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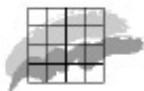
The Danish Dioxin Monitoring Programme II

# Dioxin in the Atmosphere of Denmark

A Field Study at Selected Locations

*NERI Technical Report No. 565*

*[Tom side]*



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The Danish Dioxin Monitoring Programme II

# Dioxin in the Atmosphere of Denmark

A Field Study at Selected Locations

*NERI Technical Report No. 565*  
**2005**

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# Data sheet

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Abstract: Occurrence and geographical distribution of dioxin was investigated in air and deposition at selected locations in Denmark, three forest sites in the background area, a city site in Copenhagen and a village site. At two sites simultaneously determination of dioxins concentrations in the ambient atmosphere and bulk precipitation were carried out during a period of three years.

Keywords: Dioxin, PCDD, PCDF, PCDD/F, bulk deposition, air, through fall.

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# Summary

- Aims* The aim of the present investigation has been to measure the level of dioxins in the atmosphere and bulk deposition in Denmark. The dioxins consist of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, with the abbreviation "PCDD/F". The geographical and seasonal variations and influence from different sources have been investigated through measurements at selected rural, urban and marine sites. The annual Danish deposition is estimated from the measurements and compared to the dioxin content found in soil, lake and sea sediment and in milk and fish.
- Measuring campaign* The investigation began in the fall 2001 with preliminary experiments, and was then gradually expanded until springtime 2005. PCDD/F were measured in bulk deposition at three forest sites in the Danish background area: the western part of Jutland (Ulborg), northern part of Zealand (Frederiksborg) and Bornholm (in the Baltic Sea) and at one urban site (Copenhagen). In addition through fall was measured in Frederiksborg. Through fall is the wet deposition passing the crown of the trees. The PCDD/F concentrations in the ambient air were measured in Frederiksborg and Copenhagen and periodically in a village (Gundsømagle) close to residences with wood stoves.
- Methods* The sampling method for bulk deposition was developed for the project and is based on absorption of dioxins on a filter in the field. Air was sampled according to US-EPA specifications. Samples were taken monthly or in some cases over two months or pooled as two months values. The analytical method comprised extraction in toluene, followed by classic clean up by liquid chromatography on silica and alumina. Detection and quantification was done by high resolution GC/MS.
- Air results* The results for air show a pronounced seasonal variation with maxima in the winter and a small year to year variation. The air concentrations in North-Zealand and Copenhagen are very alike, pointing to long range transport as a potential contributor to atmospheric PCDD/F at these sites. The village winter maximum is very pronounced, being the highest measured in the programme. The high concentrations are most likely caused by local emissions from wood stoves during the heating season.
- Bulk deposition results* The bulk deposition results show a winter maxima, though not as pronounced as for the air concentrations. Some variation between the years are also observed. The geographical distribution showed the highest annual fluxes in Copenhagen and lowest in West-Jutland. Apart from Copenhagen, the geographical variation was within a factor two. This modest variation indicates that the dioxins in the bulk deposition most likely are dominated by contributions from long-range transport of dioxin from distant sources.

<i>Through fall results</i>	The through fall results show some variation throughout the seasons and the level is somewhat higher than the bulk deposition. The higher level is probably caused by a contribution from airborne PCDD/F, captured by the spruce canopy and later on transferred to the ground by precipitation or adsorbed to organic material.
<i>Annual national deposition</i>	The measurements of bulk deposition at the background stations are used to estimate an annual load to the Danish land area. The load is estimated to 4.5 pg/m <sup>2</sup> ·day I-TEQ, corresponding to a total annual bulk deposition over the Danish land area of 72 g/year I-TEQ. The Danish atmospheric emissions are estimated to be in the range 11-148 g/year I-TEQ.
<i>Congener TEQ profiles</i>	The main TEQ-contributor is 2,3,4,7,8-PeCDF followed by 1,2,3,7,8-PeCDD, 2,3,7,8-TCDD and the HxCDDs, despite the site, season and type of samples, i.e. air samples, bulk deposition or through fall.
<i>Correlation analysis</i>	Highly significant correlations are found between the air concentrations in Frederiksborg and Copenhagen. A correlation is observed between bulk deposition and through fall in Frederiksborg. No significant correlation is seen between air concentrations and bulk deposition or air concentrations and through fall in Frederiksborg.
<i>Role for soil</i>	The bulk deposition can roughly account for the dioxin content found in rural soil. Even though the bulk deposition measured in Copenhagen is higher than the rural results, it is not large enough to explain the high soil concentrations found here.
<i>Role for sediment</i>	An investigation of the content of dioxin in sediments of lakes shows results that generally are too high to be explained by bulk deposition as the only source. This is also the case for sea sediment.
<i>Human intake, fish</i>	The total atmospheric deposition to the surface of the western Baltic Sea is estimated to 1.3 mg I-TEQ/km <sup>2</sup> ·year. From measurements of the content of dioxin in fatty pelagic fish (herring and salmon) and an estimation of the yearly production of biomass, it is demonstrated that the uptake in fish corresponds to 0.4% of the flux of dioxins deposited from the atmosphere. This means, that the atmospheric deposition carries a large surplus of dioxins into the Baltic Sea available for uptake in the food chains. Fish is an important source for human intake of dioxins.
<i>Human intake, dairy</i>	From the measurements the average deposition to the Danish land area during the summer is estimated to 2.8 pg/m <sup>2</sup> ·day I-TEQ. This flux is about six times more than the amount of dioxins in the milk produced pr area unit by grazing cows in summer time. This substantial surplus makes it likely that atmospheric deposition is responsible for a major part of the PCDD/F in cow milk and related dairy products, which, next to fish, are the most important source to human intake of dioxin.



*Other studies*

The air concentrations of dioxin measured in Denmark are at the same level as reported from Sweden, all though results from the Swedish west coast show lower levels. Atmospheric concentration levels from other European sites have in general shown higher results. The results found for the bulk deposition is in good agreement with results from Northgermany.



# Sammendrag

- Formål* Formålet med nærværende undersøgelse har været at bestemme niveauet af dioxiner i luft og nedbør i Danmark. Dioxiner består af polychlorerede dibenzo-p-dioxiner og polychlorerede dibenzofuroner, der fælles forkortes til "PCDD/F". Den geografiske variation samt variation med årstid og kildepåvirkning er undersøgt ved at måle på lokaliteter i baggrundsområder, byområde og nær hav. Den samlede danske deposition er estimeret ud fra målingerne og sat i forhold til dioxinindhold fundet i jord, sø- og havsediment samt i mælk og fisk.
- Måleperiode* Undersøgelsen begyndte i efteråret 2001 og er udvidet gradvist indtil slutningen af foråret 2005. Der er målt PCDD/F i nedbør på tre skovstationer i det danske baggrundsområde: Vestjylland (Ulborg), Nordsjælland (Frederiksborg) og Bornholm samt i et byområde (København). Nedbøren er målt som bulk deposition. I Frederiksborg er der også målt dioxin i gennemdryp, d.v.s. den nedbør, der passerer trækrønen. Koncentrationen af dioxin i luft er målt i Frederiksborg og København samt periodisk i en landsby (Gundsømagle) på en lokalitet tæt på husstande med brændeovne.
- Metoder* Metoden til prøvetagning af bulk deposition er udviklet til projektet og baseres på absorption af dioxin til filtermateriale i felten. Luftprøver er udtaget iht. US-EPA forskrifter. Der er udtaget månedsprøver, i visse tilfælde to-månedes prøver, sidstnævnte enten som samlet eksponering to måneder i felten eller som sammenlægning af to månedsprøver i laboratoriet. Analysemetoden består af ekstraktion i toluen fulgt af klassisk oprensning v.h.a. væskechromatografi på silikagel og aluminiumoxid. Påvisning og kvantificering af de forskellige PCDD/F'er er udført ved højopløsende GC/MS.
- Luft resultater* Resultaterne for luftmålingerne viser en tydelig årstidsvariation med maksimum om vinteren og en relativ lille variation årene imellem. Luftkoncentrationen i Nordsjælland og København er meget ens, hvilket kan tyde på, at fjerntransporteret dioxin udgør et betydeligt bidrag til PCDD/F i luften på de pågældende lokaliteter. I landsbyen er der hovedsagligt målt i fyringssæsonen og disse målinger viser højere værdier end samtidige målinger i Nordsjælland og København. De høje værdier skyldes formentlig, at målingen er foretaget tæt på kilder (brændeovne).
- Bulk deposition resultater* Resultaterne for bulk deposition viser en årstidsvariation med maksimum om vinteren, men også med nogen variation årene imellem. Den geografiske fordeling viser den højeste deposition i København og lavest i Ulborg. Udelades København, er den geografiske variation en faktor to. Dette betragtes som en beskeden variation, der kan betyde, at dioxinindholdet i nedbøren hovedsageligt stammer fra langtransport af dioxin fra fjerne kilder.
- Gennemdryp resultater* Resultaterne for gennemdryp viser en betydelig variation året igennem og tilsyneladende er variationen ikke årstidsafhængig. Gennemdryp giver et lidt højere gennemsnitsniveau end bulk depo-

sition, formentligt fordi PCDD/F fra luften afsættes i trækrone og senere føres ned til skovbunden med regnen eller nedfaldne nåle/organisk materiale.

<i>Årlig landsdeposition</i>	Målingerne af bulk deposition i baggrundsområderne er brugt til at estimere et samlet gennemsnit til det danske landområde. Det beregnes til 4,5 pg/m <sup>2</sup> ·d I-TEQ, hvilket svarer til en samlet deposition over hele landet på 72 g/år I-TEQ. Estimatet for det samlede danske atmosfæriske udslip af dioxiner er 11-148 g/år I-TEQ.
<i>Kongener TEQ profiler</i>	Hovedbidraget til TEQ stammer fra 2,3,4,7,8-PeCDF fulgt af 1,2,3,7,8-PeCDD, 2,3,7,8-TCDD og HxCDD'erne, uanset lokalitet, årstid eller hvorvidt der er målt i luft, nedbør eller gennemdryp.
<i>Korrelationsanalyse</i>	Der er god korrelation mellem luftkoncentrationerne målt i Frederiksborg og København. Der er også en signifikant korrelation mellem bulk deposition og gennemdryp i Frederiksborg, men ingen sammenhæng mellem luftkoncentration og bulk deposition h.h.v. gennemdryp.
<i>Betydning for jord</i>	Det estimerede niveau af bulk deposition kan nogenlunde redegøre for dioxinindholdet i jord analyseret fra landområder. Selvom bulk depositionen målt i København er højere end resultaterne fra baggrundsstationerne, så er depositionen af dioxin i København ikke høj nok til at forklare de koncentrationer, der er fundet ved analyse af jorden i byen.
<i>Betydning for sediment</i>	Koncentrationerne af dioxin i sediment fra undersøgte søer er generelt for høje til at kunne forklares ved bulk deposition som eneste kilde. Dette gælder også havsediment.
<i>Human indtagelse, fisk</i>	Den totale atmosfæriske deposition af dioxin til havoverfladen af den vestlige Østersø estimeres til 1,3 mg I-TEQ/km <sup>2</sup> ·år. Ud fra målinger af dioxinindholdet i fede pelagiske fisk (sild og laks) og en estimering af den årlige biomasseproduktion kan det anskueliggøres, at optaget i fiskene svarer til ca. 0,4% af den atmosfæriske tilførsel af dioxiner til havoverfladen. Atmosfærisk deposition tilfører således Østersøen et stort overskud af PCDD/F, som er tilgængeligt for optagelse i fødekæderne. Fede fisk fra Østersøen er en betydningsfuld kilde til befolkningens indtagelse af dioxin.
<i>Human indtagelse, mælk</i>	Gennemsnitsdepositionen om sommeren til danske landområder er estimeret til 2,8 pg/m <sup>2</sup> ·d I-TEQ. Dette er omkring seks gange højere end den mængde, der findes i mælken produceret pr. arealenhed fra græssende køer over en sommer sæson. Dette betydelige overskud gør det sandsynligt, at atmosfærisk deposition er kilden til hovedparten af dioxin i komælk og afledede mejeriprodukter, som næst efter fisk er den betydeligste kilde til human indtagelse.
<i>Andre undersøgelser</i>	De fundne koncentrationer af dioxin i luft er i overensstemmelse med svenske resultater, dog måles lavere værdier ved den svenske vestkyst. Andre rapporterede luftkoncentrationer fra europæiske målestationer ligger generelt på et højere niveau. Resultaterne for bulk deposition i baggrundsområder er generelt i overensstemmelse med nordtyske målinger i baggrundsområder.

# 1 Introduction

## *The Belgian scandal*

In the Belgian dioxin scandal in 1999 PCB contaminated fodder resulted in unacceptable dioxin contamination of food. This caused an international attention focused on dioxin and food safety. Responding to this situation, the EU countries took initiatives to reduce the dioxin exposure of the populations.

## *The Danish effort*

The Danish environmental effort commenced with a literature survey of dioxin emissions in Denmark (Hansen et al. 2000 & 2003) carried out on initiative of the Danish Environmental Protection Agency (DEPA). The survey indicated a lack of data for the dioxin levels and emissions in Denmark. As a response, the DEPA initiated in cooperation with NERI in 2002 a comprehensive series of investigations, the Danish Dioxin Monitoring Programme. The programme encompassed the most relevant environmental matrixes for dioxin, such as soil, compost, percolate, bio-ash, bulk deposition, air, sediment, flue-gas and waste products from incineration and cow milk. Finally, the investigations comprise dioxin in human milk and emissions from private wood stoves; the last two investigations are still in progress.

The Dioxin Monitoring Programme has yielded important information about dioxin in the Danish environment. The present report describes the results from atmospheric measurements of dioxin, i.e. in air, bulk deposition and in through fall from a forest canopy.

The investigation has been supported financially by the Ministry of the Environment.

## *Dioxins*

Dioxin is not a single substance, but a whole family of compounds, which chemically consists of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), together referred to as PCDD/Fs. PCDD/Fs is very persistent in the environment, insoluble in water, but soluble in fat. Because of these properties PCDD/Fs concentrate in the food chains, particularly in the fat tissue of the organisms. The PCDD/Fs is introduced into the food chains largely via atmospheric deposition over land or - in particular - sea, which therefore is an important route to human exposure. PCDD/Fs are aromatic planar compounds having a high affinity to carbon, hence PCDD/Fs are easily bound to soot particles e.g. in the atmosphere.

## *Toxicological properties*

PCDD/Fs are among the most toxic environmental pollutants known. The individual PCDD/Fs congeners have widely differing toxicological properties; some are highly toxic, whereas others are not toxic at all. To cope with this, a widely used approach is to express the results in so-called toxic equivalents, TEQs, which sets the total toxicity of all congeners of a sample in relation to the one most toxic congener, the "Seveso-dioxin" 2,3,7,8-TCDD. In this way, the concentrations of all congeners in the sample can be translated to a fictitious concentration of 2,3,7,8-TCDD having the same toxicity. Thus, the PCDD/Fs concentration in a sample is expressed as a single

number, simplifying the presentation of the results. More important, the results are made more relevant for environment and health by weighting the toxic congeners according to toxicity and ignoring the ones not toxic.

#### *Sources*

Contrary to many other pollutants, PCDD/Fs are not made intentionally, but arise as unwanted by-products. According to current scientific consensus most PCDD/Fs are formed by combustion processes mainly as a consequence of human activities such as industrial production, waste incineration, power plants, heating, transportation, metal production and fires. Hence, most of the PCDD/Fs formed are emitted to the atmosphere. According to the European Dioxin Inventory, about 95% of all PCDD/Fs emissions were atmospheric, whereas the residual 5% is released to the aquatic environment, or to soil. PCDD/Fs are also formed during certain chemical processes with chlorine. Hence, a certain fraction is found in technical or chemical products such as industrial chemicals, chlorinated pesticides, sealant and paper, as well as in waste products such as fly-ash, filter dust and discarded electric appliances. In addition some natural dioxin formation is believed to take place. For instance, PCDD/Fs may be formed in forest fires, vulcanos and lightning and released to the atmosphere.

#### *Human exposure*

Humans are mainly exposed to PCDD/Fs by food intake, whereas the direct intake through the skin or by inhalation is of minor importance for the general population. Humans are placed as the last link of the food chains and are therefore particularly exposed. The human levels are subsequently higher than those found in many animals. For example, human milk contains about 15 times more PCDD/Fs than does cow milk. PCDD/Fs are suspected of being cancerogenous, and further to exert a hormone like (*anti-androgenic*) effect, which is believed to harm the human health, especially the reproductive health. The exposure of the foetus is particularly harmful, since the foetus is very vulnerable to hormones during the development *in utero*.

#### *Point source measurements*

However, the quantification of PCDD/F sources is difficult and uncertain. Estimates of the total industrial emission of PCDD/Fs in the atmosphere has traditionally been done by measurements on chimneys of large industrial point sources such as incinerators, metal works, power-plants, chemical factories etc. But this straightforward approach suffers from a number of limitations. Evidently, it requires that all sources are known, but with incomplete knowledge there is a severe risk of overlooking unknown sources. Furthermore, since it is impossible to measure on all chimneys, it is necessary to select some and make assumptions about the rest, usually by more or less uncertain analogy considerations. Aggravating the problem, the measurements on a chimney is performed over a very limited period of time, typically a few hours, thus introducing a risk of being unrepresentative by overlooking emissions peaks occurring at rare occasions during atypical operation conditions. In addition, chimney measurements cannot include diffuse sources. Finally, it requires a mathematical model to evaluate or simulate the effect on the environment from the results from the point sources.

### *Atmospheric measurements*

In contrast, air and deposition measurements include atmospheric emissions from all sources. Atmospheric measurements include contributions from all sources, both point and diffuse sources, known as well as unknown and in addition also emissions from such diffuse sources as re-evaporation (e.g. from soil). Indeed, sources may be detected and found by such measurements. Hence, using atmospheric measurements one can make more realistic estimates of the total emission, than is possible to estimate from data on point sources. However, in spite of the many virtues there are also drawbacks of atmospheric measurements, the most serious of which are the long sampling period required (years) to cover variations caused by climate, season, meteorology and emissions. Moreover, several sampling stations are necessary to cover the geographical variation. From an analytical point of view, deposition measurements are technically demanding and hampered by the lack of an international standardised method.

### *Air*

Because PCDD/Fs are emitted mainly to the atmosphere, the air is the most important medium for transport of PCDD/Fs from the sources to the environment (Harrad and Jones, 1992). Therefore atmospheric measurements are well suited for tracking the transport and fate of PCDD/F. Many researchers believe that long range atmospheric transport plays a significant role for the concentration in air, but also short-range transport and local sources may be important for the local concentrations. The relative significance of the different transport routes is poorly investigated. The climate and the meteorological conditions are important for the atmospheric transport. During the residence in the atmosphere, a large fraction of PCDD/Fs is bound to particles, especially to carbon in soot. This is particularly the case in the winter, where the atmospheric soot content is high and the temperature low. During the summer, a higher percentage of PCDD/Fs are found in the vapour phase, particularly the lighter congeners. The ultraviolet (UV) radiation in sunlight is the most important degradation mechanism for PCDD/Fs in the environment. In the absence of UV-light, e.g. in sediment, PCDD/Fs are extremely persistent, with estimated half-lives up to hundreds of years.

### *Deposition*

PCDD/Fs is transferred from the atmosphere to the terrestrial and marine environment by atmospheric deposition. Atmospheric deposition consists of the material deposited as dry deposition, comprising particles and gasses, and wet deposition i.e. material transported to the ground with precipitation, comprising particles and dissolved compounds. The processes that operate during deposition of PCDD/Fs are poorly understood and investigated. The bulk deposition is defined operationally as the substance flux collected in a funnel exposed to the atmosphere. It is believed to be a measure of the wet deposition and to a certain extent the dry deposition. However, no specific study of wet and dry deposition has been done in the present investigation.

### *Through fall*

Through fall is the bulk deposition measured below the canopy in a forest, in the present investigation a spruce plantation. It consists of precipitation that has passed through the canopy and organic matter falling from the canopy, mostly spruce needles. These absorb

PCDD/Fs from air and deposition and carry an important part of the PCDD/Fs in the through fall. The average long term through fall flux measured during a sufficiently long period (year) is believed to be a good estimate of the total deposition flux to the forest during that period. Because it presents a large and rough surface to the atmosphere, the spruce plantation has high collecting efficiency. Accordingly, spruce through fall measurements may yield an independent result for the deposition flux, which may be compared with the results for the free bulk deposition in the same area.

## 1.1 Purpose

The overall purpose of the present investigation was to quantify the PCDD/Fs contamination of rural, urban, and marine sites through measurements of bulk deposition and atmospheric concentrations. Specific purposes have been to:

- develop a sampling method for bulk deposition of PCDD/F
- estimate the bulk deposition at selected urban, rural and marine sites
- measure background level and annual variation for air and bulk deposition
- estimate the total annual Danish deposition
- compare the total annual deposition with emission from known sources
- compare bulk deposition with soil and sediment results
- measure through fall as an estimation of the total deposition flux to a forest
- compare bulk deposition with through fall results to check the method
- compare the bulk deposition with through fall at the same site to get an estimation of the dry deposition load
- measure and compare air concentration at different sites (rural, urban, village)
- investigate the relative importance of local sources/long range transport



## 2 Experimental

### 2.1 Sampling programme

The sampling of bulk deposition and through fall started at the beginning of 2002 in the forest site Frederiksborg in North Zealand. Later in 2002 the forest site Ulborg, located in Western Jutland not far from the North Sea, was added to the programme. In 2003 the programme was extended with the urban site of Copenhagen Botanical Garden. The soil investigation in the Dioxin Monitoring Programme had previously shown high PCDD/Fs concentration in parks and gardens of Copenhagen. The purpose with this urban site was to show whether atmospheric deposition could be the cause of these high soil concentrations. At the same time a site at the island of Bornholm in the Baltic Sea was included in order to investigate the importance of PCDD/Fs deposition over the Baltic Sea, where high PCDD/Fs content in salmons had recently caused public concern. This is the first study of PCDD/Fs deposition over the Baltic Sea.

The air programme started simultaneously with deposition at Frederiksborg and Copenhagen Botanical Garden. In late summer 2002 the programme was extended to the village site Gundsømagle, in order to investigate the local atmospheric environment in a village where many wood stoves were used for additional domestic heating. The programme is summarised in Table 1.

