# Sampling and Measurement of PCDD/PCDF and non-ortho PCB in Arctic Air at Ny-Ålesund, Spitsbergen.

**Martin Schlabach, Aase Biseth and Hans Gundersen**
Norwegian Institute for Air Research (NILU), P.O. Box 100, N-2007 Kjeller, Norway.

## 1. Introduction

During the last 20 years persistent organic compounds have been detected in different parts of the Arctic environment. Compounds like polychlorinated biphenyls (PCB) and chlorinated pesticides have been measured in biota, sediment, air, and water [1]. Atmospheric long-range transport is considered the main dispersion mechanism to the Arctic [2]. As a part of the Arctic Monitoring and Assessment Program (AMAP), NILU measures the concentrations of semivolatile organochlorines and polycyclic aromatic hydrocarbons (PAH) in air at Ny-Ålesund, Spitsbergen. Polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) have only been studied in Arctic biota and sediments [3-5]. To our best knowledge PCDD/PCDF have not been measured in Arctic air. During spring and summer 1995 we conducted PCDD/PCDF measurements in air. Since the PCDD/PCDF-concentration in air was expected to be extremly low, it was necessary to increase the sampling volume considerably. The sampling period was therefore increased from two days for standard organochlorines and PAH (1000 $m^3$)to a total of four times five days for PCDD/PCDF (10000 $m^3$).

## 2. Experimental

The sampling station is located at Zeppelin mountain (78°55' N, 11°53' E, 474 m above sea level) about 2 km south from Ny-Ålesund, Spitsbergen (figure 1). Today the small settlement at Ny-Ålesund hosts different research facilities and is the destination for cruise ships during the spring and summer months. The former coal mine was closed after a large explosion in 1962.

Samples were taken with a high-volume sampler described earlier [6]. The sample flow was about 20 to 25 $m^3$/h and the sampling time for a single sample was 120 hours. Particles were collected on a glass fiber filter (Gelman AE 61635). Vapor phase compounds were adsorbed on two polyurethane foam (PUF) plugs (100 mm diameter, 50 mm height) in series. Each sample was extracted separately and the extracts of four samples were combined before clean-up, to a total sampling volume of about 10000 to 11000 $m^3$.

The filter and PUF plugs were spiked with $^{13}$C-labelled internal standards and extracted with toluene for 24 h. Clean-up followed the same procedure as described for sediment samples [5] with multi column chromatography on different types of silica, alumina and activated carbon. The final extract was concentrated and spiked with $^{13}$C-labelled recovery control standards. The PCDD/PCDF and non-*ortho* PCB congeners were separated with a HP 5890 II gas chromatograph using two different fused silica capillaries CPSil-8MS (30 m * 0,25 mm * 0,1μm) and $Rt_x$-2330 (30 m * 0,25 mm * 0,1μm).

For quantification a VG AutoSpec was used at a resolution of 10000 with electron ionization (EI) in the single ion monitoring (SIM) mode.

Before starting the campaign, the blank values of a representative sampling set were determined. In order to examine field blank values one sampling set was opened and packed again at the station without placing it into the sampler (see Results table: field blank). Furthermore, several laboratory method blanks were determined and selected batches of solvents were reserved for the analysis of the Arctic air samples.


*Figure 1: Position of the Zeppelin Mountain station near Ny-Ålesund on Spitsbergen (78°55' N, 11°53' E, 474 m above sea level).*

## 3. Results

*Table 1: PCDD/PCDF and no-PCB results of the spring and summer sample and of the field blank.*

