Persistent Organic Pollutants in Soil, Sludge and Sediment

A multianalytical Field Study of Selected Organic Chlorinated and Brominated Compounds

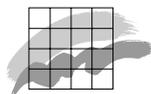*NERI Technical Report No. 402*

National Environmental Research Institute
Ministry of the Environment

Persistent Organic Pollutants in Soil, Sludge and Sediment

A multianalytical Field Study of Selected Organic Chlorinated and Brominated Compounds

NERI Technical Report No. 402
2002

Jørgen Vikelsøe
Marianne Thomsen
Lars Carlsen
Elsebeth Johansen

Data sheet

Abstract:	Occurrence, sources, geographical distribution, transport and fate of the persistent pollutants PAH, NPE, PAE, PCB, PCN and PBDE was investigated in sludge, soil and sediment in a local environment. Further investigated was the vertical distribution in cores of soils and sediment.

Miljøbutikken
Information and Books
Læderstræde 1
DK-1201 Copenhagen K
Denmark
Tel.: +45 33 95 40 00
Fax: +45 33 92 76 90
e-mail: butik@mim.dk www.mim.dk/butik

Contents

Summary

The occurrence, sources, transport and fate of persistent environmental pollutants in a local environment (Roskilde, Denmark) has been investigated. The investigation comprised samples of sewage sludge, soil and sediment selected from previous investigations of NPEs and PAEs.

The analytical program comprised PAHs, nitro-PAHs, PCBs, PCNs and PBDEs carried out on samples already analysed for NPEs and PAEs, a total number of 43 substances.

A multi-analytical method was employed, developed specifically for the present investigation, utilising high resolution GC/MS. The analyses were carried out on stored extracts from the previous investigations, much reducing the laboratory work as well as making the results more comparable.

The results yielded a wealth of information. As well the geographical and vertical distribution in soil and sediment as matrix differences, substance behaviour and persistence, correlation between substances and locations and trend in short and long time horizons could be deduced.

Some of the most important or surprising findings were:

The distribution of substance ("substance profiles") in different matrixes are similar, and more so in related matrixes.

2-nitro-fluorene, a carcinogenic compound, was abundant in sludge. PCBs were the most abundant organohalogen in the environment, even if banned in Denmark 1977 (Miljøministeriet, 1976). PCNs were measured for first time in Danish sludge, soil and sediment, but occurred in lower levels than PCBs. PBDEs were found in sludge on same level as PCB.

The level of PBDEs in sludge seems to be rising, since PBDE in recent sludge samples has already reached and exceeded the level of PCB in sludge, whereas the PBDE-level in sediment is low. The level of PCBs and PCNs seem to be decreasing everywhere.

Sludge amendment seems to be the major source of organo-halogens in soil, whereas atmospheric deposition also plays a role for PAHs and PBDEs.

Build-up of concentrations (i.e. higher concentration in environment than in source) was indicated for PCBs and PCNs in high sludge amended soil and for PAHs in sediment.

In low/no sludge amended soil most substances occurred at a depth of 0-10 cm, whereas in high sludge soils depths down to 40-50 cm were reached.

The sediment core study reaches back to 1914, showing a low level before World War II, after which a significant rise in pollution took place, culminating in the 1970-ties. A recent increase of shorter duration is most likely due to local activities.

The study demonstrates that multianalysis of persistent environmental pollutants in a local environment may yield a snapshot of the chemical state of the area. It is possible to map the geographical and the vertical distribution of the most persistent compounds, revealing important clues regarding the occurrence, sources, transport, fate and history of xenobiotics.

Resumé

Forekomst, kilder, transport og skæbne af persistente miljøfremmede stoffer i det lokale miljø ved Roskilde blev undersøgt. Undersøgelsen omfattede prøver af slam, jord og fjordsediment udvalgt fra tidligere undersøgelser af NPE og PAE.

Analyse programmet omfattede PAH, nitro-PAH, PCB, PCN og PBDE udført på prøver som allerede var analyseret for NPE og PAE, i alt 43 stoffer.

Der anvendtes en multi-analysemetode udviklet specielt til denne undersøgelse, som udnyttede højtopløsende GC/MS. Analyserne udførtes på opbevarede ekstrakter fra de tidligere undersøgelser, hvilket i høj grad har reduceret laboratoriearbejdet og medført mere sammenlignelige resultater.

Resultaterne gav et væld af information. Såvel stoffernes geografiske som vertikale udbredelse i jord og sediment samt matrix forskelle, stoffernes opførsel og persistens, korrelation mellem stoffer og steder og trend i kort og lang tidshorisont kunne udledes.

Nogle af de vigtigste eller mest overraskende resultater var:

Stoffernes indbyrdes forekomst (profiler) i forskellige miljø matricer er beslægtede, og i højere grad i beslægtede matricer.

2-nitrofluoren, et kræftfremkaldende stof, var højt forekommende i slam. PCB var det højest forekommende organohalogen overalt, selv om det blev forbudt i Danmark 1978. PCN blev målt for første gang i dansk slam, jord og sediment, men med lavere niveau end PCB. PBDE blev fundet i slam med samme niveau som PCB.

Niveauet af PBDE i slam synes at være stigende, idet PBDE i nutidige slamprøver allerede har nået og oversteget PCB niveauet, mens PBDE niveauet i sediment er lavt. PBC og PCN niveauet synes at aftage overalt.

Slamgødning synes at være hovedkilden til PCB og PCN i jord, mens deposition spiller en rolle for PAH og PBDE.

Opbygning af koncentrationer (dvs. højere niveau i miljø end i kilde) blev antydet for PCB og PCN i højt slamgødet jord og for PAH i sediment.

I lavt slamgødet og ugødet jord lå det meste stof i 0-10 cm dybde, mens de i højt slamgødet jord nåede dybder ned til 40-50 cm.

Sedimentkærne undersøgelsen går tilbage til 1914 og viser et lavt niveau før 2. Verdenskrig, efter hvilken der skete en kraftig stigning i forurening, som kulminerede i 1970'erne. En nyere kortvarig stigning skyldes sandsynligvis lokale aktiviteter.

Undersøgelsen viser, at multianalyse af persistente miljøfremmede stoffer i et lokalt miljø kan give et øjebliksbillede af områdets kemiske tilstand. Det er muligt at kortlægge den geografiske og den lodrette fordeling af de mest persistente forbindelser, og dermed afsløre vigtige oplysninger om menneskeskabte stoffers forekomst, kilder, transport, skæbne og historie.

1 Introduction

Since the 1990s, many investigations of waste water and sewage sludge have confirmed the presence of phthalates (PAEs), nonylphenol-ethoxylates (NPEs), PAHs, PCBs, bisphenol-A and an array of other pollutants as well in Denmark as elsewhere (Grüttner et al. 1994, 1995 & 1996). The emission of chemicals into the environment leads to the risk of human exposure. Many of these compounds are recognised as carcinogenic or exerting an endocrine disrupting (hormone like) activity, making them potentially harmful to human health. Thus NPEs and PAEs exert oestrogen-like and PCBs and dioxins anti-androgenic activity. The most severe effects ascribed to oestrogen-like substances seem to be on the human reproductive health, (Toppary *et al.* 1995). Many PAHs are carcinogenic, some nitro-PAHs extremely so. Recent studies in Sweden (Nylund et al., 1992) and England (Crookes & Howe, 1993) have found polychlorinated naphthalenes (PCNs) and increasing amounts of brominated diphenyl ethers (PBDEs, used as flame retardants) in the environment and in human milk. The long-term fate and effects of PCNs and PBDEs in the environment are difficult to assess. However, the lower brominated PBDEs are known to be highly bioaccumulative and effects on behaviour similar to effects of PCBs have been observed. The toxicities of PCNs are at present essentially unknown, but are possible dioxin-like because of the structural relationship.

This initiated a series of investigations of the sources, transport and fate of xenobiotics, sponsored by the Danish Environmental Protection Agency (DEPA), carried out by NERI. These investigations were limited to the local community of Roskilde city and surroundings. The present investigation is a continuation of the series.

In the previous investigations, NPEs and PAEs were investigated in an array of studies, comprising as well analytical field work as laboratory studies and modelling (Fauser et al., 2000; Sørensen et al., 2000; Thomsen et al., 2001; Vikelsøe et al., 1998, 1999 & 2001).

The present investigation expands the scope to other persistent xenobiotics and environmental pollutants, involving also halogenated compounds. The study further expands the scope from a specific matrix to the most important ones in the local environment, involving as well the technosphere as the terrestrial and aquatic environment, represented by sewage sludge, soil and fjord sediment. The occurrence, sources, geographical distribution and vertical distribution of the substances are addressed.

2 Purpose

The aims of the study has been:

- To develop a multianalytical method suitable for measurement of selected persistent pollutants, as well non-halogenated as chlorinated and brominated, in different types of environmental samples.

- To analyse for PAHs, PCBs, PCNs and PBDEs in sludge, soil and fjord sediment samples selected from previous studies, previously analysed for NPEs and PAEs.

