DECAY OF 2,3,7,8-CONGENERS IN DEPOSITION SAMPLES

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Introduction

Bulk atmospheric deposition of dioxins is usually sampled during one month. Data compiled by Lohmann & Jones[1] indicate that samples remain fairly stable during this period. Horstmann[2] et al. reported no significant difference (< 10%) between the sum of 30 daily samples and a 30-day sample. Hiester[3] however was not able to recover ^{13}C-spikes added at the start. The Bergerhoff method is used in Flanders since 1993 and a limit value based on this method was proposed. Therefore the stability of the deposition samples in different periods of the year was investigated.

Experimental

Sampling and analytical methods were described elsewhere[4]. Three Bergerhoff collectors shielded from sun light with black plastic and initially containing 1 cm of water are combined into one sample. Deposition data obtained in Mol during the year 1999 are given in table 1.

Table 1: Deposition measurements with non spiked collectors in Mol 1999, pg.d^{-1}·m^{-2}

start (day.month)	17.12	02.03	12.04	17.05	18.06	16.07	02.09	27.10	
end(day.month)	25.01	12.04	17.05	18.06	16.07	02.09	11.10	25.11	Mean
2,3,7,8-TCDF	0.48	0.26	0.24	<0.38	<0.44	0.25	<0.34	<0.32	0.25
1,2,3,7,8-PeCDF	0.28	0.09	0.08	0.03	0.02	0.01	0.03	<0.05	0.07
2,3,4,7,8-PeCDF	7.23	2.24	1.68	0.88	0.44	0.42	0.66	<0.66	1.74
1,2,3,4,7,8-HxCDF	1.45	0.39	0.85	0.18	0.14	0.11	0.11	0.19	0.43
1,2,3,6,7,8-HxCDF	1.57	0.30	0.39	0.07	0.12	0.09	<0.11	<0.16	0.33
2,3,4,6,7,8-HxCDF	2.05	0.41	0.35	0.18	0.13	0.15	<0.17	0.21	0.45
1,2,3,7,8,9-HxCDF	0.61	0.11	0.32	<0.13	0.14	0.02	<0.12	<0.16	0.18
1,2,3,4,6,7,8-HpCDF	0.54	0.11	0.46	0.06	0.05	0.06	0.04	0.12	0.18
1,2,3,4,7,8,9-HpCDF	0.13	0.02	0.15	0.00	<0.03	0.00	<0.03	<0.04	0.04
1,2,3,4,6,7,8,9-OCDF	0.03	0.01	0.30	0.00	0.01	0.01	0.00	0.02	0.05
2,3,7,8-TCDD	<3.38	0.54	0.60	1.13	<2.69	<1.37	0.33	<0.23	0.80
1,2,3,7,8-PeCDD	1.33	0.50	0.17	0.09	<0.67	0.59	0.72	<1.13	0.54
1,2,3,4,7,8-HxCDD	0.70	0.19	0.16	<0.09	<0.13	0.17	0.06	0.41	0.22
1,2,3,6,7,8-HxCDD	1.93	0.34	0.30	0.10	0.22	0.23	0.17	0.14	0.43
1,2,3,7,8,9-HxCDD	1.04	0.32	0.13	0.12	0.17	0.23	0.20	0.63	0.35
1,2,3,4,6,7,8-HpCDD	1.45	0.32	0.35	0.10	0.18	0.14	0.14	0.49	0.40
1,2,3,4,6,7,8,9-OCDD	0.20	0.08	0.13	0.03	0.04	0.03	0.07	0.07	0.08
Total TEQ (+1/2 DL)	22.7	6.24	6.64	3.27	3.63	3.18	2.91	3.74	6.42
Total TEQ (0=DL)*	21.0	6.24	6.64	2.97	1.66	2.50	2.53	2.28	5.73

A second set of samplers were spiked with all 2,3,7,8-congeners and set up simultaneously with the unspiked samplers at the same site. The amount of spike, in the order of table 1, in picogram was: 72, 72, 72, 72, 72, 72, 72, 77, 73, 145, 71, 72, 71, 73, 71, 73 and 147 respectively. The spikes were added in equal parts to the 3 collectors. The recovery rate was obtained from the difference between spiked and unspiked samplers (table 2).