| Compound | Sample 1 21.04. - 17.05.95 fg/m$^3$ | Sample 2 21.07 - 23.08.95 fg/m$^3$ | Field blank fg/m$^3$ |
|---|---|---|---|
| 2,3,7,8-TCDD | 0,19 | 0,09 | < 0,05 |
| SUM TCDD | 3,58 | 3,30 | |
| 1,2,3,7,8-PeCDD | 0,51 | 0,20 | < 0,05 |
| SUM PeCDD | 8,60 | 2,18 | |
| 1,2,3,4,7,8-HxCDD | 0,90 | 0,14 | < 0,06 |
| 1,2,3,6,7,8-HxCDD | 1,30 | 0,26 | < 0,06 |
| 1,2,3,7,8,9-HxCDD | 0,19 | 0,22 | < 0,06 |
| SUM HxCDD | 16,00 | 3,48 | |
| 1,2,3,4,6,7,8-HpCDD | n.r. | 1,61 | < 0,10 |
| SUM HpCDD | n.r. | 3,02 | |
| OCDD | n.r. | 4,35 | 0,99 |
| **SUM PCDD** | **28,18** | **16,33** | |
| 2,3,7,8-TCDF | 0,62 | 0,51 | < 0,05 |
| SUM TCDF | 23,57 | 16,90 | |
| 1,2,3,7,8-PeCDF | 1,30 | 1,63 | 0,09 |
| 2,3,4,7,8-PeCDF | 1,60 | 0,66 | 0,11 |
| SUM PeCDF | 23,12 | 15,12 | |
| 1,2,3,4,7,8/1,2,3,4,7,9-HxCDF | 3,00 | 1,38 | < 0,07 |
| 1,2,3,6,7,8-HxCDF | 2,40 | 1,40 | < 0,07 |
| 1,2,3,7,8,9-HxCDF | 0,42 | 0,71 | < 0,07 |
| 2,3,4,6,7,8-HxCDF | 0,84 | 0,43 | < 0,07 |
| SUM HxCDF | 29,80 | 11,70 | |
| 1,2,3,4,6,7,8-HpCDF | n.r. | 2,02 | 0,09 |
| 1,2,3,4,7,8,9-HpCDF | n.r. | 1,29 | < 0,07 |
| SUM HpCDF | n.r. | 3,52 | |
| OCDF | n.r. | 3,81 | 1,34 |
| **SUM PCDF** | **76.49** | **51,05** | **1,34** |
| **SUM PCDD/PCDF** | **104,67** | **67,38** | **2,33** |
| **i-TE** | **2,28** | **1,13** | **0,19** |
| 3,3',4,4'-TeCB (PCB-77) | 244,00 | 141,00 | 7,81 |
| 3,3',4,4',5-PeCB (PCB-126) | 0,85 | 0,60 | 0,45 |
| 3,3',4,4',5,5'-HxCB (PCB-169) | 0,40 | 0,01 | 0,02 |
| **TE non-*ortho*-PCB** | **0,21** | **0,16** | **0,05** |

*n.r.: no result due to very low recovery of the $^{13}$C-labelled internal standard.*

Due to the unusual large sample size with high amounts of interfering compounds, the fractionation during clean-up was disturbed. For sample 1 the recoveries of the added internal standards were low (20 %) for HxCDD/F and unacceptable (0 - 4 %) for HpCDD/F and OCDD/F. For the other congeners of sample 1 and for sample 2 the recovery rate was good (70 - 90 %). The results of the field blanks were, in general, below the detection limit or at least a factor 5 lower than the results of sample 1 and 2. This was, however, not true for OCDD and OCDF. For these congeners the results of sample 2 may be significantly influenced by contamination.

## 4. Discussion

*Table 2: Comparison of total PCDD and PCDF concentrations in air and sediment samples from the Arctic and Northern Europe.*

| | Air | | Sediment | |
|---|---|---|---|---|
| | Ny-Ålesund | Rörvik (Background values only) | Barents Sea | North Sea |
| Compound | fg/m$^3$ | fg/m$^3$ | pg/g | pg/g |
| SUM PCDD | 16 - 28 | 220 - 470 | 11,9 - 31,8 | 243 - 475 |
| SUM PCDF | 51 - 76 | 84 - 240 | 16,4 - 102 | 213 - 931 |
| SUM PCDD/PCDF | 67 - 105 | 270 - 680 | 28,4 - 130 | 456 - 1406 |
| I-TE | 1,13 - 2,28 | | 0,31 - 1,1 | 5,5 - 17,2 |

The total levels of PCDD/PCDF measured on the Zeppelin mountain are found to be a factor 5 to 10 lower than the concentration in background air at the Rörvik station at the Swedish west coast [7]. The same difference is found in sediment samples from the North Sea compared with samples from the Barents Sea [5].

