Levels and profiles of PCDDs and PCDFs in environmental samples as determined in snow deposited in Northern Sweden

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Introduction

In recent years the interest in airborne organic pollutants has been increasing. Two types of compound classes found are polychlorinated dibenzo-*p*-dioxins (PCDDs) and the related dibenzofurans (PCDFs). Due to their recognized toxicity it is of interest to elucidate the behaviour of these atmospheric trace contaminants. The aim is to have a better understanding of their origin, finding out to what extent they are being transported, degraded, transformed or accumulated. Because of the problems associated with the sampling of deposited particulate matter[1], snow seems to be a promising matrix for trapping deposited material. For example evaporation (low temperature) and resuspension from local soils (frozen) may be minimized. The known PCDD/F sources today, predominantly combustion processes and production and use of contaminated chlorinated aromatic compounds, do not explain the levels of PCDD/Fs found in deposition samples and ambient air, as reviewed by Rappe 1991[2]. There seems to be a deficit in the mass balance. An investi-gation to address this has been performed on deposited snow by Marklund et al.[3]. Comparisons will be made with earlier results because of similar sampling sites and methods.

Material and methods

The samples have been taken at four sites in and around the city of Umeå in northern Sweden. The locations were chosen to show influence on deposition from possible nearby situated sources and long-range transport. We are trying to appoint specific sources responsible for the patterns found in the deposition (source identification). This can be done by working with local meterological parameters and wind trajectories. The snow samplers have been put out for time periods ranging from two to four weeks from february to april - 91, collecting all types of deposition at these locations simultanously. Precipitation came predominantly as snow. Three samples were taken at each site. The four locations were:

- A station on the seashore approx. 20 km east from town (Rural).
- On top of the towns water tower (High suburban, 3 km from of a MSWI-plant).
- On a roof in the town centre (Urban site).
- Just outside our offices (Suburban site).

The sampler consisted of $1m^2$ pieces of untreated cotton cloth in two layers. They were put directly on the ground, which was covered with snow. Each corner was attatched to a peg. In one sample a spiked cloth (^{13}C-PCDD/F) was used to make estimates of *in situ* losses. A number of meteorological parameters were measured, including wind, temperature and precipitation.

The three time periods represented different meteorological conditions. The first 15 day long period (P1), was cold with an average temperature of -11°C with almost no snowfall yielding mainly dry deposition. The second period (P2) was 21 days. It was warmer (-6°C average) with more precipitation, giving mixed deposition, but the wet deposition still came as snow. The third period (P3) was 28 days, was more humid with tempratures occationally above 0°C (-2°C average), with both rain-and snowfall.

The snow was collected, melted and filtered through a nylon filter and a poly-urethane-foam plug. The cloth and the PUF+filter was later extracted in a soxhlet apparatus. Clean-up of PCDD/F was done according to standard prodedures[4]. Isomer specific analyses of PCDD/F was made on HRGC/HRMS using a VG 70-250 S mass spectrometer in SIR mode. Additional analyses on these samples will be made on chlorinated biphenyls, polynucleir aromatic hydrocarbons and chlorobenzenes.

Results and discussion

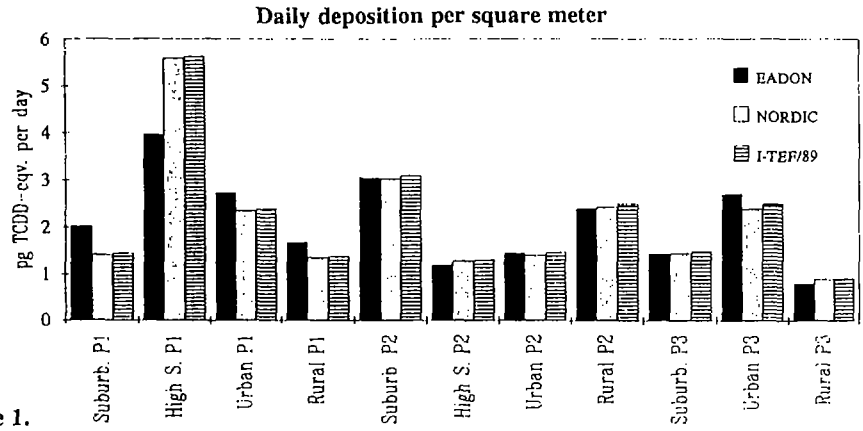

Figure 1.

The levels of PCDD/F found in the deposition (Figure 1) appear to be lower than previously noted in snow in Northern Sweden[3]. A crude estimation of the annual PCDD/F-fallout would be 1ng·TCDD-eqv.(I-TEF/89) $m^{-2}\cdot yr^{-1}$. Extrapolated on the whole of Sweden it would be about 500 g·of TCDD-eqvivalents per year, and this is about a fifth of what Marklund and co-workers found[3]. An explanation could be that the local incinerator since then has been eqipped with a dry scrubbing system to reduce its emissions. The use of leaded gasoline has also been decreasing during this time. It will be interesting to see if wind trajectories can support Egebäck et al.[5] in that the wind direction is of importance to PCDD/F-levels also in the deposition.

