LEVELS IN ABIOTIC COMPARTMENTS

DIOXINS IN DANISH SOIL

Jørgen Vikelsøe

National Environmental Research Institute, P.O.Box 358, 4000 Roskilde, Denmark.

Introduction

A literature survey of dioxin emissions in Denmark[1] indicated a lack of data for the dioxin level in the Danish environment. This initiated a series of follow-up investigations still in progress, comprising soil, compost, percolate, deposition, air and water. Further, brominated dioxin from incineration of municipal and hazardous waste was included. The present paper describes the soil investigation. The Purpose has been:

- To find the background level of PCDD/F in Danish soil
- To investigate regional and geographical differences
- To investigate the influence of sources

Methods and materials

Sampling

Top soil were sampled, preferentially from newly ploughed fields or grass fields, or grass lawn in parks or garden, according to the following criteria:

- Representative for agriculture, park, or garden soil.
- No direct contamination from ash, sludge or chemicals.
- Sampling depth 0-10 cm.

3-5 samples of topsoil from each location, taken some meters apart, were pooled (ca. 1 kg . Depth profiles were sampled by hammering a tube 10 cm Ø 50 cm into the ground, divided into sub-samples 10 cm height. The samples were stored at –20°C until analysed.

Experimantal plan

Topsoil samples collected fall 2001 from Danish locations, reaching from north to south (Skagen and Gedser) and from west to east (Esbjerg and Bornholm). In the predominantly westerly wind, the contamination from presumed sources were investigated by sampling exposed zones 1-3 km east of the sources. These comprised MSW and HSW incinerators, power plants, steel mill, larger industrial centres and urban regions. Industrial centres investigated: Ålborg, Århus, Esbjerg, Fredericia, Odense, Nyborg, Roskilde, Frederiksværk, Kyndby and Copenhagen. For comparison, reference samples from rural or remote locations were included. In addition, depth profiles in soils of low and high sludge amendment and a preserved area were analysed, sampled in a previous investigation of phthalates in soil[2].

Analytical

Grass, roots and pebbles removed, air-dryed, thoroughly mixed. 100 g dried soil spiked with 14 $^{13}C_{12}$-labelled congeners (0.4 ng tetra-hexas, 0.8 ng hepta-octas). Soxhlet extractet 20 hours in toluene. Classic clean up on silica/NaOH, silica/H_2SO_4, acidic alumina. Concentrated sample dissolved in 25 ml syringe spike (2 $^{13}C_{12}$-labelled congeners in n-dodecane). MS: Kratos Concept 1S at 10000 resolution. GC: HP 5890 series II, split/splitless injection at 290 °C, column 60 m J&W Scientific DB-5ms.

Repeatability for soil of low concentration (0.22 ng/kg I-TEQ) ca. 6 %. Detection limits 0.003 ng/kg (TCDD) to 0.5 ng/kg (OCDD). Recoveries (average all data) 74"19 %.

Results and discussion

The results of the depth profile/sludge amendment study are shown in Figure 1.

The PCDD/F found in the preserved topsoil layer indicate a build-up of concentration from air deposition during the more than 50 years of preservation. In contrast, ploughing mixes the layers of the cultured soil. In the high sludge amended soil, the concentration were roughly 100 times higher than in the other soils. This is higher than Danish average in sludge (10 ng/kg I-TEQ). The levels agree with German values[3]. The figure shows that a sampling depth of 0-10 cm is suitable for topsoil study.

In the topsoil source study, the highest concentration (15 ng/kg I-TEQ) was found in a soil containing slag from a park in Copenhagen. The remaining samples did not have any known direct contamination, their concentrations ranging from 0.25-3 ng/kg I-TEQ. The results for exposed zones in the concentrations range 2-3 ng/kg I-TEQ are shown in Figure 2.

The exposed sample (Nyborg E) near the HSW incinerator displays elevated level compared with the reference (Nyborg N). But the level is comparable with the Copenhagen samples (Rødovre & Virum). The samples near the MSW incinerator in Copenhagen (Rødovre) display slightly elevated levels compared to the reference (Virum). Consequently, it is not certain that the MSW incinerator is responsible for contamination found, which may be due to general air pollution in the Copenhagen region. This is significantly higher than the references, Copenhagen W (St. Valby), and Zealand N (Græsted, Figure 3).

