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PCDD/F IN DEPOSITION, SPRUCE THROUGHFALL AND AIR IN DENMARK.

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Introduction

A literature survey of dioxin emissions in Denmark[1] indicated a lack of data for the dioxin level in the Danish environment. Hence, the Danish government initiated a series of follow-up investigations still in progress, comprising soil, compost, percolate, deposition, air and water. Further included were brominated dioxin from incineration of municipal and hazardous waste. The present paper describes the preliminary results for the investigation of deposition and air. Deposition of dioxin over land or sea is of major importance for the human exposure, which takes place mainly from food intake.
The Purpose has been

- To develop a routine method to measure deposition of PCDD/F
- To estimate the annual deposition at selected stations in Denmark
- To compare bulk deposition with throughfall from spruce and air concentrations
- To study annual variations.

Methods and Materials

Bulk deposition sampling. After test of bulk-deposition sampling in funnels and bottles, it was found necessary to develop a new method, utilizing adsorption. Such methods have been reported[2]. The deposition is collected in glass funnel (23 or 30 cm Ø), connected to glass columns containing a quarts-wool filter, which collects particles, followed by a XAD-2 filter, which absorbs dissolved and gaseous PCDD/F. This filter combination has been routinely used for sampling of flue gas[3]. To collect sufficient amounts, the samplers are deployed in pairs or quadruples, 1.5 meters above the ground. The samplers are shielded from direct sunlight, but some stray light cannot be avoided. During the winter, electrical thermostatic heaters prevent freezing and melt snow. Samples are collected monthly, and the columns with filters are replaced.
Spruce throughfall sampling. The same method as for bulk deposition is used. Monthly samples are collected, including spruce needles falling into the funnels.
Air sampling. US EPA's method is used[4]. The sampling train contains a QFF filter and 2 PUF plugs, operating at a flow of 130 m^3/day.
Station. Fredensborg (bulk deposition, spruce throughfall and air) is located in a densely populated rural area in North Zealand 30 km North of Copenhagen.
Analytical. Performed according to European standard[3]. Before sampling, quarts wool and QFF filters are spiked with 3 $^{13}C_{12}$- PCDFs. After exposure, the filters are dried and spiked with 11 $^{13}C_{12}$-PCDD/Fs (0.4 ng tetra-hexas, 0.8 ng hepta-octas). Extraction of filters combined. Air sam-

ples are soxhlet extracted 20 hours in toluene, deposition and throughfall samples refluxed 20 h in toluene using Dean-Stark water remover. Cleanup: Silica /NaOH, silica/H_2SO_4, acidic alumina. MS: Kratos Concept 1S at 10000 resolution. GC: HP 5890 series II, column 60 m J&W DB-5ms. Repeatability for air: Ca. 6 %. Extraction recoveries (grand mean ± sd): Deposition 51 ± 19%, spruce 45 ± 9 %, air 76 ± 9 %. DL TCDD - OCDD: Deposition 0.1–8 pg/m^2/d, air 0.2-5 fg/m^3.

Results and Discussion

Figures 1-4 show the preliminary results for the investigation.

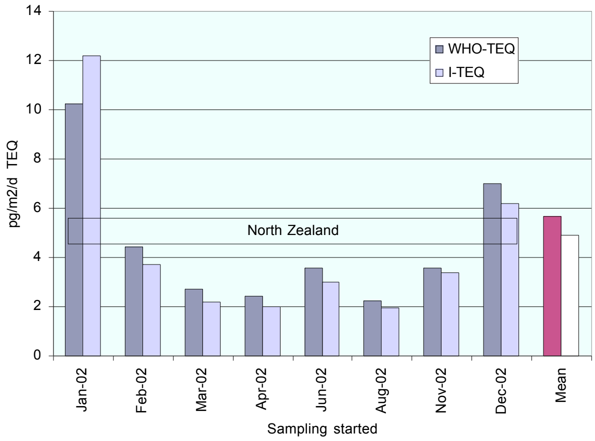

Figure 1. Results of deposition 1 year in North Zealand, pg/m^2/d TEQ. Samples taken during the summer months are combined in pools, shown as the beginning months.
I-TEQ and WHO-TEQ does not differ significantly. There is a high and sharp winter maximum and a shallow summer minimum (12 and 2 pg/m^2/d respectively). The seasonal difference may partly be due to higher emissions in the winter, e.g. from heating, but also photo-degradation in the atmosphere in the summer may play a role.

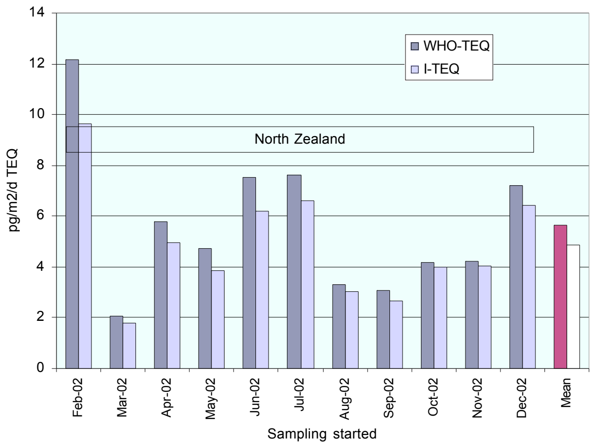

Figure 2. Results of spruce throughfall in N-Zealand 1 year monthly from the same station, pg/m^2/d TEQ. A spruce plantation in equilibrium with the atmosphere enters a steady state, as the receiving rate in the long term becomes equal to the releasing rate. Hence, spruce throughfall yields an independent check of the deposition results and sampling method. There are two local minimums at March and September and two maximums at February and July. The summer maximum may be due to more rain and higher temperatures, which may wash off the absorbed dioxin from the spruce needles.

