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A Field Study of Selected Urban and Rural Locations

NERI Tehnical Report, No. 486

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Data sheet

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Contents

Summary

The purpose of the present investigation has been to find the general level and the background level for pollution of soil with dioxins in Denmark, to investigate whether geographical or regional differences exist, to find if such differences are caused by pollution from industrial sources or urban centres. Further to study the influence of culturing and fertilising as well as the variation with depth.

The analytical method used comprised air-drying, soxhlet extraction in toluene, classic clean up on silica and alumina, and high resolution GC/MS. The method was checked on existing soil samples.

The fall 2001 samples of topsoil were collected from ploughed fields, grass fields, gardens or parks without any known contamination with chemicals, sludge or ash. The collection was nation-wide and ranged from Skagen in N to Gedser in S, and from Esbjerg in W to Bornholm in E. In the predominantly westerly wind, the contamination from presumed sources were investigated by sampling exposed zones 1-3 km east of the sources. These comprised larger industrial centres and urban regions, MSW and HSW incinerators, power plants and a steel mill. For comparison, reference samples from rural or remote locations were included. In addition, soils of low and high sludge amendment and a depth profile from a preserved area were analysed.

The results showed that in the depth profile from the preserved soil, far the most dioxin is found in the topsoil depth 0-10 cm, while deeper only minute amounts are found.

The dioxin content in the topsoil of the preserved area (0.9 ng/kg I-TEQ) is about three times higher than that of the low sludge amended soil, whereas that of the high sludge amended soil is about 100 times higher (about 30 ng/kg I-TEQ). That soil, however, has been dressed with amounts of sludge so high that it amounts to a sludge deposit. For comparison, the average in Danish sludge is 10 ng/kg I-TEQ.

In the study of the geographical distribution, the highest dioxin contents 15 ng/kg-I-TEQ were found in soils from parks and gardens in Copenhagen, and 2,2 ng/kg-I-TEQ in a football field in Nyborg near the HSW incinerator. This indicates that the soil in Copenhagen and perhaps also in other cities are considerably contaminated with dioxin.

The dioxin contents in all remaining samples, originating from rural areas, were below 1 ng/kg I-TEQ.

A remarkable result of the investigation is that the exposed zones East of the sources did not display higher dioxin content than the reference zones. Hence, the contamination from source on the surrounding land could not be demonstrated. This is the case for all exposed zones investigated near Ålborg, Århus, Esbjerg, Fredericia, Odense, Roskilde, Kyndby, Frederiksværk and Rødovre.

The total mean of the exposed zones and the reference zones were 0.74 and 0.67 ng/kg I-TEQ, respectively. The difference is neither of practical importance nor statistically significant. Hence, not either in the overall data elevated dioxin level in the exposed zones could be established.

For the reference samples, a geographical North-South gradient and a West-East gradient seem to be present.

Sammenfatning

Formålet med undersøgelsen har været at finde det generelle niveau og baggrunds niveau for forurening med dioxin af jord i Danmark, at undersøge om der findes geografiske forskelle og egnsforskelle, om hvorvidt sådanne forskelle skyldes indflydelse af industrielle kilder, punktkilder eller byområder. Desuden at undersøge om der er indflydelse af dyrkning eller gødning samt variation med dybden.

Analyse metoden bestod i lufttørring, soxhlet ekstraktion i toluen, klassisk oprensning på silikagel og aluminiumoxid samt højtopløsende GC/MS. Metoden blev tjekket på eksisterende jordprøver.

Efteråret 2001 blev indsamlet prøver af overfladejord fra pløje- eller græsmarker, haver og parker uden kendt lokal forurening med kemikalier, slam eller aske. Indsamlingen var landsdækkende med udstrækning fra Skagen til Gedser og fra Esbjerg til Bornholm. I den fremherskende vestenvind blev forureningen fra forventede flade- og punktkilder undersøgt ved prøver i eksponerede zoner 1-3 km øst for kilderne. Disse omfattede by- eller industri områder, forbrændingsanlæg for kommunalt eller farligt affald, elværker og stålvalseværket. Til sammenligning blev inkluderet reference prøver fra landlige og fra fjerne områder. Derudover blev en lavt og en højt slamgødet jord samt en dybdeprofil fra et fredet område analyseret.

Resultaterne viste, at i dybdeprofilen fra fredet jord befinder langt det meste dioxin sig i det øverste jordlag dybde 0-10 cm, mens der dybere nede kun findes forsvindende mængder.

Dioxin indholdet i overfladelaget af den fredede jord (0,9 ng/kg I-TEQ) er ca. 3 gange højere end i den lavt slamgødede jord, mens det i den højt slamgødede jord er omkring 100 gange højere (ca. 30 ng/kg I-TEQ). Denne jord har dog været tilført så store mængder slam at det i realiteten er et slam deponi. Til sammenligning er gennemsnittet i dansk slam 10 ng/kg I-TEQ.

I undersøgelsen af den geografiske fordeling fandtes de højeste dioxin indhold 15 ng/kg I-TEQ i park- og havejord i Københavns området og 2,2 ng/kg I-TEQ fra en sportsplads ved KK i Nyborg. Dette tyder på, at jorden inde i København og muligvis også i andre byer er kendeligt belastet med dioxin.

Dioxin indholdet i alle de øvrige prøver, som kom fra landlige områder, lå under 1 ng/kg I-TEQ.

Et bemærkelsesværdigt resultat af undersøgelsen er, at de eksponerede zoner øst for kilder ikke viste højere værdier end reference prøverne. Det betyder at der ikke kunne påvises en forurening fra kilder på det omkringliggende land. Dette er tilfældet for alle de undersøgte eksponerede områder nær Ålborg, Århus, Esbjerg, Fredericia, Odense, Roskilde, Kyndby, Frederiksværk og Rødovre.

Landsgennemsnittet af eksponerede zoner og reference zoner (inklusive fjerne områder) var hhv. 0,74 og 0,67 ng/kg I-TEQ. Forskellen er hverken af praktisk betydning eller statistisk signifikant, hvorfor der altså heller ikke i data materialet som helhed kunne der fastslås et forhøjet dioxin niveau i de eksponerede zoner.

For reference prøverne er der tegn på en geografisk nord – syd gradient og en vest – øst gradient.

1 Introduction

With the Belgian dioxin scandal in 1999, where PCB contaminated fodder resulted in unacceptable dioxin contamination of food, international attention became focused on food safety. Responding to this situation, Denmark and other EU countries took initiatives to reduce the dioxin load of the populations. The Danish effort took the form of a co-operation between the Ministry of Food and Agriculture, and the Ministry of the Environment. Whereas the former is focused on dioxin levels in food and in food safety, the latter is focused on the emission of dioxin to the environment.

The environmental effort was commenced with a literature survey of dioxin emissions in Denmark (Hansen et al. 2000). The survey indicated that a lack of data for the dioxin level in the Danish environment and emissions from the technosphere existed. As a response, an array of follow-up investigations was initiated to collect the needed data. These investigations are in progress for soil, compost, percolate, deposition, air and water. Furthermore, brominated dioxin from incineration of municipal and hazardous waste is included. Finally, the investigations examine dioxin in cow's milk and in human milk.

The present report describes the investigation of soil.

The investigation is supported financially by the Ministry of the Environment, and are carried our by co-operation between NERI and DEPA.

2 Purpose

The aims of the present study has been:

- To find the general and the background level of PCDD/F in Danish soil
- To investigate regional and geographical differences
- To investigate if point sources (such as incinerators or power plants) or diffuse sources (such as urban areas, cities or industrial zones) causes PCDD/F pollution of the surrounding country
- To study influence of sludge amendment and agriculture on the concentration of PCDD/F
- To study the variation of PCDD/F with depth.

3 Samples

3.1 Sampling

The depth profile was obtained by hammering a stainless steel drill 10 cm iØ 50 cm long into the ground. The core was subdivided into 5 sections of 10 cm height.

The topsoil in grass fields and grass lawns were sampled by hammering the drill 10 cm into the ground. Ploughed fields were sampled by collecting lumps of topsoil by means of a small shovel.

3-5 portions of topsoil from each location, taken some meters apart, were pooled to one sample of about 1 kg. In the laboratory, grass, roots and pebbles were removed, and the samples were air-dried, thoroughly mixed, and stored at –20°C until analysed.

3.2 Locations

Existing samples

At the disposal of NERI were a number of soil depth profiles from a previous investigation in the region of Roskilde (Vikelsøe et al. 1999). A selection of these was analysed prior to the collection of new samples. The results (mentioned in the results chapter) showed that a depth of 10 cm were suitable.

New samples

New samples for the present investigations were collected during the fall 2001 and the summer 2002. A new depth profile was sampled at the preserved area. The remaining topsoil samples were taken according to the following criteria:

- Representative for agriculture, parks, or garden soil.
- Contain no contamination from ash, sludge or chemicals.
- Comparable soil characteristics
- Depth 0-10 cm for topsoil study.

Efforts were made to collect soil with humus rich or clayey characteristics, to make the results comparable. Only in two cases (Skagen and Studstrup) this was not possible, and sandy soils had to be collected.

The samples are included in two separate studies. A depth profile/sludge amendment study and a topsoil/geographical distribution study.

An overview of the samples is given in Table 1.

Table 1 Overview of samples.

NERI No.	Sampled	Depth cm	County	Region	Name/position	Purpose
6,0863	5-okt-96	10-20	Roskilde	Hornsherred	Ejby	Preserved
6,0868	5-okt-96	10-20	Roskilde	Hornsherred	Ejby	Preserved
1,1232	7-nov-01	0-10	Roskilde	Hornsherred	Ejby	Preserved
1,1233	7-nov-01	10-20	Roskilde	Hornsherred	Ejby	Preserved
1,1234	7-nov-01	20-30	Roskilde	Hornsherred	Ejby	Preserved
1,1235	7-nov-01	30-40	Roskilde	Hornsherred	Ejby	Preserved
6,0971	25-okt-96	0-10	Roskilde	Roskilde	Bistrup	High sludge
6,0971	25-okt-96	0-10	Roskilde	Roskilde	Bistrup	High sludge
6,0972	25-okt-96	10-20	Roskilde	Roskilde	Bistrup	High sludge
6,0972	25-okt-96	10-20	Roskilde	Roskilde	Bistrup	High sludge
6,0901	26-sep-96	0-10	Roskilde	N Sjælland	Sundbylille	Low sludge
6,0902	26-sep-96	10-20	Roskilde	N Sjælland	Sundbylille	Low sludge
1,1544	6-dec-01	0-10	Nordjyllands	N Jylland	Skagen N	Rem DK N
1,1543	6-dec-01	0-10	Nordjyllands	N Jylland	Skagen W	Rem DK N
1,1542	6-dec-01	0-10	Nordjyllands	Ålborg E	V. Hassing	Pow
1,1570	12-dec-01	0-10	Nordjyllands	Ålborg E	V. Hassing	Exp
1,1260	11-nov-01	0-10	Århus	Århus N	Lisbjerg	MSWI
1,1258	9-nov-01	0-10	Århus	Århus E	Studstup	Pow
1,1259	9-nov-01	0-10	Århus	Århus E	Gl. Løgten	Ref
1,1261	11-nov-01	0-10	Århus	Århus W	Brabrand	Ref
1,1257	9-nov-01	0-10	Århus	M Jylland	Tåning	Rem
1,1541	6-dec-01	0-10	Ringkøbing	W Jylland	Ulfborg	Rem DK W
1,1540	6-dec-01	0-10	Ribe	Esbjerg N	Lifstrup	Ref
1,1190	29-okt-01	0-10	Ribe	Esbjerg E	Andrup	Exp
1,1256	9-nov-01	0-10	Fyns	Fredericia E	Røjle Kirke	Exp
1,1255	9-nov-01	0-10	Fyns	Fredericia E	Røjle Klint	Ref
1,1254	9-nov-01	0-10	Fyns	Odense E	Bullerup	Exp
1,1253	9-nov-01	0-10	Fyns	Nyborg N	Kerteminde	Ref
1,1252	9-nov-01	0-10	Fyns	Nyborg E	Football field	HWI
1,1193	1-nov-01	0-10	Frederiksborg	N Sjælland Ref	Græsted	Ref
1,1194	1-nov-01	0-10	Frederiksborg	Frederiksværk E	Arrenæs	Exp
1,1192	1-nov-01	0-10	Frederiksborg	Frederiksværk E	Park in city	Steel
1,1191	1-nov-01	0-10	Frederiksborg	Hornsherred	Kyndby	Pow
1,1236	7-nov-01	0-10	Københavns	Copenhagen N	Virum	Garden
1,1195	1-nov-01	0-10	Københavns	Copenhagen W	Rødovre	MSWI
1,1196	1-nov-01	0-10	Københavns	Copenhagen W	Rødovre Vold	MSWI
2,0715	1-jun-02	0-10	Københavns	Copenhagen C	Vanløse	Garden
1,1307	15-nov-01	0-10	Københavns	Copenhagen E	Amager Tiøren	Park
1,1294	14-nov-01	0-10	Roskilde	Roskilde E	St. Valby	Exp
1,1308	16-nov-01	0-10	Storstrøms	Baltic W	Gedser S	Rem DK S
1,1309	16-nov-01	0-10	Storstrøms	Baltic W	Gedser E	Rem DK S
1,1295	14-nov-01	0-10	Bornholms	Baltic E	Åkirkeby	Rem DK E