All remaining results in the topsoil source study were below 1 ng/kg I-TEQ, Figure 3.

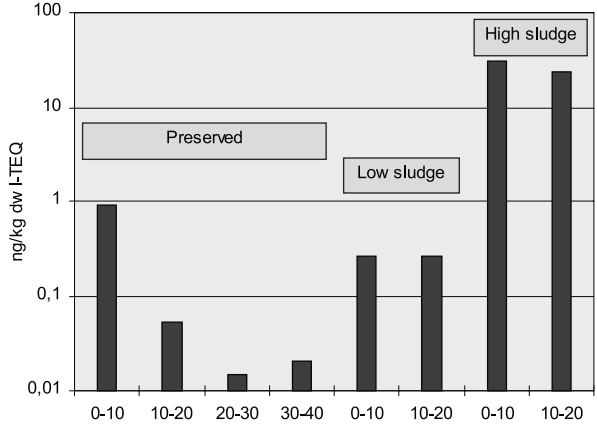

Figure 1. I-TEQ in depth profiles of differently sludge dressed soils (logarithmic scale)
Preserved. Recreational natural area not cultured >50 y, no sludge
Low sludge. Cultured field sludge amended with 0.7 t dw/ha/year (recommended amount)
High sludge. Cultured field amended with 17 t dw/ha/year of sludge through many years.

It thus seems that generally, industrial/urban centres or point sources do not give rise to significantly elevated levels, when samples of exposed zones east of such centres are compared to reference samples.

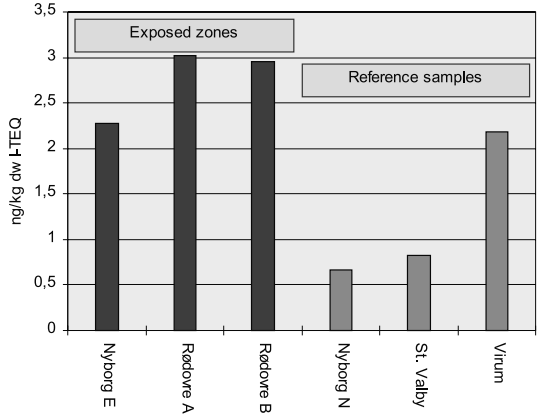

Figure 2. Results 2-3 ng/kg I-TEQ of topsoil source study
Nyborg E: Football fields 1 km E of HSW incinerator
Rødovre A&B: Grassy parks 1&2km E of large MSW incinerator in Copenhagen W
Nyborg N: Reference for Nyborg, grass field
Virum: Reference for Rødovre in Copenhagen N, grass lawn
St. Valby: Reference 25 km W of Copenhagen C, ploughed field