- To investigate the occurrence, sources, geographical distribution, transport and fate of the above compounds in the environment, comprising soil and the fjord, near Roskilde, a Danish provincial city of average size.

- To investigate the occurrence and vertical distribution of the compounds in cores 50 cm in depth in the soils, which are differently cultured and amended.

- To evaluate the historical variation and time trend in the occurrence of these compounds by study of the vertical distribution in a sediment core from Roskilde Fjord.

3 Samples

An overview of the samples is given in Table 1.

Table 1   Overview of samples.

Sample	Location	Position	Date	Depth, cm	Comment
Sludge	Bjergmarken	WWTP	Nov 96		Plant for Roskilde
Soil	Bistrup 1st	2	Oct 96	0 - 10	Very high sludge amounts
	(first sampling)			10 - 20	during many years (see text)
				20 - 30	Use: Cattle grazing)
				30 - 40	
				40 - 50	
Soil	Bistrup 2 y	2	Nov 98	0 - 10	Very high sludge
	(second sampling	2		10 - 20	
	2 years after)	2		20 - 30	
		2		30 - 40	
		2		40 - 50	
Soil	Ejby	1	Oct 96	0 - 10	No sludge
				10 - 20	preserved recreational area
				20 - 30	Use: Cattle grazing
				30 - 40	
				40 - 50	
Soil	Sundbylille	1	Sep 96	0 - 10	Normal sludge
				10 - 20	i.e. amount recommended
				20 - 30	by agricultural consultants
				30 - 40	Use: Agriculture
				40 - 50	
Sedi	Roskilde Vig	WWTP	Aug 96	0 - 3	Core
				3 – 5	(1 km from WWTP
				5 – 7	outlet)
				7 – 9	
				9 – 11	
				11 – 13	
				13 – 15	
				15 – 17	
				17 – 19	
				19 – 22	
Sedi	Roskilde Vig	Station 2	Sep 96	0 – 5	1 km from outlet
Sedi	Roskilde. Bredning	Station 60	Sep 96	0 – 5	6 km from outlet
Sedi	Isefjord	Bramsnæs	Sep 96	0 – 5	Lesser polluted fjord

Depth for sediment is below bottom of fjord. For water depths see text.

The samples of soil, fjord-sediment or sludge for the present investigation were selected from stored extracts of the previous investigations in the project reported by Vikelsøe et al. 1998, 1999 and 2001. In these reports a more comprehensive description of the sampling locations are given regarding soil characteristics, agriculture, amendment, kind and amount of fertilisers and manure etc. Below follows a short description.

Geographical region

The investigation was carried out in the region of Roskilde city as a part of a larger investigation of sources, transport and fate of xenobiotics, in a concerted effort to map the sources and distribution of xenobiotics in the area. The sludge from the municipal waste water treatment (WWTP) plant in this city (Bjergmarken) is used in several of the soil sites, and has been extensively investigated. The sediment of the nearby Roskilde fjord, which receives the discharge from the WWTP is investigated in different distances from the outlet.

3.1 Soil samples

The soil was sampled by hammering a stainless steel drill 10 cm iØ 50 cm long into the ground. Each core was subdivided into 5 sections of 10 cm height. At each location two cores were drilled at 2 positions at a distance of 5 to 10 meters. Only one of the positions was selected for the present study.

All samples were stored at -20° C until analysed.

Soil locations

The locations are shown on the map Figure 1. All the soils investigated seem to be developed on moraines from the last ice age. The soils are characterised by high clay contents, leading to low infiltration rates in comparison to sandy soils. Eight locations were investigated in the previous investigation, of which three were selected for the present study in order to get an impression of the importance of sludge dressing.

Ejby

Preserved natural area neither cultivated, dressed nor fertilised for more than 50 years, used for cattle grazing. Some artificial fertiliser has been used to improve grass growth. The location was selected as a background reference in relation to the dressed and cultured soils, and to evaluate the contribution from the deposition, since this was the expected main source of pollution in the area

Sundbylille

Cultured area amended with about 0.7 t dw/ha/y of sludge (low amounts). This sludge load is about half the amount recommended by Danish agricultural consultants (4 t/ha dw every third year = 1.3 t dw/ha/y). In addition the location had received cows manure.

Bistrup

Area used for cattle grazing. Received through a period of about 25 years all the sludge from Roskilde older WTP (in operation until the WWTP at Bjergmarken was built in 1993). The sludge load during that period amounts to about 17 t dw/ha/y, but changed to artificial fertiliser 1990. This sludge load is considerably above the maximum allowed in today Danish agriculture, which from the year 2000 has been 7 t dw/ha/y, before then 10 t

dw/t/y (Miljø- og Energiministeriet 1996, 2000). Nevertheless, such a load is allowed in other European countries. The site would give an impression of the occurrence of xenobiotics in a highly sludge loaded environment, and may be particularly relevant for other countries than Denmark.

The location was sampled again after two years to study the changes over time. Since it is not possible to sample the exact same position twice, the two positions are some meters apart.

3.2 Sediment samples

Sampling methods

The samples of fjord sediment were taken during 1996 in the upper 5 cm of the sediment. In addition, a depth core was sampled, which reached about 22 cm into the sediment. A diver sampled the sediment by hammering a stainless steel tube 6 cm iØ into the fjord bottom. The core was sawed into sections 0.5 cm high for the upper 10 cm, and 1 cm high for the lower 10 cm. The sediment core texture was very hard, and showed undisturbed horizontal layers.

All samples were stored at -20° C until analysed.

Locations

Roskilde Vig, the southern part of Roskilde Fjord, is a narrow bay (in the following sections designated the Vig), in which Roskilde Harbour and the WWTP outlet is located (map Figure 1). The sample in the Vig was taken at a position 1,5 km to the North of Roskilde Harbour at a water depth of 4 m. The site is the official measuring Station 2 for Roskilde Country, at a distance of 1 km from the WWTP outlet, which itself is located 1 km East of the harbour. The WWTP average outlet of wastewater is 19000 m^3/day.

The core site was located in Roskilde Vig 180 m N of the WWTP outlet at a water depth of 2.2 m. The site was chosen to reflect the history of variations in the wastewater.

The sample in Roskilde Bredning (in the following sections designated the Bredning) were taken 6 km N of the harbour at a water depth of 4.9 m. This is the measuring Station 60 for Roskilde County.

For comparison, a sample was included from the neighbour fjord Isefjord, regarded as lesser polluted. The sample was taken in Bramsnæs Vig, the southernmost part of Isefjord.
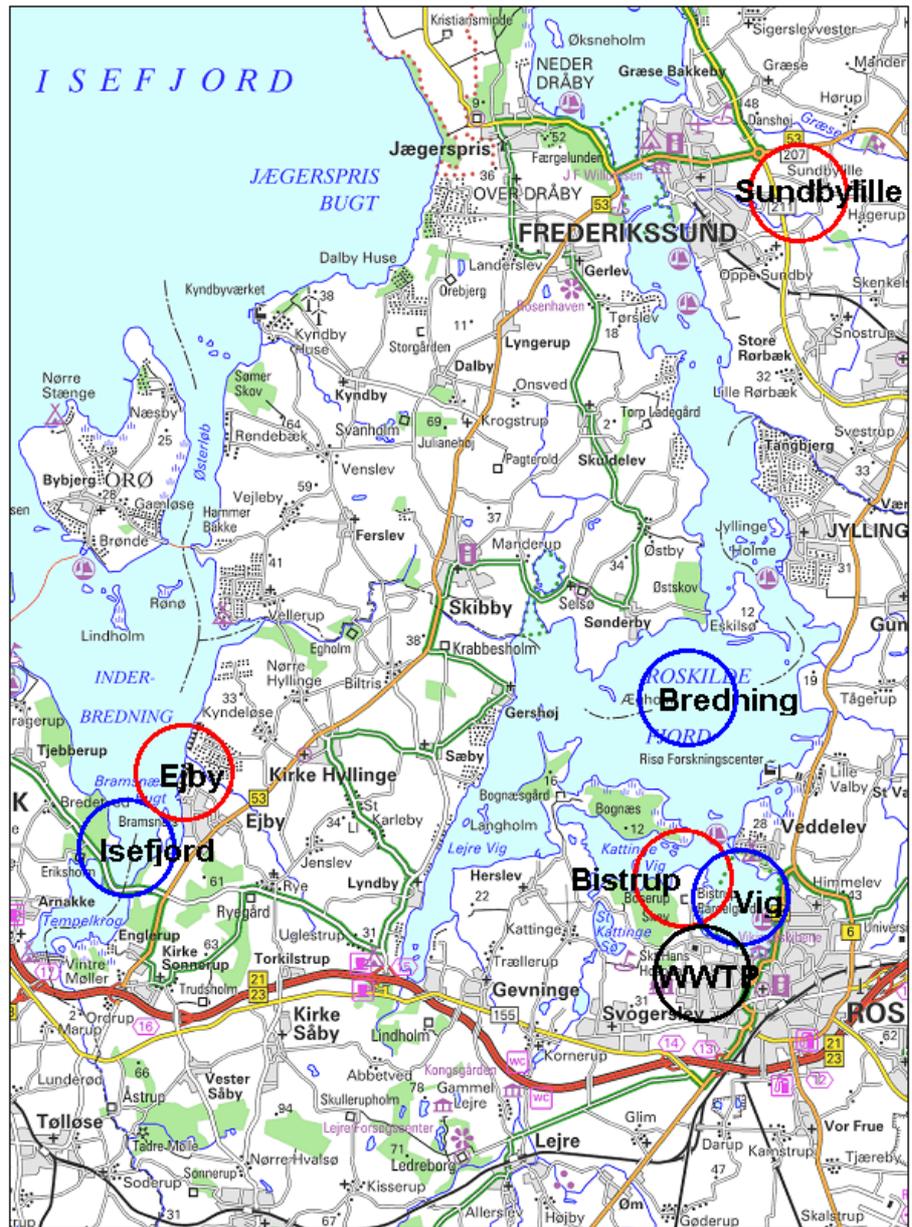
Figure 1 Map in scale 1/200,000 showing the sampling locations for WWTP (sludge, black circle), soil (red circles) and sediment (blue circles).