A short-term accumulation or release may take place. The downfall of needles carries PCDD/F into the sampler, varies with the season and increases during high wind, complicated the pattern.

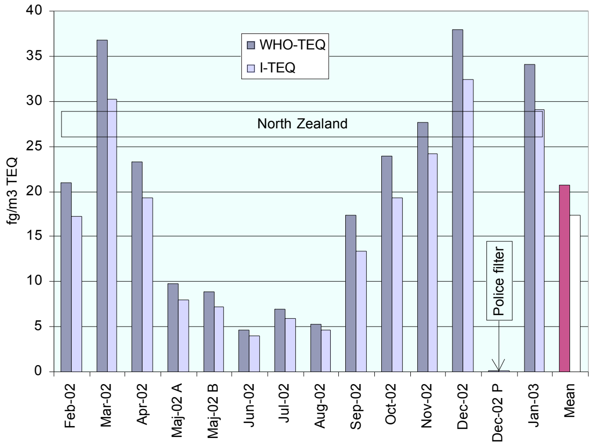

Figure 3. Results for air in North Zealand at same station as deposition and spruce, fg/m^3 TEQ.
A summer minimum in June and a winter maximum in December are seen at 4 and 32 fg/m^3 I-TEQ, respectively. The minimum is very deep and sharp, more so than for the deposition.
Method evaluation included:
Doublets May 02 A & B, CV = 6%.
Police filter experiment Dec 02 P, break-through = 0.7%.

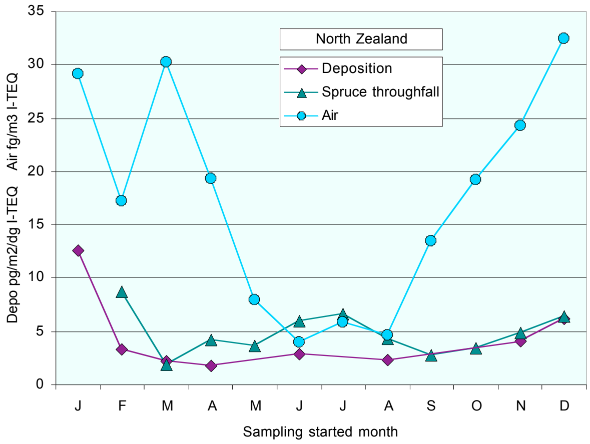

Figure 4. Annual variation of all matrixes combined (note the different units) on a common month axes.
It is seen that the spruce throughfall in the spring and fall follows the deposition closely, but deviates above that during the summer. This is probably due to contribution from dry deposition and higher uptakes of gasses and aerosols in the spruce plantation. Perhaps also due to a lesser UV degradation of collected PCDD/F in summer because the spruce-sampler is placed in shadow.

For air, the summer minimum is much narrower and deeper than for the other matrixes. The air concentration thus seems to respond more to seasonal changes than does the deposition.

Table 1.	Overview of results for deposition, spruce throughfall and air					
Location	North Zealand					
Matrix	Bulk deposition		Spruce througfall		Air	
Start	Feb-02		Feb-02		Feb-02	
Duration, d	353		353		353	
Unit	pg/m^2/d		pg/m^2/d		fg/m^3	
TEQ	WHO-	I-	WHO-	I-	WHO-	I-
Mean	4.2	3.9	5.7	4.9	21	17
Minimum	2.2	2.0	2.1	1.8	4.6	4.0
Maximum	10	12	12	9.6	38	32

Table 1 shows the mean values, minimums and maximums for the total sampling period of all matrixes. It is seen that the results for deposition and spruce throughfall are very close, particularly the minimums and maximums. This attests to the consistence of the results, and the integrity of the method. The spruce throughfall mean is, however, somewhat higher, mainly because of summer contributions as mentioned above. Absolute maximum and minimum are 9 and 2 pg/m^2/dg I-TEQ, respectively, very close to the results for the deposition.

Other studies. The present deposition results are within range of results for Flanders[5], and agree well with results from modeling of long-range transport[6]. The air results are within range of the American results[7] and agree well with results for northern winds[8]. The results are significantly lower than those reported for urban air from Korea[9] and Portugal[10], but significantly higher than modeled results for Denmark[6].

Conclusions. The PCDD/F in bulk deposition and spruce throughfall measured by an absorption method agree well on annual means. The throughfall display a complicated annual variation having 2 maximums. Air concentrations measured at the same station displays a considerably more pronounced annual variation. The annual means for all matrixes agree with other studies in similar settings.

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