Legend: High sludge = loaded with 17t/year/ha through about 25 years. Ref = rural reference area. Rem = remote area. Exp = downwind (exposed) from urban/industrial area, Pow = exposed from power plant. MSWI = exposed from municipal solid waste incinerator. HWI = exposed from hazardous waste incinerator, Steel = exposed from steel mill. Park = public urban park. Garden = private garden.

3.3 Sludge amendment/ depth profile study

During a previous study of phthalates in soil (Vikelsøe et al. 1999), depth profiles of were collected in the region of Roskilde in the fall of 1996. The locations comprised (among others) soils amended with different amounts of sewage sludge and a preserved area. Because the top layer of the latter was used up, a new depth profile was taken as mentioned above. Below follows a short description of the locations.

Preserved area

Ejby. Preserved natural area neither cultivated, dressed, nor fertilised for more than 50 years. Used for cattle grazing. The location was selected as a background reference in relation to the sludge amended soils, to evaluate the contribution from the atmospheric deposition (the only known source in this area) and to evaluate the variation with depth.

Low sludge amended

Sundbylille. Cultured area amended with about 0.7 t dw/ha/y of sludge. This sludge load is about half the amount recommended by Danish agricultural consultants (4 t dw/ha every third year = 1.3 t dw/ha/y).

High sludge amended

Bistrup. Area used for cattle grazing. Received through a period of about 25 years all the sludge from Roskilde, amounting to about 17 t dw/ha/year. This is considerably above the 7 t dw/ha/y maximum allowed in today Danish agriculture (Miljø- og Energiministeriet, 2000). The site is in fact a sludge dump. Nevertheless, such a high load is allowed in other European countries and may be of relevance for those countries. The site indicate the occurrence of dioxin in a highly sludge loaded field.

3.4 Sampling plan for geographical distribution study

The samples were collected from 32 Danish locations, reaching from Skagen in north to Gedser in south and from Esbjerg in west to Bornholm in east. In the predominantly westerly wind, the contamination was investigated by sampling *exposed zones* 1-3 km east of presumed sources, if possible. The exposed zones may receive pollution from diffuse sources such as larger industrial centres or urban regions, or from point sources such as MSW and HSW incinerators, power plants and a steel mill. The sampling stations covered a selection of the largest and most important Danish urban and industrial centres. For comparison with the exposed zones, corresponding reference samples was included, where possible taken at rural areas to the north or west of the sources. Finally, remote locations far from sources were investigated.

Because of the east-coast locations of Århus and Copenhagen, which are major urban regions and industrial centres, no “down wind “ samples could be taken.

Description of locations

Below follows very short descriptions of the sites, including name, position and purpose.

Remote rural locations

Skagen N and Skagen W. Two samples to the N and W of the town, at the northernmost tip of Denmark. Sandy grassy soil. Reference Denmark N.

Ulfborg. Grass field in at the west coast of Jutland. Reference Denmark W.

Tåning. Grass field in mid Jutland.

Gedser S and Gedser E. Ploughed fields at the south tip of Gedser Odde, the southernmost location in Denmark. Reference Denmark S

Bornholm. Eastern reference from the island in the Baltic near the south coast.

Other locations

V. Hassing. Two ploughed field in 0.5 and 2 km E of coal fired power plant, respectively.

Lisbjerg. Grass field 1 km E of MSW incinerator

Studstup. Sandy soil 0,5 km E of coal fired power plant

Gl. Løgten. Grass field, reference for Lisbjerg and Studstrup

Brabrand. Ploughed field, reference W of Århus

Lifstrup. Ploughed field, N of Esbjerg, reference

Andrup. Ploughed field E of Esbjerg (industry)

RøjleKlint. Preserved grassy area E of Fredericia (industry).

Røjle Kirke. Ploughed field, reference.

Bullerup. Ploughed field near Odense (industry).

Kerteminde. Reference for Nyborg

Nyborg. Football field 0.5 km E of HSW incinerator

Græsted. Ploughed field in N-Zealand, reference

Frederiksværk. City park 1 km E of steel mill (scrap recycling by electro process)

Arrenæs. Ploughed field 3 km E of steel mill

Kyndby. Ploughed field, 1 km E of coal fired power plant.

Virum. Grass lawn in garden in N-Copenhagen suburb

Rødovre. football field exposed from MSW incinerator

Rødovre Vold, preserved grass exposed from MSW incinerator

Vanløse. Garden in Copenhagen

Amager Tiøren. Park in Estern Copenhagen

St. Valby. Exposed Roskilde industry

Gedser S. Ploughed field, Referene Denmark S

Gedser E. Ploughed field, Reference Denmark S

Åkirkeby. Reference Denmark E.

Figure 1 Map showing sampling locations for geographical distribution study.

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4 Analytical methods

4.1 Principle

The air-dried soil is spiked with a mixture of 14 $^{13}C_{12}$-labelled PCDD/F congeners. The spiked sample is soxhlet-extracted in toluene. The extract is concentrated followed by classic clean up on silica/NaOH, silica/H_2SO_4 and acidic alumina. The analysis is performed by GC/MS at 10000 resolution. The Clean-up and MS analysis is adapted from a modified version of the European standard for analysis of dioxin in flue gasses, CEN EN 1948 2-3.

4.2 Extraction and clean-up

4.2.1 Chemicals

Toluene	Rathburn, glass destilled
n-hexane	Rathburn, glass destilled
CH_2Cl_2	Rathburn, HPLC grade
Na_2SO_4	Merck, anhydrous, analytical grade
SiO_2	Merck, Kieselgel 60, 0.063-0.20 mm
H_2SO_4	Merck, analytical grade
NaOH	Merck, analytical grade
Al_2O_3	ICN Biomedicals, Alumina A
n-dodecane	BDH, Purity > 99% (GC area)
PFK	Fluka, Perflourokerosene, High boiling, for mass spectroscopy.

4.2.2 Pre-treatment of soil

Grass, roots and pebbles are removed manually and the soil is thoroughly mixed. The soil is dried at 105°C in a thin layer for 20 hours.

4.2.3 Extraction

Approximately 100 g of pre-treated soil is weighed accurately into a Soxhlet thimble, and 100 µl of extraction spike mixture is added, containing 14 $^{13}C_{12}$-labelled congeners (0.4 ng tetra-hexas, 0.8 ng hepta-octas, Table 2). The sample is Soxhlet extracted in 700 ml of toluene for 20 hours. A volume of 0.5 ml of n-dodecane is added to the extract 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.

4.2.4 Clean-up

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

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

- 1 g anhydrous Na_2SO_4.
- 1 g SiO_2 (activated at 150 ºC),
- g SiO_2 containing 33% 1 M NaOH
- 1 g SiO_2
- g SiO_2 containing 44% conc. H_2SO_4
- 2 g SiO_2.

Column 2: (1 x 17 cm)

- 1 g anhydrous Na_2SO_4.
- g acidic Al_2O_3 (activated at 250ºC).

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

The PCDD/F fraction, which is adsorbed on the Al_2O_3, is eluted with 20 ml of a mixture of CH_2Cl_2/n-hexane 20/80.

The eluate, which contains the cleaned PCDD/F fraction, is concentrated to about 1 ml under N_2, and 25 µl of n-dodecane is added. The evaporation is continued to near dryness, and then 25 µl of syringe spike solution containing 2 $^{13}C_{12}$ labelled PCDDs is added (Table 3). The sample, which now is ready for analysis by CG/MS, is transferred to an injection vial.

4.2.5 Blanks

For each analytical series laboratory blanks were included by subjecting empty soxhlet thimble and glassware to the total extraction and clean up procedure as described above. The blanks were subtracted from the results on an amount per sample basis for each analytical series.

The blanks ranged from 0.01 to 0.02 ng/kg I-TEQ.

4.3 Standards and spikes

All unlabelled standards and labelled spikes were manufactured by CIL, Andover, Massachusetts, USA. The solutions are stored at 4 ºC.

Spikes

The extraction spike solution is a mixture of $^{13}C_{12}$ labelled PCDD/F congeners added to the sample before extraction, used for identification and quantification of the PCDD/F congeners, and for recovery calculation.

Table 2 Extraction spike solution.

Substance	ng/ml	Label
2378-TCDD	4	$^{13}C_{12}$
12378-PeCDD		
123678-HxCDD		
1234678-HpCDD	8	$^{13}C_{12}$
OCDD		
2378-TCDF	4	$^{13}C_{12}$
12378-PeCDF		
23478-PeCDF		
123789-HxCDF		
123678-HxCDF		
234678-HxCDF		
1234678-HpCDF	8	$^{13}C_{12}$
1234789-HxCDF		
OCDF		
Toluene	Solvent	

The syringe spike solution (Table 3) 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 during preparation of the external standard solutions.

Table 3 Syringe spike solution

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

External standard series

A series of external standard solutions Table 4 is analysed in 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 Table 4. All solutions further contain the $^{13}C_{12}$ labelled standards (spikes) in the same concentration given in the last column of the table.

Table 4 External standard solutions.

Substance	Unlabelled					$^{13}C_{12}$
	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 are used for quantification. To reduce the risk of carry-over from standards to unknowns, the strongest standard is not included in the analysis of a series of weak samples, such as most soil samples.

All standard solutions from 0.4 to 40 ng/ml (TCDD) are used combined for linearity test.

The weakest standard solution of level 0.4 ng/ml (TCDD) is further used for checking the sensitivity of the GC/MS system.

4.4 GC/MS analysis

4.4.1 Analytical sequence

Each analytical series is 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 are inserted between the unknowns. From time to another, a control sample of soil is analysed for quality control.