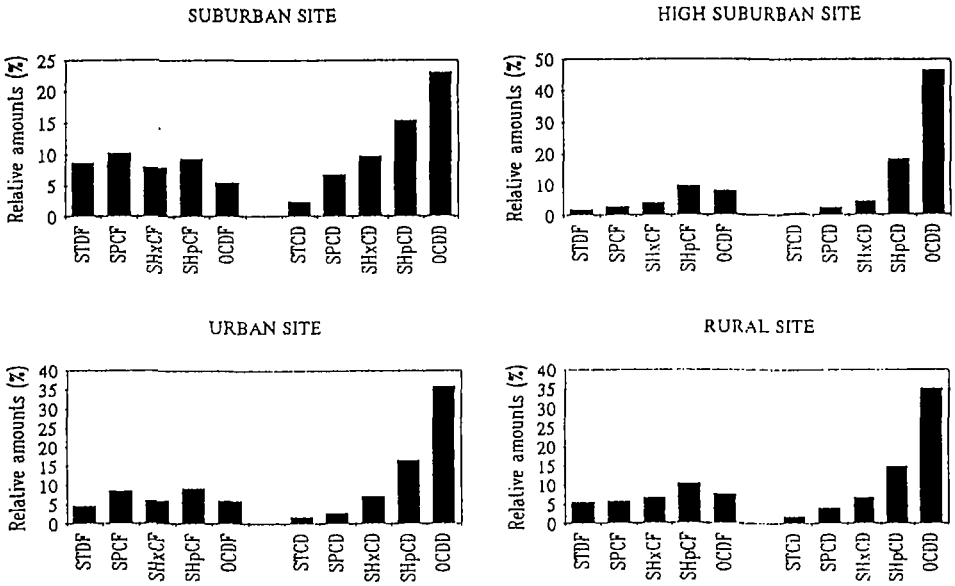

Figure 2

The columns depicted above represent the percentage of each congener group from the total PCDD/F content

The profiles obtained from this study are in general agreement with what has been found in rain[6]. We do find though, a more pronounced domination of the OCDD and other highly chlorinated congeners in these profiles (Figure 2). The urban site shows relatively small influence from local sources and looks somewhat like "aged" air, see rural site, while the suburban site is clearly affected by a local source.

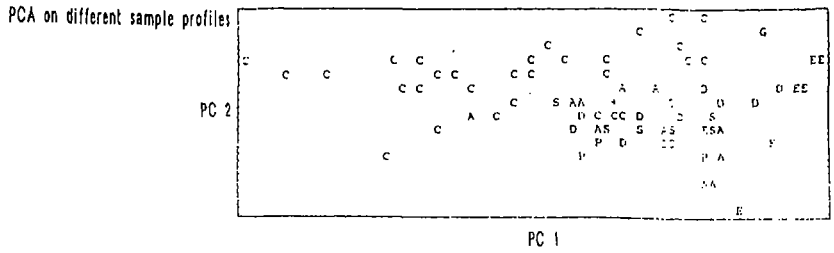

Figure 3. C= Combustion sources, P= Cutting oils, E= Environmental samples; sludge,run, ... water
G= Soil, S= Snow '86, D= Snow '91, A= Ambient air

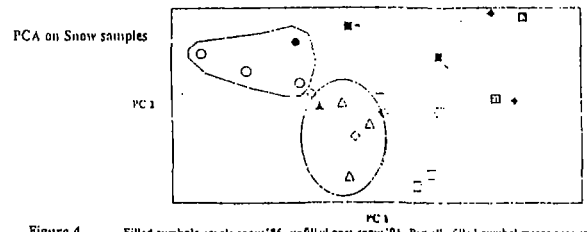

Figure 4. Filled symbols equals snow '86, unfilled ones snow '91. Partially filled symbol means near road. '86
○ High Suburban △ Urban □ Suburban ◇ Rural

Multivariate treatment of the data was made with the SIMCA 4.3 software. PCA-principal component analyses[7], yielded the scoreplots shown above. All concentrations have been normalized to the sum of PCDD/F in each sample. The variables used are the 2,3,7,8-substituted isomers (15) and the sum of each congener group of PCDD/Fs from tetra- to octachlorine (10). In Figure 3 we can see that depositon resembles ambient air closely, PLS analysis[7] gives a linear correlation (r^2=0,9). On the other hand it differs from both combustion[3], sludge[3] and soil[8] with regards to congener profiles. Looking at snow separately (Figure 4) we see differences between sites, where samples from the urban and the high suburban site respectively group together. It is also evident that car emissions have an effect on the profiles in the samples taken near a highway, but 100 m away the effect can not be seen.

Meteorology and source apportionment needs to be further examined, for examle with wind trajectories to account for the long-range transport, before final conclusions can be drawn.

An intriguing observation, concerning PCDD/Fs, is the shift in congener profiles towards a higher degree of chlorination when comparing combustion sources and deposition. This indicates that either combustion as a source is overrated, or that transformation during air transport is occuring to a large extent.

Further research is needed to clarify if there are any unknown sources for organic pollutants or how the transformation is occuring, explaining why deposition consists of the above mentioned congeners in the case of PCDD/Fs.

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