Distribution of Airborne PCDD/F in Relation to Particle Size

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Introduction

The atmosphere is a major transport pathway for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F). The majority of atmospheric PCDD/F are generally associated with particles[1]. The transport and deposition of particles is a strong function of particle size. Large particles (aerodynamic diameter d_{ae} > 10 µm) settle rapidly and have short residence times in the atmosphere while very small particles behave like gases. Similarly, large particles are relativly easily removed from receptor surfaces while small particles may be permanently retained[2]. Thus, the particle size distribution of PCDD/F will play a large role in the atmospheric transport and deposition of the compounds and will also influence the concentrations to which particle receptors are exposed.

No data on the particle size distribution of PCDD/F were found in the literature. In view of the importance of this information for understanding the enviromental behavior of dioxins and furans, we initiated a program to study PCDD/F particle size distribution. This paper presents the results of three measurements using a five stage multijet cascade impactor backed up by a glass fibre filter (GFF).

Experimental

Sampling was performed during summer of 1992 on the campus of the University of Bayreuth in northeastern Bavaria, FRG. The sampling location is considered to most closely represent rural conditions in this part of Germany. The sampling equipment and procedure have been described in detail[3]. The atmospheric particles were separated into five fractions by the impactor according to their aerodynamic diameters. The following size ranges were sampled and are subsequently referred to as stages 1 to 5: >4.05, 1.35-4.05, 0.45-1.35, 0.15-0.45, and <0.15 µm.

Three 48-hour samples, each with a volume of about 430 m^3_{NTP}, were collected between June 25 and July 1, 1992. The impactor stages and the backup filter were each analyzed separately. The samples of every run were worked up as a group together with a laboratory blank. The sample cleanup has been published elsewhere[4].

The quantification of the PCDD/F was performed on a HRGC/HRMS-system: HP 5890 Series II / VG Autospec ultima. The detection limits are listed in Table 1.

Table 1: Detection limits (pg per sample)

	run 1	run 2	run 3
ΣCl4DF	0.11-0.28	0.14-0.20	0.16-0.28
ΣCl5DF	0.04-0.13	0.04-0.15	0.06-0.12
ΣCl6DF	0.05-0.27	0.05-0.19	0.09-0.16
ΣCl7DF	0.03-0.18	0.06-0.32	0.08-0.25
ΣCl8DF	0.08-0.47	0.16-0.30	0.10-0.39
ΣCl4DD	0.15-0.35	0.10-0.22	0.14-0.30
ΣCl5DD	0.13-0.22	0.08-0.52	0.15-0.20
ΣCl6DD	0.05-0.11	0.04-0.17	0.06-0.15
ΣCl7DD	0.06-0.23	0.05-0.34	0.05-0.22
ΣCl8DD	0.11-0.39	0.06-0.34	0.10-0.18

Results and Discussion

The size spectra of the atmospheric particles are shown in Figure 1. Particles with aerodynamic diameters of less than 1.35 µm accounted for 65, 84 and 82 % of the total particle mass sampled in the impactor during runs 1, 2 and 3, respectively. The largest particle portion was found on stage 3 (0.45 µm<d ae<1.35 µm).

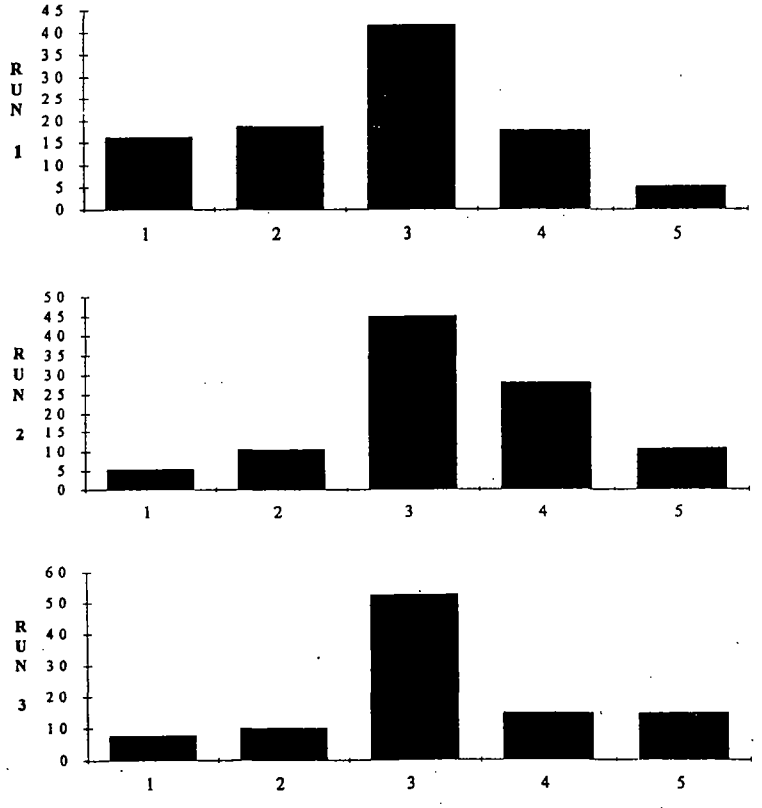

Figure 1: Size Spectra (in mass percent) of the atmospheric particles during the three runs. the numbers below the abscissa refer to the five impactor stages.

In Figure 2 the PCDD/F concentrations with respect to particle size are presented. The Cl_4- and Cl_5DD as well as the Cl_4DF were always below the quantification or the detection limits. The blanks which were worked up together with the samples showed low substance levels, but blanks of 10 pg for Cl_8DD and 4 pg for Cl_7DD have been detected in our laboratory. Thus, the results for these compounds in run 3 are associated with some uncertainty.

