Role of PCDD/F in Deposition for Soil, Percolate and Sediment

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Introduction

Denmark responded to the Belgian dioxin scandal in 1999 by initiating the Danish Dioxin Monitoring Program, a comprehensive series of investigations of PCDD/F in the environment. The present paper gives an overview of the role of deposition of PCDD/F for the relevant environmental matrixes investigated in the program, comprising air, soil, sediment, and percolate. The emphasis is on geographical variation in terms of regional differences, as well as on flux, mass flow and mass balance.

Materials and Methods

Denmark is in this context described in terms of geographical regions: N-Jutland (NW region), S-Jutland and Funen (SW region), Zealand (E region), Falster and Bornholm (SE region). Deposition was sampled at the sites Ulfborg in W-Jutland (NW region), Fredensborg in North Zealand (E region), Copenhagen central city (E region) and Bornholm (island in the Baltic Sea, SE region). Air was sampled in Fredensborg and Copenhagen in the same period as deposition. Soil and lake sediment was sampled nation-wide, sea sediment from internal Danish waters and the Baltic Sea, percolate from selected municipal and special landfills, respectively. Deposition was sampled in bulk by a method developed for the project[1]. All matrixes were sampled and analyzed as previously described[1-4]. Precipitation data is acquired from a public database[5].

Results and Discussion

Deposition results from all stations on common time axis (Fig. 1). The bars shows the average deposition in the sampling periods; these differ in length, each is shown by the beginning month. The different years displays different annual variation profiles. There is a tendency to higher results in the winter, but the winter minimum 2003-04 seems weak, and the summer 2004 comparatively high. The results from all stations are in many periods comparable, e.g. Mar-Aug 2003. Differences, when occurring, may be ascribed to the geographical location. Thus the Copenhagen results are generally highest. Oct 2003 Bornholm stands out as elevated, whereas Aug 2004 the E region is elevated.

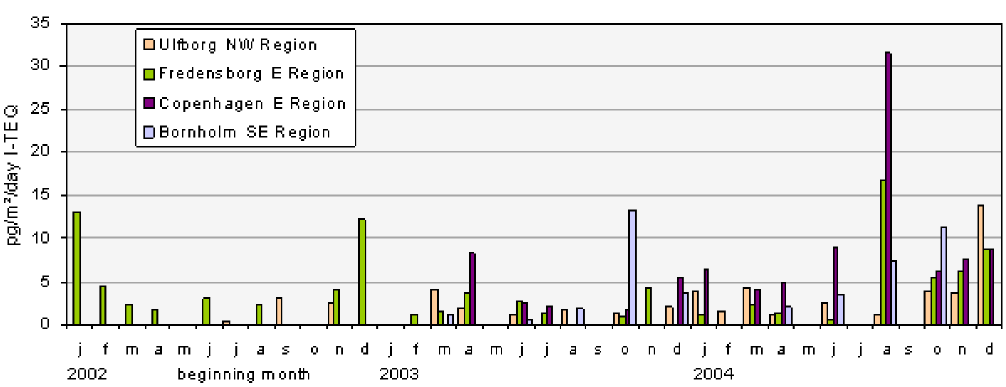
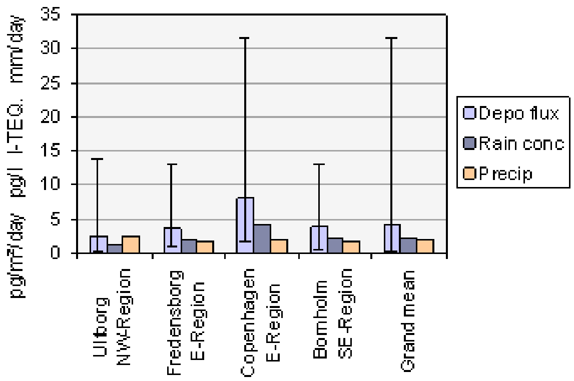


Fig. 1. Deposition

Statistics of PCDD/F deposition flux and concentrations in rainwater. (Fig. 2a). Air concentrations (Fig. 2b). Average (weighted by period length), minimum and maximum. The geographical variation of deposition spans a factor of 3 between the lowest average flux in Ulfborg and the largest one in Copenhagen; the latter is more than the double of that in Fredensborg, in spite of the short distance (30 km). This indicates that local conditions in the highly urbanized environment might play a role for the deposition there. Possibly particles are involved, but the issue has not been directly addressed. The factor between the other sites is only 2. The even geographical distribution indicates that a part of the PCDD/F is emitted far away, and has been spread out in the air during the long transport. The air concentrations, in contrast, are very near the same in Copenhagen and Fredensborg, also indicating (independently) that long-range transport is important. The PCDD/F concentration in rainwater at the different sites is near proportional to the deposition flux, which geographically seems relatively independent of precipitation.