**Table 1.** The monitoring programme for atmospheric PCDD/F

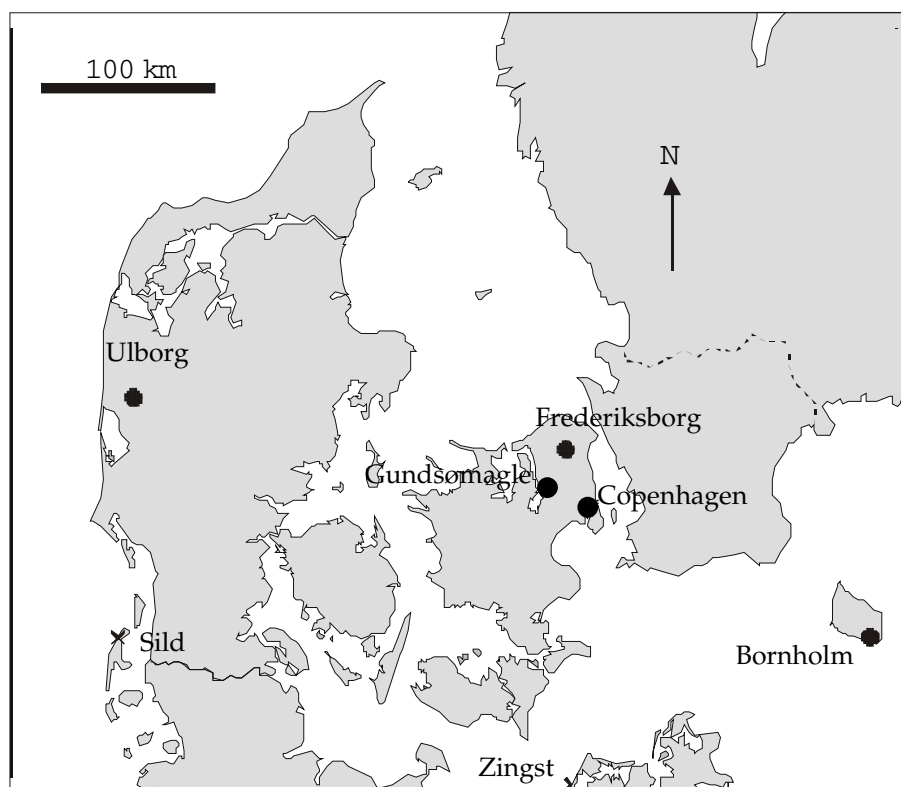
Site	Location, description	Matrix	Period
Roskilde	N-Zealand, near Roskilde fjord (preliminary test)	Depo	Nov 01 & Jan 02
Frederiksborg	N-Zealand, in Frederiksborg forest	Depo,	Feb 02 – Jun 05
- do -	- do -	Air	Feb 02 – Aug 05
- do -	- do -	Through fall	Feb 02 – Mar 04
Ulborg	Jutland W- (North Sea) coast, in Ulborg forest	Depo	Jul 02 – Mar 05
Copenhagen	Botanical Garden in central city	Depo, Air	Mar 03 – Dec 04
Bornholm	S-E corner of the Island in the Baltic Sea	Depo	Mar 03 – Apr 05
Gundsømagle	Village in N-Zealand, near Roskilde fjord	Air	Nov 02, Aug – Dec 03
-do	-do -	Air	Sep 04 – Aug 05

In connection with the wood-stove project in Gundsømagle mentioned below, the air measurements in Frederiksborg will be continued until the summer 2005.

## 2.2 Sampling sites

Since 1985 the two forest sampling sites (Frederiksborg- and Ulborg Forest Districts) have served as monitoring sites for advanced studies of atmospheric input of contaminants and studies of mineral cycling in the forest (Andersen et al. 1993; Hovmand and Bille-Hansen, 1999). Since 1989/90 the Ulborg-, Frederiksborg- and Bornholm monitoring stations have been major monitoring sites in the “Nation-wide monitoring program” on nutrient input to the aquatic environment (Kronvang et al., 1993, Hovmand et al., 1992). It is a major advantage that all sites used in the PCDD/Fs monitoring program have a long record on concentrations and depositions of other pollutants, in order to document the general pollution climate in the area and to facilitate a professional maintenance of the sampling procedures. A general description of the two experimental stations Frederiksborg and Ulborg was reported by Bille-Hansen et al. (1994), Hovmand and Bille-Hansen (1999), ICP-forest/EU-Level.II (2002). Forest growth, litter fall, water and mineral fluxes as well as air pollution inputs to the sites were well documented. Pollution levels at both stations reflect the average situation of the region.

Figure 1 shows the geographical location of the sites where atmospheric PCDD/Fs has been measured. Two German monitoring stations, to be used for comparison, were indicated (Knoth et al., 2000).



**Figure 1.** Map of sampling sites for PCDD/Fs in the atmosphere of Denmark and northern Germany.

A more specific description of the sites is given below.

### *Frederiksborg*

Frederiksborg forest district is located in a relatively densely populated rural area in North Zealand 30 km North of Copenhagen, near the town of Frederiksborg. To our knowledge no local sources of major importance to PCDD/Fs in the atmosphere could influence the measurements. At this station simultaneous sampling of air (gasses and particles), bulk deposition and through fall were performed.

Air was sampled from the top of a 12 m high scaffold in a clearing in the forest surrounded by trees with heights up to 17 m. The air intake was placed 14 m above the ground, in order to avoid a possible up-take from the air of PCDD/Fs by the tree canopies.

Open field bulk deposition samplers were placed in the clearing 10 meters from the air scaffold. The top of the two sampling funnels (having total opening area 0.14 m<sup>2</sup>, described below) were placed 2 m above the ground in scaffolds. Although the samplers were placed less than 10 m from the nearest trees, drip from the trees did not reach the bulk samplers in any measurable amount, as shown by parallel samples for other substances than PCDD/Fs taken at different positions in the clearing.

Through fall was sampled under Norway spruce (*Picea abies*) planted in 1963. Four through fall samplers having total opening area of 0.17 m<sup>2</sup> were placed in the tree-plot 1.5 m above the ground at a distance of about 100 m from the samplers for bulk deposition and air. Litter-fall consisting of needles, branches and cones were normally sampled in nets placed in a transect through the forest plot. Litter fall from the relatively young trees mainly consists of dead needles and biotic particles such as bark pollen and epiphytes. The material sampled in the through fall funnel described below is washed down with rain and drip water into the first filter of the filter train (Figure 2). The spruce needles and other litter material is included in the analysis of the through fall sample.



**Figure 2.** The 12 meter high scaffold in Frederiksborg. The rain protected air-intake is seen at the top

### *Ulborg*

Ulborg is located in a sparsely populated rural area of western Jutland 15 km east of the North Sea coast. Bulk deposition was sampled in Ulborg forest district near Ulborg. In the prevailing westerly wind, the site is believed to be representative of the deposition of PCDD/Fs over the Eastern part of the North Sea. The sampling set-up for deposition is similar to that in Frederiksborg, comprising one sampler having 0.07 m<sup>2</sup> opening. The local forest conditions were similar to those in Frederiksborg.

### *Bornholm*

Pedersker is a forest site located 0.2 km from the coast in the south-eastern corner of the island of Bornholm in the Baltic Sea. This site is exposed to air masses from the Baltic Sea by the prevailing wind directions from south, south-west and west. It may therefore be assumed that local sources play a minor role compared to long range transport of pollutants. One sampler having 0.07 m<sup>2</sup> opening was placed in a clearing in the forest surrounded by low spruce trees of a height up to 10 m. The site is described by Hovmand (2005).

## *Copenhagen*

The Botanical Garden is located in central Copenhagen. Bulk deposition (one sampler of 0.07 m<sup>2</sup>) as well as air samples were collected at the site. The downtown city is heated almost exclusively by district heating, and no large point sources such as heavy industry or incinerators were located within 2 km from the measuring site. The traffic is heavy in the city but the nearest larger road is 200 m from the sampling site. The site should give a good picture of the PCDD/Fs load in the urban environment. The sampling sites is described by Hovmand (2005).

## *Gundsømagle*

Gundsømagle is a small village located in North Zealand 5 km east of Roskilde Fjord. The village is mainly residential, having many homes with wood stoves used for additional heating as a supplement to the prevailing electrical heating. No other known atmospheric dioxin sources exist in or near the village. In the predominantly westerly wind, the village is exposed to air masses blowing from the fjord. Hence, the air is believed to be relatively free from PCDD/Fs from large point sources, and the measurements supposed to reflect local conditions. The air measuring station is placed in the village near a row of houses (< 100 m) with wood stoves.

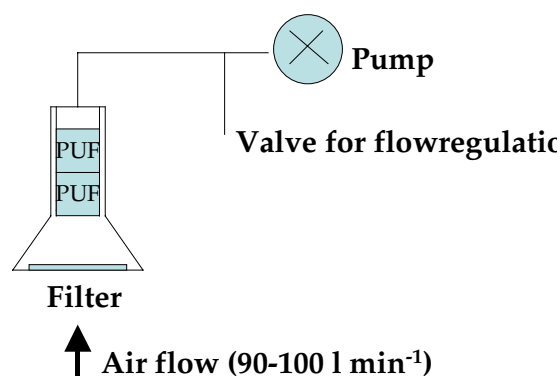
The project in Gundsømagle is connected with an investigating of PCDD/Fs emissions from wood stoves, and the significance for the local atmosphere. That project, which will be reported separately, includes measurements of PCDD/Fs in flue gas in chimneys in the village. The air measurements will be continued until the summer 2005.

A study of PAHs and particles emission from wood stove is also in progress at the same site. The results from this study will also be reported separately (Glasius et al., 2005).

## **2.3 Equipment**

### *Air*

A dual-sampling module (type GPS1-1, Andersen Instruments Inc., Smyrna, Georgia, USA), shown in Figure 3, is employed for the sampling of air (gasses and particles). The sampler is made of aluminium. The front part of the sampler contains a planar quartz fibre particle filter (Whatman QM-A, 0.6 µm, 10.2 cm in diameter), supported by a net made of stainless steel. The sampler narrows down to the second part, containing a glass cylinder with two polyurethane foam (PUF) plugs in series (Søm og Plastskum Fabrikk, Sunde, Norway). The density of the PUF is 0.02 g/cm<sup>3</sup>. Each plug is 5 cm long and with a diameter of 6.5 cm. The method is the same as used in the US EPA's National Dioxin Air Monitoring Network (Ferrario et al., 2001).



**Figure 3.** Flow diagram of the Andersen sampler used at Frederiksborg and in The Botanical Garden of Copenhagen.

The sampler is operating at a flow rate of about 95 l/min. The sampling duration is one month, giving a total volume of about 4000 m<sup>3</sup>. The flow is measured at the start and end of each exposure. In most of the wintertime exposure periods, a shift of the front filter has been done in the middle of the period in order to avoid too large a flow drop. A linear drop in flow over time is assumed when calculating the total sampled volume. Of the 21 observation from Frederiksborg, five periods had an end flow that had decreased more than 10% of the start flow (March 2002 (13%), December 2002 (28%), February 2003 (38%), March 2003 (28%) and November 2003 (13%)). The samples taken in the late spring and summer 2003 were pooled into two-month samples, thus dividing the year into nine periods. This approach leads to higher sensitivity during the summer months, where the concentrations were low. The lower temporal resolution obtained in this way in the summer is believed to be sufficient to get an adequate picture of the annual profile, because of the slow summer variation.

### *Bulk deposition*

As mentioned above, there is no standardised and reliable method for measurements of the bulk deposition of PCDD/F. Different sampler designs have been employed by a number of research groups. The most widely used bulk deposition sampler is the Bergerhoff gauge, which employs a small open funnel with flat bottom (Kirschmer et al., 1992). The present design comprises a funnel connected to a particle filter (quartz-wool) followed by an organic absorbent (XAD-2). The particles collected in this type of samplers are mainly larger than 10 µm.

All parts of the equipment in direct contact with collected rain and through fall water were made of borosilicate glass in order to avoid adsorption of PCDD/F, which can be a problem with stainless steel, plastic or other more porous materials. Furthermore, there may be a catalytic effect of metal surfaces, which may promote degradation of PCDD/Fs in the sampler.

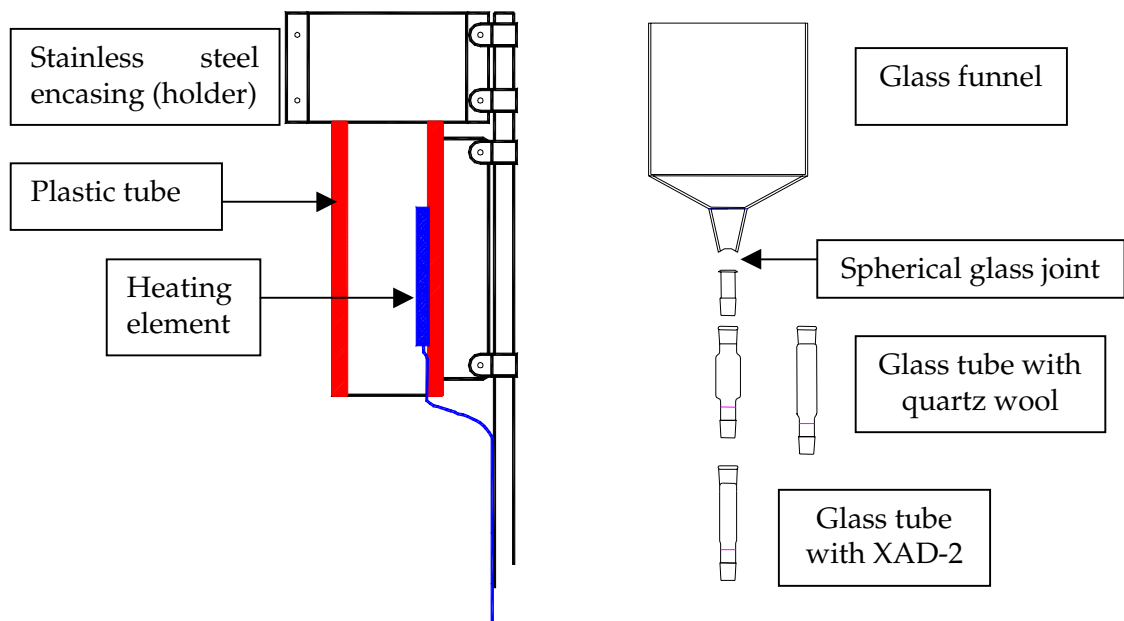
In order to collect sufficient material in the monthly samples of deposition and through fall (drip from the canopy) to detect and quantify

PCDD/F, large sampling areas were required. It would have been best to use 1 m<sup>2</sup> sampling area, but because the handling of the fragile glass funnels under field conditions is difficult, we realised that a total weight of the funnel exceeding 10 kg, corresponding to 0,07 m<sup>2</sup> collecting area, would be impractical to handle. In addition, larger funnels are not standard glassware, and they are difficult to manufacture. In order to increase the total collecting area, samplers were sometimes employed in pairs or quadruples.

Laboratory bottles (Scott Mainz, Cat. No 21 801 91) with a volume capacity of 10 l (through fall) or 20 l (deposition) were converted to funnels by removing the bottom. The collecting areas of the sampling funnels were 0.043 m<sup>2</sup> and 0.07 m<sup>2</sup>, respectively. The height of the rim is 30 cm, giving sufficient sampling capacity for snow under Danish winter conditions, and further reducing splash-back and light intensity on the filter. This funnel is comparable to the modified German sampler (VD 2119) used by Horstmann and McLachlan (1997), Knoth et al. (2000) for sampling of PCDD/Fs and PCB, and by Guerzoni et al. (2004).

A spherical ground glass joint was fused to the bottleneck of the funnel (Figure 4), connected via a long glass tube, which adds pressure to the gravity-assisted flow, to a sampling train comprising two filters: a quartz wool plug that retains particles from rainwater followed by a XAD-2 filter that absorbs dissolved PCDD/Fs. The filter materials were supported by glass frittes in the filter tubes. All tubes were suspended in the funnel, connected by ground glass joints secured by clamps.

A stainless steel casing surrounds the glass funnel, keeping it in position. A rubber seal mounted on the upper rim of the encasing tightens between encasing and funnel, to avoid leakage of rainwater on the outer side of the funnel and filter train. The funnel was protected from light by the steel encasing and the filters by a black plastic tube as shown in Figure 4. The long suspension tube reduces the intensity of light falling on the quartz-wool filter. For further light protection each glass filter tube is wrapped in aluminium foil. The plastic tube is insulated and a low voltage thermostatic heating element keeps the glass tubes frost-free. This precaution is necessary, since in preliminary experiments the glass broke because of ice formation during the subsequent freezing and thawing often encountered in Danish winters.



**Figure 4.** Schematic diagram of sampler for bulk-deposition and through fall.

Our sampler design differs from other similar samplers in the following ways:

- We use an all-glass system without plastic or steel surfaces in contact with the sample
- Particle and absorption filters are used instead of collecting the rainwater
- Quartz-wool depth filter are used instead of planar filter or Soxhlet crucible
- XAD-2 is used as absorbing material instead of PUF
- Heating is applied to avoid glass breakage due to freezing and to melt snow

The design offers several advantages compared to other deposition samplers

- The all-glass system gives lesser absorption and catalytic degradation
- It is easier to clean than plastic or metals
- The filters were easy to ship and store compared to samples collected in bottles, or to Bergerhof gauges.
- The quartz-wool filters were less likely to clog compared to planar filters.
- The light protection is much better than the more open designs (e.g. Bergerhof).

In Frederiksborg, the samplers were employed in pairs, giving a total area of 0.14 m<sup>2</sup>. For through fall, four parallel smaller funnels of 0.043 m<sup>2</sup> were used, giving a total area of 0.17 m<sup>2</sup> (Table 2). At other stations only one deposition sampler is employed.



The combined sampling area and the collected average annual amount of water is shown in Table 2 in addition to the actual registered amount of water sampled during the one-year experimental period.

**Table 2.** Sampling area of samplers and amount of water in combined samples. Air volume sampled by the high volume sampler.

Site	Deposition sample	Funnel area	n	Sampling area	Sampled water amount	Sampled air volume
Unit		m <sup>2</sup>		m <sup>2</sup>	l/year	m <sup>3</sup> /year
Frederiksborg	Open field	0.07	2	0.14	82	48,000
Frederiksborg	Through fall	0.043	4	0.17	83	
Ulborg	Open field	0.070	1	0.07	60	
Copenhagen	Open field	0.070	2	0.14	82	48,000
Bornholm	Open filed	0.070	2	0.14	70	
Gundsømagle						48,000

## 2.4 Sampling procedure

### *General*

Samplers were changed with an interval of one or two, occasionally three months for deposition samples. A check schema was filled out with sampling data and observations concerning the state of the samplers. Exposed samples were kept cool and dark in transport boxes, and sent to the laboratory for analyses.

### *Deposition filter shift*

The filter tubes were packed in the laboratory and shipped to the station. Before use, the quartz-wool is cleaned by soxhlet extraction in CH<sub>2</sub>Cl<sub>2</sub>, XAD-2 in toluene. After air-drying, 2.5 g of quartz-wool or 20 g of XAD-2 is carefully packed into clean filter tubes, which contain glass frittes to support the filter material. The quartz-wool filter is then spiked with sampling spike solution as described in the analytical section.

At the station, the funnel is rinsed with distilled water, which is allowed to run through the exposed filter train. This is then removed, and a new one mounted, leaving the funnel in place. Snow collected in the funnel was normally left over for the next sampling period. However, in case of very severe snowfall in prolonged frost periods, it has been necessary to thaw the snow using an electrical heating lamp.

### *Funnel cleaning*

In the first years of the programme, the funnels were rinsed with solvents at rare occasions at the station in field conditions. Once a year the funnel was dismounted and cleaned thoroughly in the laboratory, finished by annealing at 450 °C. However, to clean the funnel completely after an exposure period that long proved very difficult. Furthermore, it was feared that the dirt and soot residing in the funnel could bind PCDD/F, preventing it from reaching the filter train; this could in theory lead to loss of PCDD/F. Hence, a more rigorous rinsing procedure was introduced. According to this, after the water rinse and after the exposed filter train has been removed, the funnel was further rinsed with acetone (to remove residual water and pre-

liminary dissolve PCDD/F) followed by toluene (to dissolve residual PCDD/Fs and desorb it from soot). The solvents were collected in a bottle, and analysed together with the sample. To check the importance of the rinsing, the solvents have been analysed separately on a single occasion, as reported in the section on Analytical performance.

*Air*

Before use, the PUF was cleaned by soxhlet extraction in toluene. The PUF plugs were dried and packed into clean glass tubes in the laboratory, and were then mounted in the clean sampler. The particle (QFF) filter was mounted in the sampler and spiked with sampling spike mix as described in the Analytical chapter. The complete sampler was then shipped to the sampling station.

In wintertime the particle load on the QFF filter increased, and a midway change of particle filter was necessary in order to avoid flow-drop. This operation was performed at the station. The halfway-exposed QFF filter was removed and packed in aluminium foil, and a new spiked QFF filter mounted.

### 3 Analytical

#### *Principle*

The filters of the air (QFF and PUF) or deposition sample (Quartzwool and XAD-2) were combined, and spiked with a mixture of eleven  $^{13}\text{C}_{12}$ -labelled PCDD/Fs congeners, the extraction spike mix. The spiked combined sample was extracted in toluene. The extract was concentrated followed by classic clean up on  $\text{SiO}_2/\text{NaOH}$ ,  $\text{SiO}_2/\text{H}_2\text{SO}_4$  and acidic  $\text{Al}_2\text{O}_3$ . The analysis was performed by GC/MS at 10000 resolution. The spiking programme, as well as the clean-up and mass spectrometric (MS) analysis is adapted from a modified version of the European standard for analysis of dioxin in flue gasses (CEN, 1996).

#### 3.1 Extraction and clean-up

#### *Pre-treatment of samples*

Before sampling, the particle filter (quartz wool for a deposition sample or QFF filter for air samples, respectively) was spiked with a sampling spike mixture containing three  $^{13}\text{C}_{12}$ -labelled PCDFs in toluene (Table 3) according to European standard EN 1948-1 (CEN, 1996). In case of a midway shift of QFF filter for an air sample, the new filter was spiked in the same way as the first one.

After sampling, the quartz wool of a bulk deposition sample was sucked dry by vacuum. The exposed samples were stored at 4 °C until analysed.

#### *Chemicals*

Toluene	Rathburn, glass distilled
n-hexane	Rathburn, glass distilled
$\text{CH}_2\text{Cl}_2$	Rathburn, HPLC grade
$\text{Na}_2\text{SO}_4$	Merck, anhydrous, analytical grade
$\text{SiO}_2$ (silica)	Merck, Kieselgel 60, 0.063-0.20 mm
$\text{H}_2\text{SO}_4$	Merck, analytical grade
NaOH	Merck, analytical grade
$\text{Al}_2\text{O}_3$	ICN Biomedicals, Alumina A
n-dodecane	BDH, Purity > 99% (GC area)
PFK	Fluka, Perfluorokerosene, High boiling, for mass spectroscopy

#### *Extraction*

Before extraction, the filters of a sample (either air, deposition or through fall) were combined. In case of pools, either from parallel samplers, or consecutive monthly samples, or both, all filter material was combined in the same extraction. Then 100 µl of extraction spike mixture was added, containing eleven  $^{13}\text{C}_{12}$ -labelled congeners (0.4 ng tetra-hexas, 0.8 ng hepta-octas, Table 4). Air samples were Soxhlet extracted (without crucible) for 20 hours with 700 ml of toluene. Bulk deposition samples were refluxed using Dean-Stark water removal trap for 20 hr with 700 ml of toluene. The extract was filtered through filter paper. A volume of 0.5 ml of n-dodecane was added as a

keeper, and the extract concentrated to a volume of about 0.5 ml in vacuum using a rotary evaporator operating at 35 C, 25 torr.

#### *Clean-up*

Clean-up was then performed by classical column chromatography using SiO<sub>2</sub> /NaOH, SiO<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>, acidic Al<sub>2</sub>O<sub>3</sub>.

The extract was dissolved in 3 ml of n-hexane, and applied to the first of two columns coupled in series, containing (mentioned from top to bottom):

Column 1: (2.5 x 12 cm fitted with reservoir 250 ml)

- 1 g anhydrous Na<sub>2</sub>SO<sub>4</sub>.
- 1 g SiO<sub>2</sub> (activated at 150 C),
- 4 g SiO<sub>2</sub> containing 33% 1 M NaOH
- 1 g SiO<sub>2</sub>
- 4 g SiO<sub>2</sub> containing 44% conc. H<sub>2</sub>SO<sub>4</sub>
- 2 g SiO<sub>2</sub>

Column 2: (1 x 17 cm)

- 1 g anhydrous Na<sub>2</sub>SO<sub>4</sub>.
- 6 g acidic Al<sub>2</sub>O<sub>3</sub> (activated at 250 C).

Both columns were eluted in series with 90 ml of n-hexane. The columns were disconnected, and column 2 alone eluted with 20 of ml n-hexane. Both eluates, which contain impurities, were discarded.