4 Analytical methods

The aim of the analytical method was to analyse for a large number of substances in the same extract of the sample, utilising the low interference and background of the high-resolution mass spectrometry. It was further intended to accomplish this in as few GC/MS runs as possible. In the present investigation, extracts from the previous investigations were analysed. These have already been analysed for nonylphenols and phthalates, and were stored at -20°C. After addition of a mixture of selected isotope-labelled substances, the extracts were analysed for the substances mentioned below by means of high-resolution gaschromatography/mass spectrometry (GC/HR-MS). The sampling and extraction procedures are summarised briefly below, and have been described in detail by Vikelsøe et al. (1999; 2001). The analytical methods used are developed from the methods used in the previous parts of the project for analysis of nonylphenols and phthalates in soil, sludge and sediment (Vikelsøe *et. al.* 1999; 2001).

4.1 Substances

The following substances were analysed:

Polyaromatic hydrocarbons (PAHs)

Dimethylnaphtalene, Phenantrene, Antracene, Fluorantene, Pyrene, Retene, Benz[a]pyrene, Benz[e]pyrene, Benz[b]fluorantene, Benz[k]fluorantene, Benz(g,h,i)perylene), Indeno(1,2,3-cd)pyrene

nitro-PAHs

1-Nitronaphtalene, 2-Nitronaphtalene, 2-Nitrofluorene

Polychlorinated biphenyls (PCBs)

CB-28, CB-52, CB-101, CB-118, CB-138, CB-153, CB-180.

Polybrominated biphenylethers (PBDEs)

PBDE-47, PBDE-99, PBDE-100, PBDE-153

Polychlorinated naphthalenes (PCNs):

1256-TeCN, 2367-TeCN,
12358-PeCN, 12367-PeCN,
123467-HxCN, 123568-HxCN, 123678-HxCN, 124578HxCN, 1234567-HpCN, 1234568-HpCN.

4.2   Extraction

A sample of about 5 g of air-dried sediment or sludge or about 50 g of soil was extracted by shaking for 4 hours with 100 ml of dichloromethane. After gravity phase separation, a sub-extract of 10 ml was concentrated by careful evaporation under N_2, and the remanence re-dissolved in a volume of 1 ml phthalate syringe spike solution (Table 3). The extracts were analysed for nonylphenols and phthalates during the previous investigations (Vikelsøe et al. 1997; 1998; 2001), and were stored at –20°C in vials with screw-caps.

Exclusively new glassware, annealed at 450°C, was used for sampling and laboratory procedures. All solvent used was HPLC grade.

4.3   Pre-treatment of extracts

For the present investigation the stored extracts were brought to laboratory temperature and concentrated under N_2 to near dryness. The previous investigation had shown an unnecessary fine division of the core (0.5-1 cm). Hence, before concentrating the core extracts were pooled corresponding to depth intervals of approximately 2 cm (the actual corresponding depths are given in table 1). The remanences were re-dissolved in a syringe spike mix specifically prepared for the present investigation (Table 4) in volumes (Table 2) adjusted to the expected concentration levels based on the phthalate levels already known.

Table 2   Pre-treatment of extracts, volumes of syringe spike

Sample	Location	ml	Comment
Soil	Ejby	0.25	Preserved, no sludge
Soil	Sundbylille	0.5	Low (normal) sludge
Soil	Bistrup	1	High sludge
Sediment	All samples	0.25	Including core
Sludge	Bjergmarken	1	Diluted 5 x

The sludge sample was diluted with syringe spike solution. The extracts were analysed directly by high-resolution GC/MS without further clean up.

4.4   Blanks

Empty laboratory glassware was extracted for determination of the blank value for about every 10 samples. The blanks were subtracted from the results on an amount per sample basis for each analytical series.

4.5 Spikes and standards

The labelled spike solutions and standard solution are used for identification and quantification. Extraction spikes are added before the extraction, syringe spikes before GC/MS analysis. For the present investigation, only syringe spikes were used.

Table 3   Extraction spike solution for phthalate analysis of previous investigations.

Substance	Acronym	µg/ml
Di-(n-butyl)phthalate	D_4-DnBP	
Benzylbutylphthalate	D_4-BBP	10
Di-(2-ethylhexyl)phthalate	D_4-DEHP	

Table 4   Syringe spike solution for phthalate analysis of previous investigations.

Substance	Acronym	µg/ml
Di-(n-octyl)phthalate	D_4- DnOP	0.1

Table 5   Syringe spike solution for present investigations.

Substance	Formula	ng/ml
PAHs		
$^{13}C_6$-Anthracene	$^{13}C_6{}^{12}C_8H_{10}$	10
$^{13}C_6$-Phenanthrene	$^{13}C_6{}^{12}C_8H_{10}$	10
D_{10}-Flouranthene	$C_{16}D_{10}$	13
$^{13}C_6$-Flourene		10
$^{13}C_6$-Pyrene	$^{13}C_6{}^{12}C_{10}H_{10}$	10
$^{13}C_6$-Benz[b]fluorantene	$^{13}C_6{}^{12}C_{14}H_{12}$	10
D_{12}-Benz[e]pyrene	$C_{20}D_{12}$	8
$^{13}C_6$-Benz[a]pyrene	$^{13}C_6{}^{12}C_{14}H_{12}$	10
$^{13}C_6$-Indeno(1,2,3-cd)pyrene	$^{13}C_6{}^{12}C_{16}H_{12}$	10
PCBs		
$^{13}C_{12}$-CB-28	$^{13}C_{12}H_7Cl_3$	10
$^{13}C_{12}$-CB-52	$^{13}C_{12}H^6Cl_4$	10
$^{13}C_{12}$-CB-101	$^{13}C_{12}H_5Cl_5$	10
$^{13}C_{12}$-CB-118	$^{13}C_{12}H_5Cl_5$	10
$^{13}C_{12}$-CB-138	$^{13}C_{12}H_4Cl_6$	10
$^{13}C_{12}$-CB-153	$^{13}C_{12}H_4Cl_6$	10
$^{13}C_{12}$-CB-180	$^{13}C_{12}H_3Cl_7$	10
$^{13}C_{12}$-CB-209	$^{13}C_{12}H_2Cl_8$	10
Toluene, solvent	C_7H_8	

For the present investigation, a single standard solution was prepared, containing all analytes and spikes (Table 6).

Table 6   Standard solution for GC/MS.