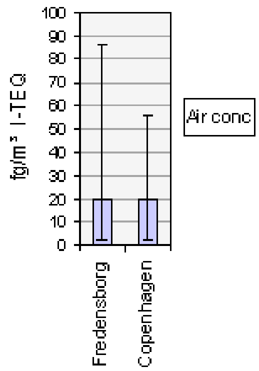


Fig. 2a. Average deposition and rain **Fig. 2b.** Air

Total flux compared to sources. The average deposition flux in the regions range from 2.5-8.0 (grand mean 4.2) pg/m^2/day I-TEQ, corresponding to an annual deposition of 41-128 (68) g/year I-TEQ over the 44000 km^2 of Danish land area. The atmospheric emission from Danish sources have been estimated to 11-148 g/year I-TEQ[6], encompassing the deposition results. This remarkable agreement makes it unlikely that the emission estimate have overlooked important PCDD/F sources.

Percolate from municipal and special landfills, respectively, compared with grand mean of rainwater (Fig. 3); the error bars refer to mean concentrations of the regions. The concentrations in percolate are much lower than those in rainwater, by a factor 36 between the means. Contrary to expectations, the garbage seems to absorb PCDD/F rather than to release it. There is thus a large surplus of PCDD/F in rainwater, making it possible that the content in percolate derives mainly from this source. However, the concentrations in percolate from special landfills are somewhat higher than those from municipal ones, indicating that some leakage of PCDD/F from the special garbage takes place. This effect overshadows the regional differences in percolate and conceals a possible regional influence from the concentration in rainwater. Percolate does not pose a threat for ground water contamination, since the amount of PCDD/F countrywide is negligible compared to that carried down by rainwater.

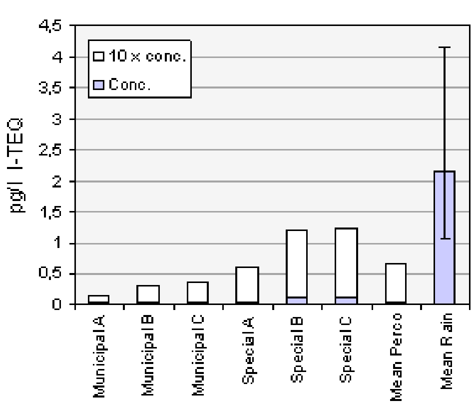


Fig. 3. Percolate

Soil. PCDD/F concentrations, mean, maximum and minimum in regions and zones, 72 samples (Fig. 4). An increase is seen in rural soils from the NW to the SE region. This follows the same tendency as the deposition, but is much weaker. The differences seems to be smoothed out in rural soil, possibly an effect of plowing and culturing. Alternatively to the geographical regions, the rural soil results have been divided into two zones: Reference zones located far from known sources. Exposed downwind impact zones located some km leeward (E) from point sources or diffuse sources with respect to the predominant wind directions (W, SW). However, no difference between those zones is found. Hence, there is no indication of deposition from point or diffuse sources via short-range transport.

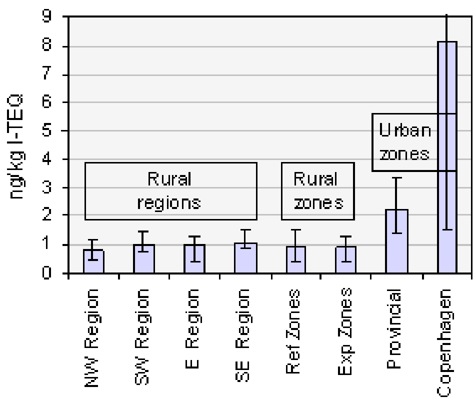


Fig. 4 . Soil

Soil and deposition flux. The time required to accumulate the amount found in the upper 10 cm of soil at the present deposition flux can be calculated for the different regions. The accumulation times of rural soils in the NW region, E region and SE region are thus calculated to 86, 81 and 75 years, respectively. This is a remarkable agreement. The concentrations in urban soil are considerably higher, leading to accumulation times of 177 years for provincial cities and 280 years for Copenhagen. This indicates that urban soil has been contaminated with PCDD/F from other sources than deposition, possibly ash, chemicals or the like. In addition, maybe a funnel effect concentrates PCDD/F deposition in cities because of the high coverage with buildings and other impermeable structures. Further, since city soil is not plowed, a lower breakdown rate must be operating there. Deposition in provincial cities has not been measured in this study. However, applying the deposition result for Copenhagen on provincial city soil leads to an average accumulation time of 77 years.