The PCDD/Fs fraction, which was adsorbed on the Al<sub>2</sub>O<sub>3</sub>, was eluted with 20 ml of a mixture of CH<sub>2</sub>Cl<sub>2</sub>/n-hexane 20/80 (v/v).

The eluate, which contains the cleaned PCDD/Fs fraction, was concentrated to about 1 ml under N<sub>2</sub>. Then 25 ml of syringe spike solution containing two <sup>13</sup>C<sub>12</sub> - PCDDs in n-dodecane (Table 5) was added, the spike also functioning as a keeper. The evaporation was continued to near 25 ml. The sample was transferred to an injection vial, ready for analysis by GC/MS.

#### *Blanks*

For each analytical series blanks were included by subjecting unexposed filters and glassware to the total extraction and clean up procedure as described above. For air, laboratory blanks were made by analysing a QFF filter and two PUF plugs. For deposition, sampling blank (so-called "box-blank) were made by keeping a spiked filter train in a box on the sampling station during the sampling period. The blank results were subtracted from the results of the unknown on an amount per sample basis for each analytical series. For results of blanks see section on Analytical Performance.

### 3.2 Standards and spikes

Spikes were PCDD/Fs standards labelled with stable isotopes, added in precise amounts to the sample at different stages during the laboratory procedure. Exclusively  $^{13}\text{C}$  (carbon-13) labelled spikes were used. Sampling spikes were added before sampling, extraction spikes before extraction, and syringe spikes before injection in the CG/MS. The spikes were chemically identical with the unlabelled PCDD/Fs (the *analytes*), and therefore follow those during the analytical procedure. They can be distinguished because of their higher mass during the MS. They were used for the identification and quantification of analytes (isotope dilution principle), and further for evaluation of losses encountered (recovery determination) and check of instrument performance (signal to noise ratio). All standards and spikes were manufactured by CIL, Andover, Massachusetts, USA. The solutions were stored at 4 °C.

The sampling spike solution (Table 3) is a mixture of three  $^{13}\text{C}_{12}$  labelled PCDF congeners added to the particle filter (i.e. QFF for air, quartz-wool for deposition) before exposure, used for determination of sampling recovery, indicative of losses during sampling.

**Table 3.** Sampling spike solution

Substance	ng/ml	Label
12378-PeCDF	4	$^{13}\text{C}_{12}$
123789-HxCDF		
1234789-HxCDF		
Toluene	Solvent	

The extraction spike solution (Table 4) is a mixture of eleven  $^{13}\text{C}_{12}$  labelled PCDD/Fs congeners added to the sample before extraction, used for identification and quantification of the PCDD/Fs congeners, and for determination of extraction recovery, indicative of losses during extraction and clean-up.

**Table 4.** Extraction spike solution

Substance	ng/ml	Label
2378-TCDD	4	$^{13}\text{C}_{12}$
12378-PeCDD		
123678-HxCDD		
1234678-HpCDD OCDD	8	$^{13}\text{C}_{12}$
2378-TCDF	4	$^{13}\text{C}_{12}$
23478-PeCDF		
123678-HxCDF		
234678-HxCDF		
1234678-HpCDF OCDF	8	$^{13}\text{C}_{12}$
Toluene	Solvent	

The syringe spike solution (Table 5), containing two  $^{13}\text{C}_{12}$  labelled PCDD congeners in n-dodecane, is used for re-dissolving and dilution of the sample. The presence of syringe spikes in the sample is necessary to calculate the recoveries. It is further used to check the injection, function and signal of the GC/MS system for each GC/MS run. Finally, it is used during preparation of the external standard solutions. EN-1948 prescribes  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD as syringe spike. This is synthesised solely for this purpose and is the only spike in the spiking programme which does not have a corresponding analyte.

**Table 5.** Syringe spike solution

Substance	ng/ml	Label
1234-TCDD 123789-HxCDD	16	$^{13}\text{C}_{12}$
n-dodecane	Solvent	

#### External standards

A series of external standard solutions (Table 6) was analysed by CG/MS for identification and quantification of the individual congeners, and for checking the performance of the mass spectrometer during the analysis. The solutions form a series of dilution, containing all the 2,3,7,8-substituted congeners in increasing concentrations, given in the first columns of the table. All solutions further contain the  $^{13}\text{C}_{12}$  labelled standards (spikes) in the same concentration given in the last column of the table.

**Table 6.** External standard solutions

Substance	Unlabelled					$^{13}\text{C}_{12}$
	ng/ml	ng/ml	ng/ml	ng/ml	ng/ml	ng/ml
1234-TCDD	-	-	-	-	-	4
2378-TCDD	0.4	1	4	10	40	4
12378-PeCDD	0.4	1	4	10	40	4
123478-HxCDD	0.4	1	4	10	40	-
123678-HxCDD	0.4	1	4	10	40	4
123789-HxCDD	0.4	1	4	10	40	4
1234678-HpCDD	0.8	2	8	20	80	8
OCDD	0.8	2	8	20	80	8
2378-TCDF	0.4	1	4	10	40	4
12378-PeCDF	0.4	1	4	10	40	4
23478-PeCDF	0.4	1	4	10	40	4
123478-HxCDF	0.4	1	4	10	40	-
123678-HxCDF	0.4	1	4	10	40	4
123789-HxCDF	0.4	1	4	10	40	4
234678-HxCDF	0.4	1	4	10	40	4
1234678-HpCDF	0.8	2	8	20	80	8
1234789-HpCDF	0.8	2	8	20	80	8
OCDF	0.8	2	8	20	80	8
n-dodecane	Solvent					

The standard solutions of levels 1, 4 and 10 ng/ml 2,3,7,8-TCDD were used for quantification. To reduce the risk of carry-over from standards to unknowns, the strongest standard was not included in the analysis of a series of weak samples, such as deposition samples. The weakest standard solution (0.4 ng/ml TCDD) was used for checking the signal to noise ratio (sensitivity) of the GC/MS system.

All standard solutions from 0.4 to 40 ng/ml (TCDD) were used for linearity test of the GC/MS.

### 3.3 GC/MS analysis

#### *Analytical sequence*

Each analytical series was analysed by GC/MS in the following sequence:

Dilution series of external standards, a sample of pure n-dodecane for control of carry-over, blank, the unknown samples, dilution series of external standards.

During long analytical series, extra standard series were inserted between the unknowns.

#### *Gaschromatography (GC)*

Gaschromatograph: Hewlett-Packard 5890 series II  
Injection: Automatic, CTC autosampler, 3 ml split/splitless, 290 C, purge closed 40 sec, Restek gooseneck insert 4 mm  
Pre-column: Chrompack Retention Gap, fused silica, 2.5 m x 0.32 mm i.Ø.  
Column: Agilent J&W Scientific DB-5MS, fused silica, 60 m x 0.25 mm i.Ø, cross-linked phenyl-methyl silicone 0.25 µm film thickness  
Carrier gas: He, 150 kPa  
Temperature-programme: 40 sec at 200 C, 20 C/min to 230 C, 3 C/min to 230 C, 28 min at 290 C  
Transfer line: 290 C

#### *Mass spectrometry*

Instrument: Kratos Concept 1S, high resolution magnetic sector mass spectrometer  
Resolution: 10,000 (10% valley definition)  
Ionisation: Electron impact (EI). Source temperature 290 C, electron energy 35-45 eV depending on tuning, electron current 5 mA  
Interface: Direct to ion source, 290 C  
High voltage: Acceleration 8 kV, electron multiplier 2,5-3 kV  
Noise filter: 300 Hz digital  
Magnet stabilisation: Current  
Solvent filament delay: 10 min

Coolant temperature: 19-21 C  
 Calibration gas: Perfluoro kerosene (PFK)  
 Scan parameters: Cycle time 1 sec  
 Electrostatic analyser (ESA) sweep 10 ppm  
 Lock-mass sweep 300 ppm  
 Lock-mass dwell 100 msec  
 Check-mass dwell 20 msec  
 Dwell per monitored mass 90-100 msec  
 Inter mass delay 10 msec  
 Fixed fly-back time 20 msec

Detection mode: Selected Ion Monitoring (SIM) using 5 windows with different mass combinations ("descriptors", Table 7)

The descriptors contain masses for analytes and spikes. For each substance class (i.e. sum formula) two masses were monitored, corresponding to the most intense lines in the molecular ion group of the mass spectrum. In all windows was further used a lock-mass to correct (automatically) for magnet instabilities, and a check-mass as a documentation of correct mass-lock and instrument signal. Both were prominent lines in the PFK mass spectrum.

**Table 7.** Selected ion monitoring (SIM) programme for mass spectroscopy

Substance	m/z 1	m/z 2	m/z 3 <sup>13</sup> C <sub>12</sub> <sup>-</sup>	m/z 4 <sup>13</sup> C <sub>12</sub> <sup>-</sup>	Intensity % mz1/mz2
Group 1, Cl <sub>4</sub>			10-18 min		
Lock/check	292.9824	304.9824			
TCDF	303.9016	305.8987	315.9419	317.9389	77.3
TCDD	319.8965	321.8936	331.9368	333.9339	77.2
Group 2, Cl <sub>5</sub>			18-24 min		
Lock/check	330.9792	342.9792			
PeCDF	339.8597	341.8567	351.9005	353.8976	154.3
PeCDD	355.8546	357.8517	367.8954	369.8925	154.3
Group 3, Cl <sub>6</sub>			24-28 min		
Lock/check	392.9760	392.9760			
HxCDF	373.8207	375.8178	385.8610	387.8579	123.5
HxCDD	389.8156	391.8127	401.8559	403.8530	123.5
Group 4, Cl <sub>7</sub>			28-34 min		
Lock/check	442.9729	442.9729			
HpCDF	407.7818	409.7788	419.8220	421.8189	102.9
HpCDD	423.7767	425.7737	435.8169	437.8140	102.9
Group 5, Cl <sub>8</sub>			34-45 min		
Lock/check	442.9729	442.9729			
OCDF	441.7428	443.7398	453.7860	455.7830	88.2
OCDD	457.7377	459.7348	469.7780	471.7750	88.2



### 3.4 Toxic equivalents (TEQ)

The result is calculated in toxic equivalents according to the formula:

$$E_{\text{tox}} = \sum C_{ip} \cdot T_i$$

where:

- $E_{\text{tox}}$  = Toxic Equivalents concentration in sample (TEQ, ng/kg)  
 $C_{ip}$  = Concentration of i'th isomer  
 $T_i$  = Toxic Equivalent Factor (TEF) for i'th isomer, either International or WHO (Table 8)

International toxic equivalent factors (I-TEF) have been generally used for many years. The newer WHO-TEF is regarded as more relevant for toxicity in humans. In the present investigation, the results have been calculated both systems. In Figures, I-TEQ are used to make them comparable with other investigations.

**Table 8.** Toxic equivalent factors (TEFs)

Substance	I-TEF	WHO-TEF
2378-TCDD	1	1
12378-PeCDD	0.5	1
123478-HxCDD	0.1	0.1
123678-HxCDD	0.1	0.1
123789-HxCDD	0.1	0.1
1234678-HpCDD	0.01	0.01
OCDD	0.001	0.0001
2378-TCDF	0.1	0.1
12378-PeCDF	0.05	0.05
23478-PeCDF	0.5	0.5
123478-HxCDF	0.1	0.1
123678-HxCDF	0.1	0.1
123789-HxCDF	0.1	0.1
234678-HxCDF	0.1	0.1
1234678-HpCDF	0.01	0.01
1234789-HpCDF	0.01	0.01
OCDF	0.001	0.0001

Abbreviations: I-TEF = International toxic equivalent factor,  
 WHO-TEF = World Health Organisation toxic equivalent factor

### 3.5 Performance of analytical method

*Air*

To evaluate repeatability, in May 2002 a parallel sampling was performed at Frederiksborg and the results showed good agreement. Furthermore, to evaluate the collecting efficiency, a breakthrough experiment was performed in December 2002 by placing two extra PUF-plugs (a so-called "police filter") after the normal filter train. The police filter was analysed separately.

**Repeatability** for two parallel samples: 6%.

**Breakthrough** in police filter experiment: 0.6%.

**Recoveries** (mean – sd all data): Sampling recovery 67% – 21%, extraction recovery 79% – 14%.

**Detection limits**, defined by signal to noise ratio on 2s level of significance, (mean all data): Ranging from 0.02 fg/m<sup>3</sup> (OCDD) to 0.5 fg/m<sup>3</sup> (PeCDD).

Laboratory blanks

*Bulk deposition*

To evaluate repeatability, a parallel sampling was performed in January 2004 at Frederiksborg, by pooling the four filter trains in two pairs, which were analysed separately. The results showed a relative standard deviation of 45%. This considerable deviation was probably caused by the different amounts of spruce needles in the funnels, which was substantially larger for the pair having the highest result. Hence, this variation is inherent in the through fall itself because of the uneven spatial distribution of the litter over the forest floor, and is not caused by the sampling method itself. However, a lower variation will result when all four funnels were analysed together, as is the normal practice. This was anticipated during the planning of the campaign, and it is the reason for the use of four funnels analysed together.

To evaluate the absorption efficiency, a breakthrough experiment was performed in April 2004 by collecting the rainwater flowing through the normal filter train in a bottle. The rainwater was analysed separately (using NERI in-house analytical method for PCDD/Fs in water by extraction in toluene).

A solvent rinsing experiment was performed in Frederiksborg September 2004 in order to measure the amount of remaining PCDD/Fs in the funnel, and to test the efficiency of the rinsing procedure. After the water rinse, the funnels were rinsed with acetone followed by toluene. The rinsings were collected and analysed separately.

**Repeatability** for through fall (two parallel pairs of samples): 45%.

**Breakthrough** by collecting water through bulk deposition train: 0.2%.

**Funnel solvent rinse** performed after water rinse (rinse/sample, %): First rinse with acetone 1.1%, second rinse with toluene 0.1%.

**Detection limits** for monthly samples, defined by signal to noise ratio on 2s level of significance (mean all data): Ranging from 0.1 pg/m<sup>2</sup>-d (TCDD) to 8 pg/m<sup>2</sup>-d (OCDD).

**Sampling recoveries** for <sup>13</sup>C<sub>12</sub>-1,2,3,7,8-PeCDD (mean – sd all data): Bulk deposition 40 – 23%, through fall 38 – 33%

**Sampling recoveries** for <sup>13</sup>C<sub>12</sub>-1,2,3,4,7,8,9-HpCDD (mean – sd all data): Bulk deposition 13 – 15%, through fall 26 – 11%.

**Extraction recoveries** (mean – sd all data): Bulk deposition 51 – 19%, through fall 45 – 9%.

*Note on sampling recovery*

The sampling recoveries were somewhat lower than the extraction recoveries, because during the sampling exposure, the compounds were inevitably lost to evaporation, breakthrough and degradation.

It is noteworthy that the bulk deposition average sampling recovery for <sup>13</sup>C<sub>12</sub>-1,2,3,7,8-PeCDD is 40%, whereas the corresponding figure for <sup>13</sup>C<sub>12</sub>-1,2,3,4,7,8,9-HpCDD is only 13%, even if the latter higher chlorinated congener is more chemically stable than the former one. An explanation for this anomaly could rely on the higher water solubility of the lower congeners. Hence, during the sampling exposure, the rain water predominantly washes the more soluble <sup>13</sup>C<sub>12</sub>-1,2,3,7,8-PeCDD out of the quartz-wool filter onto the XAD-2 filter. Adsorbed here, it is protected from photo-degradation. In contrast, the low water soluble <sup>13</sup>C<sub>12</sub>-1,2,3,4,7,8,9-HpCDD preferentially remains on the quartz-wool where it is more exposed to light. This interpretation is supported by an annual variation of the field recoveries, which has a pronounced summer minimum. Further indications come from the corresponding recoveries for through fall, which displays substantially lesser difference between the sampling spikes. This can be explained by the low light intensity in the shadow of the spruce plantation. Provided the above considerations were correct, they demonstrate the importance of light protection. But in practice it is difficult to devise better light protection measures than the present ones in use, without impeding the collecting properties of the sampler. In addition, the location in forests reduces the direct sunlight falling on the samplers. However, the evidence is indirect, since only spikes were involved; the significance of light protection for native PCDD/Fs during the residence in the sampler has not been investigated directly.

*Note on extraction recovery*

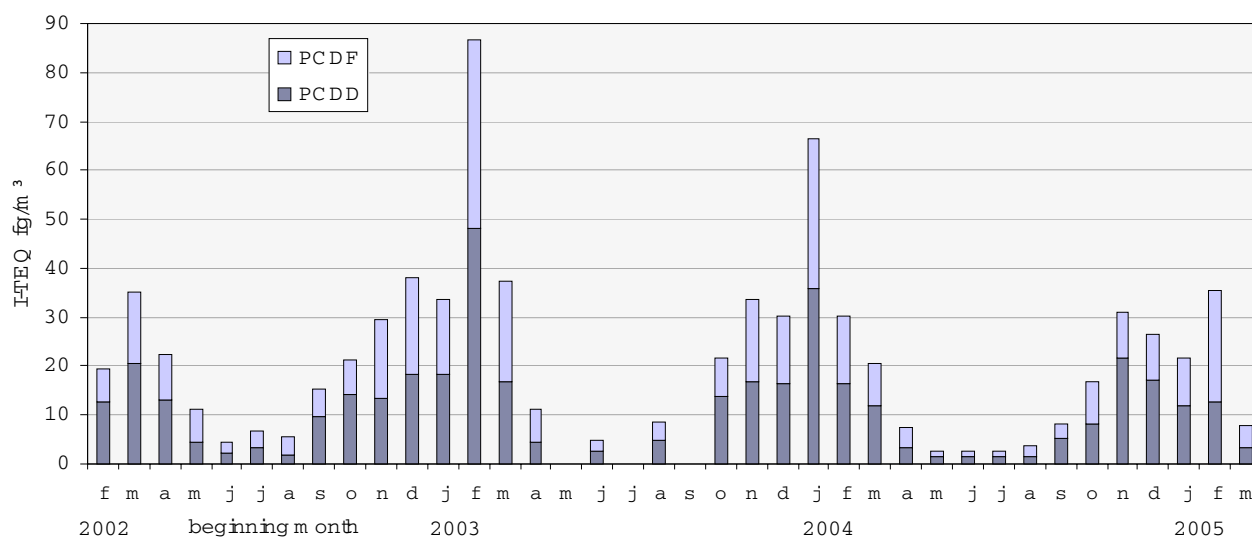
Whereas the extraction recovery grand mean for air is 79%, which is entirely acceptable, the recovery for deposition is somewhat lower, and that for through fall were even lower. A reason for this is the use of reflux extraction for deposition and through fall samples, in stead of the more efficient soxhlet extraction used for air. This is dictated by practical reasons, because it has turned out to be very difficult to dry the very wet exposed XAD-2 material sufficiently for soxhlet extraction. During the reflux extraction, the water is boiled out of the sample as an azeotrope with toluene and removed with the Dean-Stark trap, which is a very efficient method to remove water. If any water is left in the XAD-2 material, the extraction efficiency will suf-

fer. Furthermore, the reflux is somewhat overloaded, being designed for one sampling train only; this will lead to lower extraction efficiency when multiple samples are pooled. Particularly the through fall extraction is overloaded with the pooled materials from four (in some cases eight) parallel sampling trains.

## 4 Results

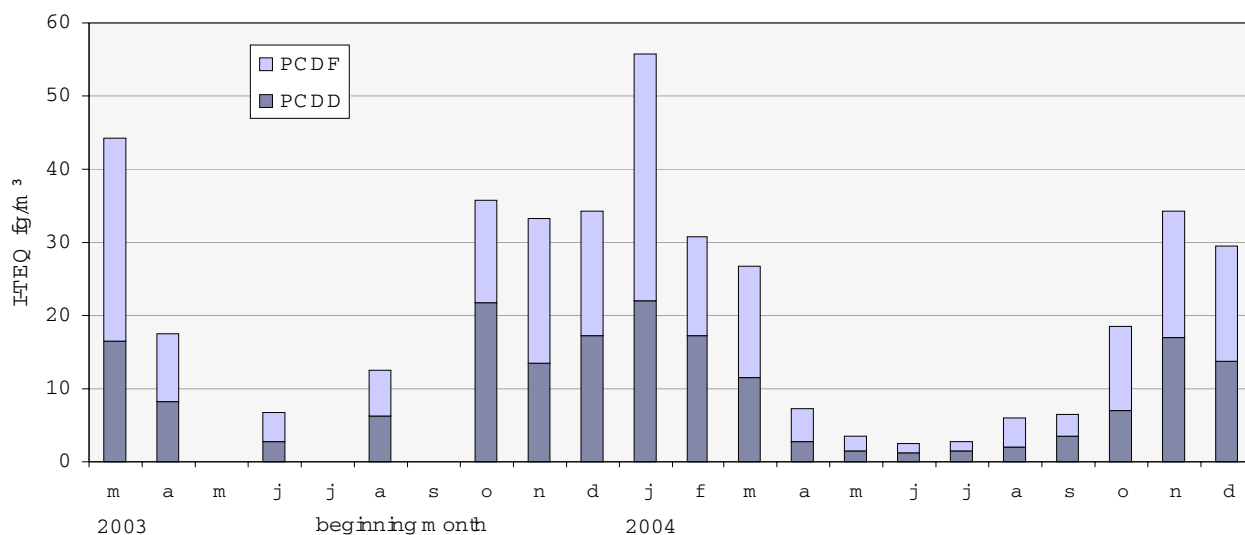
### 4.1 Concentrations in air

Figure 5 shows the results for PCDD/Fs in air in Frederiksborg. A strong seasonal variation is observed in all years, the minimum occurring during the summer and the maximum during the winter. The winter maxima stand out sharply and well defined. The annual variation profile seems very alike in the different years. The variations span a factor of 35. The average winter concentration is  $31 \text{ fg/m}^3$  I-TEQ, the summer average  $8 \text{ fg/m}^3$  I-TEQ and the total average  $20 \text{ fg/m}^3$  I-TEQ. An almost equal distribution between PCDD and PCDF is found for most of the measurements; the average PCDF/PCDD ratio is 0.9.

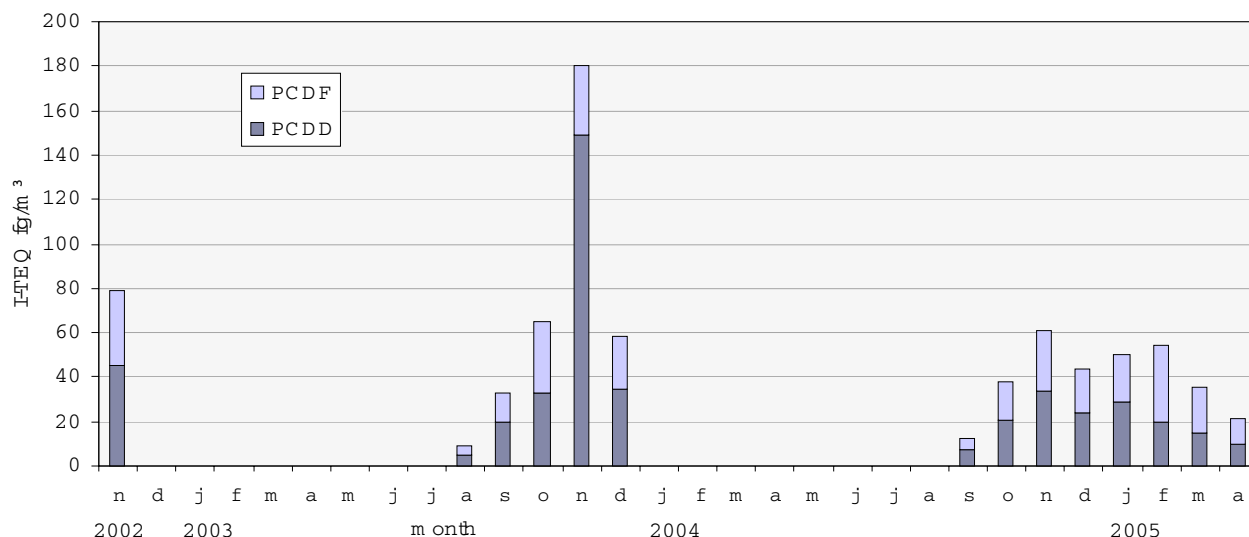


**Figure 5.** PCDD/Fs in the ambient atmosphere of Frederiksborg State Forest expressed as I-TEQ contributions from PCDD and PCDF respectively. April/May, June/July and August/September 2003 were sampled monthly, though analysed as pooled samples.