4.4.2 Gaschromatography (GC)

The following gaschromatographic operating conditions were used:

Gaschromatograph:	Hewlett-Packard 5890 series II
Injection:	Automatic, CTC autosampler, 2 µl split/ splitless, 270ºC, 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:	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
Temperatureprogram:	40 sec at 200ºC, 20ºC/min to 230ºC, 3ºC/min to 230ºC, 28 min at 290ºC
Transferline	250ºC.

4.4.3 Mass spectrometry (MS)

The following instrument conditions were used:

Mass spectrometer:	Kratos Concept 1S, high resolution magnetic sector instrument
Resolution:	10,000 (10% valley definition)
Ionisation:	Electron impact (EI)
Ionisation energy	35 - 45 eV depending on tuning
Ionisation current	5 µA
Ion source temperature	270ºC
Interface:	250ºC direct to ion source
Acceleration voltage	8 kV
Multiplier voltage	2,5-3 kV
Noise filter	300 Hz digital
Magnet stabilisation	Current
Solvent filament delay	10 min

Coolant temperature	19,5-20,5ºC
Calibration gas:	Perfluorokerosene (PFK)
Scan parameters	Cycle time 1 sec Electrostatic analyser (ESA) sweep 10 ppm Lock-mass sweep 300 ppm Lock-mass dwell 100 msec Dwell per monitored mass 90-100 msec Dwell for check-mass 20 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 5).

The descriptors contain masses for analytes and spikes. For each substance class (i.e. sum formula) 2 masses are monitored, corresponding to the most intense lines in the molecular ion group of the mass spectrum. In all windows is further used a lock-mass and a check-mass, which are prominent lines in the PFK mass spectrum.

Table 5 MID masses for mass spectroscopy

Substance	m/z 1	m/z 2	m/z 3 $^{13}C_{12}$-	m/z 4 $^{13}C_{12}$-	I mz1 /I mz2, %
Group 1, Cl_4	**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_5	**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_6	**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_7	**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_8	**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

4.4.4 Toxic equivalents (TEQ)

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

$$E_{tox} = \Sigma\ C_{ip} \bullet T_i$$

where:

E_{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 according to Table 6.

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 to make them comparable with other investigations.

Table 6 Toxic equivalent factors.

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

4.4.5 Performance of analytical method

- Repeatability: (low concentration 0.2 ng/kg I-TEQ): about 6 %.
- Detection limits: 0.01 ng/kg for TCDD to 0.8 ng/kg for OCDD
- Recoveries: Mean and standard deviation all data: 74±21%.
- Blanks: 0.01 to 0.02 I-TEQ.

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5 Results and discussion

5.1 Depth profile/sludge amendment study

The results showing the influence of sludge amendment and of sampling depth are shown in Table 7. Several conclusions can be drawn.

Analytical performance

The first two columns in Table 7 show the results of a double determination of the preserved soil (Ejby depth 10-20 cm sampled Oct/96). It is seen that almost all congeners can be detected, and that the doublet results correspond fairly well. The coefficient of variation (repeatability) of I-TEQ is 6%, even in this very low-contaminated soil. Hence, it may be concluded that the performance of the analytical method is satisfactory in the soil matrix.

Depth profiles

The depth profile of the preserved soil (sampled Nov/01) in the following table-columns shows that 90% of the I-TEQ occurs at depth 0-10 cm, 5% at 10-20 cm and only 1% at 20-30 cm. This demonstrates that in such uncultured soils with no ploughing, the downward PCDD/F migration – even over many years – is insignificant. The comparatively high concentration in the top layer is surprising, since the only known source at the location is the atmospheric deposition, having a considerable lower concentration (in rainwater). Thus an enhancement has taken place i.e. concentrations builds up over the years. This is only possible if PCDD/F have a considerable persistence. Finally, the vertical distribution shows that a sampling depth of 0-10 cm is sufficient for such locations. There is a discrepancy between the results for the preserved soil depth 10-20 cm for the two samplings (Oct/96 and Nov/01). However, the Oct 96 result is in between the Nov 01 result for depth 0-10 cm and 10-20 cm, suggesting difference in the exact depth of the PCDD/F-layers at the different sampling positions, which are some meters apart in the hilly terrain. It is unlikely that a time trend is causing the discrepancy, since no human activities has taken place. The only changes in the input conditions in the preserved area has been the decade- slow changes in the deposition.

Sludge amendment

Remarkably, the I-TEQ from the preserved area 0-10 cm depth is higher than the same depth of the low sludge amended cultured field, whereas the opposite holds for 10-20 cm depth. These findings demonstrate that low sludge amendment does not lead to build up of PCDD/F in cultured fields. In contrast, the I-TEQ for the high sludge soil is about 100 times higher than in the low sludge soil. Actually it is higher than in sludge, the Danish average being 10 ng/kg dw I-TEQ (unpublished results by Vikelsøe 2000, cited by Hansen et al., 2000). This demonstrates that the high amended soil exceeds a threshold for sludge amendment, above which a build-up takes place. Below the threshold, the degradation/removal keeps pace with the influx. For phthalates, similar conclusions were drawn by Vikelsøe et al. (1998).

The I-TEQ in 0-10 cm and 10-20 cm depth are not significantly different in the low sludge soil or in the high sludge soil. This is very likely due to mixing by ploughing (both fields has been regularly ploughed). Further, it shows that also for ploughed fields a sampling depth of 10 cm is sufficient.

The depth/sludge study results are summarised in Figure 2.

Figure 2 shows the results for the depth profile/sludge amendment study. The steep decreasing gradient is seen in the preserved soil, declining 20 times between the upper and the next layer, until a low plateau is reached below 20 cm. Almost identical concentrations in the upper layers of the ploughed soils is found. Remarkably, higher concentration is seen in the top layer of the preserved soil compared to the low sludge soil.

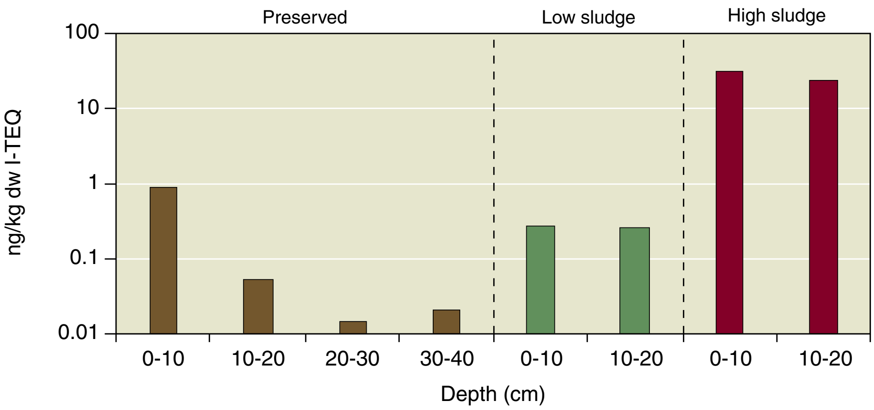

Figure 2 I-TEQ of depth profile/sludge amendment study (logarithmic scale).

Table 7 PCDD/F in soils differntly sludge amended, ng/kg dm.

Location	Ejby						Sundbylille		Bistrup		QA	
Use	Preserved						Agriculture		Cattle grazing			
Sludge amendm.	No						Low		High			
Sample No.	6.0863	6.0868	1.1232	1.1233	1.1234	1.1235	6.0901	6.0902	6.0971	6.0972	Blank	DL
Sampled, date	Oct/96	Oct/96	Nov/01	Nov/01	Nov/01	Nov/01	Sep/96	Sep/96	Oct/96	Oct/96	mean	mean
Depth, cm	10-20	10-20	0-10	10-20	20-30	30-40	0-10	10-20	0-10	10-20		
2378-TCDD	nd	nd	0.08	0.02	nd	nd	0.003	0.004	0.86	1.1	0.01	0.01
12378-PeCDD	0.04	0.04	0.24	nd	nd	nd	0.03	0.02	7.8	6.0	0	0.01
123478-HxCDD	0.12	0.25	0.31	nd	nd	0.12	nd	nd	2.3	3.8	0	0.02
123678-HxCDD	0.08	0.07	0.48	nd	nd	nd	0.15	0.13	33	23	0	0.01
123789-HxCDD	0.13	0.12	0.68	nd	nd	nd	0.17	0.12	11	11	0	0.01
1234678-HpCDD	1.6	1.6	6.1	0.67	0.42	0.51	2.0	2.10	400	390	0.17	0.22
OCDD	4.0	4.5	59	2.2	nd	1.5	10	14	8200	3700	0.78	0.87
2378-TCDF	0.22	0.11	0.49	0.05	0.02	0.02	0.24	0.30	14	12	0.04	0.06
12378-PeCDF	0.11	0.07	0.19	nd	nd	nd	0.13	0.14	3.7	3.3	0	0.01
23478-PeCDF	0.26	0.17	0.75	0.02	nd	nd	0.46	0.43	13	12	0.04	0.03
123478-HxCDF	0.24	0.36	0.73	0.10	0.05	nd	0.28	0.25	9.6	13	0	0.01
123678-HxCDF	0.13	0.15	0.50	0.04	0.03	nd	0.11	0.08	6.3	6.8	0	0.01
123789-HxCDF	0.03	nd	0.27	nd	nd	nd	0.01	0.01	0.41	1.5	0	0.01
234678-HxCDF	0.11	0.10	0.34	nd	nd	nd	0.15	0.13	9.2	8.3	0.02	0.01
1234678-HpCDF	0.81	0.71	5.36	0.31	0.05	nd	1.7	1.8	230	161	0.03	0.04
1234789-HpCDF	0.06	nd	0.37	nd	nd	nd	0.03	0.02	2.7	6.5	0	0.02
OCDF	1.04	0.75	10	0.46	nd	0.10	1.8	1.7	660	430	0	0.03
WHO-TEQ	0.24	0.23	0.96	0.05	0.01	0.02	0.27	0.26	27	23	0.02	
I-TEQ	0.23	0.21	0.90	0.05	0.01	0.02	0.27	0.26	31	24	0.02	

Recovery corrected, blank subtracted. Legend: nd, not detected; *Italics,* uncertain detection; DL, detection limit.

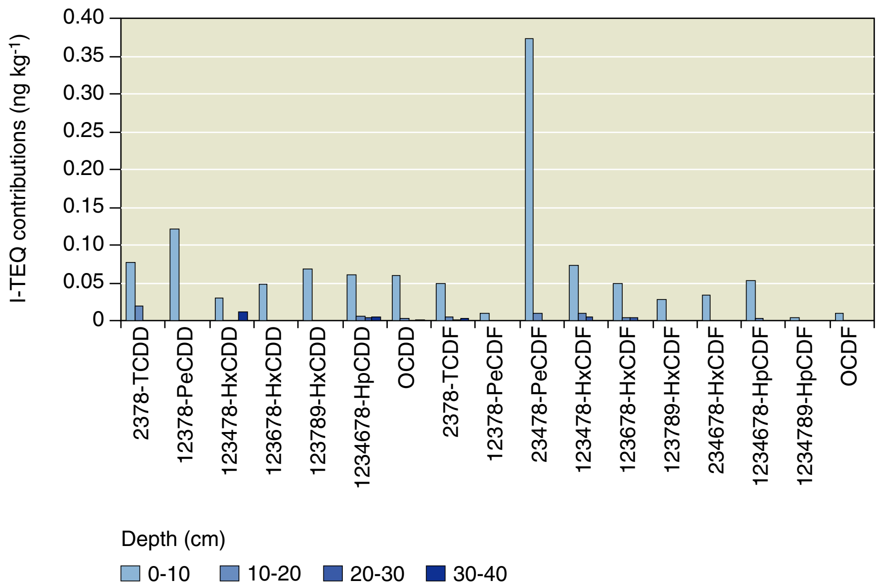

Figure 3 I-TEQ contributions of congeners in preserved soil.