Substance	Acronym	Unlabelled		Spikes	
		Formula	ng/ml	Label	ng/ml
Polyaromatic hydrocarbons	*PAHs*				
Dimethylnaphthalene		$C_{12} H_{12}$	11		
Antracene		$C_{14} H_{10}$	10	$^{13}C_6$	10
Phenanthrene		$C_{14} H_{10}$	10	$^{13}C_6$	10
Flouranthene		$C_{16} H_{10}$	17	D_{10}	13
Flourene				$^{13}C_6$	10
Pyrene		$C_{16} H_{10}$	10	$^{13}C_6$	10
Retene		$C_{18} H_{18}$	7		
Benez[b]fluoranthene		$C_{20} H_{12}$	12	$^{13}C_6$	10
Benez[k]fluoranthene		$C_{20} H_{12}$	10		
Benz[e]pyrene		$C_{20} H_{12}$	13	D_{12}	8
Benz[a]pyrene		$C_{20} H_{12}$	13	$^{13}C_6$	10
Indeno(1,2,3-cd)pyrene		$C_{22} H_{12}$	8	$^{13}C_6$	10
Benz(g,h,i)perylene		$C_{22} H_{12}$	10		
Nitro-PAHs	*NPAHs*				
1-Nitronaphtalene		$C_{10} H_7 N O_2$	50		
2-Nitronaphtalene		$C_{10} H_7 N O_2$	50		
2-Nitrofluorene		$C_{13} H_9 N O_2$	50		
3-Nitrofluoranthene		$C_{16} H_9 N O_2$	50		
1-Nitropyrene		$C_{16} H_9 N O_2$	50		
6-Nitrobenez(a)pyrene		$C_{20} H_{11} N O_2$	50		
1,3-Dinitropyrene		$C_{16} H_8 N_2 O_4$	50		
Polychlorinated biphenyls	*PCBs*				
244'-TriCB	CB-28	$C_{12} H_7 Cl_3$	10	$^{13}C_{12}$	10
22'55'-TeCB	CB-52	$C_{12} H_6 Cl_4$	4	$^{13}C_{12}$	10
22'455'-PeCB	CB-101	$C_{12} H_5 Cl_5$	5	$^{13}C_{12}$	10
23'44'5-PeCB	CB-118	$C_{12} H_5 Cl_5$	5	$^{13}C_{12}$	10
22'344'5'-HxCB	CB-138	$C_{12} H_4 Cl_6$	10	$^{13}C_{12}$	10
22'44'55'-HxCB	CB-153	$C_{12} H_4 Cl_6$	4	$^{13}C_{12}$	10
22'344'55'-HpCB	CB-180	$C_{12} H_3 Cl_7$	10	$^{13}C_{12}$	10
Octa-CB	CB-209	$C_{12} H_2 Cl_8$		$^{13}C_{12}$	10
Polychlorinated naphthalenes	*PCNs*				
1256-TeCN		$C_8 H_4 Cl_4$	10		
2367-TeCN		$C_8 H_4 Cl_4$	10		
12358-PeCN		$C_8 H_3 Cl_5$	10		
12367-PeCN		$C_8 H_3 Cl_5$	10		
123467-HxCN		$C_8 H_2 Cl_6$	10		
123568-HxCN		$C_8 H_2 Cl_6$	10		
123678-HxCN		$C_8 H_2 Cl_6$	10		
124578-HxCN		$C_8 H_2 Cl_6$	10		
1234567-HpCN		$C_8 H Cl_7$	10		
1234568-HpCN		$C_8 H Cl_7$	10		

Table 6   *Continued.*

Substance	Acronym	Unlabelled		Spikes	
		Formula	ng/ml	Label	ng/ml
Polybrominated diphenylethers	*PBDEs*				
22'44'-TeBDE	PBDE-47	$C_{12} H_6 Br_4 O$	10		
22'44'5-PeBDE	PBDE-99	$C_{12} H_5 Br_5 O$	10		
22'44'6-PeBDE	PBDE-100	$C_{12} H_5 Br_5 O$	10		
22'44'55'-HxBDE	PBDE-153	$C_{12} H_4 Br_6 O$	10		
Phthalates	*PAEs*				
Di-(n-butyl)phthalate	DnBP	$C_{16}H_{22}O_4$		D_4	100
Benzylbutylphthalate	BBP	$C_{19}H_{20}O_4$		D_4	100
Di-(2-ethylhexyl)phthalate	DEHP	$C_{24}H_{38}O_4$		D_4	100
Di-(n-octyl)phthalate	DnOP	$C_{24}H_{38}O_4$		D_4	100

The standard was analysed by GC/MS for about every 5 samples.

4.6 Gaschromatography

For analyses of all substances, the same column and gaschromatographic operating conditions were used.

Gaschromatograph:	Hewlett-Packard 5890 series II
Injection:	CTC autosampler. 2 µl split/splitless 270°C, purge closed 30 sec.
Pre-column:	Chrompack Retention Gap, fused silica, 2.5 m x 0.32 mm i.Ø.
Column:	J&W Scientific DB-5ms, fused silica, 30 m x 0.25 mm i.Ø, crosslinked phenyl-methyl silicone 0.25 µm film thickness.
Carrier gas:	He, 120 Kpa
Temperature-program:	30 sec at 110°C, 8°C/min to 290°C, 17 min at 290°C.

4.7 Mass spectrometry (GC/MS)

The aim was to analyse for all substances in as few runs as possible. It was feasible to analyse PAHs and PBDEs in separate runs, and analyse PCBs and PCNs together.

Mass spectrometer:	Kratos Concept 1S, high resolution, magnetic sector instrument
Resolution:	10,000 (10% valley definition)
Ionisation:	Electron impact 40 - 50 eV depending on tuning, ion source temperature 270°C
Interface:	250°C direct to ion source
Acceleration voltage	8 kV
Calibration gas:	Perfluorokerosene (PFK)
Scan:	Selected Ion Monitoring (SIM) mode. SIM descriptors depending on substances (Tables 7-9).

The descriptors contain masses for analytes and spikes of the present study, and furthermore for the masses of phthalate extraction and syringe spikes. These are present in the extracts from the phthalate analysis of the previous studies. This makes possible to use the phthalate recovery for correction of the present analytes, assuming that the losses during extraction and storage are the same for all substances. This is only an approximation, but useful in the absence of specific extraction spikes for all analytes.

Table 7   HR-MS SIM program for analysis of PAHs.

Substance	Formula	Label	m/z, native	m/z, label	R/T, min:sec
Group 1, 5-13 min					
Lock/check	C_4F_7		180.9888		
Dimethylnaphthalene	$C_{12}H_{12}$		156.0939		5:53
1-Nitronaphthalene	$C_{10}H_7NO_2$		173.0477		8:35
2-Nitronaphthalene	$C_{10}H_7NO_2$		173.0477		9:12
Phenanthrene	$C_{14}H_{10}$	$^{13}C_6$	178.0783	184.0984	11:06
Anthracene	$C_{14}H_{10}$	$^{13}C_6$	178.0783	184.0984	11:15
Group 2, 13-18 min					
Lock/check	C_6F_9		242.9856		
DnBP	$C_{16}H_{22}O_4$	D_4		227.1221	13:13
Flouranthene	$C_{16}H_{10}$	D_{10}	202.0783	212.1410	14:43
Pyrene	$C_{16}H_{10}$	$^{13}C_6$	202.0783	205.0883	15:26
2-Nitrofluorene	$C_{13}H_9NO_2$		211.0633		15:20
Retene	$C_{18}H_{18}$		234.1409		16:28
Group 3, 18-35 min					
Lock/check	C_6F_9		242.9856		
Benz[b]fluorantene	$C_{20}H_{12}$	$^{13}C_6$	252.0939	258.1140	22:17
Benz[k]fluorantene	$C_{20}H_{12}$		252.0939	258.1140	22:22
Benz[e]pyrene	$C_{20}H_{12}$	D12	252.0939	264.1692	23:01
Benz[a]pyrene	$C_{20}H_{12}$	$^{13}C_6$	252.0939	256.1073	23:10
Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	$^{13}C_6$	276.0939	282.1140	26:45
Benz(g,h,i)perylene	$C_{22}H_{12}$		276.0939	288.1342	27:45
DEHP	$C_{24}H_{38}O_4$	D_4		283.1847	19:48
DnOP	$C_{24}H_{38}O_4$	D_4		283.1847	21:46

Table 8   HR-MS SIM program for analysis of PBDEs.

Substance	Formula	Label	Native m/z 1	m/z 2	Labelled m/z 3	m/z 4	R/T min:sec
Group 1, 6-19 min							
Lock/check	C_6F_9		242.9856				
D_4-BBP	$C_{19}H_{20}O4$	D_4			210.1194		18:16
D_4-DnBP	$C_{16}H_{22}O_4$	D_4			227.1221		13:37
Group 2, 19-30 min							
Lock	$C_{10}F_{17}$		442.9729				
Check	$C_{11}F_{19}$		492.9697				
^{13}C-CB-209	$C_{12}H_2Cl_8$	$^{13}C_{12}$			439.8038	441.8008	23:35
PBDE-47	$C_{12}H_6Br_4O$		483.7133	485.7114			20:11
PBDE-153	$C_{12}H_4Br_6O$		483.7133	485.7114			25:37
PBDE-100	$C_{12}H_5Br_5O$		563.6219	565.6200			22:09
PBDE-99	$C_{12}H_5Br_5O$		563.6219	565.6200			22:47

Table 9   SIM HR-MS program for analysis of PCBs and PCNs.