Table 2: Percentual recovery of spikes during deposition experiments

	Dec - Jan	March- April	April- May	May- June	June- July	July- Aug	Sept- Oct	Oct- Nov	Mean
2,3,7,8-TCDF	5	5	11	8	7	12	17	6	9
1,2,3,7,8-PeCDF	12	11	18	8	6	8	10	17	11
2,3,4,7,8-PeCDF	19	17	19	11	9	4	9	26	14
1,2,3,4,7,8-HxCDF	25	20	18	12	8	3	6	40	17
1,2,3,6,7,8-HxCDF	28	20	18	10	9	4	6	36	16
2,3,4,6,7,8-HxCDF	46	28	31	12	11	4	10	54	24
1,2,3,7,8,9-HxCDF	19	22	23	12	7	4	7	53	18
1,2,3,4,6,7,8-HpCDF	75	42	7	13	11	-1	7	80	29
1,2,3,4,7,8,9-HpCDF	19	30	16	12	9	3	5	62	20
1,2,3,4,6,7,8,9-OCDF	50	40	0	11	10	1	6	52	21
2,3,7,8-TCDD	11	20	51	34	18	38	26	24	28
1,2,3,7,8-PeCDD	16	18	30	14	13	8	15	43	20
1,2,3,4,7,8-HxCDD	20	30	34	14	12	5	8	50	22
1,2,3,6,7,8-HxCDD	38	44	37	20	17	4	11	59	29
1,2,3,7,8,9-HxCDD	23	47	38	17	20	6	16	68	29
1,2,3,4,6,7,8-HpCDD	82	38	30	25	22	-1	15	78	36
1,2,3,4,5,6,7,8,-OCDD	129	50	18	24	18	7	7	52	38
TEQ	18	21	34	20	14	17	16	34	22

Estimation of half life times

The breakdown of PCDDs and PCDFs in these experiments is most likely caused by indirect sun light and atmospheric oxidants. Evaporation may play a role since the losses increase with temperature, however they are not proportional to the vapor pressures of the congeners. The deposition sample is a mixture of water and particles and degradation may be similar to aqueous samples. O'Keefe et al[5] measured half life times of 4 hours for TCDD and TCDF, and 14 to 16 hours for OCDF and OCDD respectively in natural waters exposed to sun light. Although the decay here is not continuous, it can be approximated by a first order model on a time scale of days:

$$y = y_0 \,.\, \exp(-r \,.\, t) \qquad (1)$$

where y is the amount of any congener present at time t in days, y_0 is the initial amount present, in picograms, and r is the fraction of congener lost per day. The decay rate r and the half life time $t_{1/2}$ are calculated from the recovery y/y_0 as:

$$r = -1/t \ln(y/y_0) \qquad \text{and} \qquad t_{1/2} = 1/r \,.\, \ln 2$$

Results for half life times are given in table 3.

If we further assume that the deposition rate during the sampling period is constant:

$$dy = D \, . \, dt - r \, . \, y \, . \, dt$$

then the amount y of deposition in the collector at any moment t, and the integrated total deposition D.t, not taking into account any decay, are given by:

$$y = D/r \, . \, (1 - \exp(-r \, . \, t)) \qquad (2)$$

$$D \, . \, t = y \, . \, r \, . \, t / (1 - \exp(-r \, . \, t)) \qquad (3)$$

Table 3: Half life times of congeners in days

Period	1	2	3	4	5	6	7	8	Mean
2,3,7,8-TCDF	8.8	8.6	11	8.1	6.6	16	14	6.4	9.9
1,2,3,7,8-PeCDF	12	12	14	8.8	6.9	13	12	11	11.3
2,3,4,7,8-PeCDF	16	15	15	10	7.9	10	11	15	12.4
1,2,3,4,7,8-HxCDF	19	17	14	10	7.8	9.8	9.9	22	13.7
1,2,3,6,7,8-HxCDF	21	16	14	9.6	7.9	10	9.5	19	13.5
2,3,4,6,7,8-HxCDF	34	21	21	11	8.7	10	11	32	18.6
1,2,3,7,8,9-HxCDF	16	18	17	10	7.5	10	9.4	31	14.8
1,2,3,4,6,7,8-HpCDF	96	29	8.9	11	8.6	-	9.9	74	29.6
1,2,3,4,7,8,9-HpCDF	16	22	13	10	7.8	9.3	8.4	40	15.8
1,2,3,4,6,7,8,9-OCDF	39	29	-	10	8.3	7.9	8.9	31	16.7
2,3,7,8-TCDD	12	17	37	21	11	34	20	14	20.6
1,2,3,7,8-PeCDD	14	16	20	11	9.5	13	14	23	15.2
1,2,3,4,7,8-HxCDD	16	22	22	11	9.0	11	11	29	16.5
1,2,3,6,7,8-HxCDD	27	32	24	14	11	10	12	38	21.1
1,2,3,7,8,9-HxCDD	18	35	25	13	12	12	15	52	22.5
1,2,3,4,6,7,8-HpCDD	141	28	20	16	13	-	14	81	39.2
1,2,3,4,5,6,7,8,-OCDD	∞(*)	38	14	16	12	12	10	31	41.6