Figure 3 shows the contribution of the congeners to the I-TEQ in the preserved soil, depth 0-40 cm. The bar-heights have been calculated by multiplying the concentrations with the corresponding International Toxicity Equivalent Factors (I-TEF). An advantage of this system is that each congener is displayed as the toxicological importance of that congener. A further advantage is an improved readability, the very high concentration of OCDD is scaled down to manageable dimensions because of the low I-TEF of that congener.

As observed from Figure 3, 2,3,4,7,8-PeCDF stands out as by far the most prominent contributor, followed by much lower contributions from 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD. It is further observed that in samples below a depth of 20 cm, the results are very low compared to the top layer.

Congener profile

The question is now how this profile compares with the lower concentrations in the deeper layers, which would give clues about the origin of the deeper layers. Further, how it compares with the sludge amended soils. For this purpose, relative profiles are useful, in which each congener contribution is normalised with the sum of contributions, set to 100%. This makes it possible to compare profiles with widely different concentrations in the same diagram. Also important, it makes it feasible to compare results expressed in incommensurable units (e.g. for soil ng/kg, for air fg/m^3 and for deposition pg/m^2/day).

In Figure 4, relative congener profiles are shown for preserved soil and sludge amended soils for the two upper layers. The concentrations in the lower layers of the preserved soil are too low to yield consistent profiles.

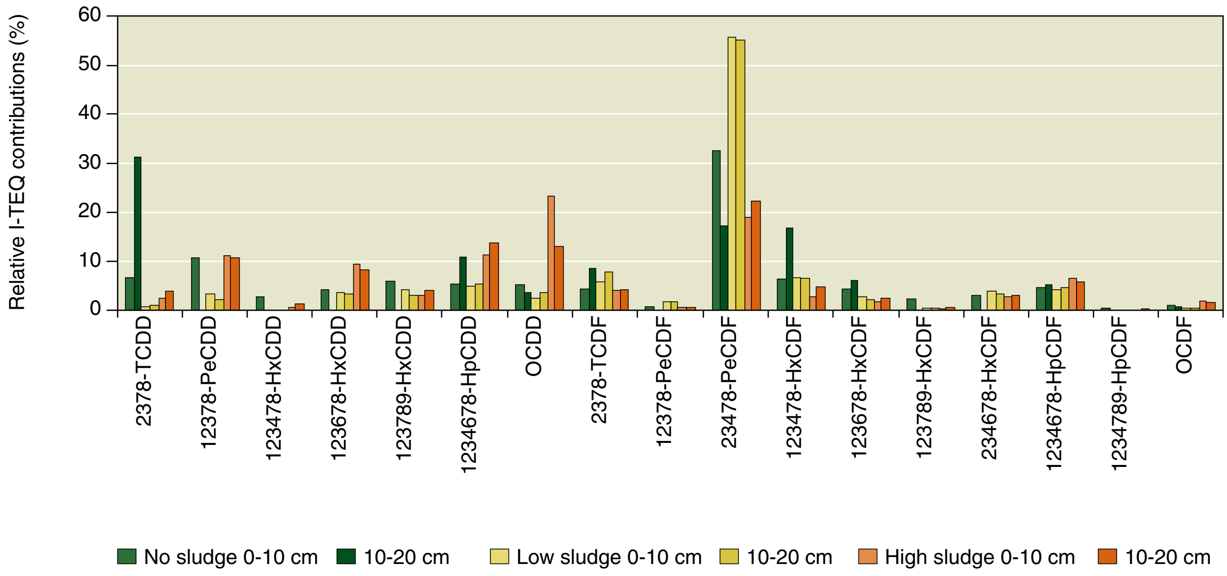

Figure 4 Congener profiles in soil (i.e. relative I-TEQ % contributions of congeners). Preserved soil compared to low and high sludge amended soil, respectively. Depth 0-20 cm.

One would predict a more uniform distribution between the layers of the ploughed (amended) soils, and this is also more or less seen in Figure 4. *A priori* one would further expect that the profiles for the low sludge amended soil would be intermediate between the others. This is because the only known source for the preserved soil is atmospheric deposition, which also should play a role for the low amended soil, whereas a sludge pattern should be imposed on the amended soils. But as observed from Figure 4, the low sludge soil stands apart from the others, particularly for the most contributing congener 2,3,4,7,8-PeCDF. A possible reason for this may be that the low amended soil is normal with respect to culturing and fertilisation, having a normal bacterial flora. In contrast, the high amended soils is extreme, since the site amounts to a sludge deposit. Studies of phthalates (Vikelsøe et al. 1998) indicate that an abnormal low biological breakdown of phthalates takes place in the high sludge soil, and the same might be the case for dioxin. A specific study of bacterial processes has not been carried out, however. Also the preserved soil is special because of the lack of ploughing and fertilisation.

Sources

The important question of the sources remains. In Figure 5 the profile of the top layer of the preserved soil is compared with the profiles of the most important known sources, i.e. air, deposition, compost and sludge. Also a profile of fjord sediment is shown. One should *a priori* expect that the profile of the preserved soil would correspond to the deposition, if this is the main input to that matrix. This is indeed the case for many congeners, such as the penta, hexa and octachloro dioxins, and for the tetra, hexa and hepta-chloro-furans. However, the preserved soil seems to be depleted in 2,3,7,8-TCDD, 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8-PeCDF compared to deposition, but surprisingly enriched in 2,3,4,7,8-PCDF. Thus, in spite of certain similarities between these profiles, there are also significant differences. In other words, a simple correspondence between profiles of deposition and preserved soil cannot be established. This indicates that the condi-

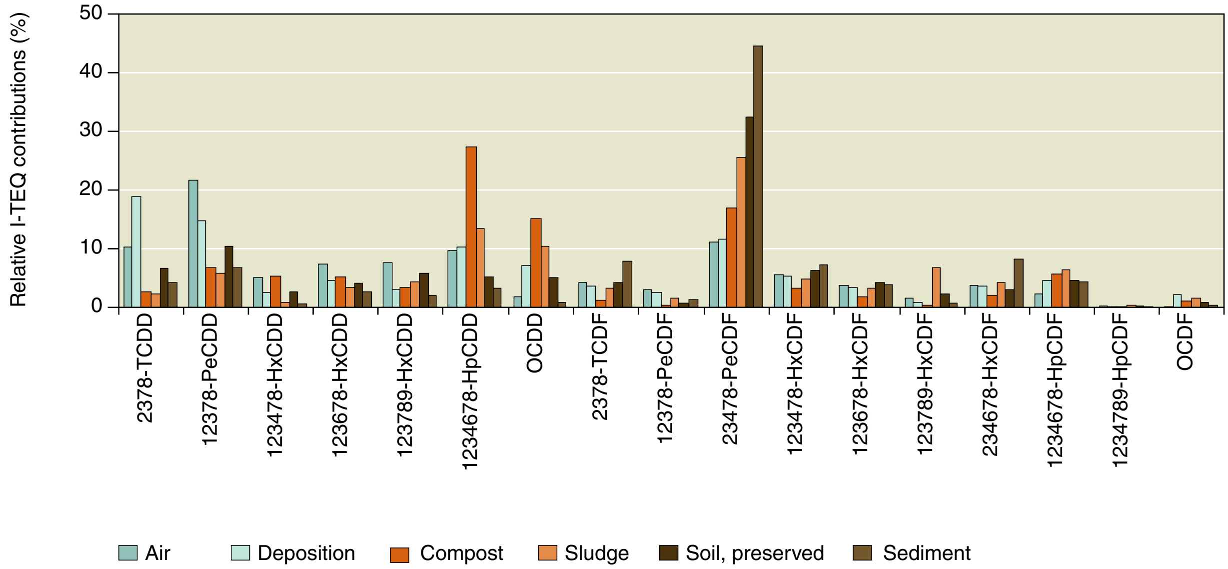

Figure 5 Congener profiles (i.e. relative I-TEQ % contributions of congeners in air (mean 2002 Fredensborg), deposition (mean 2002 Fredensborg), compost (mean of 13 samples from N-Sjælland) and sludge (mean all NOVA data since 1996, 100 samples) compared to preserved soil (Ejby 0-10 cm) and fjord sediment (Roskilde Bredning Station 60).

tions are more complicated. This may reflect variation in profile during history of the dioxin, since the soil contains a frozen-in pattern many years old, whereas the deposition contains an actual profile. The differences may also be caused by selective degradation in the soil, either chemical or biological, evaporation or percolation.

5.2 Geographical distribution in topsoil

The abundance and geographical distribution of PCDD/F in topsoil are addressed in this chapter. The results are shown in Table 8, divided according to counties. The sequence is largely from north to south and from west to east.

Table 8 Geographical distribution of PCDD/F in topsoil, ng/kg dm.

County	Nordjylland				Århus					Ringkøbing
Location	N Jylland		Ålborg E		Århus N	Århus E		Århus W	M Jylland	W Jylland, DK W
NERI No.	1.1544	1.1543	1.1542	1.1570	1.1260	1.1258	1.1259	1.1261	1.1257	1.1541
Sampled date	6/Dec/01	6/Dec/01	6/Dec/01	12/Dec/01	11/Nov/01	9/Nov/01	9/Nov/01	11/Nov/01	9/Nov/01	6/Dec/01
Name	Skagen N	Gl Skagen	V. Hassing	V. Hassing	Lisbjerg	Studstup	Gl. Løgten	Brabrand	Tåning	Ulfborg
Remarks	Rem DKN	Rem DKN	Power	Expo	MSWI	Power	Expo	Ref	Rem	Rem
2378-TCDD	0.03	0.04	nd	0.06	0.05	0.03	0.05	0.02	0.02	0.03
12378-PeCDD	0.21	Nd	nd	0.30	0.17	0.06	0.28	0.15	0.09	0.14
123478-HxCDD	0.09	0.10	0.22	0.22	0.14	0.07	0.19	0.08	0.08	0.15
123678-HxCDD	0.15	0.14	0.20	0.44	0.09	0.68	0.49	0.19	0.20	0.26
123789-HxCDD	0.09	0.16	0.26	0.33	0.22	0.25	0.50	0.20	0.19	0.24
1234678-HpCDD	2.3	3.0	3.9	8.6	1.86	28	6.1	3.5	1.8	4.6
OCDD	22	38	35	88	13	300	56	35	13	40
2378-TCDF	0.21	0.56	0.45	0.79	0.96	0.27	0.64	0.79	0.30	0.59
12378-PeCDF	0.10	0.19	0.11	0.17	0.16	0.07	0.17	0.15	0.12	0.15
23478-PeCDF	0.47	0.84	0.44	0.75	0.68	0.32	0.69	0.70	0.47	0.68
123478-HxCDF	0.00	0.51	0.31	0.41	0.28	0.16	0.60	0.37	0.31	0.42
123678-HxCDF	0.00	0.28	0.12	0.28	0.24	0.14	0.24	0.28	0.20	0.23
123789-HxCDF	0.05	0.09	nd	nd	0.11	nd	0.13	0.10	0.08	0.12
234678-HxCDF	0.15	0.41	0.20	0.26	0.21	0.14	0.23	0.22	0.20	0.24
1234678-HpCDF	2.6	5.2	2.1	12	1.7	5.5	2.9	6.0	2.1	3.6
1234789-HpCDF	0.15	0.22	0.14	0.21	nd	0.24	0.20	0.15	0.15	0.16
OCDF	3.7	8.40	2.5	11	1.9	24	4.0	6.5	3.0	4.3
WHO-TEQ	0.44	0.49	0.31	0.97	0.60	0.69	0.86	0.60	0.39	0.59
I-TEQ	0.36	0.53	0.35	0.91	0.53	0.95	0.77	0.56	0.36	0.56

Recovery corrected, blank subtracted. Legend: nd, not detected, detection limit in last section of table; *Italics,* uncertain detection; Power, power plant (coal fired); MSWI municipal solid waste incinerator (0.1 ng/Nm3 stack emission); Expo, diffuse exposed from urban area; Ref, reference for urban area; Rem, remote area; DKN, northernmost site in Denmark.