Figure 6 shows the PCDD/Fs concentrations in the air in central Copenhagen. The results were very similar to the results from Frederiksborg, with respect to the seasonal variation and the order of magnitude. Also here, an almost equal distribution between PCDD and PCDF is found for most of the measurements, the average PCDF/PCDD ratio being 1.2. The variation spans a factor of 23, somewhat lower than in Frederiksborg. The average winter concentration is  $34 \text{ fg/m}^3$  I-TEQ, the summer average  $8 \text{ fg/m}^3$  I-TEQ and the total average  $20 \text{ fg/m}^3$  I-TEQ, i.e. very close to those found in Frederiksborg.

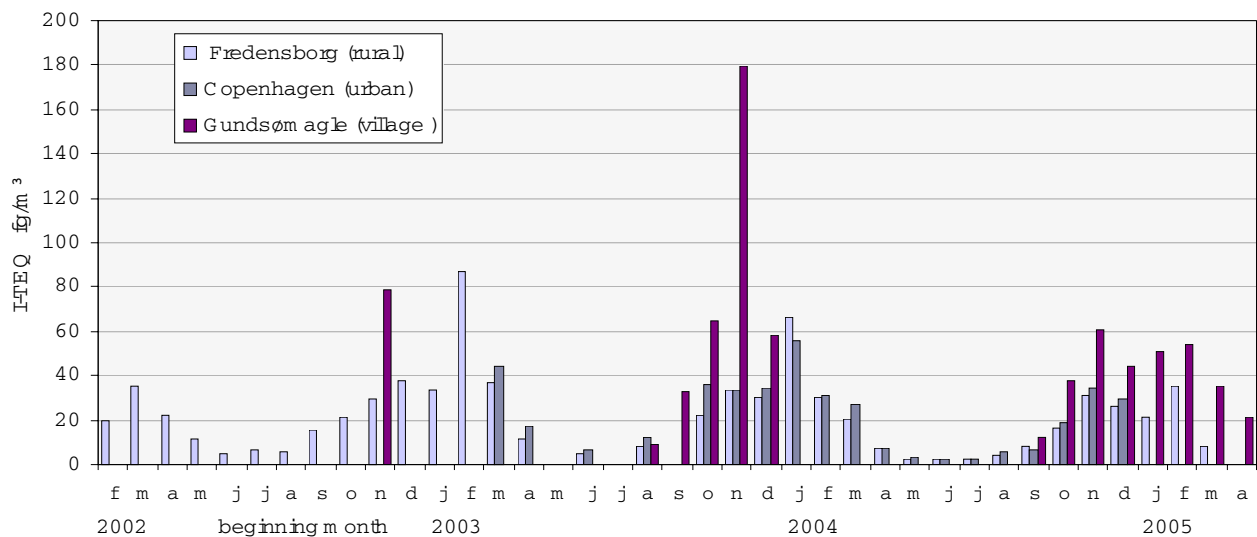


**Figure 6.** PCDD/Fs in the ambient atmosphere of central Copenhagen (Botanical Garden) expressed as I-TEQ contributions from PCDD and PCDF, respectively. April/May, June/July and August/September 2003 were sampled monthly, though analysed as pooled samples.



**Figure 7.** PCDD/Fs in the ambient air of Gundsømagle, a small village in North Zealand having many homes with wood stoves. The measurements cover a single result from November 2002, and the late summer and heating season autumn 2003, expressed as I-TEQ contributions from PCDD and PCDF, respectively.

Figure 7 shows the PCDD/Fs concentrations in the air in Gundsømagle. The concentrations rise sharply during the heating season beginning in October 2003, reaching a maximum of 180 fg/m<sup>3</sup> I-TEQ in November 2003. The heating season 2004-05 displays a similar rise, but does not include a pronounced maximum comparable with the one in 2003. The variation spans a factor of 20; this comparatively low factor is caused by the lack of a complete summer period. In the maximum, the distribution between PCDD and PCDF is dominated by PCDD, in contrast to the other air measurements, which show an average PCDF/PCDD ratio of 0.9.

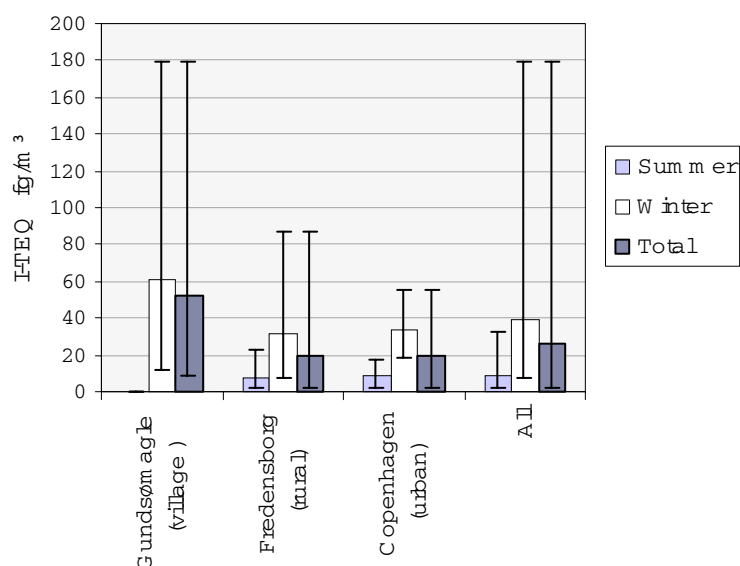


**Figure 8.** PCDD/Fs concentrations in air at all stations Frederiksborg (rural forest), Copenhagen (urban) and Gundsømagle (village) shown on a common time axis.

Figure 8 shows the results for PCDD/Fs in air from all three stations on a common time axis. The parallel measurements in urban Copenhagen 40 km from the forest site Frederiksborg follow each other closely and synchronously in spite of the distance and different characteristics of the sites. This strongly suggests the hypothesis that the seasonal variation in background concentrations is a regional phenomenon, not a local one. This issue is further addressed in the discussion section.

In contrast, the concentrations in Gundsømagle deviate much from those of the other sites. In August and September 2004 the results are comparable with Frederiksborg and Copenhagen, but in November 2003 the concentrations at Gundsømagle are clearly elevated, being more than five times higher than at the other sites. However, the subsequent maximum in November 2004 is much lower. One could expect that this difference might reflect differences in the meteorological conditions. Comparing monthly averages of temperature and wind speed show little differences between 2003 and 2004, though sampling with average times of one month, single or few meteorological events i.e. with stable air conditions can affect the sampling without affecting the meteorological average values.

Figure 9 and Table 9 shows descriptive statistics of the air results from all stations. As seen, the average concentrations for summer, winter and total are nearly identical in Frederiksborg and Copenhagen, the total being 20 fg/m<sup>3</sup> I-TEQ at both sites. The winter averages in Frederiksborg and Copenhagen are higher than the summer averages by a factor 4. The winter average in Gundsømagle, 61 fg/m<sup>3</sup> I-TEQ, is twice that of the I-TEQ winter average of 31 fg/m<sup>3</sup> in Frederiksborg.



**Figure 9.** Descriptive statistics of PCDD/Fs concentrations in air, all results from all stations Frederiksborg (rural), Copenhagen (urban) and Gundsømagle (village). Average (weighted by duration of sampling periods), maximum and minimum for summer, winter and total, respectively. Summer for Gundsømagle has been omitted because data do not cover a whole summer period.

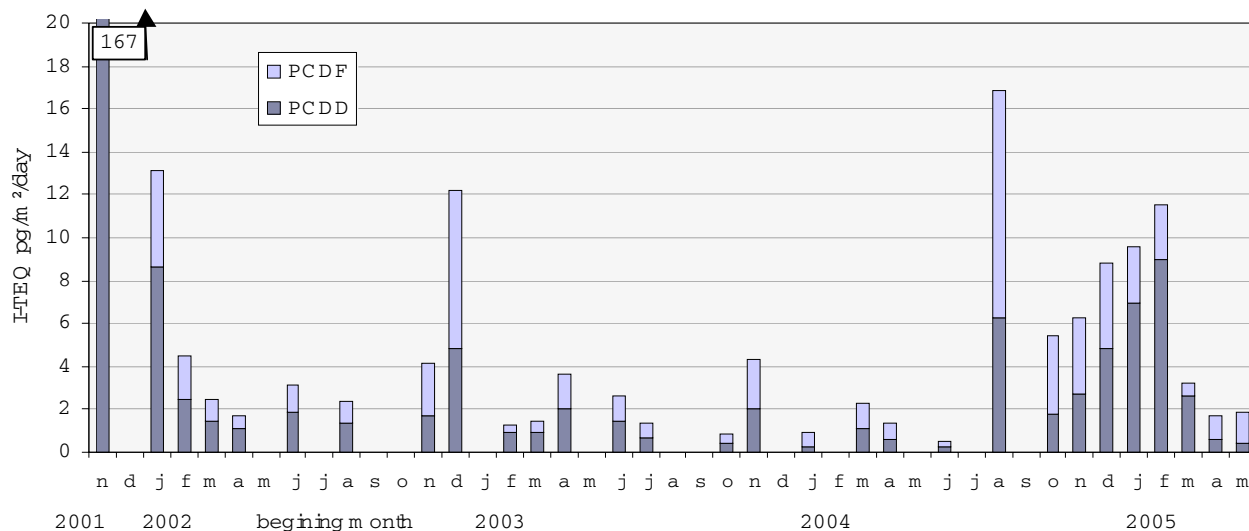
**Table 9.** Descriptive statistics of results for PCDD/Fs concentrations in air, fg/m<sup>3</sup> I-TEQ

Site	From	To	Season	n	Mean	Median	Min	Max
Gundsømagle	06/11-02	02/05-05	Total	14	52.7	47.2	8.9	179.9
			Summer	3	21.0	21.0	8.9	33.0
			Winter	11	60.7	54.3	12.2	179.9
Frederiksborg	05/02-02	05/04-05	Total	37	20.0	20.6	2.5	86.7
			Summer	16	7.9	7.2	2.5	22.5
			Winter	21	31.1	30.2	7.9	86.7
Copenhagen*	28/03-03	04/01-05	Total	19	20.0	18.6	2.5	55.7
			Summer	9	8.4	6.6	2.5	17.6
			Winter	10	34.0	33.7	18.6	55.7
All	02/04-02	05/04-05	Total	70	26.0	22.1	2.5	179.9
			Summer	28	30.0	7.1	2.5	33.0
			Winter	42	39.6	33.9	7.9	179.9



## 4.2 Bulk deposition and through fall

Monthly bulk deposition fluxes for Frederiksborg Forest District are shown in Figure 10 and through fall results in Figure 11, expressed in  $\text{pg I-TEQ/m}^2\cdot\text{day}$ .

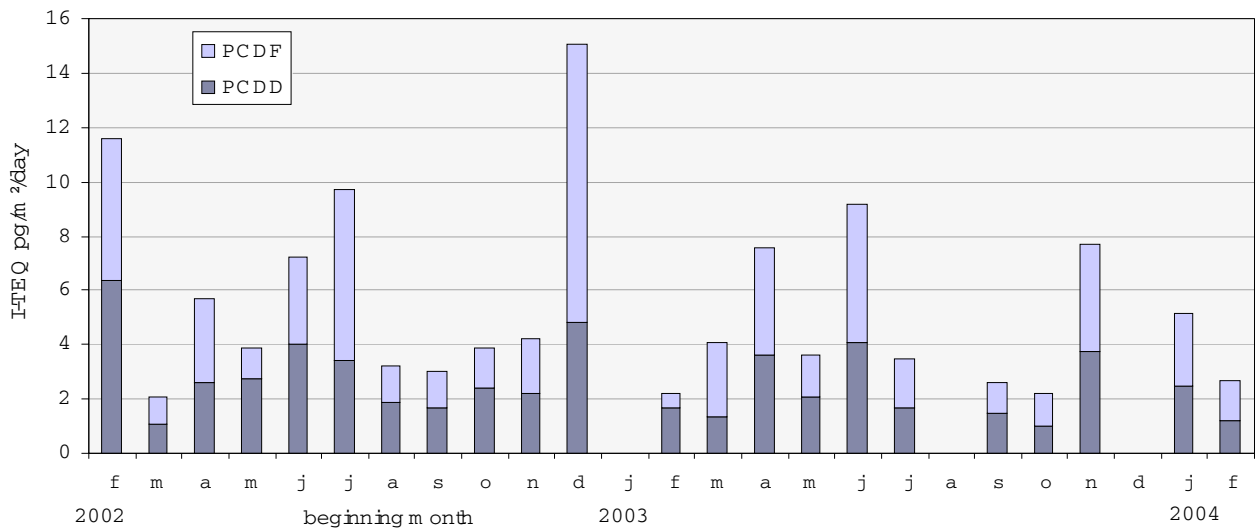


**Figure 10.** PCDD/Fs flux in bulk deposition at Roskilde November 2001 and January 2002 and in Frederiksborg from February 2003 to February 2005. Summer samples were pooled, pools and long periods are shown as the beginning month.

Figure 10 shows the bulk deposition of PCDD/Fs at Roskilde in November 2001 and January 2002 and at Frederiksborg from February 2002 to February 2005. The very high result in Roskilde from November 2002 is obviously an outlier, perhaps caused by birds' droppings in the sampler. A regular variation profile is seen in 2002, having maxima in the winter. A more erratic pattern prevails in 2003 with a very weak winter maximum 2003-04. The result from August 2004 stands out as the maximum in the series. There is a pronounced winter maximum 2004-05, which ends abruptly in March 2005. The variation spans a factor 33 omitting the outlier November 2001. The ratio between PCDF and PCDD is more variable than for air, fluctuating around an average PCDF/PCDD ratio of 1.0.

The average winter deposition flux is  $5.1 \text{ pg/m}^2\cdot\text{day I-TEQ}$ , the summer average  $3.6 \text{ pg/m}^2\cdot\text{day I-TEQ}$  and the total average  $4.4 \text{ pg/m}^2\cdot\text{day I-TEQ}$ .

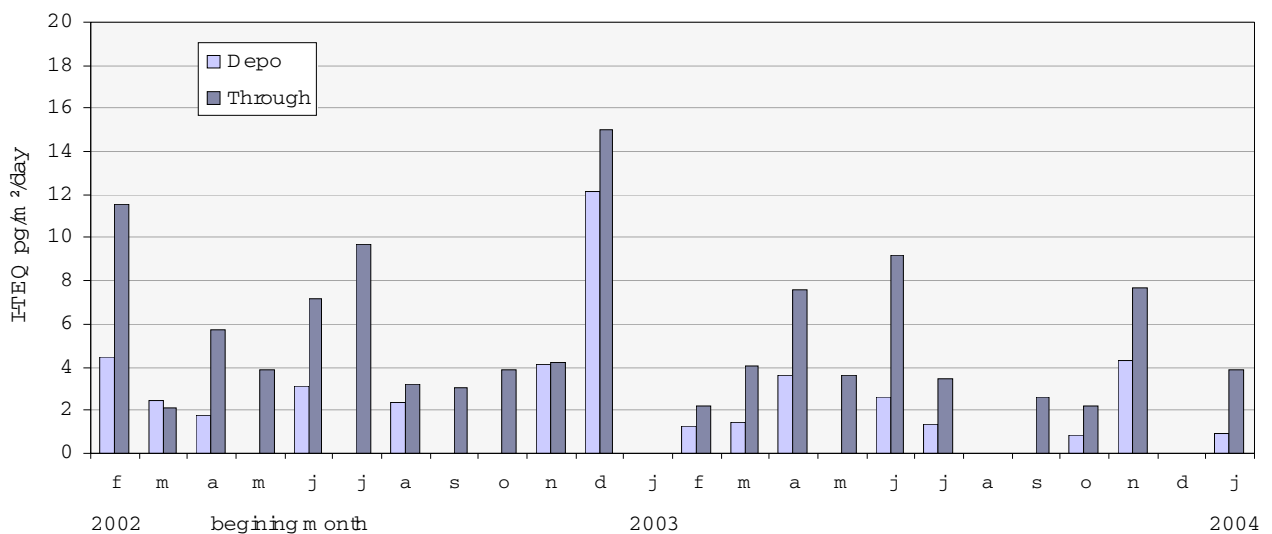
Figure 11 shows the results for through fall in Frederiksborg from February 2002 to February 2004. Several local peaks and valleys are seen, making a rather erratic variation profile. The variation spans a factor of 7, considerably lower than for air and bulk deposition. The average PCDF/PCDD ratio is 1.1, somewhat higher than for bulk deposition. The average winter through fall flux is  $5.3 \text{ pg/m}^2\cdot\text{day I-TEQ}$ , the summer average  $5.2 \text{ pg/m}^2\cdot\text{day I-TEQ}$  and the total average  $5.3 \text{ pg/m}^2\cdot\text{day I-TEQ}$ , i.e. the winter-summer difference for through fall is negligible.



**Figure 11.** PCDD/Fs in through fall sampled at Frederiksborg State Forest 2002-04. Some summer samples were pooled due to low concentrations. Each sampling period is shown by the start month.

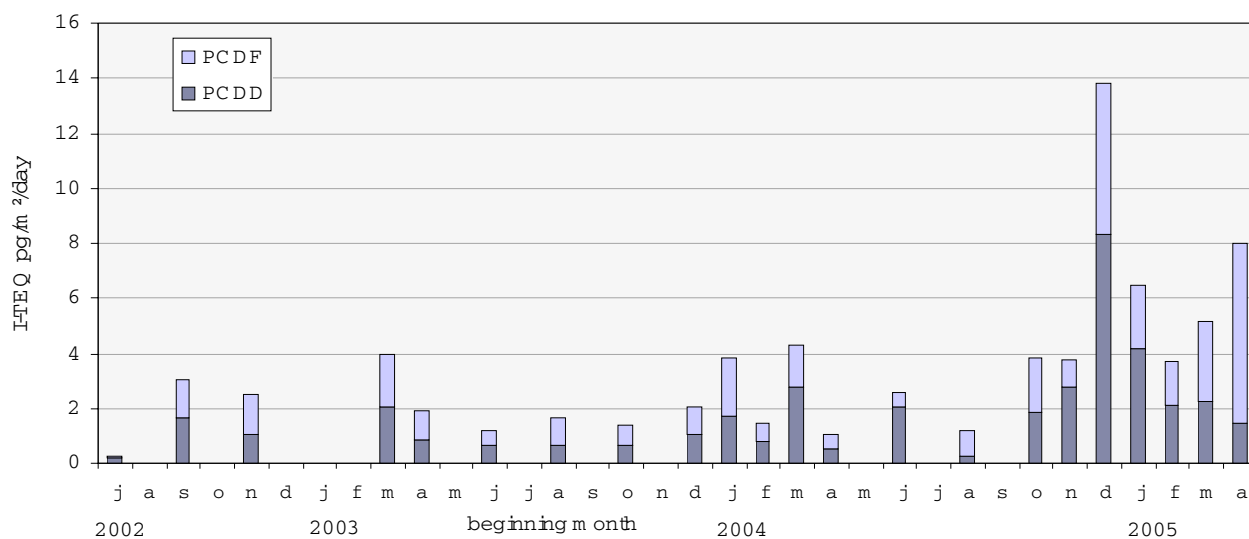
Figure 12 shows the results for bulk deposition and the spruce through fall at Frederiksborg on a common time axis. In many cases the results are nearly identical but in general the through fall are higher and the variation profile more erratic. Most likely, this is caused by irregular shedding of spruce needles during the course of the year. The low overall variation for through fall may be due to a buffering effect for absorbed PCDD/Fs of the canopy, causing a levelling effect.

Even so, the through fall variation profile is highly correlated with the bulk deposition profile, as shown in the correlation section 6.10 below. During the through fall campaign, the bulk deposition average flux at that site was 2.8 pg/m<sup>2</sup>-day I-TEQ, and the through fall flux a factor 1.9 higher. These issues are further addressed in the discussion section.



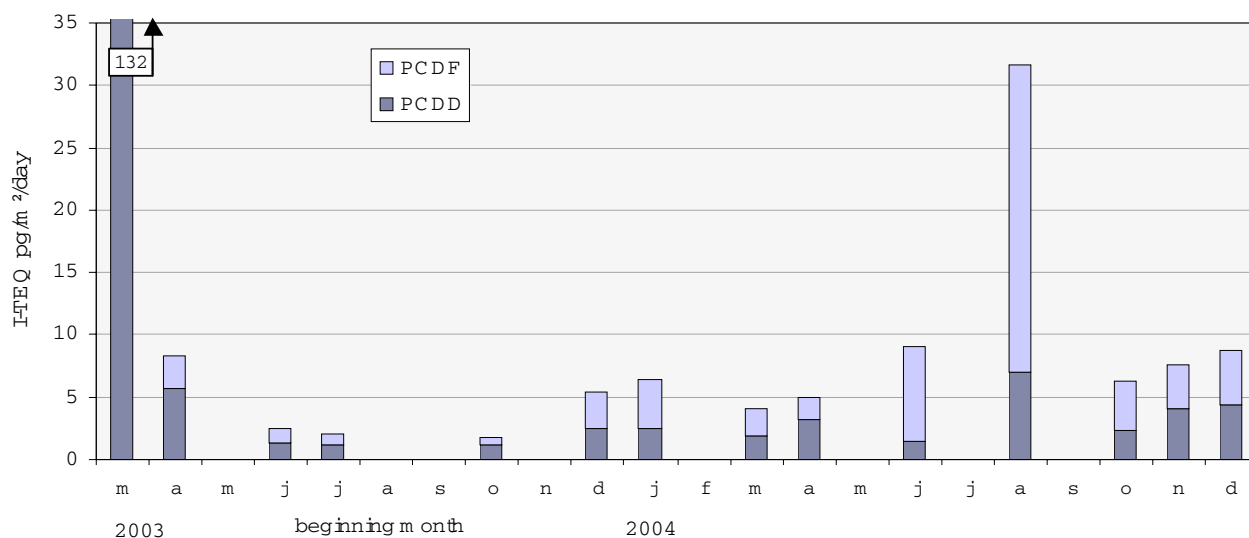
**Figure 12.** PCDD/Fs in through fall and deposition at Frederiksborg 2002-04 shown on a common time axis. Some samples were pooled, pools and long sampling periods being shown by the start month.

Figures 13 to 15 show the bulk deposition results for Ulborg, Copenhagen and Bornholm, respectively.



**Figure 13.** PCDD/Fs in bulk deposition in Ulborg State Forest. Some sample were pooled, pools are shown by the start month.