Substance	Formula	Label	Native		Labelled		R/T
			m/z 1	m/z 2	m/z 3	m/z 4	min:sec
Group 1, 5-15 min							
Lock/check	C_6F_9		242.9856				
D4-DnBP	$C_{16}H_{22}O_4$	D_4			227.1221		13:44
CB-28	$C_{12}H_7Cl_3$	$^{13}C_{12}$	255.9613	257.9584	268.0016	269.9986	12:49
1256-TeCN	$C_8H_4Cl_4$		263.9067	265.9037			13:53
2367-TeCN	$C_8H_4Cl_4$		263.9067	265.9037			14:30
CB-52	$C_{12}H_6Cl_4$	$^{13}C_{12}$	289.9224	291.9194	301.9626	303.9597	13:41
Group 2, 15-17 min							
Lock/check	C_7F_{11}		292.9824				
12358-PeCN	$C_8H_3Cl_5$		299.8648	301.8618			16:31
12367-PeCN	C_8H_3Cl5		299.8648	301.8618			16:43
CB-101	$C_{12}H_5Cl_5$	$^{13}C_{12}$	325.8804	327.8775	337.9207	339.9178	15:47
Group 3, 17-19 min							
Lock/check	C_9F_{15}		392.9760				
CB-118	$C_{12}H_5Cl_5$	$^{13}C_{12}$	325.8804	327.8775	337.9207	339.9178	17:23
123467-HxCN:	$C_8H_2Cl_6$		333.8258	335.8229			18:09
123568-HxCN	$C_8H_2Cl_6$		333.8258	335.8229			18:29
124578-HxCN	$C_8H_2Cl_6$		333.8258	335.8229			18:43
123678-HxCN	$C_8H_2Cl_6$		333.8258	335.8229			19:35
CB-138	$C_{12}H_4Cl_6$	$^{13}C_{12}$	359.8415	361.8385	371.8817	373.8788	17:49
CB-153	$C_{12}H_4Cl_6$	$^{13}C_{12}$	359.8415	361.8385	371.8817	373.8788	18:29
Group 4, 20-23 min							
Lock/check	C_7F_{11}		292.9824				
D₄-DEHP	$C_{24}H_{38}O_4$	D_4			283.1847		20:16
D₄-DnOP	$C_{24}H_{38}O_4$	D_4			283.1847		22:14
1234567-HpCN	C_8HCl_7		367.7868	369.7839			21:00
1234568-HpCN	C_8HCl_7		367.7868	369.7839			21:05
CB-180	$C_{12}H_3Cl_7$	$^{13}C_{12}$	393.8025	395.7996	405.8428	407.8398	20:03
Group 5, 23-30 min							
Lock/check	$C_{10}F_{17}$		442.9729				
CB-209	$C_{12}H_2Cl_8$	$^{13}C_{12}$	427.7635	429.7606	439.8038	441.8008	23:35

Overview of GC/MS   Figure 2 displays an overview of masses versus retention times for the GC/MS analysis.
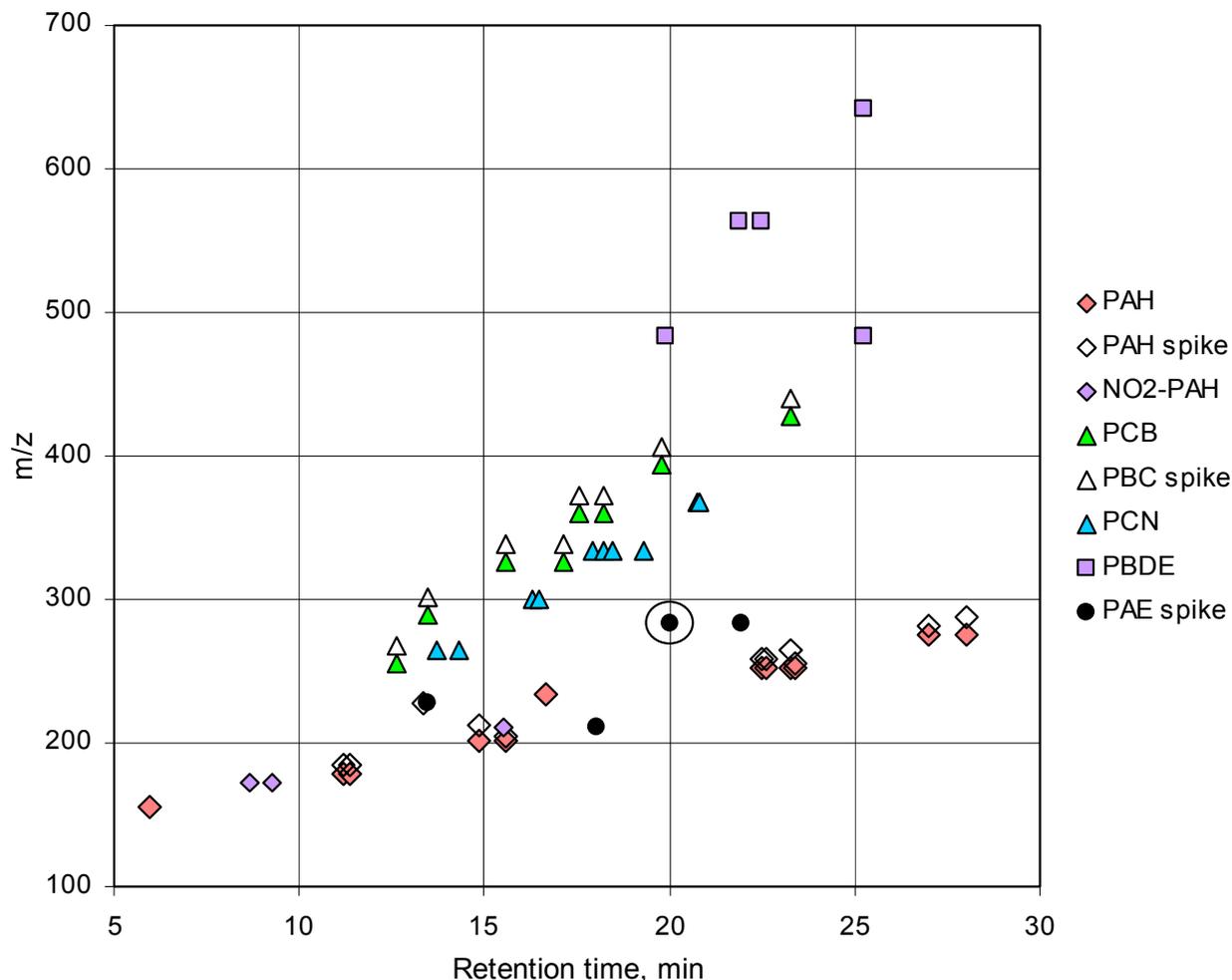

Figure 2   Overview of the GC/MS analysis, masses versus retention times.

In Figure 2, the retention times of the different GC runs have been normalised in relation to DEHP spike set to 20:00 min (marked with a circle), very close to the actual retention time of that substance, to compensate for small variations. Figure 2 shows that each class of substances is approximately linearly distributed in the diagram. PAHs/nitro-PAHs and phthalate spikes are within a narrow mass-corridor, which is also the case for PCBs/PCNs. The brominated compounds stands out with their exceptionally high masses in relation to their retention times. For this reason, and because of the narrow mass range in high-resolution mass spectrometry, it has been found feasible to analyse the PBDEs in a separate run. Thus, the analytical program can be covered in 3 separate GC/MS runs with specific SIM-descriptors.

5 Results and statistics

5.1 Average occurrence of substances

The average concentrations and standard deviations for the results of the samples investigated are shown for each location in Table 10. The last column show the mean and standard deviation for all samples, the former being the total average (equal to the mean of means weighted by the number n of samples in each mean). In the first section of Table 10 on this page, the results for NPEs and PAEs are given, compiled from the archived raw data previously measured during the investigations by Vikelsøe et al. 1999 and 2001. In the remainder of Table 10 on the following pages, the results measured during the present study are shown.

The correlation between different substances is evaluated in a correlation analysis described in a later section.

Table 10   NPEs and PAEs, mean concentrations and standard deviations, µg/kg dm.
Results compiled from archived raw data measured by Vikelsøe et al. 1999 and 2001.

Location	Stat	Bjerg-marken	Bistrup 1st	Bistrup 2 y	Sund-bylille	Ejby	Vig	Bred-ning	Ise-Fjord	Core	All samples
Sample type		*Sludge*	*Soil*	*Soil*	*Soil*	*Soil*	*Sedi*	*Sedi*	*Sedi*	*Sedi*	*All*
	n	2	10	10	10	10	2	2	2	20	68
NP	mean	675	1526	2996	0	0.7	347	149	214	33	715
	sd	51	541	2236	0	0.7	u	u	8.7	39.5	1359
NPDE	mean	23723	1306	3177	24.5	4.4	276	23	0	20.2	1376
	sd	6205	480	2502	54.9	4.6	u	u	0	26.7	4205
ΣNPE	mean	24398	2832	6172	24.5	5.1	623	172	214	53.0	2091
	sd	17801	359	4734	54.9	5.2	u	u	152	54.2	4824
DnBP	mean	8.5	544	474	1.7	3.6	78	45.6	43.9	30.2	164
	sd	12.1	344	428	1.0	6.9	u	u	4.6	67.6	299
DPP	mean	0	3.7	1.1	0.01	0.02	0.6	0.8	0	0.2	0.8
	sd	0	3.7	0.6	0.01	0.02	u	u	0	0.2	1.8
BBP	mean	28.2	38.1	43.1	0	0.1	5.4	4.4	2.7	1.9	13.7
	sd	10.5	21.9	30.0	0	0.1	u	u	0.3	1.1	22.4
DEHP	mean	24638	1270	2278	10.8	27.6	161	52	80.3	226	1327
	sd	377	395	764	9.6	33.1	u	u	27.5	252	4211
DnOP	mean	188	59.2	68.1	0.7	1.2	9.9	1.8	1.1	1.7	25.4
	sd	13.0	8.6	20.5	0.3	1.1	u	u	0.1	1.2	41.3
DnNP	mean	214	181	256	0.3	0.1	24.8	1.7	0.6	5.6	73.0
	sd	3.8	26.4	89.8	0.5	0.2	u	u	0.9	4.6	109
DiNP	mean	5626	159	805	4.9	22.2	na	na	na	na	504
	sd	474	65	401	1.4	24.9	u	u	na	na	1232
ΣPAE	mean	30702	2254	3926	18.4	54.8	280	106	129	266	1916
	sd	13961	201	1225	10.7	31.8	u	u		318	5304

0 = not detected, u = undefined, sd = standard deviation,
Bistrup 2 y sampled 2 years after Bistrup 1st at the same location

Table10 *Continued.* PAHs, mean concentrations and standard deviations, μg/kg dm. Results measured during present study.