Table 8 cont. Geographical distribution of PCDD/F in topsoil, ng/kg dm.

County	Ribe		Fyns					Frederiksborg			
Location	Esbjerg N	Esbjerg E	Fredericia E	Fredericia E	Odense E	Nyborg N	Nyborg E	Frederiksværk E	Frederiksværk E	Hornsherred	N Sjælland
NERI No.	1.1540	1.1190	1.1256	1.1255	1.1254	1.1253	1.1252	1.1194	1.1192	1.1191	6.0901
Sampled date	6/Dec/01	29/Oct/01	9/Nov/01	9/Nov/01	9/Nov/01	9/Nov/01	9/Nov/01	1/Nov/01	1/Nov/01	1/Nov/01	26/Sep/96
Name	Lifstrup	Andrup	Røjle Kirke	Røjle Klint	Bullerup	Kerteminde	Nyborg, KK	Arrenæs	Frd.værkv. Skole	Kyndby	Sundby-lille
Remarks	Ref	Expo	Expo	Ref	Expo	Ref	HWI	Expo	Steel	Power	Low sludge
2378-TCDD	0.03	nd	0.07	0.02	0.04	0.04	0.11	0.09	0.13	0.09	nd
12378-PeCDD	0.10	0.32	0.25	0.27	0.21	0.29	0.84	0.20	0.24	0.20	0.03
123478-HxCDD	0.13	0.32	0.25	0.23	0.15	0.17	0.44	0.15	0.23	0.25	nd
123678-HxCDD	0.27	0.63	0.34	0.36	0.18	0.21	0.86	0.27	0.36	0.41	0.15
123789-HxCDD	0.27	0.60	0.54	0.44	0.33	0.49	1.2	0.41	0.36	0.33	0.17
1234678-HpCDD	6.6	8.1	4.2	4.9	1.7	2.3	11	2.3	4.8	3.9	2.0
OCDD	75	76	22	29	9.9	22	90	17	120	24	10
2378-TCDF	0.40	0.49	0.60	0.39	0.33	0.53	0.96	0.74	0.91	0.86	0.24
12378-PeCDF	0.21	0.15	0.21	0.14	0.19	0.19	0.64	0.18	0.23	0.25	0.13
23478-PeCDF	0.99	0.67	0.97	0.66	0.72	0.82	3.1	0.63	0.89	0.95	0.46
123478-HxCDF	0.60	0.57	0.68	0.97	0.49	0.56	2.0	0.49	0.62	0.65	0.28
123678-HxCDF	0.50	0.48	0.43	0.40	0.34	0.35	1.30	0.31	0.41	0.54	0.11
123789-HxCDF	0.19	0.17	0.15	nd	nd	0.13	0.31	0.12	0.10	0.17	0.01
234678-HxCDF	0.23	0.39	0.35	0.30	0.23	0.28	1.01	0.22	0.35	0.36	0.15
1234678-HpCDF	6.5	8.5	4.3	2.7	4.0	2.3	21	3.0	4.8	4.1	1.7
1234789-HpCDF	0.34	0.47	0.40	0.33	0.21	nd	0.84	0.22	0.28	0.36	0.03
OCDF	8.7	13	6.93	3.6	4.2	3.5	44	3.9	5.4	6.3	1.8
WHO-TEQ	0.69	0.97	0.90	0.79	0.64	0.78	2.58	0.74	0.97	0.91	0.27
I-TEQ	0.72	0.89	0.80	0.68	0.55	0.66	2.28	0.66	0.96	0.84	0.27

Recovery corrected, blank subtracted. Legend: nd, not detected, detection limits in last section of table; *Italics,* uncertain detection; HWI, exposed from hazardous waste incinerator (0.1 ng/Nm^3 stack emission); Expo, diffuse exposed from urban industrialised area; Ref, reference for urban area; Rem, remote area.

Table 8 cont. Geographical distribution of PCDD/F in topsoil, ng/kg dm

County	Roskilde		Københavns					Storstrøm		Bornholm	Quality assurance	
Location	Hornsherred	Roskilde E	Copenhagen W	Copenhagen W	Copenhagen N	Copenhagen C	Copenhagen E	Rem DK S		Rem DK E		
NERI No.	1.1232	1.1294	1.1195	1.1196	1.1236	2.0715	1.1307	1.1308	1.1309	1.1295		
Sampled date	7/Nov/01	14/Nov/01	1/Nov/01	1/Nov/01	7/Nov/01	1/Jun/02	15/Nov/01	16/Nov/01	16/Nov/01	14/Nov/01		
Name	Ejby	St. Valby	Rødovre Sportspl.	Rødovre Vestvold	Virum	Vanløse	Amager Tiøren	Gedser S	Gedser E	Åkirkeby	mean of	meain
Remarks	Preserved	Expo	MSWI	MSWI	Garden	Garden	Park	Baltic W		Baltic C	Blanks	DL
2378-TCDD	0.08	0.08	0.18	0.31	0.09	0.98	0.98	0.07	0.03	0.02	0.01	0.01
12378-PeCDD	0.24	0.29	0.95	1.1	0.72	3.0	2.88	0.28	0.15	0.17	0	0.01
123478-HxCDD	0.31	0.00	1.8	0.81	0.68	2.0	1.28	0.14	0.13	0.09	0	0.02
123678-HxCDD	0.48	0.27	1.6	1.5	1.2	3.5	3.06	0.25	0.06	0.17	0	0.01
123789-HxCDD	0.68	0.48	1.4	1.4	1.1	3.4	2.45	0.27	0.24	0.12	0	0.01
1234678-HpCDD	6.1	4.76	32	16	19	43	36	6.0	3.7	1.91	0.17	0.22
OCDD	59	53	360	95	140	190	350	85	48	18	0.78	0.87
2378-TCDF	0.49	0.87	2.6	2.5	0.75	8.2	17	1.22	0.99	1.1	0.04	0.06
12378-PeCDF	0.19	0.21	0.44	0.65	0.48	2.3	3.5	0.26	0.18	0.19	0	0.01
23478-PeCDF	0.75	0.83	2.2	3.1	1.9	5.3	16	1.36	0.74	0.79	0.04	0.03
123478-HxCDF	0.73	0.74	1.6	1.9	1.7	5.5	8.8	0.77	0.53	0.53	0	0.01
123678-HxCDF	0.50	0.33	1.3	1.7	1.3	4.1	6.0	0.45	0.30	0.23	0	0.01
123789-HxCDF	0.27	0.00	0.39	0.51	0.37	1.1	1.4	0.14	0.07	0.13	0	0.01
234678-HxCDF	0.34	0.33	1.1	1.3	1.0	3.8	4.3	0.39	0.22	0.17	0.02	0.01
1234678-HpCDF	5.4	4.48	16	18	21	51	450	5.7	3.2	3.9	0.03	0.04
1234789-HpCDF	0.37	0.25	0.85	0.88	0.93	2.5	3.9	0.27	0.12	0.16	0	0.02
OCDF	10	7.05	23	21	29	36	720	8.0	4.3	5.7	0	0.03
WHO-TEQ	0.96	0.91	3.2	3.4	2.4	9.6	16	1.0	0.64	0.64	0.02	
I-TEQ	0.90	0.82	3.0	3.0	2.2	8.3	15	0.98	0.62	0.57	0.02	

Recovery corrected, blank subtracted. Legend: nd, not detected; *Italics,* uncertain detection; detection limit in last section of table. Steel, steel mill; Power, power plant (coal fired); MSWI municipal solid waste incinerator (0.1 ng/Nm3 stack emission); Expo, diffuse exposed from urban area.

5.2.1 Distribution in zones

Figure 6 shows an overview of all the data divided into zones, i.e. Rural Reference, Rural Exposed and Urban zones, respectively, sorted according to increasing order of ng/kg I-TEQ.

As noted from Figure 6, the level in the rural zones are of the same order of magnitude, whereas the level in the urban zone is an order of magnitude higher. It is further observed that the urban zone displays a considerably larger and more random variation. In the Copenhagen zone an increase from west to east is noted (Rødovre, Vanløse, Tiøren). In the westerly wind prevailing in Denmark, this should be expected if the content in the soil of Copenhagen originates from atmospheric deposition from local sources. However, the data are too few to draw such a conclusion with certainty.

Figure 7 shows the descriptive statistics (mean, median and range) for the same data. The level of PCDD/F in the soil of the rural reference zones is 0.7 ± 0.2 ng/kg I-TEQ (mean ± standard deviation) and the level in the exposed zones, i.e. zones east of industrialised or urban zones or point sources, is likewise 0.7 ± 0.2 ng/kg I-TEQ. No statistical significant difference between the means of those zones is found (by t-test), nor between their standard deviations (by F-test). Hence, no significantly elevated PCDD/F level in the exposed rural zones could be established, or, in other words, that no pollution from point sources or diffuse sources into the soil of the surrounding environment was found. Accordingly, the two zones can be merged into a combined rural zone, having a mean level of likewise 0.7 ± 0.2 ng/kg I-TEQ.

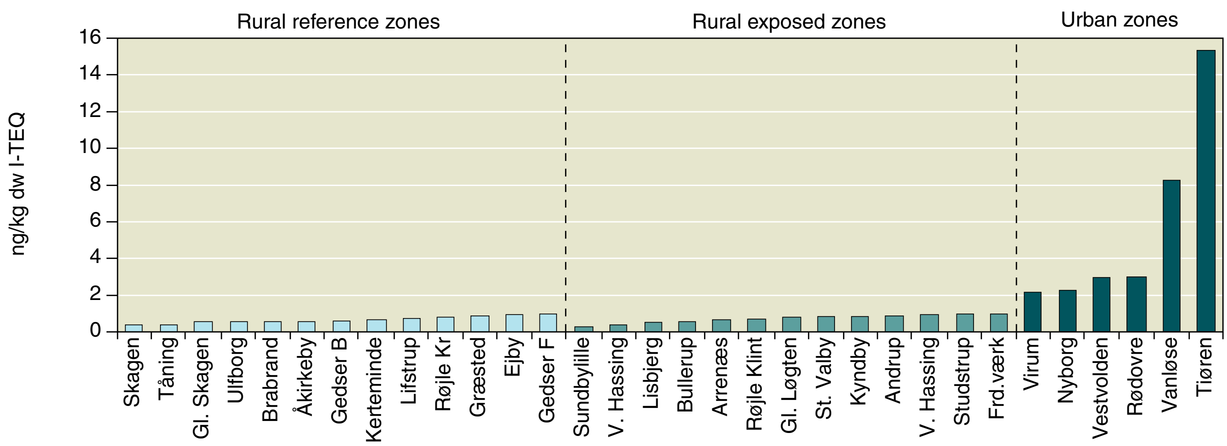

Figure 6 Concentration of I-TEQ in rural reference zones, rural exposed zones and urban zones, respectively. In each zone sorted according to concentration.