Sediment from lakes and fjords in all regions, from internal Danish waters and Baltic Sea and from small and large harbors, respectively. Mean, maximum and minimum, 28 samples (Fig. 5). The concentration in lake sediments increase from NW to E region. The increase is much more pronounced than the corresponding one for deposition. The mean concentrations are considerably higher than those of rural soils, attesting to long half-lives in sediment, where the concentrations seem to build up. The deposition of PCDD/F may have been higher in the past, before the introduction of efficient incinerator flue gas cleaning; the PCDD/F from then might still be present in sediment today. However, not shown, is a pronounced variation between individual lakes in the same geographical region. Since deposition is evenly distributed, this variation points to significant contributions from other sources. The accumulation time for sediment in the lakes at the present deposition flux range from a plausible 60 to 1800 years. The latter value indicates significant pollution in some lakes, most likely from waterborne sources. Also the water pollution might have been worse in the past, particularly before efficient wastewater treatment was introduced in Denmark in the 1990^{ties}. Some researchers believe natural formation of dioxin takes place in lake sediment[7]. However, this reportedly is characterized by a high PCDD/PCDF TEQ ratio, in contrast to the almost unity ratio in all lakes in the present investigation. For sea sediment, the accumulation times range from 300-2500 years, which is considerably more than can be explained by the present deposition. For the sea, in contrast to lakes, contamination through water sources is no option to explain the high values, because such sources worldwide only amounts to a few percent of the air emissions. The sea is the ultimate reservoir for PCDD/F on the planet, therefore PCDD/F accumulates there, whereas most lakes are washed through. Also possibly, hot spots in the Baltic sea sediment are re-distributed by sea currents. For harbor sludge the accumulation times range from 13 years for a small harbor to 2300 years for large harbors, indicating that the PCDD/F in the small harbors may originate from deposition only, whereas large harbors are highly contaminated.

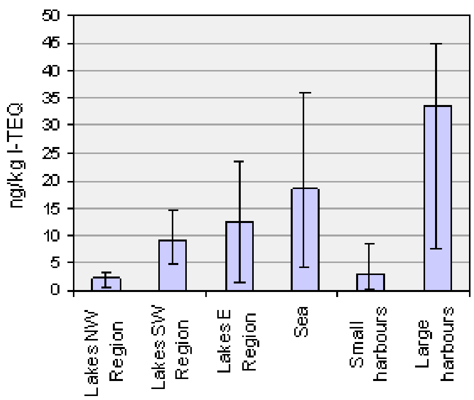


Fig. 5. Sediment

Deposition over sea and biouptake. The average deposition flux at Bornholm in the Baltic Sea is 3.9 pg/m^2/day, or 1.4 mg/km^2/year. We apply this figure for the Western part of the Baltic Sea, although the deposition over the sea surface may be somewhat lower than on the island. The production of bio-mass in the western Baltic is estimated to 2400 kg/km^2/year [8]. The concentration in herring in this sea region has been measured to 2-8 (average 3.2) ng/kg WHO-TEQ[9,10]. Applying the average concentration as valid for all bio-mass, the content in the produced bio-mass amounts to 8 mg/km^2/year WHO-TEQ, or about 0.5 % of the deposition on the sea surface. Hence, there is a very large surplus of PCDD/F from deposition available for uptake in the marine food chains. This makes it likely that PCDD/F in pelagic fish mainly originates from atmospheric deposition on the sea surface.

Acknowledgements

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References

1. Vikelsøe J., Hovmand M. and Andersen H.V. (2003) *Organohalogen Compounds* 61: 454.

2. Vikelsøe J. (2002) *Organohalogen Compounds* 57: 373-376.

3. Vikelsøe J. (2001) *Organohalogen Compounds* 50: 488-491.

4. Vikelsøe J. (2004) DMU Statusrapport, Dioxinmåleprogrammet. www.dmu.dk

5. Danish Meteorological Institute Weather Archive Database. www.dmi.dk

6. Hansen E. and Hansen C.L. (2003) Environmental Project no. 811, Danish EPA. www.mst.dk.

7. Rappe C, Öberg L, Andersson R (1999). *Organohalogen Compounds* 43, 249-253.

8. ICES CM 2003/ACFH:17. O:\ACFM\WGREPS\HAWG\REPORTS\2003\I-Introduction.doc

9. Danish Institute for Food and Veterinary Research (2004). Samlet rapport over dioxin ilaksogsildfraØstersøen.

10. Karl H. and Ruoff U. (2004) *Organohalogen Compounds* 66, 1886-1892.