Location	Stat	Bjerg mark	Bistrup 1st	Bistrup 2 y	Sund bylille	Ejby	Vig	Bred ning	Isefjord	Core	All samples
Sample type		*Sludge*	*Soil*	*Soil*	*Soil*	*Soil*	*Sedi*	*Sedi*	*Sedi*	*Sedi*	*All*
	n	1	5	5	5	5	1	1	1	10	34
Dimethyl-	mean	33.9	26.5	29.5	0.1	0.03	30.7	15.7	32.8	1.7	12.1
naphthalene	sd	u	10.9	7.9	0.1	0.04	u	u	u	2.0	14.7
Anthracene	mean	44.7	44.7	50.8	0.4	0.6	21.2	9.7	4.8	5.0	18.0
	sd	u	16.2	17.0	0.4	0.7	u	u	u	5.0	22.8
Phenanthrene	mean	98.8	70.7	90.0	2.1	3.3	44.1	22.2	8.3	8.0	31.9
	sd	u	16.4	19.6	2.0	5.4	u	u	u	7.9	37.8
Fluoranthene	mean	193	88.7	119	6.7	5.7	146	110	59.5	29.7	56.0
	sd	u	22.3	12.8	7.2	6.8	u	u	u	13.8	52.6
Pyrene	mean	173	90.7	99.5	5.4	5.8	119	125	44.1	18.0	48.5
	sd	u	14.2	8.7	5.7	7.0	u	u	u	8.9	48.6
Retene	mean	260	8.9	11.9	0.5	0.6	17.8	12.9	14.6	4.5	13.5
	sd	u	4.5	2.0	0.2	0.5	u	u	u	3.2	43.8
Benz[b]-	mean	250	293	388	7.6	8.1	634	409	75.9	66.6	162
fluoranthene	sd	u	24.8	41.4	7.8	10.0	u	u	u	32.2	173
Benz[k]-	mean	83.0	82.2	114	1.9	1.9	170	114	25.2	28.8	49.5
fluoranthene	sd	u	14.7	46.2	1.9	2.0	u	u	u	18.1	51.1
Benz[a]pyrene	mean	102	116	172	3.4	4.2	270	172	31.5	38.9	71.9
	sd	u	39.0	32.7	3.6	5.3	u	u	u	19.2	74.5
Benz[e]pyrene	mean	145	256	325	4.5	4.7	341	220	41.4	60.8	127
	sd	u	50.7	40.1	4.5	5.6	u	u	u	38.8	131
Benz(g,h,i)-	mean	116	343	429	4.7	5.3	339	210	44.2	75.1	158
perylene	sd	u	59.0	66.0	4.6	6.5	u	u	u	68.3	171
Indeno(123-cd)	mean	97.8	261	333	4.2	4.7	297	185	37.2	64.5	126
pyrene	sd	u	37.6	43.5	4.2	5.7	u	u	u	57.7	132
1-Nitro-	mean	79.8	1.7	1.1	0	0.1	8.8	12.2	20.8	1.2	4.4
naphthalene	sd	u	1.1	2.5	0	0.1	u	u	u	0.8	14.0
2-Nitro-	mean	0	1.7	5.7	0.3	0	3.3	0.0	6.9	0.03	1.4
naphthalene	sd	u	1.8	8.3	0.5	0	u	u	u	0.09	3.7
2-Nitrofluorene	mean	941	141	144	1.5	0.4	40	16.7	4.5	13.6	76
	sd	u	28	27	2.1	0.3	u	u	u	13.8	166
ΣPAH	mean	4132	2007	2520	46.1	47.0	2581	1677	475	438	1069
	sd	u	341	218	46.8	55.7	u	u	u	269	1143

0 = not detected, u = undefined, sd = standard deviation,
Bistrup 2 y sampled 2 years after Bistrup 1st at the same location

Table 10 *Continued.* Halogenated compounds, mean concentrations and standard deviations, µg/kg dm. Results measured during present study.

Location	Stat	Bjerg-marken	Bistrup 1st	Bistrup 2 y	Sund-bylille	Ejby	Vig	Bred-ning	Isefjord	Core	All samples
Sample type		*Sludge*	*Soil*	*Soil*	*Soil*	*Soil*	*Sedi*	*Sedi*	*Sedi*	*Sedi*	*All*
	n	1	5	5	5	5	1	1	1	10	34
CB-28	mean	22.7	1.9	1.8	0.006	0.01	0.9	0.5	0.2	0.1	1.3
	sd	u	1.3	0.7	0.008	0.01	u	u	u	0.1	3.9
CB-52	mean	17.0	7.8	12.9	0.025	0.005	0.9	0.4	0.1	0.1	3.6
	sd	u	2.1	8.5	0.024	0.01	u	u	u	0.1	6.2
CB-101	mean	16.4	51.5	55.2	0.042	0.01	2.4	1.1	0.3	0.3	16.4
	sd	u	23.2	40.1	0.048	0.007	u	u	u	0.2	29.3
CB-118	mean	17.5	0.0	4.3	0.029	0.005	6.3	1.7	0.5	0.8	1.6
	sd	u	0.0	9.7	0.031	0.006	u	u	u	0.8	4.7
CB-138	mean	40.0	313.5	301	0.158	0.04	15	6.2	1.8	1.9	92.8
	sd	u	134.6	221	0.158	0.05	u	u	u	1.6	167
CB-153	mean	7.9	56.4	52.3	0.03	0.01	3.2	1.3	0.4	0.4	16.5
	sd	u	25.0	38.6	0.03	0.01	u	u	u	0.4	29.6
CB-180	mean	13.6	122	130	0.08	0.02	3.7	1.8	0.5	0.5	37.7
	sd	u	55.3	95.2	0.07	0.02	u	u	u	0.4	69.3
ΣPCB	mean	135	553	558	0.37	0.10	32	13.0	3.8	4.0	170
	sd	u	241	400	0.36	0.09	u	u	u	3.6	301
1256-TeCN	mean	0.7	2.7	2.5	0.002	0.001	0.1	0.1	0	0	0.8
	sd	u	1.2	0.7	0.003	0.001	u	u	u	0.0	1.3
2367-TeCN	mean	1.1	2.8	2.5	0.005	0	0.1	0.0	0	0	0.8
	sd	u	1.9	1.4	0.006	0	u	u	u	0.0	1.5
12358-PeCN	mean	0	1.2	0.9	0.001	0	0.0	0	0	0	0.3
	sd	u	0.7	0.3	0.002	0	u	u	u	0.0	0.5
12367-PeCN	mean	0	1.4	1.2	0	0	0.0	0	0	0	0.4
	sd	u	0.9	0.4	0.001	0	u	u	u	0.0	0.7
123467-HxCN	mean	0.3	0.2	0.2	0	0	0.0	0	0	0	0.1
	sd	u	0.04	0.02	0	0	u	u	u	0.0	0.1
123568-HxCN	mean	0.4	0.3	0.3	0	0	0.0	0	0	0	0.1
	sd	u	0.0	0.1	0	0	u	u	u	0.0	0.1
123678-HxCN	mean	0	0	0.3	0	0	0.0	0	0	0	0.0
	sd	u	0	0.1	0	0	u	u	u	0.0	0.1
124578-HxCN	mean	0.7	0.4	0.4	0	0	0.0	0	0	0	0.1
	sd	u	0.1	0.1	0	0	u	u	u	0.0	0.2
HpCN	mean	0	0.2	0.3	0	0	0.0	0	0	0	0.1
	sd	u	0.04	0.1	0	0	u	u	u	0.0	0.1
ΣPCN	mean	3.2	9.1	8.4	0.01	0.001	0.2	0.13	0	0	2.7
	sd	u	4.8	2.9	0.01	0.001	u	u	u	0.1	4.5
PBDE-47	mean	69.3	3.3	11.0	0.03	0.003	0.1	0.00	0.1	0.1	4.2
	sd	u	1.1	7.8	0.04	0.003	u	u	u	0.0	12.4
PBDE-99	mean	92.0	5.3	23.5	0.05	0.002	0.0	0	0	0	7.0
	sd	u	2.5	19.1	0.07	0.005	u	u	u	0.1	18.4
PBDE-100	mean	14.2	0.9	3.5	0.01	0.001	0.0	0	0	0	1.1
	sd	u	0.3	3.0	0.01	0.003	u	u	u	0.0	2.8
PBDE-153	mean	0	1.6	2.1	0.01	0.02	0.0	0	0	0	0.6
	sd	u	2.4	1.5	0.02	0.01	u	u	u	0.0	1.3
ΣPBDE	mean	175.5	11.1	40.1	0.10	0.03	0.1	0.00	0.1	0.2	12.8
	sd	u	4.8	31.2	0.15	0.01	u	u	u	0.1	33.9