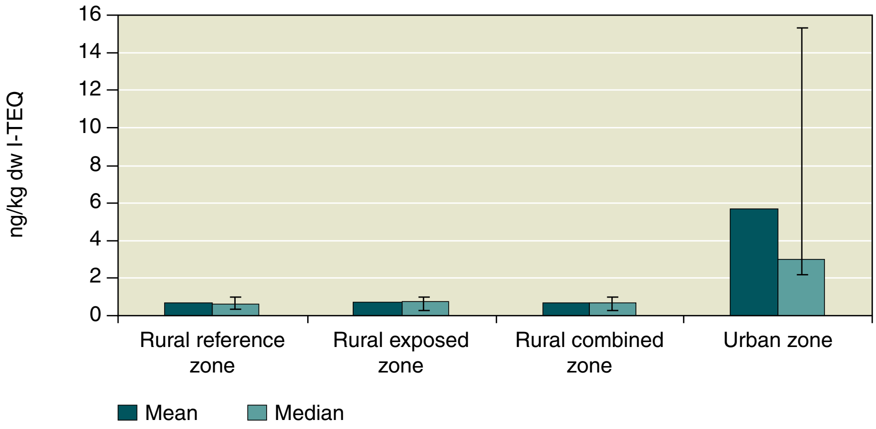

Figure 7 Geographical distribution of PCDD/F in topsoil. I-TEQ in rural zones (reference, exposed and combined) and urban zones, mean, median and range (minimum and maximum).

The lack of difference between the exposed and reference rural zones is surprising and against expectations.

In contrast, the urban zone level mean, 6.2 ± 5.6 ng/kg I-TEQ, is about 8 times higher than the combined rural zone, without any overlap between the zones. The difference is highly statistically different by t-test (p=0.03). The variation in the urban zone is considerably higher, as seen by the large standard deviation and range. Furthermore, unlike what is the case in the rural zone, the range of the urban zone is positioned highly asymmetrical around the median, which is considerably below the mean and close to the minimum. This indicates an asymmetrical distribution, pointing to a more "patchy" and random concentration geometry in the urban zone.

Figure 8 shows a more detailed view of the geographical distribution in the rural zones alone, each zone being arranged from North to South. The data contains results for double samplings in the same location at positions about 1 km apart, namely Skagen, V. Hassing and Gedser. As Figure 8 reveals, for those results the within-location difference (e.g. Gedser F - Gedser B) is comparable with the between location difference (e.g. Gedser - Skagen). This indicates that - for the rural zones – the local scale variation may comparable with the geographical scale variation. This further attests to the similarity between the dioxin level in the reference zone and the exposed zone.

As mentioned above, no statistical significant difference between the means of these zones was found. However, this test is insensitive, since comparing the means ignores the information about the individual positions in each zone, meaning that the correspondence is lost between exposed positions and references.

Paired test

By the application of a more sensitive paired test, the demonstration of smaller differences would in principle be feasible. This is illustrated in Figure 9, showing the same data as Figure 8 arranged in corresponding pairs of reference and zones exposed from power plants, incinerators, diffuse sources and steel mill. As observed, in several cases the exposed positions are higher than the references, whereas in other cases they are lower.

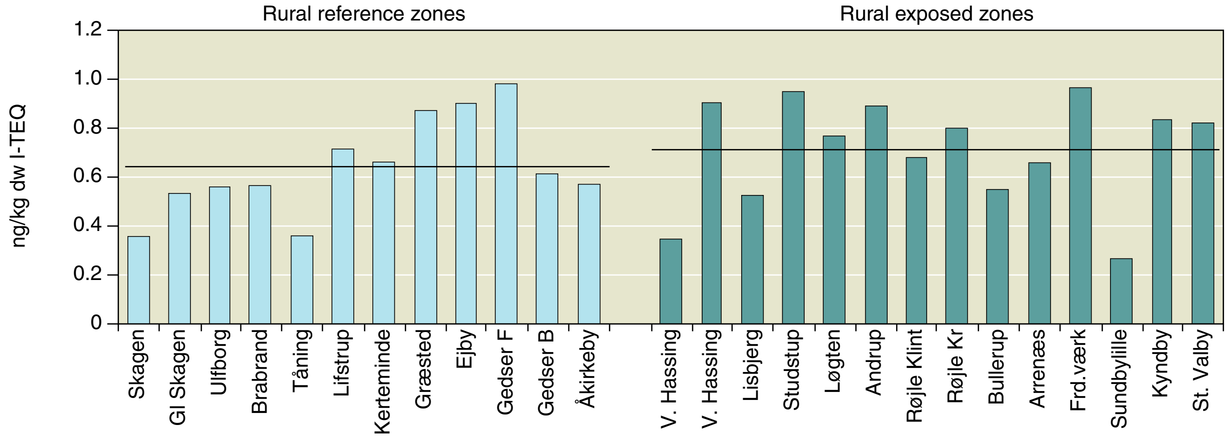

Figure 8 Geographical distribution of PCDD/F in topsoil arranger N-S and E-W in each zone. The horizontal lines show the means of the zones.

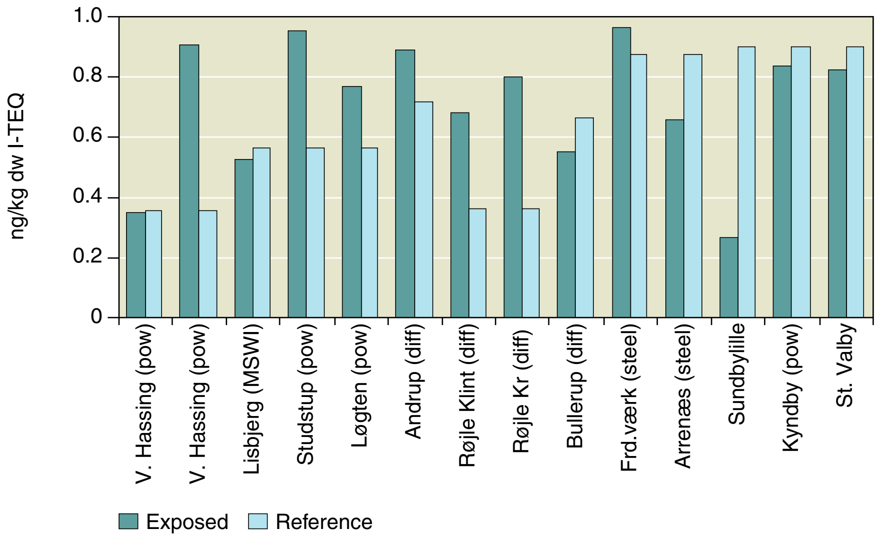

Figure 9 Geographical distribution of PCDD/F in rural topsoil showing the data of Figure 8 arranged in corresponding pairs of exposed and reference positions. Pow = power plant, diff = diffuse.

The situation is illustrated more clearly in Figure 10, displaying the corresponding differences of the rural zones, of the same data set as Figure 9. A positive bar designates that the I-TEQ of the exposed position is higher than that of the corresponding reference position. A weak tendency is seen for positive differences on the left side if the figure. This pattern, however, is highly dependant on the choice of reference positions, and no significant difference is found (paired t-test, p=0.2).

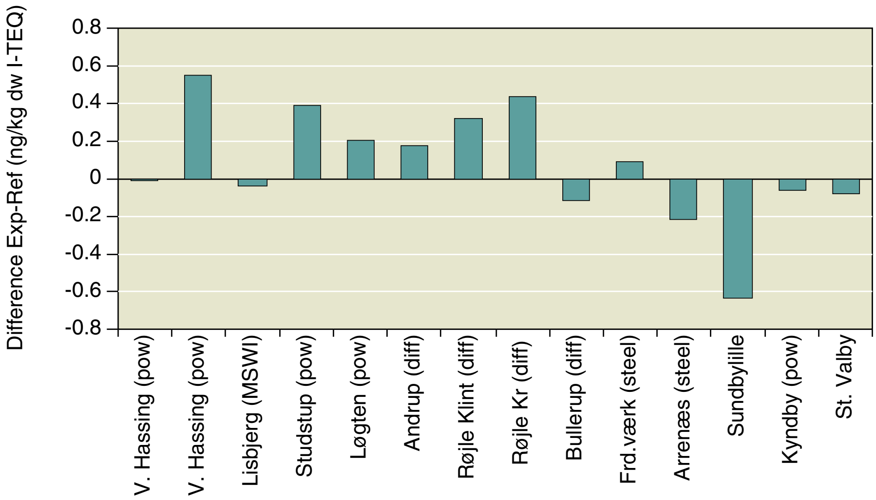

Figure 10 Geographical distribution of PCDD/F in rural topsoil showing differences between corresponding pairs of exposed / reference positions (named after exposed positions), ng/kg I-TEQ.

In Figure 11, the view of Figure is 10 expanded to include the urban zone, encompassing the whole data set. As seen, the urban differences are all positive and much larger than the rural ones. The differences for the urban zone alone are highly statistically significant (paired t-test, p=0.04). The incinerators in urban zone (Rødovre and Nyborg) do display positive differences, but these are not higher than the urban zone in general. Hence, the elevated levels seen in Nyborg and Rødovre cannot with certainty be ascribed to the incinerators.

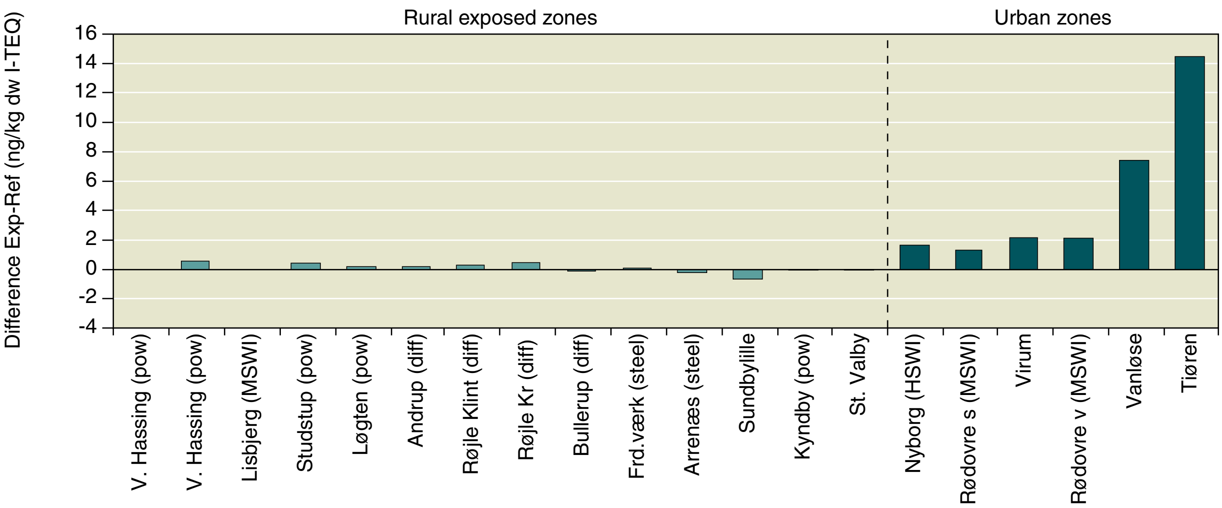

Figure 11 Geographical distribution of PCDD/F in topsoil for all data, showing differences between corresponding pairs of exposed / reference positions (named after exposed positions), ng/kg I-TEQ.

5.2.2 Overall geographical distribution

Figure 12 shows the overall geographical distribution in rural topsoil in the counties (excluding Copenhagen, which is predominantly urban), expressed as mean ± standard deviation and median in ng/kg I-TEQ.