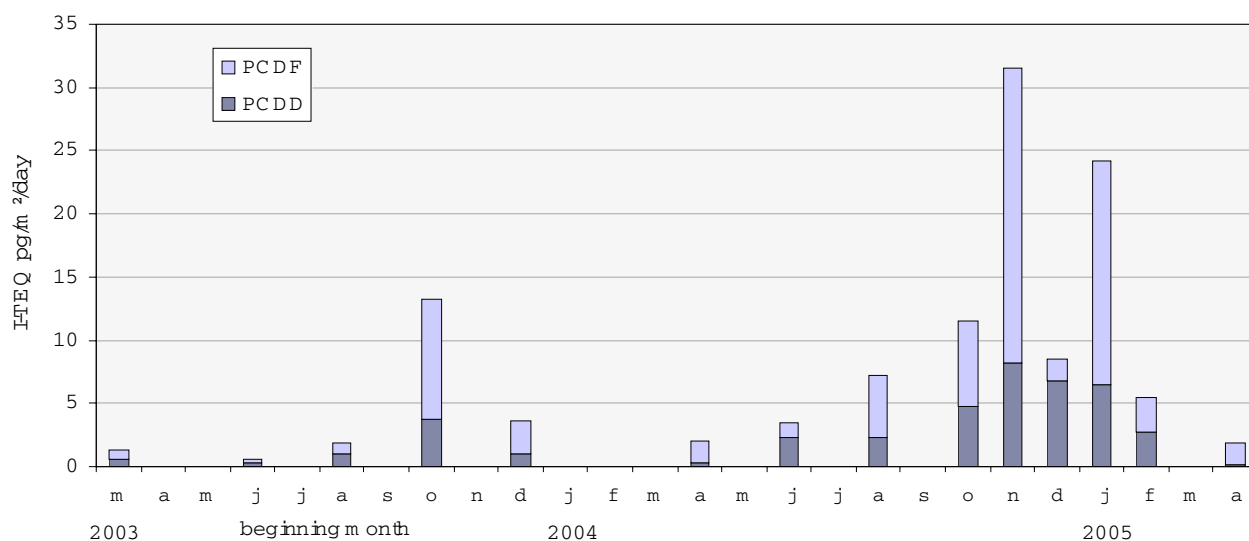
Figure 13 shows PCDD/Fs in bulk deposition sampled in Ulborg State Forest January 2002 to April 2004. As seen, the variation is comparatively modest, apart from the minimum in January 2002 and the maximum in December 2004. The variation spans a factor 50 including all data, but only a factor 13 omitting July 2002. The average PCDF/PCDD ratio is 1.0. The average winter flux is 4.0 pg/m<sup>2</sup>·day I-TEQ, the summer average 2.0 pg/m<sup>2</sup>·day I-TEQ i.e. the winter is the double of the summer; the total average is 2.9 pg/m<sup>2</sup>·day I-TEQ.



**Figure 14.** PCDD/Fs in bulk deposition sampled in Copenhagen Botanical Garden Summer samples were pooled due to low concentrations, pools being shown as the start month.

Figure 14 shows the results for bulk deposition sampled in Copenhagen Botanical Garden March 2003 to December 2004. The very high result from March 2003 is an outlier, possibly caused by bird's droppings in the sampler. However, this has not been further investigated, and the cause of the outlier remains hypothetical. Omitting the outlier, the maximum result from August 2004 stands out. The varia-

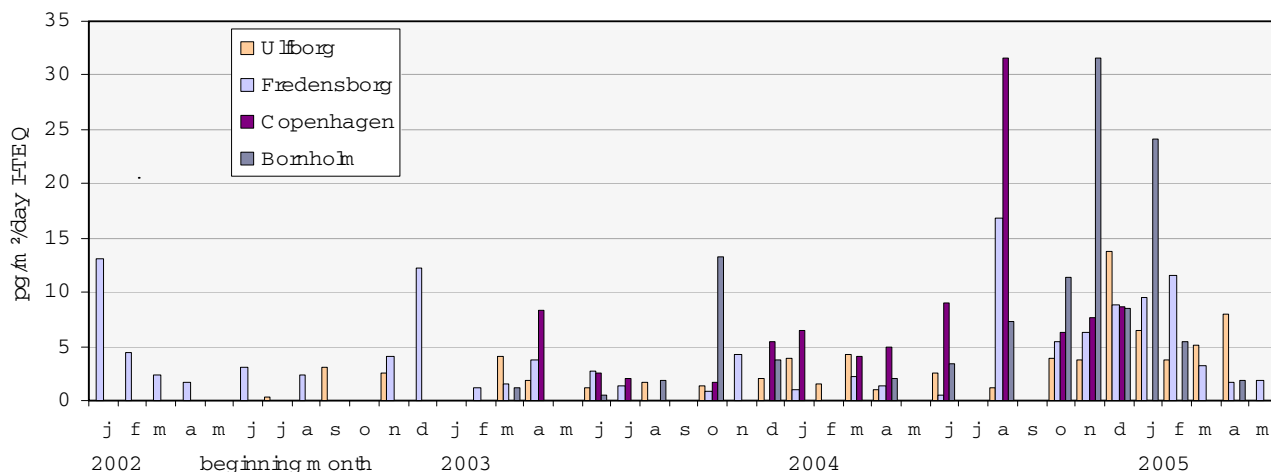
tion spans a factor 18 including August 2004, but only a factor 5 omitting that result. The average PCDF/PCDD ratio is 1.5. The average winter flux is 5.5 pg/m<sup>2</sup>·day I-TEQ, the summer average is 9.8 pg/m<sup>2</sup>·day I-TEQ, i.e. the summer is higher than the winter; the total average is 8.0 pg/m<sup>2</sup>·day I-TEQ.



**Figure 15.** PCDD/Fs in bulk deposition sampled at Bornholm March 2003 – April 2005. Some samples were pooled and in some cases the sample duration was more than month. Pools and long sampling periods are shown by the start month.

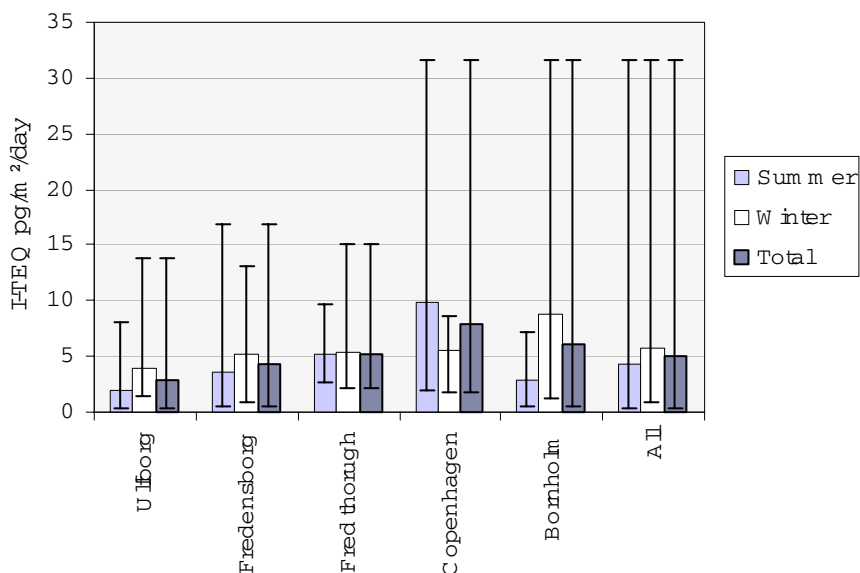
Figure 15 shows the results of bulk deposition on Bornholm. As seen, all summer values are low. A conspicuous feature of the variation profile is the large difference between the winters 2003-04 and 2004-05, respectively. There is a pronounced winter peak 2004-05 with maximum in November 2004. The PCDF/PCDD ratio varies erratically, it seems that PCDF fluctuates more than PCDD do; hence, the average ratio is not meaningful. The winter flux average is 8.8 pg/m<sup>2</sup>·day I-TEQ, the summer average is 2.9 pg/m<sup>2</sup>·day I-TEQ, i.e. the winter is more than the double of the summer; the total average is 6.1 pg/m<sup>2</sup>·day I-TEQ.

Figure 16 shows results of bulk deposition flux at all stations on a common time axis. As seen, the results from all stations are in many periods comparable, e.g. March-August 2003. Differences, when occurring, may in most cases be ascribed to the geographical location. Thus the Copenhagen results are generally highest. In October 2003 Bornholm, isolated in the Baltic Sea, stands out as elevated compared to the other sites; the same is the case the winter 2004-05. In August 2004 the concentrations in Copenhagen and Frederiksborg are elevated especially compared to Ulborg. A general tendency to higher results in the winter is observed, particularly the winter peak 2004-05.



**Figure 16.** PCDD/Fs in bulk deposition at all stations shown at common time axis. Each sample period is shown as the start month. The two outliers (Roskilde November 2001 and Copenhagen March 2003) have been omitted.

Figure 17 and Table 10 shows descriptive statistics of the deposition results, for each station arranged in summer, winter and total, respectively. For example, “Winter” represents the mean for all winter months (i.e. October to March, incl.) encompassing all years from a particular station, weighted by period length. “All” represents the grand mean for all stations. As seen, the overall geographical variation spans a factor of only 2.7 between the lowest average total flux in Ulborg and the highest one in Copenhagen. For all sites except Copenhagen, the bulk deposition winter average is higher than the summer average. For through fall the winter-summer difference is negligible.



**Figure 17.** Descriptive statistics for deposition of PCDD/Fs at all stations and for through fall at Frederiksborg for summer, winter and total, respectively. The average (weighted by length of sampling periods) is shown as column height, minimum and maximum by error bars.

**Table 10.** Descriptive statistics of results for PCDD/Fs in bulk deposition and through fall, ng/m<sup>2</sup>-day I-TEQ

Site	From	To	Season	n	Mean	Median	Min	Max
Ulborg	01/07-02	30/04-05	Total	22	2.9	2.8	0.3	13.8
			Summer	9	2.0	1.6	0.3	8.0
			Winter	13	4.0	3.9	1.4	13.8
Frederiksborg 1)	01/01-02	06/06-05	Total	28	4.4	2.9	0.5	16.9
			Summer	11	3.6	1.8	0.5	16.9
			Winter	17	5.1	4.3	0.8	13.2
Fred through	01/02-02	31/03-04	Total	21	5.3	3.9	2.1	15.1
			Summer	11	5.2	3.9	2.6	9.7
			Winter	10	5.3	4.0	2.1	15.1
Copenhagen 2)	01/04-03	04/01-05	Total	13	8.0	6.2	1.7	31.6
			Summer	6	9.8	6.7	2.0	31.6
			Winter	7	5.5	6.2	1.7	8.7
Bornholm	14/03-03	21/04-05	Total	14	6.1	4.6	0.5	31.5
			Summer	6	2.9	2.0	0.5	7.2
			Winter	8	8.8	10.0	1.2	31.5
All	01/01-02	06/06-05	Total	98	5.0	3.7	0.3	31.6
			Summer	43	4.3	2.0	0.3	31.6
			Winter	55	5.7	4.3	0.8	31.5

1) Roskilde January 2002 included. 2) High outlier March 2003 omitted

## 5 Discussion and statistics

### 5.1 Air

#### *Rural and urban sites*

It is remarkable that dioxin concentrations in Frederiksborg and Copenhagen (see figure 8) follow each other very closely and almost synchronously in spite of the distance of 40 km and the location in rural and urban zone, respectively. This suggests that a substantial contribution is due to long-range transport, because it is highly unlikely that zones so different in type could have synchronous emissions from local sources. Whereas the main domestic heating form in the North Zealand region is by oil firing, central Copenhagen is largely heated by district heating based on waste heat from electrical power generation (most of them gas fired), incineration and industry. Hence, domestic heating by individual stoves plays a minor role in the city. The total average for air in Frederiksborg and Copenhagen were found to 20.0 fg/m<sup>3</sup> I-TEQ at both sites i.e. practically without any difference (Figure 9). However, there is an appreciable difference in the corresponding deposition fluxes in Frederiksborg and Copenhagen, amounting to a factor 1.8 of between the total averages. We can conclude that air concentrations cannot explain the difference between urban and rural deposition fluxes, as further discussed below in the deposition section.

#### *Village*

As noted from Figure 8 the concentrations in the air of the rural village deviate considerably from the variation profile prevailing in Frederiksborg and Copenhagen. The village is a residential area, where many houses have wood stoves used for domestic heating as supplement to the electrical heating that is prevailing in the village. During a NERI monitoring campaign for particles and PAHs in air (Wåhlin et al., 2003), a sample taken in November 2002 was analysed for dioxin. The concentration found was significantly higher than the corresponding one in Frederiksborg. The wood stoves were suspected to be the source of this high concentration, since the sample was taken in the heating season, and because no other known local dioxin sources exist in the village. As a consequence, the present investigation was initiated. This also comprise an investigation on emission from the wood stoves in the village. This investigation is still in progress, but results from the first part of the study has been reported separately (Glasius et al., 2005). As noted from Figure 8, the August 2002 result is on level with Frederiksborg and Copenhagen, but as the heating season begins in October the PCDD/Fs concentration increases to a very high level in November. The much higher levels compared to Frederiksborg (which as mentioned is suspected mainly to reflect long range transport) indicate that the increase is caused by local sources. Local emissions were confined to an air layer at low altitude; hence the dilution is much lower than is the case for long range transport, enhancing the concentrations in the local atmosphere.

The simultaneous increase in the level of PAHs, which are known to be emitted by wood stoves (Wåhlin et al., 2003) supports the hypothesis that the observed PCDD/F increase in air is caused by domestic heating.

## 5.2 Through fall

### *Through fall*

For substances with no or little internal cycling between soil and vegetation, the through fall can be an approximation of the total deposition to the forest canopy. This applies for PCDD/Fs which do not participate in an internal cycling in a forest ecosystem, since the input of PCDD/Fs to the canopy comes from the atmosphere and the uptake through the roots is negligible (Hülster & Machner, 1993). In addition, PCDD/Fs are extremely persistent. A spruce plantation in equilibrium with the atmosphere enters a steady state, as the receiving rate of PCDD/Fs in the long term becomes equal to the releasing rate. Therefore, the through fall measured below the canopy is a good estimate of the total deposition of PCDD/Fs to the forest. Contrary to the conditions encountered for in the free bulk deposition sampler, the plantation presents a very large and "rough" surface to the atmosphere, leading to high uptake efficiency. The waxy surface of the spruce needles has high uptake of the lipophilic substances like PCDD/F, which dissolves in the wax. Accordingly, spruce needles have been used frequently as a convenient monitoring method for PCDD/Fs in air, and this method is widely accepted internationally (Rappolder et al., 2004). Most likely, the erratic variation profile observed for through fall reflects irregular variations in the shedding of spruce needles, which in turn depend on season and are caused by varying meteorological conditions e.g. wind, rainfall, draughts, temperature, and by the needle life cycle. This being the case, a large part of the through fall PCDD/Fs flux must be carried by the needles, and not by rainwater or particles. A further indication of this is the large difference observed between the parallel sampling experiments, mentioned in the Analytical performance section, which can be explained by the different amounts of spruce needles in the samplers. In spite of the erratic variation profile, the variations span only a factor of 7, much less than for free deposition. This may be explained by a certain damping caused by the canopy acting as a buffer and reservoir for PCDD/F.

The through fall samples in this project includes needle fall in the sampling period, i.e. the flux estimate is based on water soluble PCDD/F and particulate bound PCDD/F including needles and other organogenic particles sampled in the funnel.

Because of the erratic variation and the buffer effect in the canopy, only the average long term through fall is a good estimate of the total flux deposition to the forest. Of course, the same can be said of free deposition, because of the substantial difference between years.

As mentioned in the results section, the through fall flux is a factor of 1.9 higher than the bulk deposition flux at Frederiksborg and may be caused by dry deposition, mainly uptake of gaseous PCDD/Fs and particles, on the spruce trees. This is also observed for other sub-



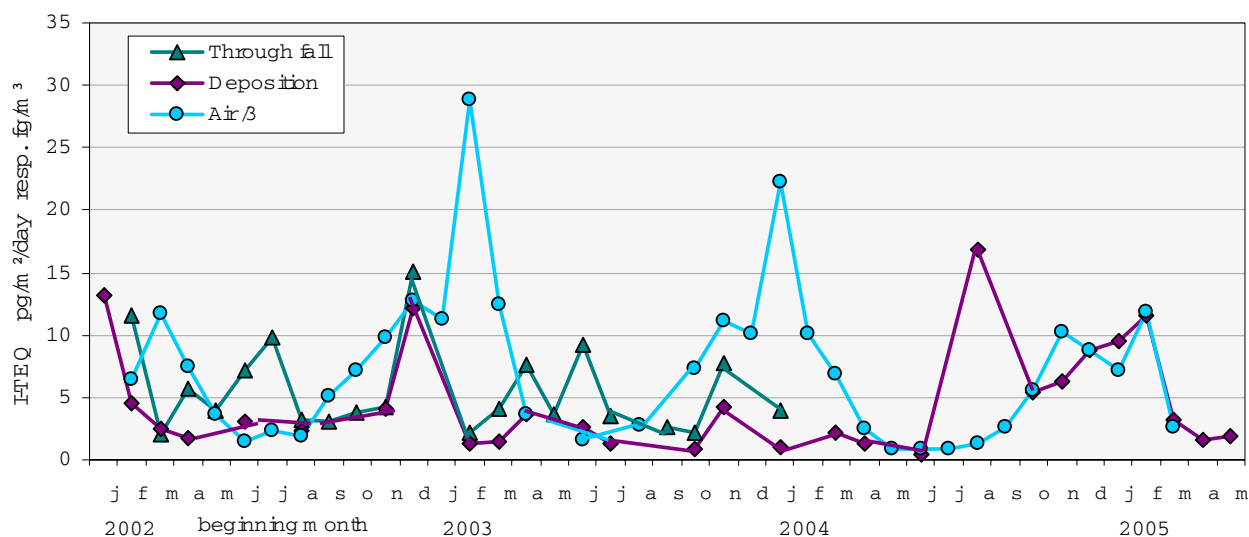
stances, e.g. sulphur compounds (Hovmand & Kemp, 1996). In addition, the deep shadow in the spruce plantation would theoretically reduce the photo-degradation of PCDD/Fs in the sampler, which could lead to higher results compared to free deposition.

#### *Dry deposition*

The atmospheric deposition of a substance is defined as the total flux of the substance from the atmosphere per unit surface area. Atmospheric deposition includes wet deposition, which in Danish conditions means mainly with rain, and dry deposition of gasses and particles. Net-through fall is defined as the difference between through fall and bulk deposition. In Frederiksborg, the total average flux for bulk deposition and through fall is 2.8 and 5.3 pg/m<sup>2</sup>·day I-TEQ, respectively. The difference is the net-through fall 2.4 pg/m<sup>2</sup>·day I-TEQ. For some substances, the net-through fall is a good estimate of the dry deposition. If it also applies for PCDD/F, this figure will be an approximation to the dry deposition in the plantation. However, this cannot be validated, since dry (or wet) deposition has not been measured directly in the present investigation. This would have required the development and construction of special samplers, and further a considerably more comprehensive analytical programme. The particle fraction in the quartz-wool filter, which would be a measure of the particle fraction in the dry deposition, has not been measured separately in the present study. However, even if the through fall is a good estimate for the deposition to the forest, it does not necessarily mean that it is a good overall estimate. On the open land no spruce trees are available to absorb gaseous PCDD/F. The interpretation of through fall measurements of PCDD/Fs is further discussed by Hovmand et al. (in prep.).

#### *Variation profiles*

In Figure 18, the variation profiles of bulk deposition, through fall and air concentrations measured at Frederiksborg Forest District are compared on a common time axis. Roughly speaking, the bulk deposition and through fall flux have episodes with close correspondence interspersed with episodes with higher through fall. For example, there are near identical values in March 2002, August 2002-February 2003 and August 2003, whereas elevated through fall episodes occur in April -July 2002 and March and June 2003. As mentioned, the high episodes very likely reflect the shedding of needles from the spruce trees. This indicates that in the absence of needle shedding, there is a close correspondence between through fall and deposition. This in turn shows that in the absence of needles falling, the sampler collects deposition which has passed more or less unchanged through the spruce trees. From an analytical point of view, this further demonstrates that under the field conditions in Frederiksborg, the samplers for free deposition and for through fall yield comparable, indeed sometimes nearly identical, results. Hence, the photo-degradation suspected to occur in the free deposition sampler cannot be of practical importance for the operation of that sampler.



**Figure 18.** PCDD/Fs in air, deposition and through fall from the spruce canopy sampled at Frederiksborg State Forest January 2002 – May 2005. Note that deposition and through fall have the unit I-TEQ pg/m<sup>2</sup>-day. Air concentrations expressed in I-TEQ fg/m<sup>3</sup> divided by 3 to make the comparison easier.

The bulk deposition flux follows the air concentrations in broad terms. This is because the deposition flux is transferred from the air, which is the primary transport medium. In other words, PCDD/Fs must be present in the air in order for deposition of PCDD/Fs to occur, as reflected in the curves for air and deposition. However, the contrary is not necessarily true. Thus, the two winter peaks in air concentrations in February 2003 and January 2004 are not reflected in corresponding peaks in bulk deposition flux. This is perhaps due to special meteorological conditions such as precipitation, humidity or by other factors, which have impeded or prevented the transfer from air to deposition. One could think that the peaks might be due to local air concentrations in low altitude, which presumably will not be reflected in deposition. This explanation is unlikely, however, because the Copenhagen air data also displays a peak in January 2004 (see Figure 6) in spite of the long distance between the sites, ruling out local conditions as a plausible explanation.

### 5.3 Bulk deposition

As seen from Figure 17 and Table 10 showing descriptive statistics for bulk deposition at all stations, the overall geographical variation of deposition is of a limited range, spanning a factor of 2.7 between the largest average total flux in Copenhagen and the lowest one in Ulborg. Omitting Copenhagen, which is reasonable because of the special character of this highly urbanised site, the factor between the Ulborg and next highest deposition flux at Bornholm is only 2.1. This is a relatively small difference, considering that the geographical distance between the Ulborg in west and Bornholm in east is more than 500 km. The even geographical distribution indicates that a part of the PCDD/Fs is emitted far away, and has been spread out in the air during the long transport. This conclusion supports the independent finding in the air study mentioned above, based on synchrony between in air concentrations in Frederiksborg and Copenhagen.

#### *Copenhagen deposition*

It is noteworthy that the Copenhagen bulk deposition flux is 1.8 times higher than the one in Frederiksborg, in spite of the almost identical levels of the air concentrations at these sites, as seen from the corresponding Figure 9 in the Air chapter. This difference, as well as the winter-summer anomaly for Copenhagen mentioned below, suggests that special conditions exist in the highly urbanised environment, which affects the transfer of PCDD/Fs from air to deposition. Possibly particles are involved in this, but the issue has not been further investigated. Local atmospheric sources can be excluded as the cause, since these ought to be reflected in the air concentrations, in stark contrast to what is found. However, an influence of the urban environment directly on the bulk deposition sampling cannot be excluded, such as soot or dust blown up from soil collecting in the sampler funnel. Of course, this will also happen in the rural sampler, but the considerable higher concentration in urban soil (discussed below) will yield a correspondingly higher contribution. Furthermore, the urban surface area is largely covered with buildings, concrete and asphalt which do not bind dust as well as the rural vegetation.

#### *Winter/summer ratios*

The winter average for bulk deposition is a factor 2 higher than the summer average for Ulborg, 3 for Bornholm and 1.4 for Frederiksborg. This is probably due to higher atmospheric emissions during winter e.g. from heating, and faster atmospheric photo degradation during summer. In Copenhagen, we observe the opposite relationship with a ratio of 0.6. This might be due to dust collecting in the sampler during the more dusty conditions in the dry summer. For through fall, the winter-summer difference is negligible, very likely because of an equalising effect of the spruce canopy.