0 = not detected, u = undefined, sd = standard deviation,
Bistrup 2 y sampled 2 years after Bistrup 1st at the same location

5.1.1 Overall abundance in sludge, soil and sediment

As seen from Table 10, the data spans a very large concentration range, as well between substances as between locations. The last column, the total, contains the mean and standard deviations for the concentrations of all samples and thus comprises sludge, soil, sediment, and all locations. This gives an overview of the general abundance and concentration span. Particularly the sums of substances give an overview of the general occurrence of the substance groups, shown in Figure 3 as the total means and total standard deviations in a logarithmic bar graph.
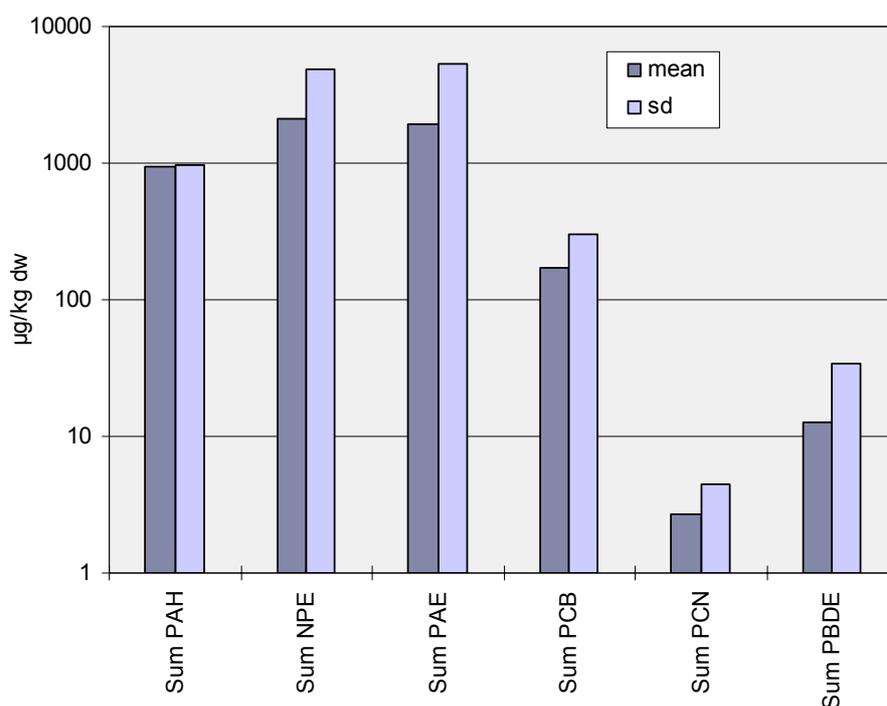
Figure 3   Total abundance of sums of substance groups. Mean and standard deviation (sd) of all samples (n=34).

As seen from Table 10 and Figure 3, the total average concentrations of the non-halogenated substance groups, ΣPAH, ΣNPE and ΣPAE, are of the same order of magnitude ranging from 1000-2000 μg/kg dm. In contrast, the halogenated substances occur in much lesser concentrations, PCBs being most abundant with ΣPCB of 170 μg/kg dm. The other groups occur in much lesser concentrations, ΣPBDE about 13 and ΣPCN only 3 μg/kg dm, respectively. This is in spite of the fact that PCBs have been banned in Denmark since 1977 (Miljøministeriet, 1976). The PBDEs (Poly Brominated Diphenyl Ethers, a type of brominated flame retardant) have increasingly been used in recent years, but have by far not yet reached a level in the environmental samples (soil and sediment) comparable with the PCBs. The current consumption of penta-BDE in the EU is estimated to < 150 t/y. A similar amount is estimated in imported goods, but with great uncertainty. A substantially larger consumption of higher BDEs, particularly deca-BDE, is estimated. In the past, the consumption has been estimated to 1100 t/y (European Commission, 2001).

PCNs have been synthesised for similar use as PCBs, but were phased out in the 1980s (Brinkman & Reymar, 1976; Crookes & Howe, 1993). PCNs occur as a by-product in technical PCB-preparations (Yamashita et al.,

2000). It is further seen that the standard deviations are somewhat higher than the means, because these standard deviations reflect as well the geographical and natural variation and sample differences as the analytical error.

The sample type difference is illustrated in Figures 4-7, showing graphs of same type for all soil samples and for all sediment samples.
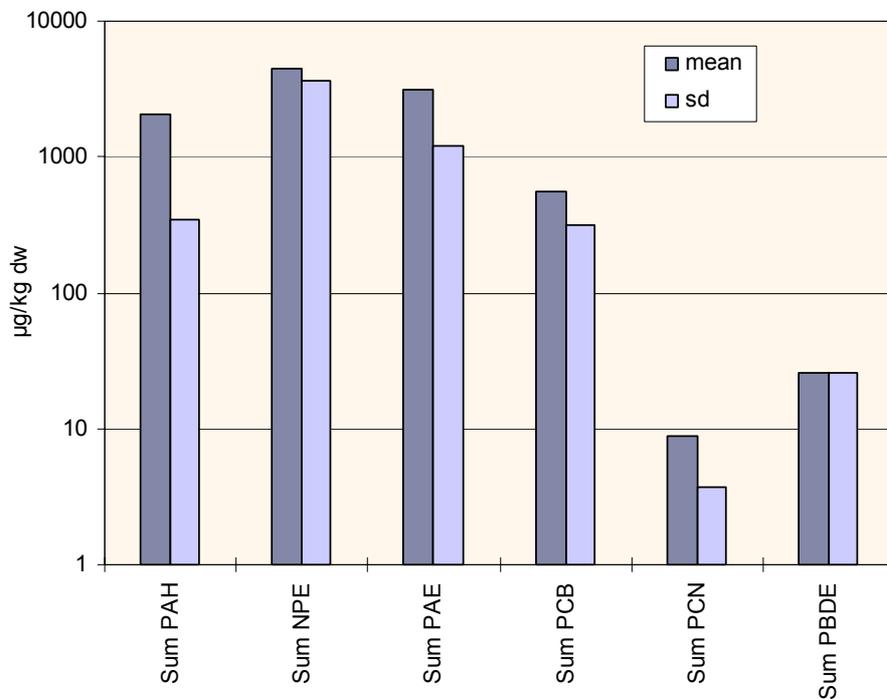
Figure 4　Abundance in high-amended soil. Mean and standard deviation (sd) of substance sums (n=10).
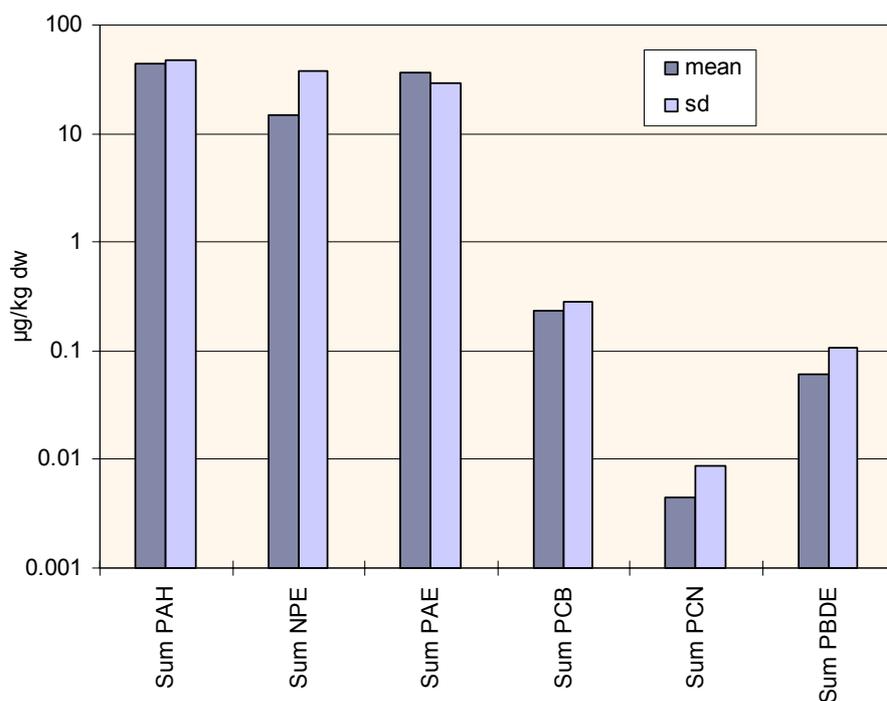
Figure 5　Abundance in low-amended soil. Mean and standard deviation (sd) of substance sums (n=10).
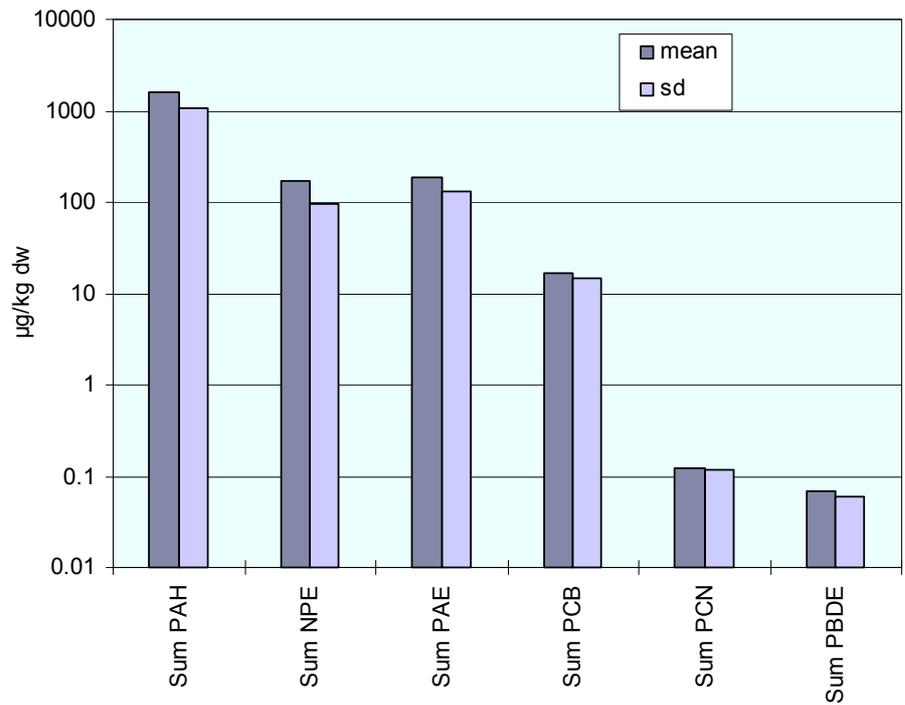
Figure 6 Abundance in fjord sediment from Roskilde Vig, Bredning and Isefjord. Mean and standard deviation (sd) of substance sums (n=3).
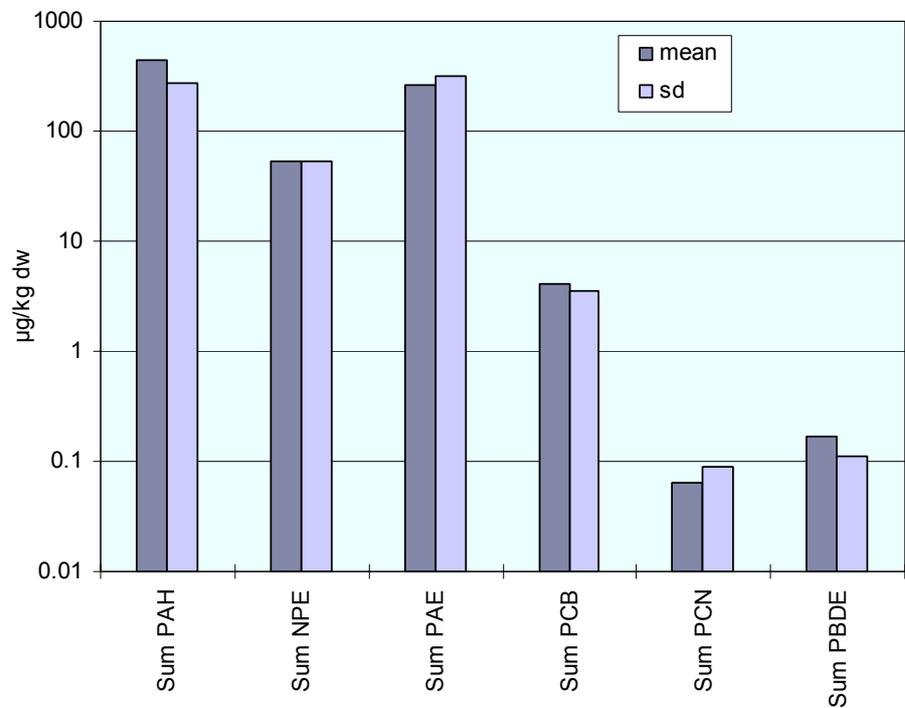
Figure 7 Abundance in sediment core from Vig. Mean and standard deviation (sd) of substance sums (n=10).