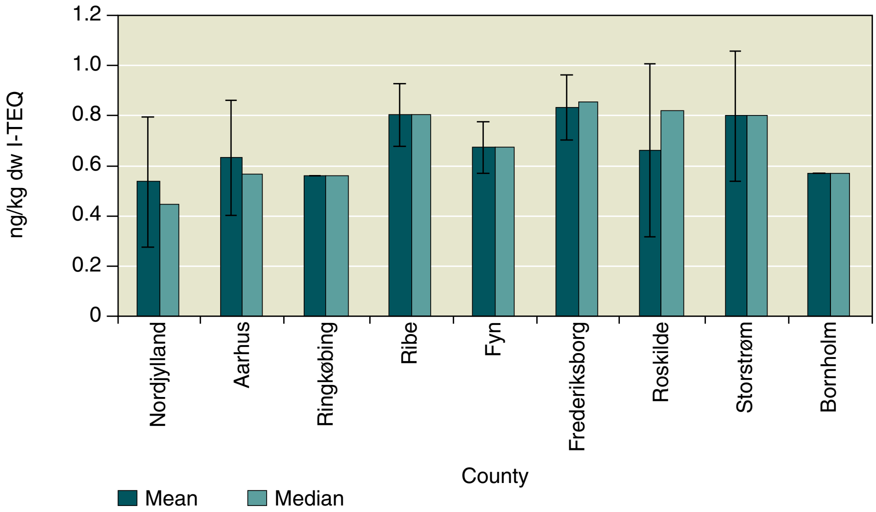

Figure 12 Geographical distribution of PCDD/F in rural topsoil in counties, pooled reference zones and exposed zones in ng/kg I-TEQ mean ± standard deviation and median .

Figure 13 shows the same data as Figure 12 in a 3-dimensional bar graph arranged in a "map". The columns represents means of counties. As seen, the level seems to rise from N to S in the western counties. Hence, in this part of the country a N-S gradient seems to exist.

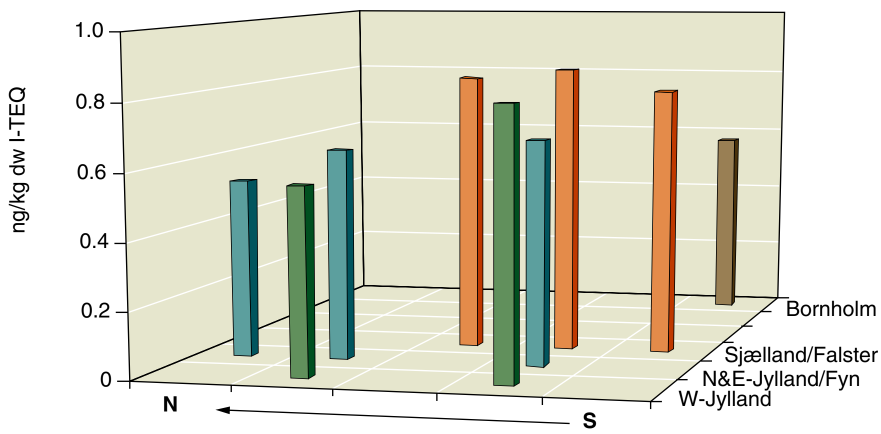

Figure 13 Geographical distribution of PCDD/F in rural topsoil, pooled reference zones and exposed zones. Columns represents means of counties arranged in a "map".

Figure 14 shows the overall geographical distribution in Denmark. The I-TEQ concentration in the outermost (i.e. northernmost etc.) remote positions (Table 1, Remote DK N, S, E & W) is shown in a 3-dimensional bar graph similar to Figure 13. A weak increase from N to S is also indicated. Such an increase should be expected because Denmark is situated between the more industrialised Europe in South and the thinly populated regions in North.

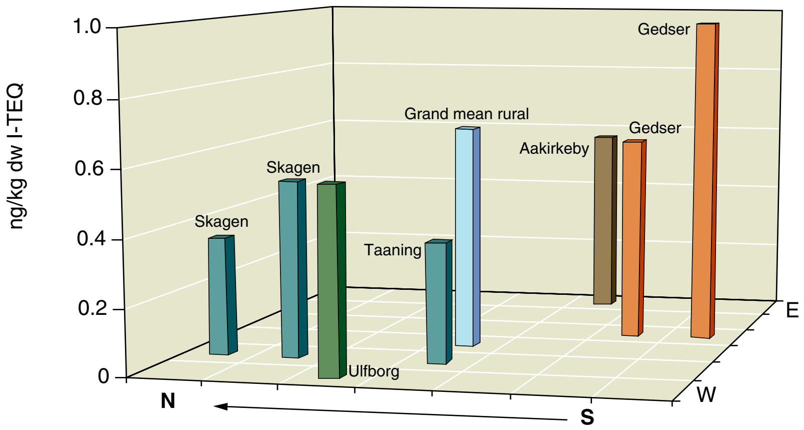

Figure 14 Geographical distribution of PCDD/F topsoil. Rural remote zones representing outer geographical limits arranged in a "map".

5.2.3 Congener profiles

The question arises whether the distribution of the individual congeners – the so-called congener profiles – are different in the zones. The profile can be considered as a "fingerprint" characteristic for the sources. In particular, one might expect that the urban zone with the generally high level would stand out from the rural ones, since the sources very well could be different.

Figure 15 shows the relative congener profiles (explained in section 5.1) for the means of the rural reference zone, rural exposed zone and urban zone. As seen from the figure, the profiles in the three zones are very much alike. The main contributor in all zones is 2,3,4,7,8-PeCDF followed by 1,2,3,7,8-PeCDD, and for these congeners, the profiles are close to each other. Some difference is noted for 1,2,3,4,6,7,8-HpCDD and OCDD, apparently being higher for the exposed rural zone. Another conspicuous feature is the high profile for 1,2,3,4,6,7,8-HpCDF in the urban zone, which could be explained by contamination from chemicals. However, the difference is not statistically significant (t-test unequal variances, p=0.13).

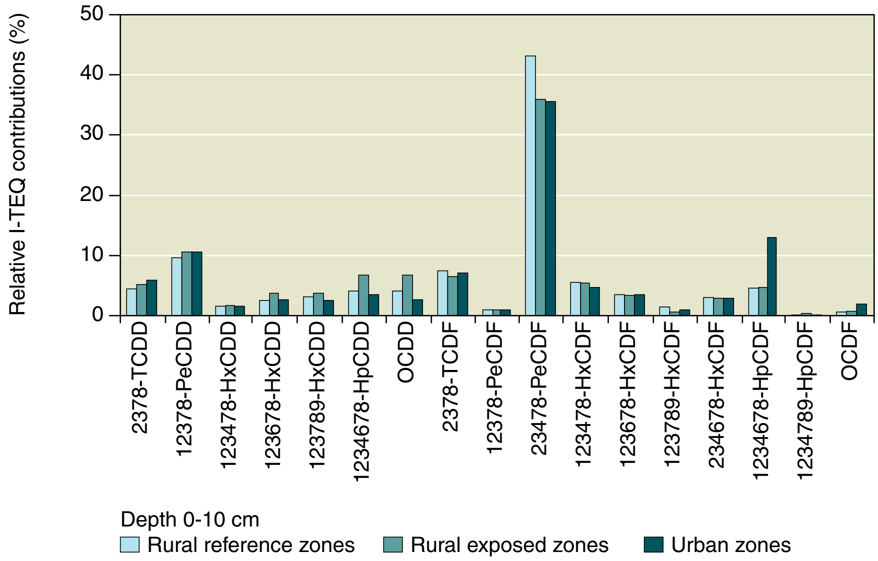

Figure 15 Relative congener profiles of rural reference, rural exposed and urban zones. Mean of all data.

In Figure 16, the relative congener profiles are shown for the mean of counties. This does not change the general picture significantly, as the same remarks apply with respect to most contributing congeners.

As noted, 1,2,3,4,6,7,8-HpCDF stands out for Copenhagen County (København), as was the case for the urban zone in Figure 15.

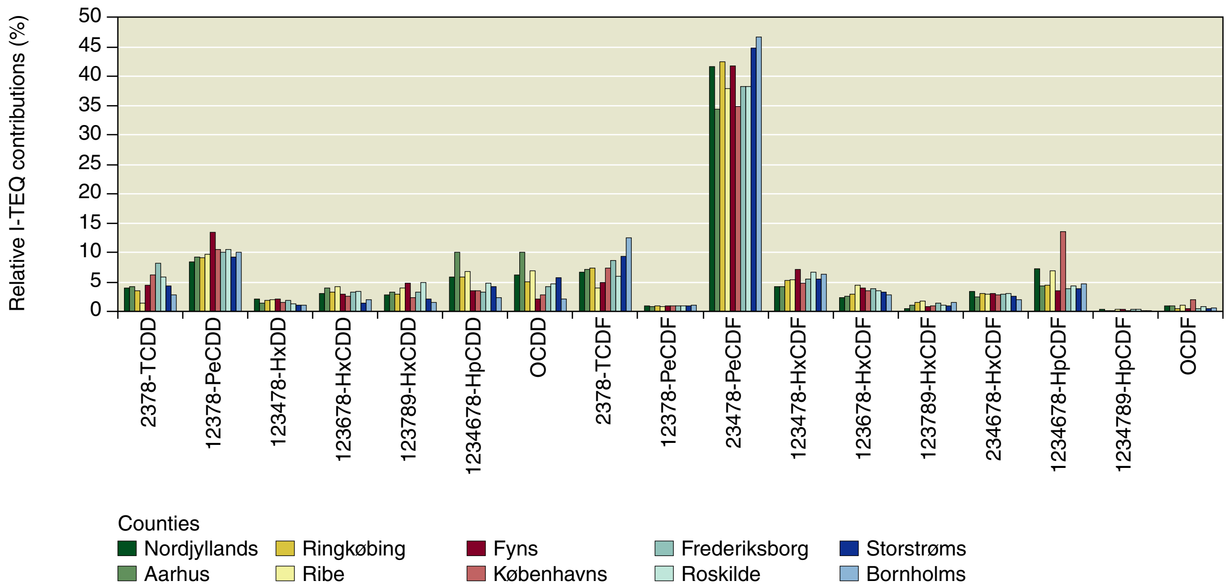

Figure 16 Relative cogener profiles of county means. All counties contain rural samples only with the exception of Copenhagen County (København) which contains urban samples alone.

5.3 Other studies

5.3.1 Parallel study of Copenhagen soil

The consulting company NIRAS has in co-operation with DEPA carried out a parallel investigation of PCCDD/F in soil from the Copenhagen area. Figure 17 adapted from NIRAS shows a selection of NIRAS and NERI results.

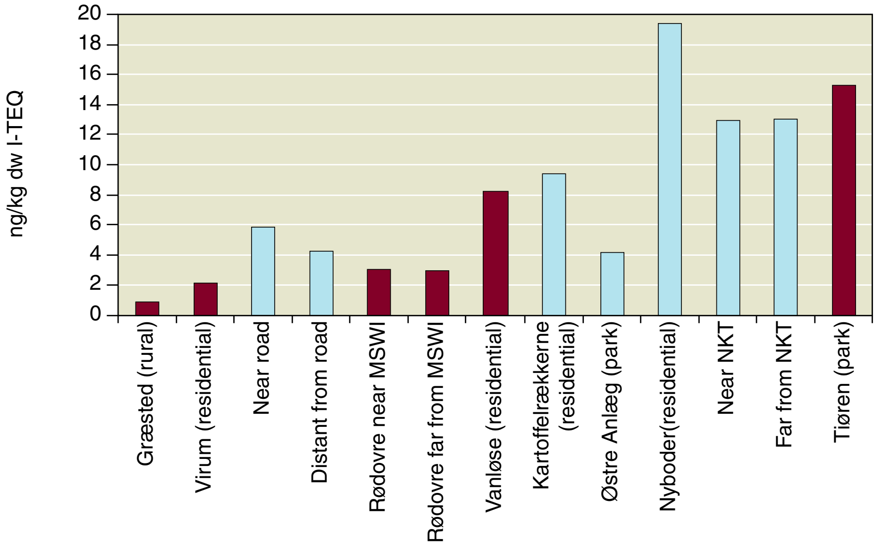

Figure 17 Comparison between results from NIRAS and NERI for dioxin in soil from Copenhagen (see text), ng/kg I-TEQ. The figure is adapted from NIRAS (with persimission). The light (blue) columns are the NIRAS results.