The PCDD/F homologue patterns for each sample were very similar for all five stages of a particular run. Hence, the particle mediated transport and deposition should be similar for all PCDD/F.

Figure 2 also illustrates that the PCDD/F were found primarily on small particles. The particles of d_{ae}<1.35 µm contained 91%, 90% and 85% of the PCDD/F for runs 1, 2 and 3, respectively. The Cl_7DD and Cl_8DD levels measured on stage 1 in run three were unusually high and deviated significantly from the uniform pattern in the remainder of the dataset. We suspect that these two values may have been due to laboratory contamination as mentioned above. There is no indication of significant levels of PCDD/F on the first impactor stage of runs 1 and 2 where the PCDD/F concentrations were higher than in run 3.

The fact that the PCDD/F are found mainly on accumulation mode particles (0.1µm<d_{ae}<1µm) has consequences for their atmospheric transport and deposition. Accumulation mode particles have the longest residence times of any particles in the atmosphere, so long range transport is to be expected.

References

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TRANS

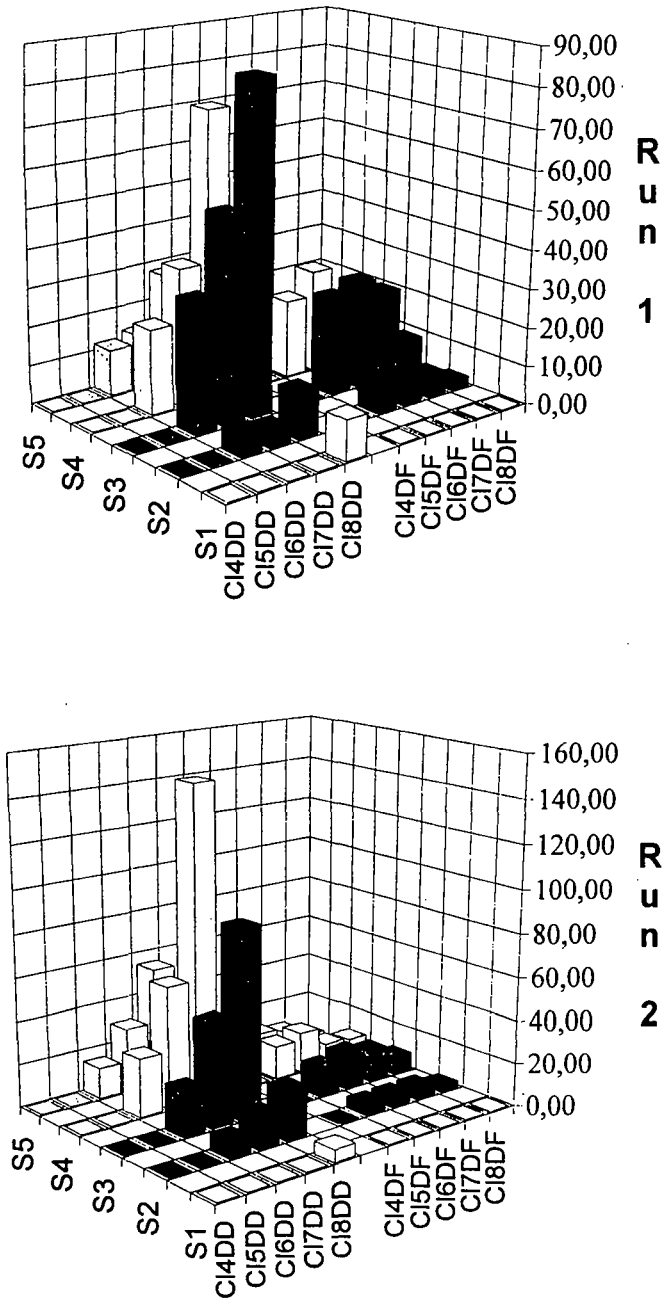

Figure 2 a,b: Concentrations of the PCDD/F homologues (fg m^{-3}) with respect to particle size of run 1 and run 2

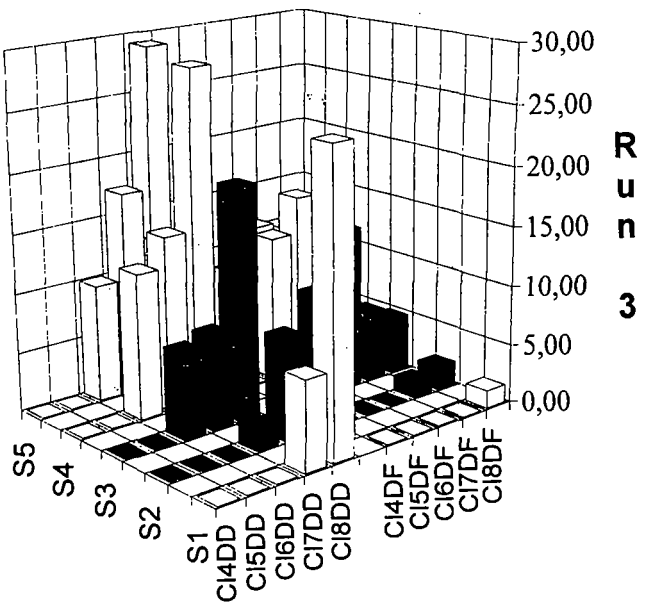

Figure 2 c: Concentrations of the PCDD/F homologues (fg m^{-3}) with respect to particle size of run 3