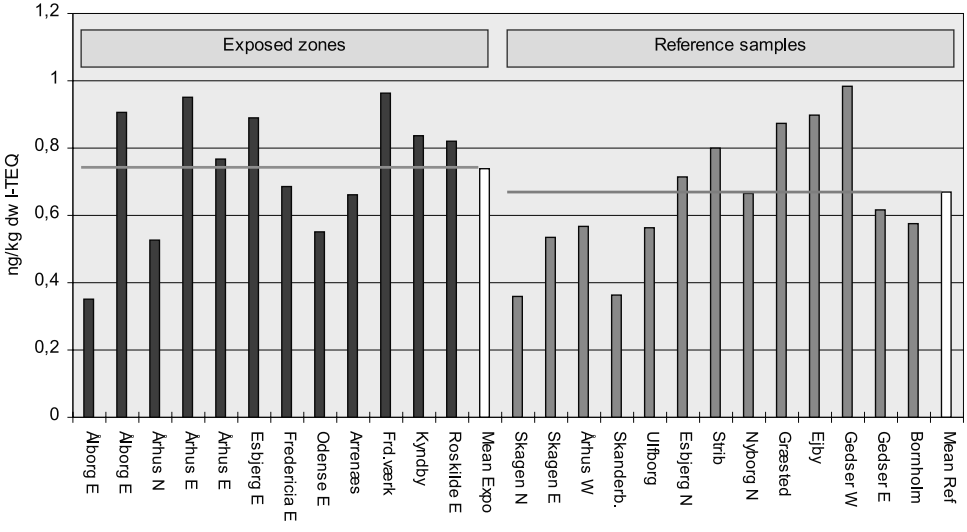

Figure 3. Results of topsoil source study <1 ng/kg I-TEQ. Soils in exposed zones east of industrial/ urban centres compared to reference samples from rural and remote locations. Slightly elevated levels are in some cases seen in the exposed samples. The differences are small, however, and in many cases negligible or negative. The mean of the exposed zone samples (0.74"0.18 ng/kg I-TEQ) is close to the mean of references i.e. the *Background Level* (0.67"0.20 ng/kg I-TEQ). The means are not statistically different by a t-test (p=0.13).

LEVELS IN ABIOTIC COMPARTMENTS

Comparing Figures 2 and 3, it might seem that the Copenhagen area is more contaminated than the other cities. However, the figures are not directly comparable, since no park or garden soils inside the other cities were investigated.

A geographical-scale north-south gradient seems to be discernible in the reference soils in Figure 3, which are largely arranged from north to south.

The PCDD/F -levels found in the present topsoil source study are comparable with Spanish[4] results, whereas Australian[5] or New Zealand[6] results are lower. Typical results for urban UK soils are higher[7]. The present results for sludge amended soils are comparable with Swedish[8] and Spanish[9] results

Conclusions

- Preserved topsoil layer indicates a build-up of PCDD/F from air deposition. Almost all PCDD/F is found in the upper 0-10 cm. Level in low-sludge soil comparable with preserve soil, in high-sludge soil roughly 100 times higher, suggesting a threshold for sludge-amendment.
- The I-TEQ of the source topsoil study ranged from 0.25-3 ng/kg I-TEQ
- The background level (i.e. mean of reference samples) was 0.67"0.20 ng/kg I-TEQ
- Near HSW incinerator I-TEQ level elevated compared with local rural reference, but not compared with the Copenhagen area.
- Level near the MSW incinerator in Copenhagen slightly elevated compared to the reference, but probably not significant.
- Contamination in the Copenhagen area is significantly higher than references W and N of Copenhagen.
- Mean of exposed zone samples east of industrial/urban centres not statistically different from the mean of corresponding rural references. Hence, the study does not in general indicate significantly elevated levels near larger industrial/urban centres or point sources.
- A geographical-scale north-south gradient seems to be discernible in the reference soils.

Acknowledgements

The project was funded by a grant from the Danish Environmental Protection Agency. The author wishes to thank the Danish counties and municipalities, private field owners, and management of power plants and incinerators for help in collecting the soil samples. E. Johansen is gratefully acknowledged for the skilful analytical work.

References

1. Hansen E., Skårup S. and Jensen A.A. (2000) Environmental Project No. 570, Danish EPA (electronic publication)
2. Vikelsøe J., Thomsen M., Johansen, E. and Carlsen, L. (2002) Sci Total Environ (in press)
3. Pieper A., Lorenz W., Kolb M. and Bahadir M. (1997) Chemosphere 34, 121
4 Eljarrat E., Caixach J. and Rivera, J. (1997) Environ Sci Technol 31, 2765
5. Gaus C., Päpke O., Dennison N., Haynes D., Shaw G.R., Connell D.W. and Müller J.F. (2001) Chemosphere 43, 549
6. Buckland S.J., Ellis K.H., Salter R.T and Scobie S.E (1998) Organohalogen Compounds 39, 101
7. Holmes S., Green N., Lohmann R. and Jones K. (1998) Organohalogen Compounds 39, 257
8. Rappe C., Anderson R., Nilsson C. and Nilsson P. (1997) Organohalogen Compounds 32, 45
9. Eljarrat E., Caixach J. and Rivera, J. (1997) Organohalogen Compounds 39, 103