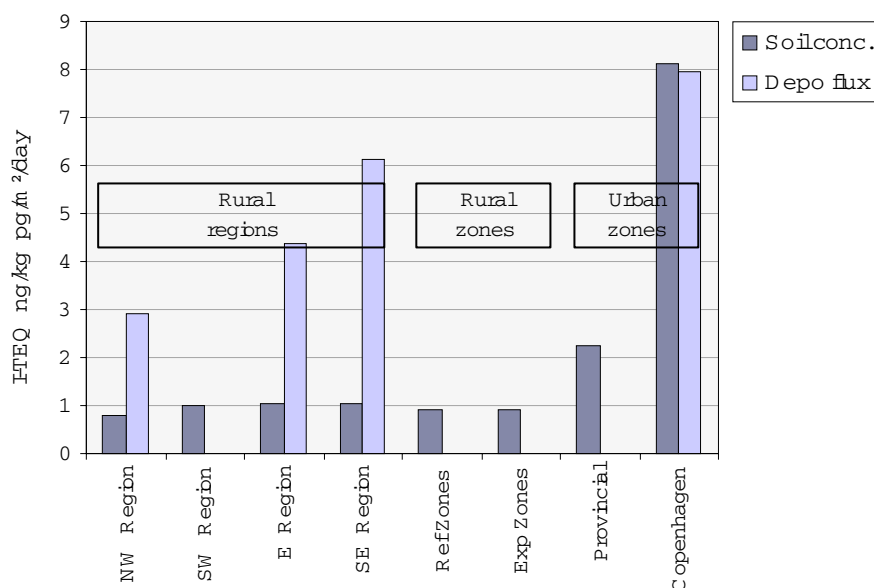
### **5.4 Role of deposition for soil**

#### *Geographical regions*

The Danish Dioxin Monitoring Programme included a comprehensive investigation of PCDD/F in soil (Vikelsøe 2003, 2004a, 2004b). The soil study was planned in such a way that it is possible to evaluate the role of deposition for the contamination of soil. In soil context Denmark is in the following described in terms of geographical regions: N-Jutland (NW region), S-Jutland and Funen (SW region), Zealand (E region), Falster and Bornholm (SE region). The deposition sampling sites are located in regions as follows: Ulborg in W-Jutland (NW region), Frederiksborg in North Zealand (E region), Copenhagen central city (E region) and Bornholm (SE region). Figure 19 shows the average PCDD/Fs concentrations in soil (72 samples) in the regions together with the total averages of the bulk deposition flux at all stations placed in their respective regions/zones. The average for rural soil is 0.8 ng/kg I-TEQ. 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. Thus, the variation originating from deposition seems to be smoothed out in rural soil, possibly an effect of ploughing or culturing.

## Rural zones

An important question is whether the atmospheric sources – either diffuse or point sources – contaminates the surrounding land. To address this, alternatively to the geographical regions, the soil results have been divided into zones: rural reference zones located far from known sources, and rural exposed impact zones located some km leeward (E) from point sources or diffuse sources with respect to the predominant wind directions (W, SW). Contrary to a region, a zone does not form a coherent area, but is patched together from many separate sites of similar characteristics. As seen from Figure 19, no difference between those zones is found, the average soil concentrations in both zones being 0.93 ng/kg I-TEQ. Hence, somewhat contrary to expectation, there is no indication that deposition from larger point sources or diffuse sources via short-range transport contaminates the surrounding land.



**Figure 19.** Concentrations in soil in geographical regions and zones compared to deposition flux. The deposition stations are placed in their respective regions/zone. Note different units on the y-axis.

## Urban zones

In addition to the rural zones, provincial cities form a zone, and the Copenhagen area is regarded as a large urban zone. The average for park and garden soil in provincial cities are 2.2 ng/kg I-TEQ, for Copenhagen it is 8 ng/kg I-TEQ. Thus urban zones are substantially higher than rural zones. In soil from Frederiksborg was found 1.3 ng/kg I-TEQ, thus Copenhagen is a factor 6 higher. However, the corresponding factor for deposition is only 1.8. Hence, the difference in soil concentrations in Copenhagen and Frederiksborg cannot be explained by difference in deposition alone.

## Accumulation times

PCDD/Fs in soil is extremely persistent, therefore the PCDD/Fs found today has been accumulated from contamination in the past during many years. Hence, the PCDD/Fs will build up in the soil under a steady influx from deposition. The time required to accumulate the PCDD/Fs amount found in the upper 10 cm of soil at the present deposition flux – the simple accumulation time - can be calculated. The accumulation times of the rural regions are thus calculated to 86 years in Ulborg, 81 years in Frederiksborg and 75 years on Bornholm. These consistent and plausible accumulation times make

it likely that deposition has been the main source for PCDD/Fs in soil in the rural regions. Unfortunately, we have no deposition results for provincial cities, and can therefore not calculate the accumulation times.

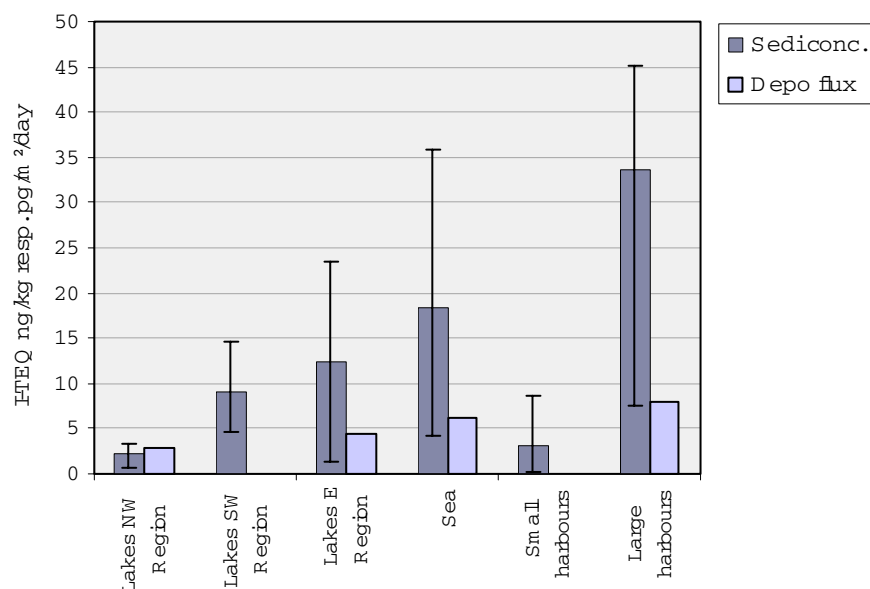
#### *Copenhagen contamination*

In contrast, the accumulation times for Copenhagen average is 280 years, ranging up to 1300 years for the highest concentration in Copenhagen soil. These very long accumulation times show that deposition alone is not enough to account for the present concentrations, thus other sources must have contributed. On the other hand, the present deposition flux in Copenhagen agree with a finding in the soil of a preserved fortress in the easternmost part of the city (Kastupfortet very close to the East coast) which has remained undisturbed since it was built in 1887. Because of the prevailing Westerly wind direction, this specific location ought theoretically to be particularly exposed to the atmospheric pollution from Copenhagen. Nevertheless, the concentration found in the soil there was only 1.5 ng/kg I-TEQ, much lower than in the central city, and only slightly higher than that in Frederiksborg. An accumulation time of 50 years is calculated for this site. Very likely, the PCDD/Fs concentration in the soil of the preserved fortress comes close to the true contamination from atmospheric deposition in the Copenhagen area.

In conclusion, the present deposition fluxes cannot explain the present high concentrations in soil of Copenhagen. It is likely that the deposition flux was considerably higher before the introduction of incinerator flue gas cleaning and lead-free gasoline during the 1990<sup>ties</sup>; but this would be reflected in the concentration at Kastupfortet. Furthermore, the dioxin concentrations in the atmosphere are geographically evenly distributed and cannot explain why there is so large a variation (a factor 25) in the soils of Copenhagen. Most likely, the soil with concentrations exceeding that found at Kastupfortet, has been contaminated with chemicals, garbage, ash, slag etc. This would explain both the high concentrations and the large variation in the Copenhagen soil. The highest concentrations are found at former industrial sites, and in parks built on former garbage dumps.

## **5.5 Role of deposition for sediment**

The Danish Dioxin Monitoring Programme included an investigation of sediment from lakes and fjords, from internal Danish waters, from the Baltic Sea and from small and large harbours, respectively. In addition, it was anticipated that the sediment study would reveal the importance of deposition over lakes and fjords for sediment but also aquatic and marine biota. The reason is the very long persistence of PCDD/F in sediment, which as mentioned previously is due to the absence of UV-light and the low O<sub>2</sub>-level. Of course, PCDD/F in sediment is also important in its own right. In total 28 samples of sediment were analysed. To evaluate the geographical distribution in lake sediment, the lakes were assigned to the same geographical regions as mentioned in the preceding section on soil.



**Figure 20.** Concentrations in lake sediment in geographical regions, sea sediment and harbour sludge compared to deposition flux. The deposition stations are placed in their respective regions/zone. Mean (column height) minimum and maximum (error bars). Note different units on the y-axis.

### Lake sediment

Figure 20 shows descriptive statistics (mean, maximum and minimum) for fjords and lakes in the regions, harbour sludge and sea sediment, compared where possible to deposition fluxes. As seen, the concentration in lake sediments increase from NW to E region. The increase seems almost proportional with the corresponding one for deposition, but is more pronounced. The mean concentrations in sediments are considerably higher than those of soils (see Figure 19), attesting to long persistence in sediment, where the concentrations seem to build up. The deposition of PCDD/F on the lake surfaces 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, as shown by the error bars, there is a pronounced variation between individual lakes in the same geographical region. Since deposition is evenly distributed in a region, this variation must originate from contributions from other sources.

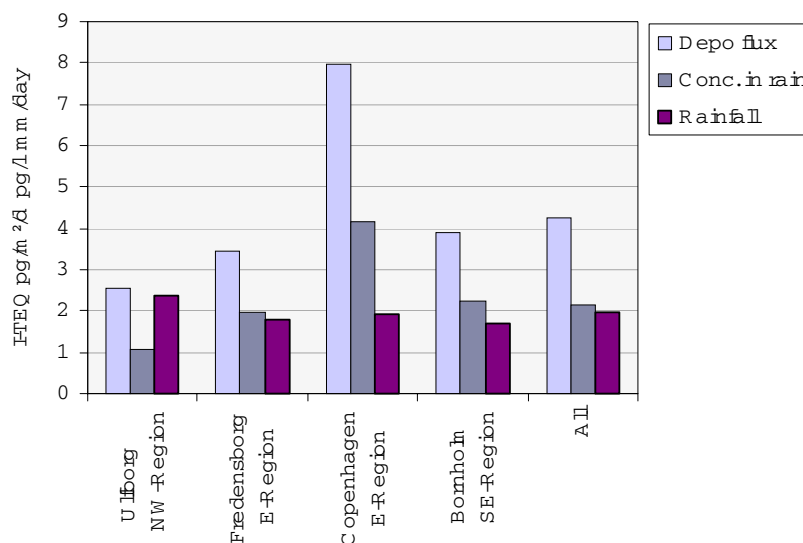
### Accumulation times

The accumulation time for sediment in the lakes at the present deposition flux range from a plausible 60 years to 1800 years. The latter value indicates that significant pollution takes place in some lakes, most likely from waterborne sources, or in some cases possibly from direct contamination (e.g. with sludge or ash). Also the water pollution might have been worse in the past, particularly before efficient wastewater treatment was introduced in Denmark in the 1990<sup>ties</sup>. In addition to the anthropogenic pollution, some researchers believe that natural formation of dioxin takes place in lake sediment; however, this reportedly is characterised by a high PCDD/PCDF TEQ ratio (Rappe et al., 1999a & b), contrary to the almost unity ratio found 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 world-wide 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. Hence, theoretically 95% of PCDD/Fs in sea sediment globally originates from deposition on the sea surface. It is also possible, that hot spots in the very polluted Baltic sea sediment are re-distributed by sea currents. For harbour sludge the accumulation times range from 13 years for a small harbour to 2300 years for large harbours, indicating that the PCDD/F in the small harbours may originate from deposition only, whereas large harbours are highly contaminated.

## 5.6 Role of rain for bulk deposition

Figure 21 shows deposition flux total averages all stations, compared to concentrations in rainwater and rainfall in geographical regions (the same designations as used in the soil and sediment discussion above). As seen, the rainfall is not very different in the regions, being highest in Ulborg. The concentration in the rainwater is lowest in Ulborg and highest in Copenhagen, as is also the case for the deposition flux. Thus the flux seems to follow the concentrations and not the rainfall, indicating that the flux is independent of the rainfall. As shown in the correlation section, there is a highly significant correlation between deposition flux and concentration in rainwater, but not between flux and amount of rainfall.



**Figure 21.** Bulk deposition averages at all stations and as averages of all locations (until December 2004), compared to concentrations in rainwater and rainfall in geographical regions (see text in soil discussion). Note that there are three different units on the y-axis.

Also for phthalates, which like PCDD/Fs are ubiquitous substances insoluble in water, the bulk deposition seems to be relatively independent of the amount of rainfall as found by Vikelsøe et al. (1997 & 1998).

## 5.7 Role of deposition for cows' milk

An important question is the role of deposition over the agricultural land, particularly the importance for the human intake via food. It has long been known that milk and other dairy products account for a substantial part of the human intake with PCDD/Fs. Since cows are grazing during the summer, we use the average summer deposition values at rural sites Ulborg and Frederiksborg, which amounts to 2.8 pg/m<sup>2</sup>·day. According to questionnaire data collected during the cows' milk study (Vikelsøe, 2002 & 2003), the production of milk fat per hectare range from 1-27 kg/ha/day with average 5.7 kg/ha/day (Vikelsøe, unpublished). Setting the average PCDD/F concentration in cows' milk to 0.8 pg/g fat WHO-TEQ, this corresponds to 0.08-2.1 pg/m<sup>2</sup>·day with average 0.45 pg/m<sup>2</sup>·day I-TEQ. This in turn amounts to 2.8-76% with average 16% compared to the average land-deposition above. Thus on the average, 6 times more PCDD/F is carried to the ground than is excreted in the milk of grazing cows. This substantial surplus available for uptake in cows makes it likely that a substantial part of the PCDD/Fs enter milk - and hence, dairy products - via atmospheric deposition over agricultural grassland.

## 5.8 Role of deposition for the sea

Deposition was measured at three coastal stations in the western part of the Baltic Sea (including The Belts) and a coastal station on Sild in the North Sea only 80 km west of the Baltic Sea (see figure 1 and table 12). Results from these four stations (including two German stations) give us the possibility to make a first approximation of the atmospheric input of PCDD/Fs to the western Baltic Sea.

The measurements represent an area of approximately 43,000 km<sup>2</sup> of sea surface. The average bulk deposition flux measured at the four stations is 3.3 pg/m<sup>2</sup>·day I-TEQ, corresponding to 1.2 mg/km<sup>2</sup>·year I-TEQ. The dry deposition input to water surfaces has to our knowledge not been measured, so we estimate an extra input from PCDD/Fs in particles and gasses directly to the water surface to 10% of the bulk deposition. This leads to a total dry- and wet-deposition of 1.3 mg/km<sup>2</sup>·year I-TEQ, corresponding to 57 g/year I-TEQ on the 43,000 km<sup>2</sup> of sea surface considered. This seems to be a small amount, but it is of the same order of magnitude as the 72 g/year I-TEQ bulk deposition over the Danish land area. Furthermore, it should be compared to other sources. According to the latest assessment reports (Jensen, 2003) the outlet emissions directly to water are world-wide between 1% and 4% of the emissions to the atmosphere. Riverine loads to the Western Baltic Sea should consequently be small; but it must be remembered that the Baltic Sea may be unrepresentative since it is closed and receives input from a number of presumably polluted rivers. Unfortunately, we have at this point no information on other major PCDD/Fs sources to the Western Baltic Sea.

We speculate if a total atmospheric input of PCDD/Fs on 1.3 mg I-TEQ/km<sup>2</sup>·year could lead to measurable concentrations of PCDD/Fs in fat pelagic fish as herring, sprat and wild salmon. Recent investi-



gations (Jensen, 2003) show an average concentration in herring of 2.2 ng WHO-TEQ PCDD/Fs /kg fresh weight. This unit is in our investigation close (within in a factor 1.1 see table 2.) to the I-TEQ unit otherwise used in this report. It should be stressed that coplanar PCB is not included in the toxicity evaluation below.

Rough estimates on fish-biomass production in the Western Baltic indicate a fresh weight production of pelagic fish as herring and sprat of 2400 kg/km<sup>2</sup>·year. The annual pelagic fish production in western Baltic Sea is based on data of landed herrings and sprat reported by ICES (2003) and an estimated natural fish death of 50%.

We are aware that herring and sprat are migratory fish, so yearly fish bio-mass production and exposure is not attributed to a fixed area. However, neighbouring areas have the same PCDD/Fs exposure as the Western Baltic Sea. PCDD/Fs are cumulated in the marine food web and fatty fish such as herring, sprat and salmon have higher PCDD/Fs concentrations than other fish.

Herring is the dominating pelagic fish in the Western Baltic Sea and the Belts. Based on the above reported PCDD/Fs concentrations in herring, we estimate an average PCDD/Fs accumulation of (2400\*2.2 ng =) 5.3 µg WHO-TEQ/km<sup>2</sup>·year (fresh weight) in pelagic fish production (Hovmand and Vikelsøe, 2005).

Comparing the atmospheric deposition of PCDD/Fs to the Western Baltic Sea of 1.3 mg I-TEQ/ km<sup>2</sup>·year with a yearly pelagic fish accumulation of 5.3 µg WHO-TEQ/km<sup>2</sup>·year we find that the pelagic fish bio mass production amounts approximately 0.4% of the flux to the sea surface. Thus, a large surplus of PCDD/Fs is available in the sea for bio-uptake from atmospheric deposition on the sea surface alone. This makes it likely that most of the PCDD/Fs in fish originate from this source, even if some may be taken up from sediment or originate from rivers. Only a minor part of the deposition flux to the sea ends up in the biomass near the top of the food web. The major part is precipitated to the sediments, where in the case of the Western Baltic Sea concentrations found in the Danish Dioxin Monitoring Programme are in the range of 4-36 ng/kg I-TEQ (see Figure 20). According to other studies are reported 10-30 ng WHO-TEQ/kg dry matter (Jensen, 2003) or 4-36 ng/kg I-TEQ (Verta et al., 2005).

## 5.9 National annual deposition

The modest geographical variation makes it possible to use the average deposition to calculate the total national deposition. The total average bulk deposition and through fall all data is 5.0 pg/m<sup>2</sup>-day I-TEQ, corresponding to 1.8 mg/km<sup>2</sup>-year I-TEQ, which in turn corresponds to 80 g/year on the 44000 km<sup>2</sup> of land area in Denmark. However, it is reasonable to omit the results for through fall and Copenhagen from the calculation, because of their special character. The average of the total deposition fluxes of the more representative data from Ulborg, Frederiksborg and Bornholm is 4.5 pg/m<sup>2</sup>-day I-TEQ, corresponding to 1.6 mg/km<sup>2</sup>-year I-TEQ, which in turn corresponds to 72 g/year on the Danish land area. Using the lowest total average flux in Ulborg and the highest one on Bornholm for the calculation yields 47 and 98 g/year, respectively; these values can be regarded as limits.

Hence, according to the present study, the annual bulk deposition of PCDD/Fs on the Danish land area can be estimated to:

47-98 g/year with best estimate 72 g/year.

This may be compared to the emission from the known Danish sources. According to Hansen et al. (2003), the annual Danish emissions are estimated at 9-45 g/year I-TEQ, including incinerators, power plants, industry, traffic and heating. Attempting to include unknown sources Hansen et al. (2003) estimate the emission to 11-148g/year I-TEQ. Both known sources and the estimate including unknown sources are of the same order of magnitude as the deposition above.

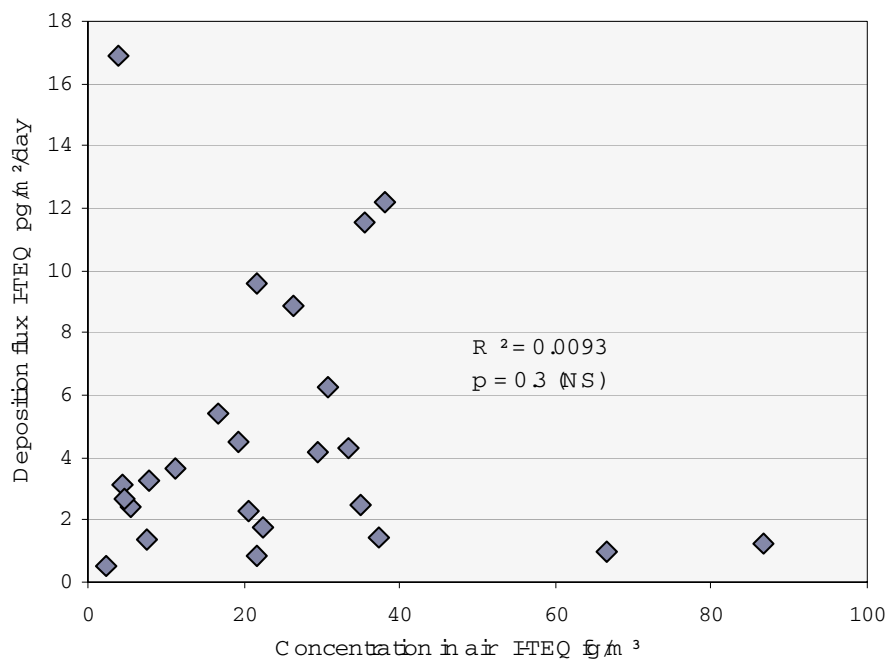
It is likely that some of the deposition originates from long-range transport of dioxins and furans from foreign sources. However, this can only be confirmed by model calculations that are also needed to quantify this contribution more closely as well as the fraction of indigenous emissions exported abroad.

## 5.10 Correlation and regression analysis

### *Correlation analysis*

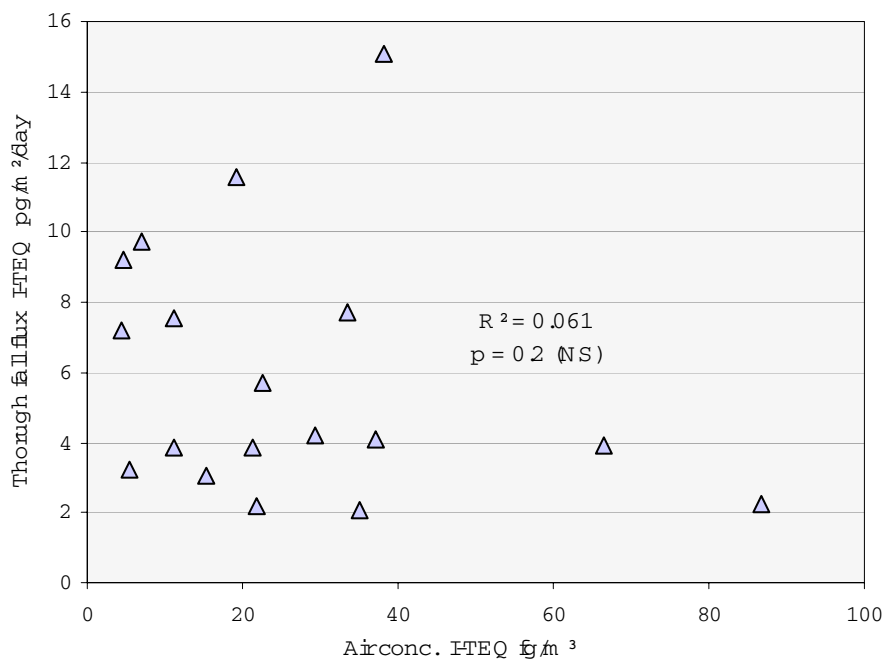
This section addresses the aspect of the statistical significance by means of correlation and regression analysis. A significant correlation between two parameters indicates (but does not prove) that there might a causal effect. Regression analysis indicates if there exists a linear relationship between two parameters. The analysis of correlation was performed on the z-transformed (normal parametric) correlation coefficients that are approximately normally distributed, allowing a t-test for statistical significance of the correlation coefficients to be performed

The following figures show the correlation between the most important or interesting pairs of parameters. In all cases the correlation coefficient squared ( $R^2$ ) is shown together with the level of significance ( $p$ ). In case of pairs with significant correlation, linear regression analysis is performed, shown by the regression line and equation.