(*) recovery > 100% half life of 200 days assumed to calculate mean

Discussion

As a general trend the recovery of congener spikes is highest in the cold season and increases from tetra to octa. On the average all PCDDs are more resistent to decomposition than PCDFs, except for the most stable 2,3,4,6,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF. 2,3,4,6,7,8-HxCDF is significantly more stable than the other HxCDFs. Unexpected high recoveries for 2,3,7,8-TCDD are found in the warmer months. This could indicate that 2,3,7,8-TCDD is the most persistent congener in summer, which seems contradictory with other data[1,3,5] . An explanation may be that this congener is formed as a product of photochemical dechlorination of higher PCDDs. If we set a limit of 20 % spike recovery, corresponding to 50 % sample recovery according to equation (2), then the method would be inadequate for TCDF, PeCDF and PeCDD for nearly all samples. During the warmer months from May to September the loss of all spikes exceeds 70 %. In the cold season hexa, hepta and octa spikes can be recovered at rates higher than 30 % which is considered adequate. Applying the model of equations (2) and (3) the relation between loss of spikes and loss of sample was calculated for all congeners (figure 1). Furthermore this model allows to answer to some interesting questions related to artefacts of the method:

1. How much of the sample in TEQ is approximately lost during sampling?

With the calculated decomposition rates, we reconstructed the integral deposition, assuming no decay, by applying equation (3). The results in table 4 are based on the reconstructed congener profiles in the unspiked experiments and were calculated for a sampling period of 30 days. The calculated loss of TEQ is a factor 2.0 as an annual average, and is highest in summer.

Figure 1: Annual average recovery of spikes and calculated recovery in a 30 day sample

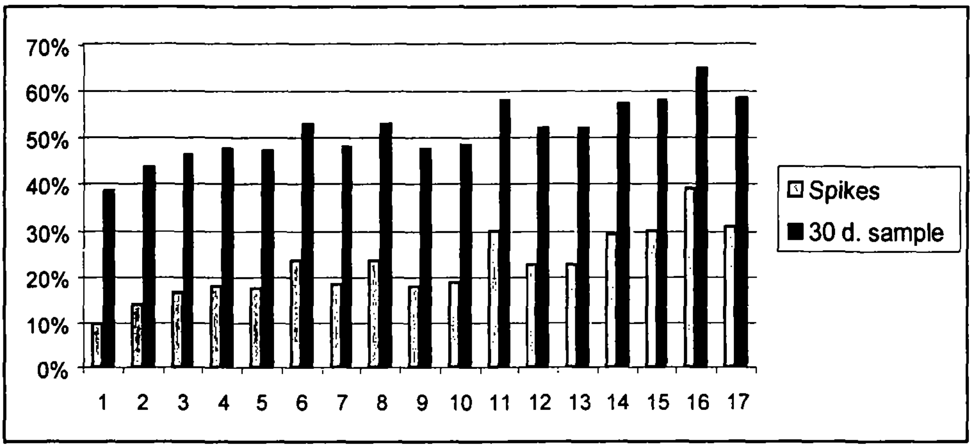

Table 4: Calculated TEQ loss ratio in deposition samples over 30 days

Period	1	2	3	4	5	6	7	8	Mean
Loss Ratio	1.89	1.99	1.94	2.15	2.36	2.61	2.41	1.48	2.00

2. Can the decay in the collectors account for the difference between seasons?

When the data in table 1 are recalculated to the original values using equation (3) and the decay rates for each period, the time trend curve is only slightly smoothened. Consequently we find no significant effect of the measurement technique on the observed seasonal variation.

3. Is the typical congener profile in deposition samples biased by the method?

The transformation of the congener patterns can be calculated for all periods with equation (1) for spikes and equation (3) for samples. As figure 1 illustrates for the annual averages the change in profile for a sample is not as drastic as the difference between emission and deposition profiles. Our data for the winter periods result in the most differentiated pattern change. The calculated changes however are limited and when applied to typical emission profiles do not result in the typical deposition profiles, which leads to the conclusion that processes in the atmosphere are more decisive in shaping the typical deposition congener pattern.

References

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