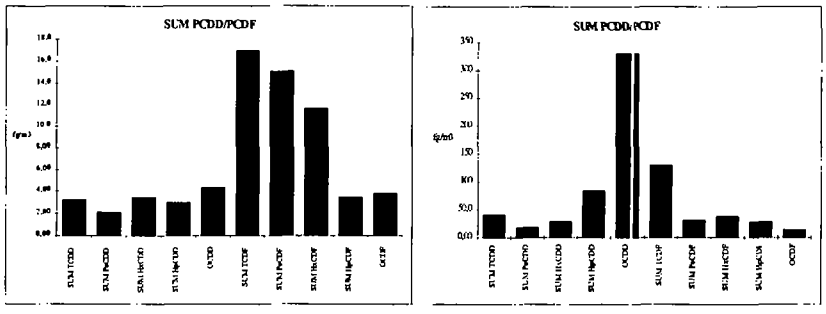


*Figure 2: PCDD/PCDF congener profiles in sample 2 from Ny-Ålesund (left) and from a background air sample from Rörvik at the Swedish west coast (right).*

ΣTCDF, ΣPeCDF and ΣHxCDF were the most dominant congener groups in the Arctic samples, while OCDD is prevalent in the samples from Rörvik. This might be caused by a higher volatility of the lower chlorinated compounds with only a minor fraction adsorbed to particles. As a consequence the overall deposition rate will be lower for these congeners.

Very recently, the PCDD/PCDF-concentration in air around McMurdo station in Antarctica have been monitored. Close to the station, the total PCDD/PCDF levels ranged from 140 up to 4570 fg/m$^3$. This is up to a factor 50 higher than the concentrations found at Ny-Ålesund. At the remote site Black Island about 30 km away from McMurdo station no PCDD/PCDF could be detected [8].

## 5. Acknowledgment

This work was supported by the Norwegian Pollution Control Authority (SFT, Oslo).

## 6. References

[1] Anonymous (1995): Distribution of contaminants in the Arctic biosphere. Sci. Total Environ. **160/161,** 233-519.

[2] Oehme, M., J.-E. Haugen and M. Schlabach (1995): Ambient air levels of persistent organochlorines in spring 1992 at Spitsbergen and the Norwegian mainland: comparison with 1984 results and quality control measures. Sci. Total Environ. **160/161,** 139-152.

[3] Oehme, M., M. Schlabach, K. Hummert, B. Luckas and E.S. Nordøy (1995): Determination of levels of polychlorinated dibenzo-*p*-dioxins, dibenzofurans, biphenyls and pesticides in harp seals from the Greenland Sea. Sci. Total Environ. **162,** 75-91.

[4] Oehme, M., A. Biseth, M. Schlabach and Ø. Wiig (1995): Concentration of Polychlorinated Dibenzo-*p*-dioxins, Dibenzofurans and non-*ortho* substituted Biphenyls in Polar Bear Milk from Svalbard (Norway). Environ. Pollut. **90,** 401-407.

[5] Oehme, M., J. Klungsøyr, A. Biseth and M. Schlabach (1993): Quantitative Determination of ppq-ppt Levels of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Sediments from the Arctic (Barents Sea) and the North Sea. Anal. Methods Instrument. **1,** 153-163.

[6] Oehme, M. and H. Stray (1982): Quantitative determination of ultra-traces of chlorinated compounds in high-volume air samples from the Arctic using polyurethane foam as collection medium. Fresenius Z. Anal. Chem. **311,** 665-673.

[7] Tysklind, M., I. Fängmark, S. Marklund, A. Lindskog, L. Thaning and C. Rappe (1993): Atmospheric Transport and Transformation of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans. Environ. Sci. Technol. **27,** 2190-2197.

[8] Lugar, R.M., R.L. Harless, A.E.j. Dupuy and D.D. McDaniel (1996): Results of Monitoring for Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Ambient Air at McMurdo Station, Antarctica. Environ. Sci. Technol. **30,** 555-561.