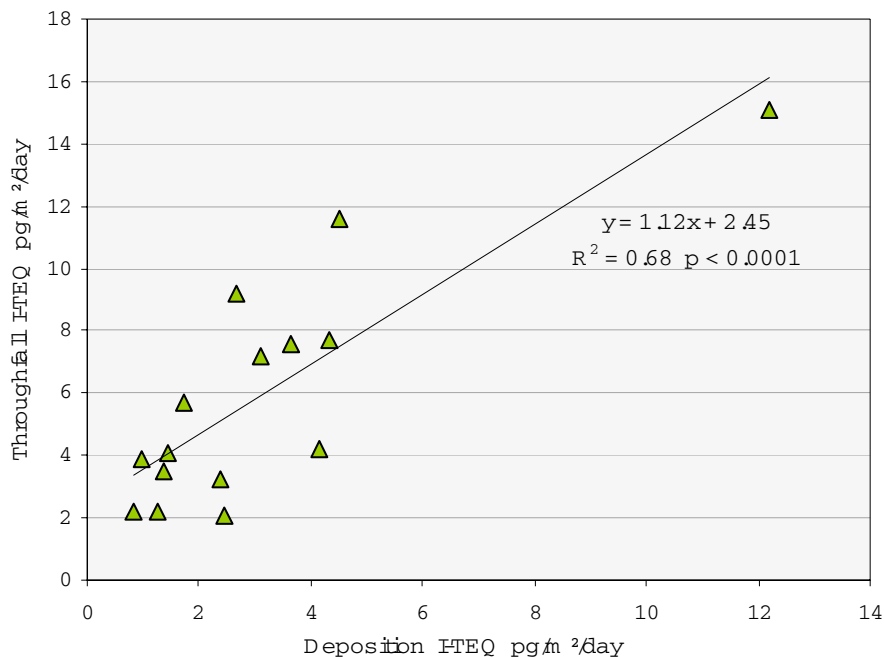
**Figure 22.** Correlation of bulk deposition and air concentration in Frederiksborg.

Figure 22 shows the bulk deposition versus the air concentrations in Frederiksborg. No significant correlation was found ( $p = 0.3$ ). The lack of correlation indicates that a complicated process takes place in the transfer of dioxin from the air to deposition.



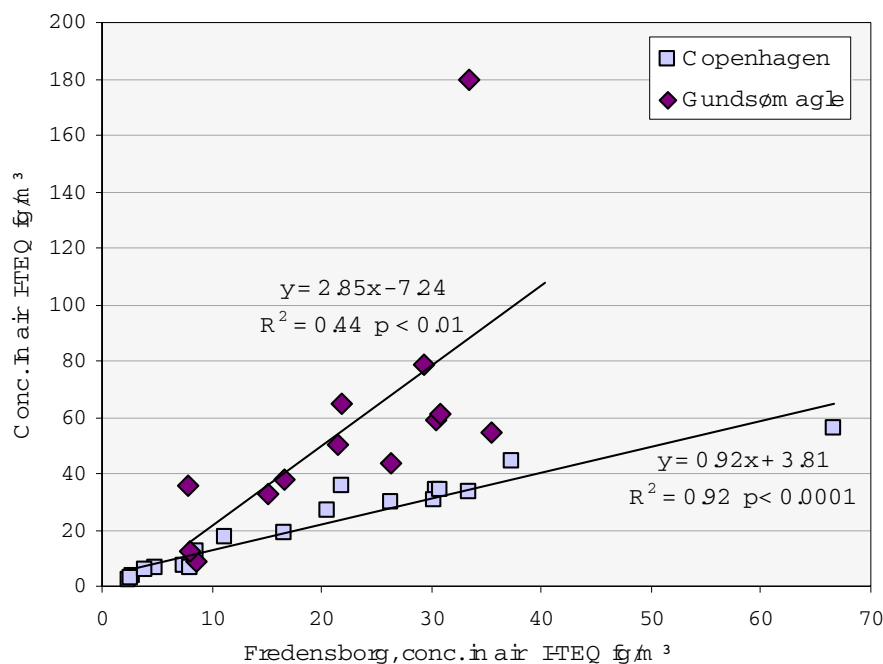
**Figure 23.** Correlation of air concentrations and through fall in Frederiksborg.

Figure 23 shows the air concentrations versus the through fall data. No significant correlation was found ( $p = 0.2$ ). This indicates that the uptake from air in the spruce needles is delayed before arriving as through fall at the sampler.



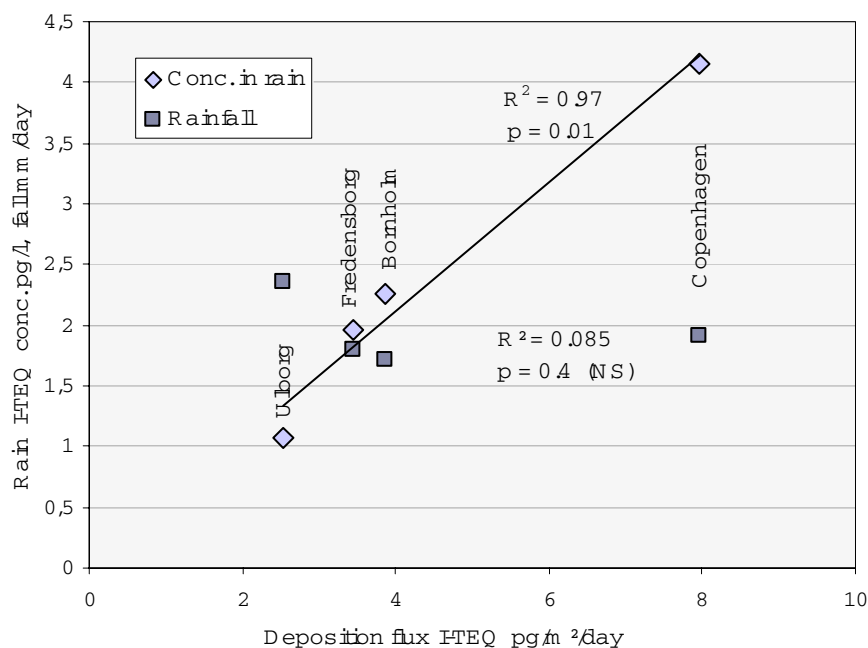
**Figure 24.** Correlation of bulk deposition and through fall in Frederiksborg.

Figure 24 shows through fall data versus the bulk deposition data. A highly significant correlation was found. The slope near 1 indicates that the through fall flux closely follows the deposition flux. One could suspect that the high through fall episode June-July 2002 (Figure 12) might negatively affect the correlation. However, this is not the case, since repeating the correlation analysis with that episode omitted from the data did not result in a higher level of significance. A correlation between sulphur in net-through fall and atmospheric concentrations of sulphur-containing gasses and aerosols was also observed by Hovmand and Kemp (1996).



**Figure 25.** Correlation of concentrations in air in Frederiksborg with Copenhagen and Gundsømagle.

Figure 25 shows the air concentrations measured at Frederiksborg versus the data from Copenhagen and Gundsømagle, respectively. A highly significant correlation was found between Frederiksborg and Copenhagen ( $p < 0.0001$ ). The slope near 1 indicates that the concentrations covariate synchronously, presumably because both sites receive contributions from long range transport. Also between Frederiksborg and Gundsømagle a significant correlation was found ( $p < 0.01$ ). However, the higher slope (2.5) indicate a contribution from local sources in Gundsømagle.



**Figure 26.** Correlation of yearly average of PCDD/Fs in bulk deposition versus the concentrations in rainwater and rainfall, respectively.

Figure 26 shows the yearly average of PCDD/Fs bulk deposition versus the concentrations in rainwater and rainfall, respectively. Total averages all stations until December 2004. A significant correlation was found between flux and concentration in rainwater ( $p < 0.01$ ). Between flux and rainfall, no significant correlation was found ( $p = 0.4$ ). This indicates that on a geographical scale, the deposition flux is independent of the rainfall. That is, a higher (average) rainfall does not result in a higher (average) deposition flux, but instead dilutes the PCDD/Fs in the rainwater.

## 5.11 Congener profiles

The concentrations of the 7 PCDD-congeners and the 10 PCDF-congeners analysed form a characteristic pattern, which can be considered as a "fingerprint" for each sample. This can be used to compare mutual similarities in different samples, and to compare samples with sources. It is not useful to directly display the concentrations of the 17 analysed congeners in a diagram, because of the wide range of concentrations in a single sample, and because the toxicity of the congeners differ widely. The analysis below does not take into consideration, that the recoveries of the different congeners show a variation (see section 4.5).

### *Relative congener profiles*

To cope with this, so-called relative congener profiles are useful; these show the relative I-TEQ contribution from each congener in a sample as % of the total I-TEQ. Relative profiles are calculated by multiplying the concentration of each congener in the sample with the corresponding International Toxicity Equivalent Factors (I-TEF), obtaining the contributions to I-TEQ. The congener contributions are then normalised by division with the sum of all contributions, which is set to 100%. The relative congener profiles displays the toxicological importance of each congener. The very high concentration of OCDD in air and deposition samples is scaled down because of the low I-TEF of that congener, making the diagram more readable. Furthermore, it is possible to compare profiles of samples with widely different concentration levels in the same diagram. Finally, it is feasible to compare results expressed in incommensurable units (e.g. for air  $\text{fg}/\text{m}^3$  and for deposition  $\text{pg}/\text{m}^2\cdot\text{day}$ ). Because of these virtues, relative congener profiles are used in the following.

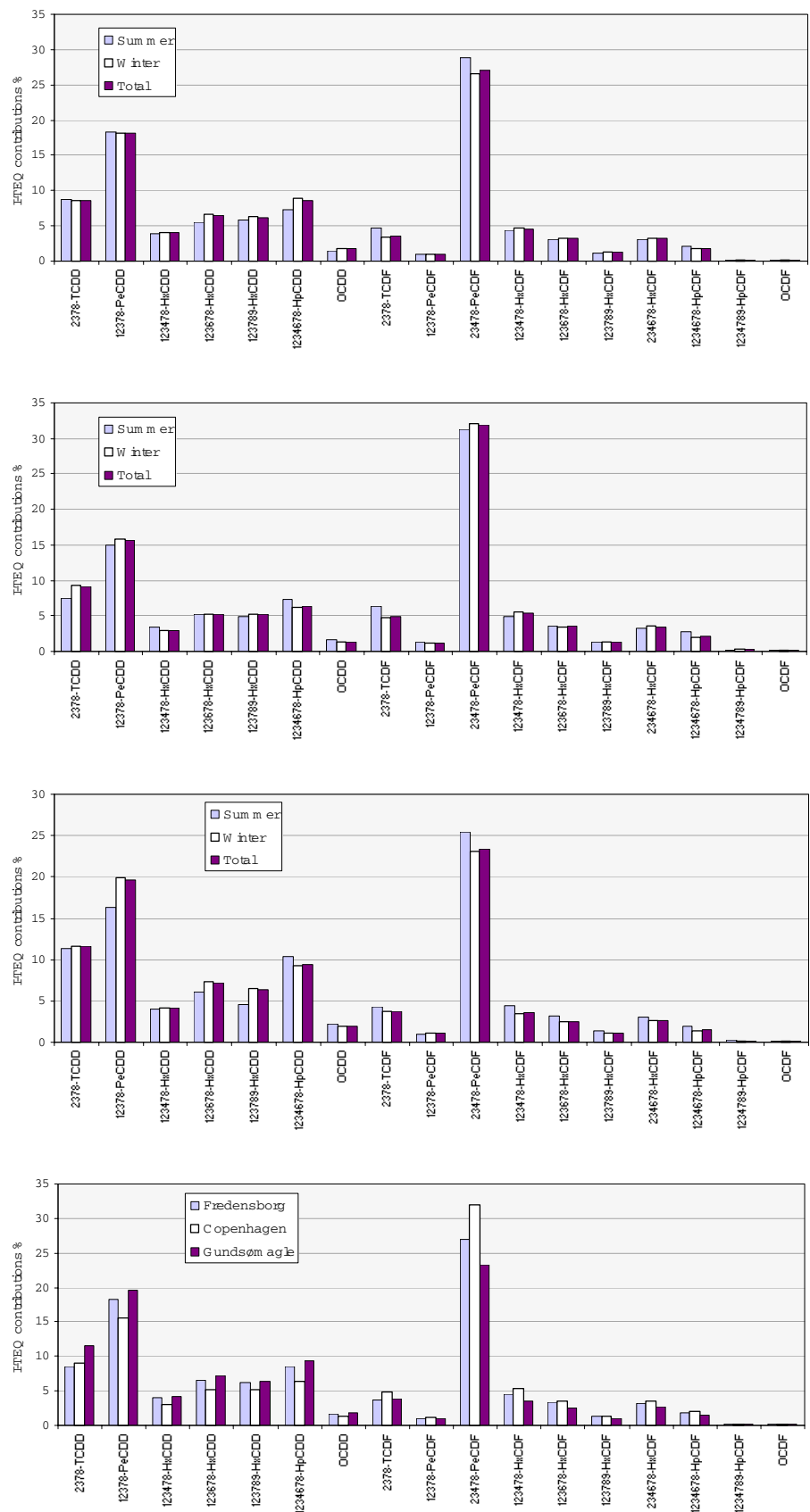
An important question is the difference between air, deposition and through fall, between the different sites, and between summer and winter. In the following figures, relative congener profiles are shown for selected averages of air and deposition. The profiles are calculated from the respective averages, which have been calculated from the concentrations.

### *Air congener profiles*

Figure 27 shows the relative congener profiles of air from all air-sites. The upper three panels show summer, winter and total averages, respectively from Frederiksborg, Copenhagen and Gundsømagle, respectively. It is noted that the main TEQ contributor for all sites is 2,3,4,7,8-PeCDF, followed by 1,2,3,7,8-PeCDD, 2,3,7,8-TCDD, and 1,2,3,4,6,7,8-HpCDD.

No substantial difference is seen between summer and winter for any site. One might expect that the air temperature would affect the ratio between the lower, more volatile congeners, compared to the higher, lesser volatile ones, which should condense at low temperatures. However, several studies have shown that low temperature merely shifts the equilibrium from gaseous to the more particle-bound state, without changing the overall concentration in the air. As mentioned, the profile is a "fingerprint" characteristic for the sources. In particular, one might expect that the winter results would stand out from the summer ones, since the former would be characterised by emission from heating. But as noted, it does not seem to be the case. Even in Gundsømagle, where wood stoves are known to emit considerable amounts of PCDD/Fs during the winter, the difference seems to be as modest as is the case for the other sites.

Figure 27 lower panel compare the total means of the three air sites. As seen, the profiles for all sites are alike. This support the notion mentioned previously, that that the PCDD/Fs in air is a large-scale phenomenon, the profiles being similar everywhere.



**Figure 27.** Relative congener profiles of air in Frederiksborg, Copenhagen and Gundsømagle, average of summer, winter and total (3 upper panels), average totals all 3 stations (lower panel).



Figure 28 shows the relative congener profiles of deposition for summer, winter and total averages, from Ulborg (upper panel), Frederiksborg, Copenhagen and Bornholm, respectively. It is noted that the main TEQ contributor for all sites is 2,3,4,7,8-PeCDF as was the case for air,. This is very pronounced, more so than for air, and is followed by the lower PCDDs, and then the PCDFs. In contrast to air, no pronounced contribution from 2,3,7,8-TCDD and 1,2,3,7,8-PePDD is seen. A further conspicuous feature of Figure 27 is the relationship between Ulborg and Frederiksborg, characterised by the comparatively high and evenly descending contributions from the lower PCDDs. Also Copenhagen and Bornholm are related. Contrary to Ulborg and Frederiksborg, their profiles are dominated by 2,3,4,7,8-PeCDF, the contributions from all other congeners being low and rather erratic.

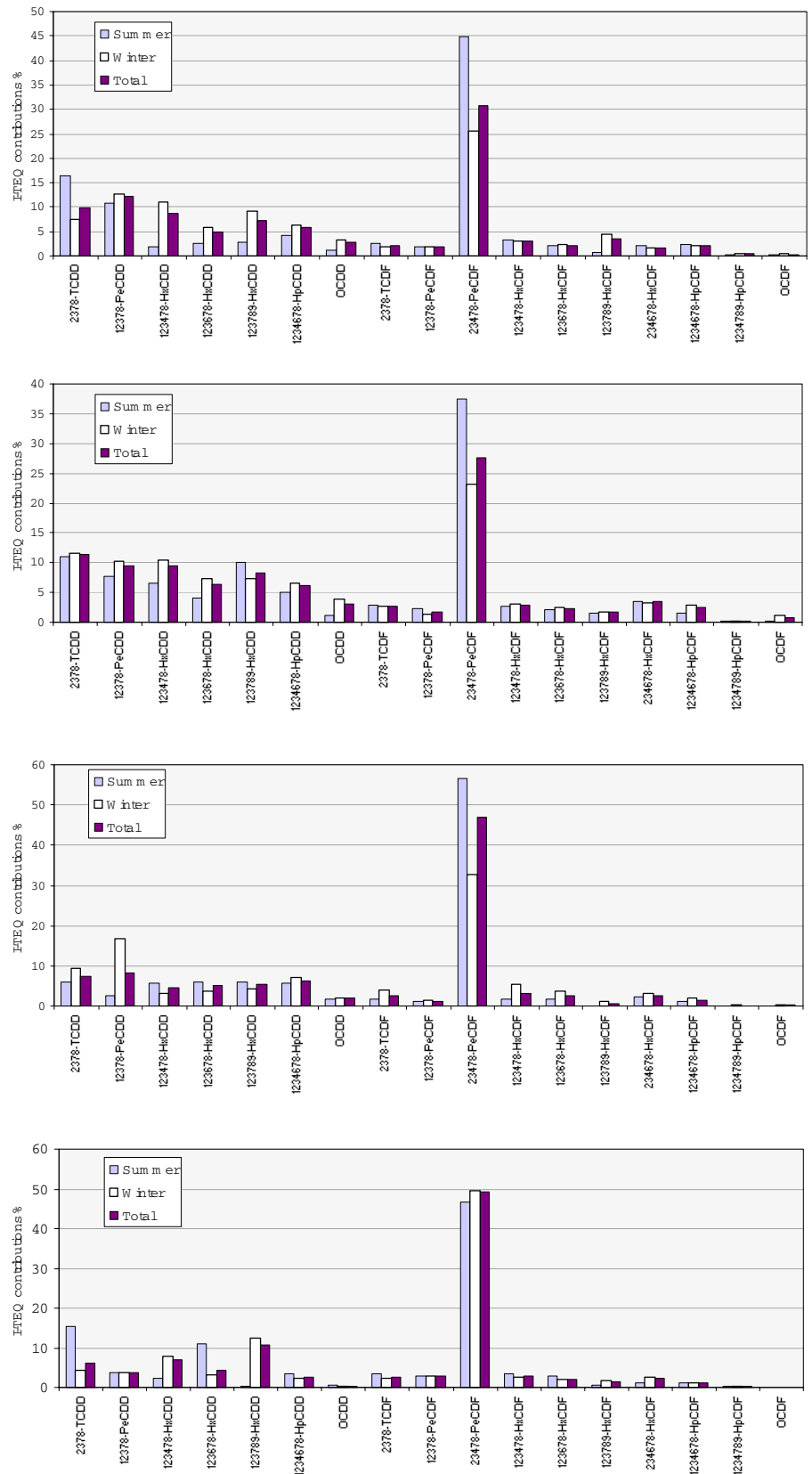
Contrary to air, a difference is seen between summer and winter for deposition. This is particularly evident for 2,3,4,7,8-PeCDF in the upper 3 panels of Figure 28, being higher during the summer. Otherwise, the summer winter difference does not seem well defined. The explanation for this may be that - in contrast to air - it seems that the deposition profile depends on the particle bound fraction, which in turn is dependent in a complicated way on kind, amount and size of the particles, temperature etc.

Figure 29 upper panel shows relative congener profiles of through fall in Frederiksborg summer, winter and total. No appreciable difference between summer and winter is seen. The profile and the air profiles is alike (Figure 26). Thus air-uptake dominates the profile, independently confirming the previous conclusion that dry deposition of gaseous substance plays a major role for through fall.

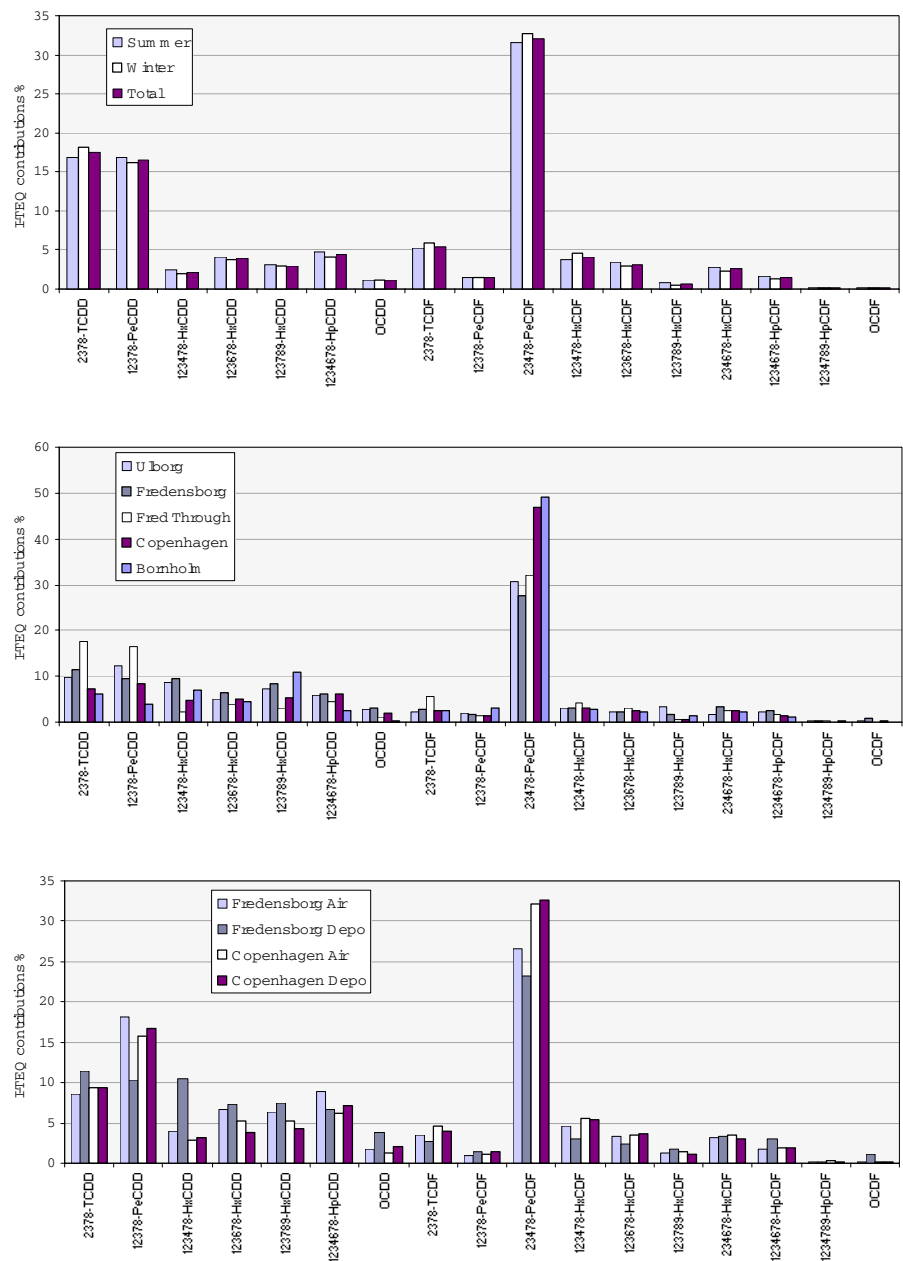
Figure 29 middle panel shows average total bulk deposition and through fall for all stations. As seen, for the highest contributing congeners, Ulborg and Frederiksborg are close together, confirming the relationship between those stations. The same remarks apply to Copenhagen and Bornholm. For through fall in comparison, the two lower PCDD congeners stands out as elevated.

