

Environmental deposition of PCDDs and PCDFs as determined by the analysis of Snow Samples from the North Part of Sweden

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Abstract

A series of snow samples have been analyzed. In all samples detectable levels of PCDDs and PCDFs were found. The congener profiles of the snow samples have been compared to combustion samples and ambient air samples. The results show that local sources of PCDDs and PCDFs can be identified in the general background levels of chlorinated dioxins and dibenzofurans in snow samples.

Introduction

The environmental deposition of PCDDs and PCDFs to the ground has become a matter of scientific and public concern during the last years. Models for the estimation of environmental deposition from known emissions sources are not in agreement with the actual levels found in the environment. Attempts to establish the significance of different sources have been made by analysis of soil, ambient air, spruce needles and sediment samples, however in these matrices the total deposition time is difficult to measure or estimate. Earlier we have reported on analysis of snow samples collected after accidental fires to establish the deposition of PCDDs and PCDFs. In this paper we introduce snow samples as a method of measuring background deposition of PCDDs and PCDFs in the environment.

Snow samples have shown to be an excellent matrix for environmental deposition studies during the winter season. The cold environment prevents the PCDDs and PCDFs from evaporation and slow down the degradation rate. The snow is very easy to collect and the deposition time can be defined by keeping a record of the meteorological data.

Experimental

Snow samples were collected 1) close to a heavy traffic highway passing through Umeå, 2) beside a road downtown Umeå and 3) on the top of the watertower in Umeå. A background sample was collected on the ice of the Golf of Bothnia 1000 m from the coastline 10 km SE of Umeå. A sampling area of 0.5 x 0.5 m with a depth of 20 mm was chosen for all snow samples except the sample of the watertower. The highway snow samples were collected at two locations and at a distance of 5 m and 100 m from the road. The levels of PCDDs and PCDFs in the snow samples correspond to a

two weeks' period of environmental deposition. In the watertower sample, a snow core was collected down to the roof with an area of 0.1 m^2 . This corresponds to a deposition time of 5 months.

Earlier we have reported on analyses of snow samples after an accidental fire in a plastic carpet factory outside Umeå, Sweden¹. Background snow samples were also taken at locations other than the downwind direction after the fire. The levels of PCDDs and PCDFs in the background samples correspond to two weeks deposition.

Snow samples were taken after a fire on a municipal solid waste (MSW) landfill in Lycksele, Sweden. Two snow samples were collected in downwind from the dumpsite at a distance of 100m and 1000 m from the fire. A background snow sample was taken 8 km upwind from the dumpsite on a field without any heavy traffic roads in the surroundings.

All snow samples were analyzed on a HRGC-HRMS. As the levels of PCDDs and PCDFs in the samples were very close to the detection levels, it was impossible to calculate the total concentrations of each homolog series. Furthermore, all levels of tetra- to hexaCDDs were under the detection level ($10\text{-}100 \text{ pg/m}^2$). However, interpretation of the data from the toxic isomers of the PCDFs gives valuable information about the environmental deposition of PCDDs and PCDFs.

Results

The results of the snow samples taken near to traffic roads in Umeå all showed detectable amounts of most of the toxic PCDF isomers. The levels of the TCDFs and the PeCDFs are higher close to the road than 100 m away. This points to a measurable contribution of dibenzofurans to the environment from car emissions, which normally has a pronounced emission of TCDF and PeCDF². However, the increase is low, the level of 2,3,7,8-TCDF in the samples 5 m from the roads is only 3 - 4 times higher than for the level in the samples collected at a distance of 100 m from the road in which the level of 2,3,7,8-TCDF is comparable with other background samples. This indicates that a slight direct contribution of the PCDD and PCDF emission to the environment can be derived from cars. However the results also show that the deposition of PCDDs and PCDFs which originate from car emissions are very local and are found close to the roads.

The snow samples collected in the wind direction after the accidental fire on an MSW dumpsite in Lycksele show an increased levels of PCDDs and PCDFs. However the dioxin levels in the snow taken 100 m from the dumpsite were only 4 -10 times higher than the background level, and at 1000 m the levels were almost identical with the background sample. Comparison of the levels of PCDFs in snow samples after the dumpsite fire in Lycksele and after the accidental PVC fire in Holmsund¹ shows one order of magnitude lower levels in Lycksele.

The levels of PCDFs found in the snow around Umeå are in the same range as the background levels found on the ice of the Golf of Bothnia, the background levels in Holmsund and in the snow

of Lycksele. Some of the samples from Umeå could have been exposed for fall outs from the MSW incinerator in Umeå. Neither Holmsund nor Lycksele has MSW incinerators in the surroundings and no other dioxin sources of important significance have been localized there. However, the background snow samples from Umeå did not show higher levels of PCDF than Lycksele or Holmsund. The levels on the top of the watertower are 10 times higher than other samples which corresponds well with the other data, because the "sampling time" was 5 months on the watertower and half a month for all other samples. The consistent levels of PCDFs in all background samples indicate that long-range transport is a more significant source for the environmental dioxin immission than a local MSW incinerator with normal emission levels. However if the incinerator is not working properly, levels of PCDDs and PCDFs can be detected in the surroundings³.

Principal component analysis (PCA)⁴ was performed in order to illustrate the differences and similarities in profiles between samples with different original. The calculations was based on all 2,3,7,8-substituted isomers and the total of each congener group, in total 25 variables. The resulting score-plot, PC1 versus PC2, is shown in Figure 1. The two components explain 67 % of the variation.

The different combustion related profiles are distributed over a large area depending of the type of process studied. The environmental samples, i.e. run-off water and sludge samples, and the air samples are drawn towards a profile with higher chlorinated congeners not typical for combustion sources.

The congener profiles found in the snow samples are in good agreement with other environmental samples. However, a minor shift towards higher chlorinated congeners can be observed. It is known that photolysis of PCDDs and PCDFs favours the degradation of the lower chlorinated congeners resulting in a higher proportion of the higher chlorinated isomers.

Conclusion

Snow sampling is an excellent matrix for environmental immission studies. It is easy to sample, the deposition time can be established and the clean-up and analysis is easy. The dispersion from a source can be studied by snow sampling in different directions and distances. It is suggested that new snow samples should be collected and analyzed to verify the expected trends in the environmental levels.

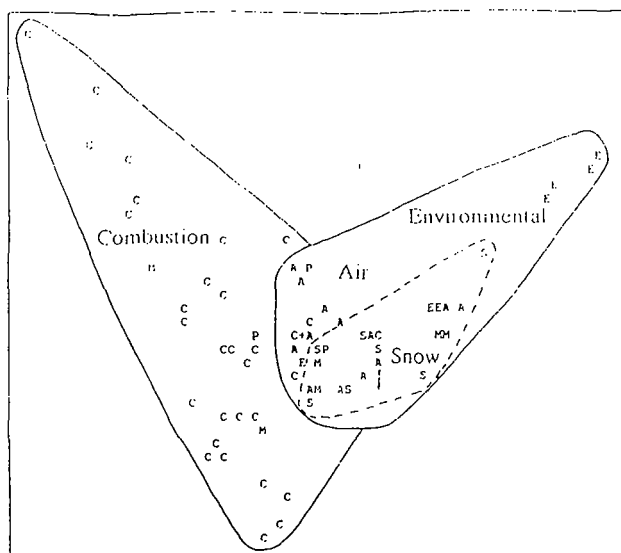


Figure 1. The score plot from the principal component analysis. A = Air Samples, C = Combustion related samples, E= Environmental Samples, M= Two Objects, P= Oil Products and S= Snow Samples .

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