Græsted is a rural reference in N-Zealand having the absolute lowest result, all other samples are from the Copenhagen area. It is seen that the NIRAS results "Near road" and "Distant from road" (a highly trafficked road in the northern outskirts) are nearly equal with "Østre Anlæg" (a park in the central city), comparable with the two NERI results from "Rødovre" (in the western outskirts, at different distances from a large MSWI incineration plant). The NIRAS result from "Nyboder" (a downtown residential quarter) is absolute highest with about 19 ng/kg I-TEQ, followed by NERI result "Tiøren" (a park in the easternmost part) and NIRAS results from NKT (a large industrial plant). The NIRAS result from "Kartoffelrækkerne" is very close to the NERI result from "Vanløse", both residential quarters.

Hence, the results of the NIRAS and NERI studies appear to be consistent.

The highest TEQ-values are found in the central and eastern parts, whereas the results from the western and northern parts are lower, in agreement with the discussion on this subject in the Distribution in Zones Section. Deviating from the overall pattern, "Nyboder" is exceptionally high, whereas "Østre Anlæg" is exceptionally low.

Note that "NKT near" and "NKT far" display similar TEQ-levels, even if sampled in different distances form the industrial plant (a cable manufacturer). This is the case as well for "Near road" and "Distant from road", as well as for the "Rødovre near MSWI" and "Rødovre far from MSWI" (taken 1 and 2 km from MSWI, respectively). These findings indicate that in urban areas, no well-defined or local effect form point sources can be established with certainty in these data. It looks as if the dioxin is spread over the whole area. This is hardly surprising, considering that the maximal downfall takes place at varying distances from the sources, which by high smoke stacks may go up to several kilometres (see also the discussion on the French sinter plant below). In this way the downfall zones from many sources overlap and may be mixed in an urban region with a high source density. In addition, the high urban activity in transport and construction probably contributes to a mixing.

5.3.2 Sludge amendment

In Sweden, Rappe et al., (1997) found untreated soils containing 0.53-1.1 ng/kg I-TEQ; after 4 t/ha sludge amendment 0.92-1.1 ng/kg I-TEQ i.e. no or low increase, in close accordance with the results of the present study for low sludge amended soil.

In Spain Eljarrat et al., (1997) found I-TEQ values of untreated soil 0.3 –3.1 ng/kg I-TEQ, which after 22-74 t/ha sludge treatment through several years increased to 3.7-8.6 ng/kg I-TEQ (i.e. 1.2 to 11.6 times higher than untreated areas) depending on pH, soil type and sludge supply. This result agrees with the findings of present study for heavy sludge amendment.

5.3.3 Urban and rural levels

Holmes et al. (1998) reported 30 ng/kg I-TEQ average for soil in typical English urban zone, somewhat higher than the present study for urban zone.

A comprehensive German soil survey by Knoth et al. (1999) reported the following TEQ values: Forests 5.4-112 (mean 34.6) ng/kg I-TEQ, grasslands 0.4-4.8 (mean 1.9) ng/kg I-TEQ, plowlands 0.3-3.7 (mean 1.6) ng/kg I-TEQ. According to the German Dioxin Database (Fiedler et al., 2002) compiling 2500 soil data, the median PCDD/F concentrations in German soil is 3 ng I-TEQ/kg dry matter (dm) in urban centres, 2 ng I-TEQ/kg dm at the urban fringe, and 1 ng I-TEQ/kg dm in rural areas. The maximums were 112, 88 and 26 ng/kg I-TEQ, respectively. The German mean and median values are close to those of the present study, but the maximums are significantly higher, in part because of the larger data set.

In Spain Eljarrat et al. (1997) found TEQ levels in rural soils of 0.3-3.1 ng/kg I-TEQ. Although the lower limits are comparable with the present study, the maximum values are somewhat higher.

For Russian soils, extremely low results of 0.022-0.1 ng/kg I-TEQ are reported for sparsely inhabited places, whereas up to 40 ng/kg I-TEQ was found in a heavily industrialised city (Mamontov et al., 1998).

From USA Yake et al. (2000) reported the following TEQ levels in soil: Urban 0.13-19 ng/kg TEQ, forest 0.033-5.2 ng/kg TEQ, open land

0.04-4.6 ng/kg TEQ and agricultural 0.078-1.2 ng/kg TEQ. These results comply with the present study, but have wider ranges. Also concurrent is the finding that agricultural soil has the lowest TEQ-level.

For New Zealand soils Buckland et al. (1998) reported TEQ levels for hill country pasture 0.37-0.90 (median 0.58) ng/kg I-TEQ and for pristine grassland 0.35-0.85 (median 0.54) ng/kg I-TEQ. This correspond closely to the combined rural zone of present study, 0.27-0.98 (median 0.67) ng/kg I-TEQ.

In Japan, high TEQ values of 71 ng/kg were found in rice fields (Ono & Ikegushi, 2001). Also in Japan, incredible high dioxin contamination were found in the densely populated Saitama province, ranging from 7.9-424 ng/kg I-TEQ (Nakao et al., 1999). These findings by far exceed all the above-mentioned results. The sources have not been located with certainty.

5.3.4 Industrial contamination of soil

A Canadian study of the soil in the surroundings of a hazardous incinerator found no elevated levels in the exposed downwind impact zone (Mills, 2002). This is in agreement with the findings of the present study.

Contrary to the findings of the present study, however, an Italian study of similar design (Della Sala et al., 1999) found a significant increase in the exposed zones (called downgradient) from an industrialised zone (Mestre near Venezia). In the urban centre 3.6 ng/kg I-TEQ was measured, 0.2-1.6 km from centre 13 ng/kg I-TEQ, 2-15 km from centre 2.3 ng/kg I-TEQ and the rural background only 0.14 ng/kg I-TEQ. Note that the maximal contamination does not occur in the urban centre itself, but some kilometres downgradient. The sampling plan of the present study is in accordance with this finding.

Also contrary to the findings of the present study, significant contamination in soils near French sinter plants were found by Berho et al. (1999). In the plume impact centre was measured 5.29 ng/kg I-TEQ, whereas outside the plume impact only 0.12-0.33 ng/kg I-TEQ and in background zone 0.35 ng/kg I-TEQ were found. In the present study, no elevated levels were found in the (estimated) plume impact centre of the steel mill (Frederiksværk).

In Korea, Im et al. (2001) reported a staggering 3270 ng/kg I-TEQ from soil in industrial areas, which amounts to the absolute record for soil contamination with PCDD/F. Contrary, a study by Kim et al. (2001) also in Korea found industrial and urban soils containing 4-8 ng/kg I-TEQ, close to the results of the present study.

5.3.5 Long term changes from archived soils

An study of archived soil from British agricultural research was carried out by Wood et al. (1999). In soil from the years 1856, 1881, 1904, 1913 were found 0.79, 0.73, 0.94 and 1.4 ng/kg TEQ, respectively, demonstrating a rise in TEQ-level setting in early in the preceding century. Note that in 1856, detectable amounts of dioxin were present, hence, dioxin contamination of (British) soil cannot be an exclusively modern phenomenon. The results are on similar level as those for the present Danish rural soil.

6 Conclusions

Preserved topsoil layer indicates a build-up of PCDD/F from air deposition. Almost all PCDD/F is found in the upper 0-10 cm, whereas in ploughed soil it is found in the upper 0-20 cm. The level in low-sludge soil is surprisingly comparable with preserved soil, but the level in high-sludge soil is roughly 100 times higher. This suggests a threshold exist for sludge-amendment below which no build-up takes place.

The background level (i.e. mean of rural reference samples) was 0.7±0.2 ng/kg I-TEQ, as was the mean of exposed zone samples east (i.e. downwind) of industrial/urban centres and point sources such as incinerators, power plants and steel industry. These means are not statistically different. Accordingly, the two zones can be merged into a combined rural zone, having a mean level of likewise 0.7 ± 0.2 ng/kg I-TEQ. Hence, no significantly elevated PCDD/F level in the exposed rural zones near larger industrial/urban centres or point sources could be established.

The urban zone level mean was 6.2 ± 5.6 ng/kg I-TEQ, about 8 times higher than the combined rural zone.

Near urban HSW and MSW incinerators elevated I-TEQ level were found compared with local rural references, but not compared with the urban zone. Hence, the elevated level found may be due to other sources in the urban zone, and cannot with certainty be ascribed to the incinerators.

A geographical-scale north-south gradient seems to be discernible in the reference soils.

The congener profiles of the means in the zones are alike. The main TEQ-contributors in all zones are 2,3,4,7,8-PeCDF followed by 1,2,3,7,8-PeCDD.

The levels found in rural and urban soil in the present study agree with similar other studies, but are generally found in the lower range in comparison.

6.1 Acknowledgements

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8 Abbreviations

2378-TCDD	2,3,7,8-tetrachlordibenzo-p-dioxin
12378-PeCDD	1,2,3,7,8-pentachlordibenzo-p-dioxin
123478-HxCDD	1,2,3,4,7,8-pentachlordibenzo-p-dioxin
123678-HxCDD	1,2,3,6,7,8-hexachlordibenzo-p-dioxin
123789-HxCDD	1,2,3,7,8,9-hexachlordibenzo-p-dioxin
1234678-HpCDD	1,2,3,4,6,7,8-heptachlordibenzo-p-dioxin
OCDD	octachlorodibenzo-p-dioxin
2378-TCDF	2,3,7,8-tetrachlordibenzofuran
12378-PeCDF	1,2,3,7,8-pentachlordibenzofuran
23478-PeCDF	2,3,4,7,8-pentachlordibenzofuran
123478-HxCDF	1,2,3,4,7,8-hexachlordibenzofuran
123678-HxCDF	1,2,3,6,7,8-hexachlordibenzofuran
123789-HxCDF	1,2,3,7,8,9-hexachlordibenzofuran
234678-HxCDF	2,3,4,6,7,8-hexachlordibenzofuran
1234678-HpCDF	1,2,3,4,6,7,8-heptachlordibenzofuran
1234789-HpCDF	1,2,3,4,7,8,9-heptachlordibenzofuran
OCDF	octachlorodibenzofuran
µg	microgram, 10^{-9} kg
dm	Dry matter
HR-MS	High resolution mass spectrometry
HWI	Hazardous waste incinerator
I-TEQ	International toxicity equivalent
Max	Maximum value
Min	Minimum value
MSWI	Municipal solid waste incinerator
n	Number (in statistics)
nd	not detected, non-detect
ng	nanogram, 10^{-12} kg
PCDD	polychlorinated dibenzo-p-dioxins
PCDD/F	PCDD and/or PCDF
PCDF	polychlorinated dibenzofurans
sd	Standard deviation
TEF	Toxicity equivalent factor
WHO-TEQ	WHO toxicity equivalent

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Occurrence and geographical distribution of dioxin was investigated in soil in selected rural and urban locations in Denmark.

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