Figure 29 lower panel compares relative profiles of the winter averages for air and deposition in Frederiksborg and Copenhagen. Shown in this way, it seems that the profiles for air and deposition are alike for each site, the only (minor) difference being 1,2,3,4,7,8-HxCDD in Frederiksborg. Also the difference between sites seems modest.

It must be concluded that the congener profiles of deposition and air are similar in many respects, but also differs from each other as well as mutually in subtle ways. It is difficult to get an overview of the differences and similarities between the profiles by visually comparing the diagrams. To cope with this, a new approach is needed, such as pattern recognition.



**Figure 28.** Relative congener profiles of bulk deposition in Ulborg (upper panel), Frederiksborg, Copenhagen and Bornholm, average of summer, winter and total.



**Figure 29.** Relative congener profiles. Through fall in Frederiksborg summer, winter and total (upper panel). Average total bulk deposition and through fall all stations (middle panel). Air compared to deposition (winter average) in Frederiksborg and Copenhagen (lower panel).

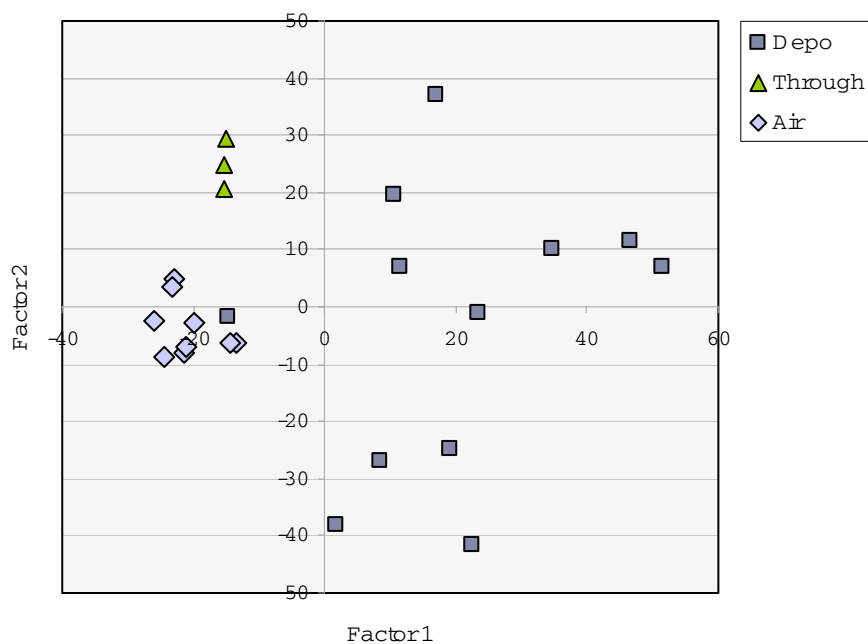
## 5.12 Principal component analysis (PCA)

The different profiles in the previous section may be difficult to compare. In this connection, pattern recognition techniques may be helpful, and for these reasons a principal component analysis was performed. The analysis was carried using the FACTOR routine in UNESCO's free software package WinIDAM downloaded from the Internet. The PCA was done on correlation coefficients and limited to 6 principal components. The relative congener profiles of the averages mentioned in the preceding section were used as input. The data were ranked in order of total averages all data, leading to the sequence (in descending order):

23478-PeCDF, 12378-PeCDD, 2378-TCDD, 1234678-HpCDD, 123789-HxCDD, 123678-HxCDD, 123478-HxCDD, 123478-HxCDF, 2378-TCDF, 123678-HxCDF, 234678-HxCDF, OCDD, 12378-PeCDF, 123789-HxCDF.

1234789-HpCDF and OCDF were left out because of low average.

The results of the PCA showed that the eigenvalues of the first 2 principal components (factors) were 5.42 and 3.89, explaining 36 and 25% respectively of the variation, i.e. 61% together. In the following, only these two factors are considered.



**Figure 30.** Results of PCA on first two factors on the average relative congener profiles deposition, through fall and air all sites, summer winter and total, signatures showing matrix.

### *Air and through fall*

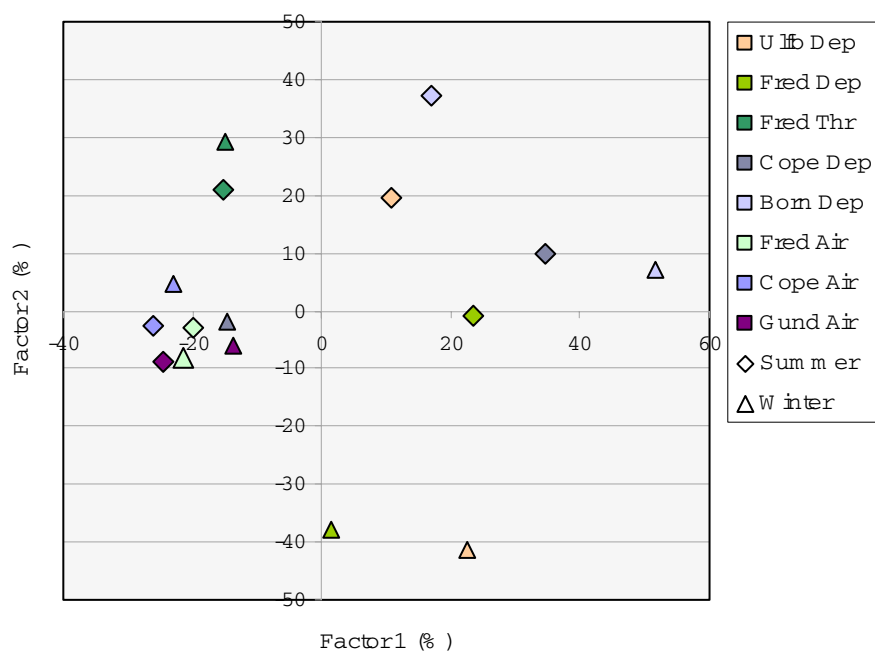
Figure 30 shows the results of the PCA with signatures for the matrix. It is remarkably that the air results form a tight, well-defined group on the left side of the y-axis close to the x-axis. This group includes summer winter and total for all air-sites. Also the through fall forms a very tight group within the x-range (factor 1) of the air group, but higher y-range (factor 2). The distinct groups at near identical primary factor attest to a close relationship between the profiles of air and through fall, and confirm that the uptake of PCDD/Fs from the air in spruce needles is an important process for through fall. That the through fall is higher in factor 2 indicates subtle differences in the profiles, possibly caused by different solubilities of congeners in the waxy needles. However, one must consider the possibility that the (slight) difference also might be due to the different sampling techniques employed for air and deposition/through fall. The existence of such well-defined groups so close together confirms that the methods of sampling and analysis yield consistent and comparable results, even if the sampling campaign extends over several years. On the other hand, the distinct air-group show that the profiles in (Danish) air are closely related and ubiquitous, and hence, unsuited for source identification and backtracking studies. Thus, the idea to use PCA on air profiles for source identification and transport studies is not supported by the present results.

### *Deposition*

In stark contrast to air and through fall, the deposition results are spread out in the right side of the PCA diagram, occupying space near the x-axis and the y-axis. A single point (Copenhagen winter average) is found on the left side inside the air group. The wide spread-out of the deposition points indicates that the profiles vary much more than those of air, the primary transport medium. We can conclude that the profiles are altered during the process of transfer from air to deposition. This transformation is highly variable, and the process discriminates between congeners.

### *Site and season*

The influence of season and geographical location is addressed in Figure 31, which shows the same PCA as Figure 30 with the site and matrix colour-coded and the season shape-coded. To make the summer-winter difference, clearer, the totals are omitted.



**Figure 31.** Results of PCA (same as shown in Figure 30) on first two factors on the average relative congener profiles deposition, through fall and air all data, summer and winter (totals are omitted). Site and matrix colour-coded, season shape-coded.

It is seen from Figure 31 that the deposition summer and winter results of Ulfborg and Frederiksborg display large vertical difference within a narrow x-interval. These findings indicate that the Ulfborg and Frederiksborg profiles are related, as may also be seen by close inspection of Figure 27. On the contrary, Copenhagen and Bornholm form more horizontal groups, showing a high variation along the x-axis. The PCA thus once more confirm the anomaly of Copenhagen deposition. Bornholm displays an erratic PCDD/PCDF ratio (as noted in the result section) that leads to a poorly defined profile. Otherwise, no clear picture with respect to stations emerges. Omitting Copenhagen entirely and Bornholm winter, the remainder of the data in the diagram indicates an influence of station along the x-axis (first factor), and season along the y-axis (second factor). The summer is highest in y in all cases. It may be difficult to explain the variation between stations, but the causes of the summer-winter difference are clearer. One factor responsible for this is obviously the air temperature, which affect the fraction being in the vapour phase, thus discriminating between more or less volatile congeners. Another factor may be the soot content in the air, which is considerably higher during the winter, but also varies with the site. This factor also discriminates between congeners, because the higher congeners (e.g. OCDD) are bound much stronger to soot carbon than the lower ones (e.g. 2,3,7,8-TCDF). A third factor might be air moisture and rain fall, but this seems to be of lesser importance as mentioned previously. A fourth factor could be photodegradation, because light intensity at Danish latitudes is considerably higher during the summer. However, since photodegradation takes place in the air, this factor should theoretically influence the air profiles as well, contrary to what is seen.

In conclusion, the PCA displays a clear picture of air and through fall profiles, which forms distinct and related groups close to each other in the PCA diagram. In contrast, the deposition profiles do not form groups, but are spread out in the PCA diagram, occupying space far from the air group. This indicates that the profiles, during the transfer from air to deposition, are changed in a highly variable process, which discriminates between congeners. However, the factors responsible for the variation are not entirely clear. The analysis above does not take into consideration, that the recoveries of the different congeners show a variation (see section 4.5). This might also have an influence on the results.

### 5.13 Other studies

#### *Concentrations in air*

Ambient air concentrations of PCDD/Fs from selected European sites are compared to the levels found in this study in Table 11.

**Table 11.** Comparison of atmospheric levels of PCDD/Fs in selected studies from Europe

Country	Location	Sampling period	Annual mean (min-max), fg TEQ/m <sup>3</sup>	References	Remark
Denmark	Frederiksborg	2002-2003	20 (3-87)	Present study	R
	Copenhagen	2002-2003	20 (3-56)	Present study	U
	Gundsømagle	2003	71 (9-180)	Present study	R
Belgium	Flanders	1992	110 (20-380)	Wevers et al. (1993)	U
Germany	Köln, Duisburg	1987	240	Hiester et al. (1997)	U
	Essen, Dortmund	1993	90	Hiester et al. (1997)	U
	Hessen	1994	100 (80-150)	König et al. (1993)	U
Italy	Rome	1990-1991	85 (50-280)	Turrio-Baldassarri et al. (1994)	U
Poland	Krakow	1995	12000	Grochowalski et al. (1995)	U
Spain	Catalunya	1995	250 (70-530)	Abad et al. (1997)	U
	Catalunya	1995	50	Abad et al. (1997)	R
Sweden	Rörvik	1989-1990	21 (4-60)	Tysklind et al. (1993)	R
	Göteborg	1988	22 (16-30)	Tysklind et al. (1993)	U
	Coast	1987	4	Broman et al. (1991)	B
	Stockholm	1987	19	Broman et al. (1991)	U
UK	Manchester	1991-1993	410 (ND-1800)	Duarte-Davidson et al. (1994)	U
	Cardiff	1992-1993	190	Jones et al. (1997)	U

Remarks: U = urban area, SU = suburban area, R = rural area, B = background site

It is seen from Table 11 that the dioxin concentrations found in air in Frederiksborg and Copenhagen are very similar to levels earlier reported from Sweden (Rörvik, Göteborg and Stockholm). The coast measurements from Sweden are lower. The concentrations from a rural site in Spain are somewhat higher than the Danish levels. This could be caused by climate difference, but since in Spain the reported urban concentrations are considerably higher, there must be local sources that might influence the background too. Apart from Sweden, all urban values reported are higher than the Copenhagen results. This might be due to combustion sources such as industry, in-

cineration and heating; whereas in the Copenhagen area the prevailing heating method is district heating, incinerators are equipped with special flue-gas cleaning, and there is no heavy industry.

### Bulk deposition

The atmospheric deposition fluxes of PCDDs/F (pg TEQ/m<sup>2</sup>-day) reported in selected studies in Europe are compared to the fluxes observed in the present study (Table 12).

It is seen from Table 12 that the flux in bulk deposition at the background and rural sites Ulborg, Frederiksborg and Bornholm are very similar to the levels reported from Belgium (rural site in Flanders) and Germany (rural sites in Bayreuth and Baden-Württemberg). All results from Italy are lower, even of the industrial and urban sites, and so is the German background site at Zingst. The results from Copenhagen compared to urban and suburban values are close to results reported from Flanders and Bayreuth, but lower than those from North Rhine Westphalia and Baden Württemberg.

Overall, this geographical distribution shows a general agreement between the background/rural and low urban levels, whereas some results from urban sites in Germany are higher than the Danish results. This is hardly surprising. Contrasting this pattern, the results from Italy and Zingst stand out as low in comparison. Since this discrepancy is confined to two specific studies (Guerzoni et al., 2004 and Knoth et al., 2000), it cannot be excluded that the difference might be due to the methods used in the respective studies.

**Table 12.** Comparison of atmospheric deposition fluxes of PCDD/Fs in selected studies from Europe

Country	Location	Sampling period	Flux, mean (min-max), pg/m <sup>2</sup> -day TEQ	Reference	Remark
Denmark	Ulborg	2002-2005	2.9 (0.3-13.8)	Present study	B
	Frederiksborg	2002-2005	4.4 (0.5-16.9)	Present study	R
	Bornholm	2003-2005	6.1 (0.5-31.5)	Present study	R
	Copenhagen	2003-2004	8.0 (1.7-31.6)	Present study	U
Italy	Venice	1998-1999	(0.19-0.2)	Guerzoni et al. (2004)	U
	Porto Marghera	1998-1999	(0.03-5.2)	Guerzoni et al. (2004)	I
	Venice	1998-1999	(0.03-6.2)	Guerzoni et al. (2004)	R
Belgium	Flanders	1993-1999	(3.4-25.0)	van Lieshout et al. (2001)	U
	Flanders	1993-1999	(0.68-10.0)	van Lieshout et al. (2001)	R
Germany	Bayreuth	1996	(0.71-6.4)	Hostmann et al. (1997)	B
	Bayreuth	1994-1995	(2.0-10.9)	Hostmann et al. (1998)	U
	North Rhine Westphalia	1992	(9.6-82.2)	Hiester et al. (1993)	U
	Baden Württemberg	1992	(34.0-40.8)	Wallenhorst et al. (1997)	U
	Baden Württemberg	1992	(24.1-38.1)	Wallenhorst et al. (1997)	SU
	Baden Württemberg	1992	(2.7-10.1)	Wallenhorst et al. (1997)	R
	Zingst	1996-1997	(1.1-1.7)	Knoth et al. (2000)	B

Remarks: U = urban area, SU = suburban area, R = rural area, B = background site, I = industrial area



## 6 Conclusions

<i>Air</i>	The results for air show a pronounced seasonal variation with maxima in the winter and a small year to year variation. The air concentrations in North-Zealand and Copenhagen are very alike, pointing to long range transport as a potential contributor to atmospheric PCDD/F at these sites. The village winter maximum is very pronounced, being the highest measured in the programme. The high concentrations are most likely caused by local emissions from wood stoves during the heating season. The mean concentrations at the Frederiksborg and Copenhagen sites were 20 fg/m <sup>3</sup> I-TEQ
<i>Through fall</i>	The through fall results show some variation throughout the seasons and the level is somewhat higher than the bulk deposition. The higher level is probably caused by a contribution from airborne PCDD/F, captured by the spruce canopy and later on transferred to the ground by precipitation or adsorbed to organic material.
<i>Bulk deposition</i>	Measurements of PCDD/Fs in bulk deposition 2002-2005 at three rural sites in Denmark show an even geographical distribution over the country, the difference amounting to factor two. The seasonal variation is not as pronounced as for air. The background level (i.e. mean of rural sites) was 4.5 pg/m <sup>2</sup> ·day I-TEQ. The deposition in Copenhagen is 1.8 times higher than that in Frederiksborg, in spite of the similarity in air concentration. This difference is, possibly an effect of dust contaminating the bulk deposition sampler.
<i>Role for soil</i>	The regional deposition roughly accounts for the PCDD/Fs in rural soil. The present bulk deposition flux corresponds to accumulation times of 75-86 years. In Copenhagen, the soil concentrations are much too high and variable to be explained by deposition alone.
<i>Role for sediment</i>	The concentrations of dioxin in sediments of investigated lakes are in general too high to be explained by bulk deposition alone. This is also the case for sea sediment.
<i>Connection with rain</i>	The rainfall amounts at the different sites are similar. On a regional scale, the average deposition flux follows the concentrations in rain and not the rainfall.
<i>National annual deposition</i>	The average rural deposition, 4.5 pg/m <sup>2</sup> ·day I-TEQ, corresponds to 1.6 mg/km <sup>2</sup> ·year I-TEQ or 72 g/year on the Danish land area. This is in the same range as Danish atmospheric sources, which is estimated to 11-148 g/year (all sources) or 9-45 g/year (known sources).
<i>Deposition over the Baltic Sea</i>	Atmospheric input of PCDD/Fs to the western Baltic Sea based on Danish and German measurements is estimated to 1.3 mg I-TEQ/km <sup>2</sup> ·year. From measurements of the content of dioxin in fatty pelagic fish (herring and salmon) and an estimation of the yearly production of biomass, it is demonstrated that the uptake in fish only amounts to 0.4% of the flux of dioxins deposited from the atmosphere. Therefore, atmospheric deposition to the sea surface of the western Baltic Sea can account for the PCDD/Fs found in pelagic fish being the top of the food web in the open sea.

<i>Human intake</i>	Deposition carries a large surplus of PCDD/Fs into the Baltic Sea compared to the amount contained in the pelagic fish production; hence, this transport route does have an important impact on the human intake via seafood. Also, the deposition on the Danish land area during the summer is more than sufficient to account for the PCDD/Fs contained in cow milk, hence, dairy products.
<i>Correlations</i>	The main TEQ-contributor is 2,3,4,7,8-PeCDF followed by 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD at all sites, seasons as well as matrixes. The congener profiles of air and through fall are alike, as are the deposition profiles of Ulborg/Frederiksborg and Copenhagen/Bornholm.
<i>Congener profiles</i>	The main TEQ-contributor in all sites and matrixes is 2,3,4,7,8-PeCDF followed by 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD. The congener profiles of air and through fall are alike, as are the deposition profiles of Ulborg/Frederiksborg and Copenhagen/Bornholm.
<i>Principal Component Analysis</i>	A principal Component Analysis on average congener profiles shows that the congeners found in air form a tight group, indicating that the profiles are similar (across site, summer and winter). The same is the case for profiles of through fall, which form a group close to the air group, showing the effect of gaseous dry deposition on the spruce trees. In contrast, the deposition data are spread out in another region of the PCA diagram, reflecting a much higher variation between profiles. Roughly speaking, the first component accounts for site, and the second for the summer-winter difference.
<i>Other studies</i>	The Danish concentrations of PCDD/Fs in rural air are at the same level as those found by Swedish and German measurements, whereas Spanish values are higher. Apart from Sweden, all urban values reported elsewhere are higher than the Copenhagen results. The flux of PCDD/Fs in bulk deposition at the Danish rural sites is very similar to the levels reported from rural sites in Belgium and Germany. Results from Italy and German background site at Zingst are lower, however. The results from Copenhagen are close to urban and suburban values results reported from Flanders and Bayreuth, but those from North Rhine Westphalia and Baden Württemberg are higher.
<i>Future work</i>	It is important to quantify deposition and atmospheric levels of PCDD/F over Danish waters in order to evaluate, and eventually to reduce, the flux of PCDD/Fs into seafood. In this connection it would be necessary to operate more sea stations. The Danish islands Bornholm and Falster in the Baltic Sea and Anholt in Kattegat, would be very suited for such an investigation, since deposition stations has to be located on islands. Backtracking from high time resolution studies should be used to locate atmospheric sources in the Baltic region.
<i>Final conclusion</i>	The present investigation shows that atmospheric deposition still yields an important contribution to the human intake of PCDD/Fs from seafood, milk and dairy products. The only way to cope with this is to locate atmospheric sources and reduce/eliminate their emission. This work should be continued on an international scale, and the progress followed by air and deposition studies.

## 7 Acknowledgements

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## 9 Abbreviations

2378-TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
12378-PeCDD	1,2,3,7,8-pentachlorodibenzo-p-dioxin
123478-HxCDD	1,2,3,4,7,8-pentachlorodibenzo-p-dioxin
123678-HxCDD	1,2,3,6,7,8-hexachlorodibenzo-p-dioxin
123789-HxCDD	1,2,3,7,8,9-hexachlorodibenzo-p-dioxin
1234678-HpCDD	1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin
OCDD	Octachlorodibenzo-p-dioxin
2378-TCDF	2,3,7,8-tetrachlorodibenzofuran
12378-PeCDF	1,2,3,7,8-pentachlorodibenzofuran
23478-PeCDF	2,3,4,7,8-pentachlorodibenzofuran
123478-HxCDF	1,2,3,4,7,8-hexachlorodibenzofuran
123678-HxCDF	1,2,3,6,7,8-hexachlorodibenzofuran
123789-HxCDF	1,2,3,7,8,9-hexachlorodibenzofuran
234678-HxCDF	2,3,4,6,7,8-hexachlorodibenzofuran
1234678-HpCDF	1,2,3,4,6,7,8-heptachlorodibenzofuran
1234789-HpCDF	1,2,3,4,7,8,9-heptachlorodibenzofuran
OCDF	Octachlorodibenzofuran
dm	Dry matter
HR-MS	High resolution mass spectrometry
I-TEQ	International Toxicity Equivalent
Max	Maximum value
Min	Minimum value
n	Number of measurements (in statistics)
nd	Not detected, non-detect
ng	Nanogram, $10^9$ g
$\mu$ g	Microgram, $10^6$ g
pg	Picogram, $10^{12}$ g
fg	Femtogram, $10^{15}$ g
PCA	Principal Component Analysis
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzofurans
PCDD/Fs	PCDDs and/or PCDFs
sd	Standard deviation
TEF	Toxicity equivalence factor
UV	Ultra-violet
WHO-TEQ	WHO toxicity equivalent
GC/MS	Gas Chromatography – Mass Spectrometry

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Occurrence and geographical distribution of dioxin was investigated in air and deposition at selected locations in Denmark, three forest sites in the background area, a city site in Copenhagen and a village site. At two sites simultaneously determination of dioxins concentrations in the ambient atmosphere and bulk precipitation were carried out during a period of three years.

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