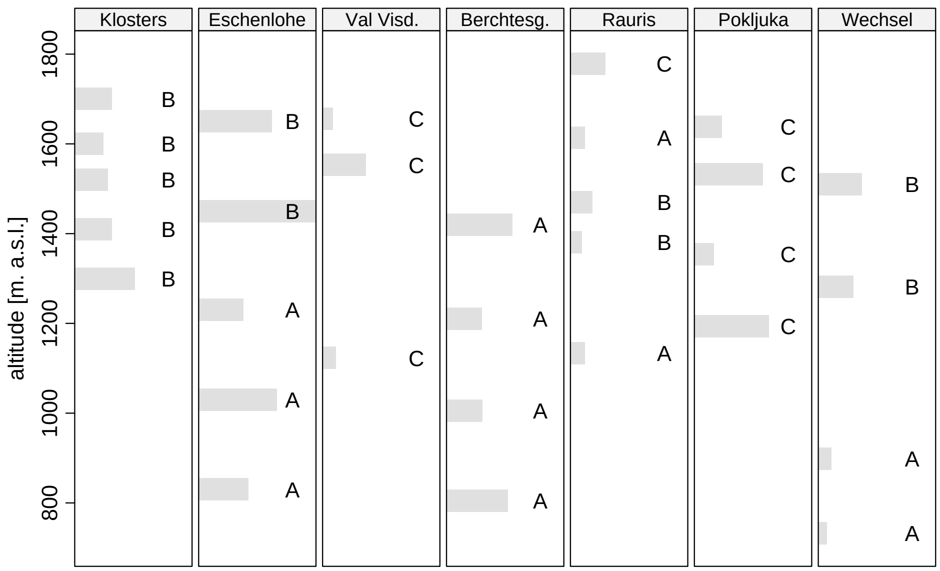

Figure 4: Similarity of PCDD/F homologue patterns across height profiles. Horizontal bars indicate PCDD/F contamination (relative to the maximum of 702 ng kg^{-1}d.m). observed at profile “Eschenlohe”).

Altitudinal variation of PCDD/F levels in 0.5 year old Norway spruce needles was as little consistent across height profiles as that of humus PCDD/F content (Figure 5). Comparison of Figures 1 and 5 also reveals that the inspection of needle and humus samples lead to entirely different estimates of vertical pollutation gradients. Confronted with these discrepancies between matrices, one has to consider that the needle samples delivered a “snapshot” of atmospheric pollution during the current vegetation period. Forest humus, especially that from coniferous stands, had accumulated PCDD/F over several years, thus reflecting the long-term situation and, other than the current year’s needles, the impact of domestic emissions during the heating season. At profile “Klosters”, e. g., PCDD/F levels in humus increased towards the populated valley bottom (Figure 1) which indicates that local emissions from wintertime domesting heating might supersede the contribution of long-range transport. Needle PCDD/F concentrations at this profile, although lacking a distinct vertical trend, peaked on the top of the profile, apparently governed by the interaction of altitudinal climate gradients with atmospheric PCDD/F burdens from long-range transport.

Not only PCDD/F levels but also homologue patterns differed between matrices: needle samples had a higher dioxin:furan ratio than humus. This has been reported earlier [7,8] and appears to be typical for remote sites. The furan fraction was dominated by the tetrachlorinated homologues (TCDF) in needles and the pentachlorinated ones (PeCDF) in humus. Cluster analysis of needle PCDD/F patterns revealed only two distinct site groups, one of which had significantly higher PCDD/F contents and was characterised by the dominance of the volatile TCDF (almost equalling the portion of OCDD). Needle PCDD/F patterns, where thus – in contrast to humus – connected to the degree of contamination.

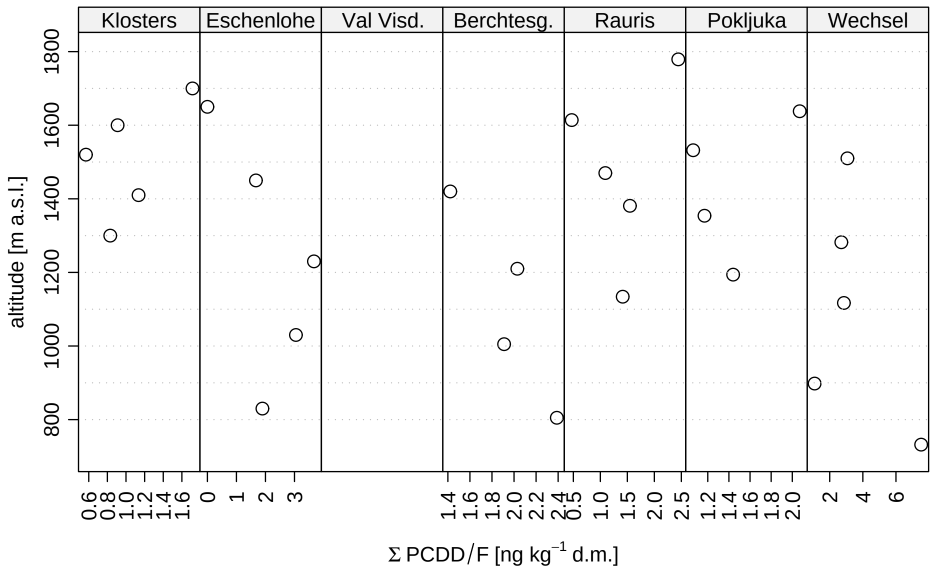

Figure 5: Altitudinal variation of the PCDD/F content of 0.5 year old Norway spruce needles from background sites (no full set of 2004 data available for profile "Val Visdende".) Note differing x-scales.

Acknowledgements

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[b] `http://www.monarpop.at`

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