Soil compared to sediment

Figures 4 and 5 display virtually identical pictures, showing that the substance distributions in high and low sludge amended soil are roughly similar. This is in spite of the fact that the concentration levels in the high-amended soil are approximately two orders of magnitude above those in the low-amended soils. From Figures 6 and 7 is seen that there is relatively lesser NPEs and more PAHs in sediment compared to soil. Furthermore, the proportion of PBDEs to PCNs is notably higher in the soils. The persistent pollutants are conserved in the layers of sediment, hence, these samples contain an "archived" record of pollution. The 5 cm depth of the sample covers approximately 20 years. In contrast, the upper layers of cultured soils are fertilised with sludge of current composition and mixed by ploughing in a more oxidising environment. Hence, the differences between soil and sediment to a certain extent reflect the historical development of the pollution with these substances. They further reflect the physico-chemical difference between soil and water. Thus, the low proportion of NPEs in sediment may be explained by the relatively high solubility in water characteristic for surfactants (6 mg/l for NPs according to OECD, 1997), compared to PAHs, PAEs etc. (0.16 mg/l for DEHP according to Thomsen & Carlsen, 1998). This will impede the sedimentation process by keeping the NPEs dissolved in the water.
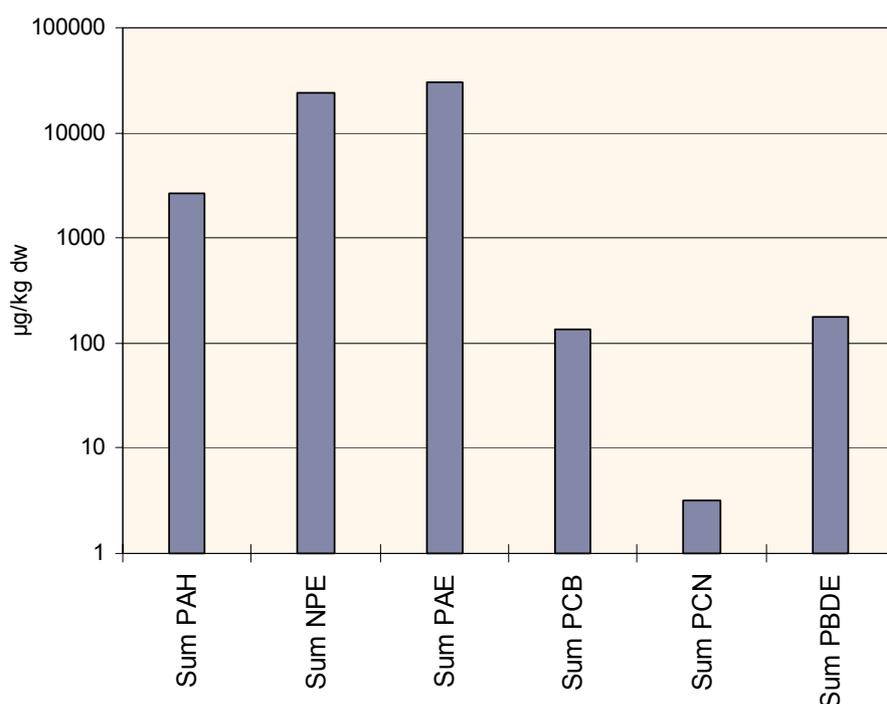
Figure 8   Abundance in sludge sample. Substance sums (n=1).

Sludge versus sediment

These differences are further enhanced comparing the mean sediment concentrations (Figure 6) with the sludge (Figure 8). In the sediment, which reflect the pollution in the past, the ΣPBC is two orders of magnitude (i.e. factors of 10) lower than ΣPAH, and this also the case in the sludge, which yields an actual picture of the present state of pollution in wastewater. Hence, the ratio of ΣPCB to ΣPAH has remained approximately constant during the about 20 years covered by the sediment. ΣPBDE, in contrast, is 4 orders of magnitude lower (i.e. 10^{-4}) than ΣPAH in sediment, but only 2 orders of magnitude lower than ΣPAH in sludge, where it occurs at about

the same level as ΣPCB. Hence, ΣPBDE is more abundant relative to ΣPAH, ΣPCB and ΣPCN in the "actual" matrix sludge compared to the "historical" matrix sediment. Taken together, these observations suggest that a rise in the level of PBDEs in sludge has taken place during the time span of about 20 years covered by the sediment. In this view ΣPBDE in sludge has reached and now exceeds the level of ΣPCB, which on the other hand is believed to be slowly decreasing since it was phased out in 1977. The present results are based on only a single sample and should therefore not be over-interpreted. Nevertheless, the levels of PBDEs found here agree with unpublished results on 10 other WWTPs (Larsen, 2001).

ΣPCN is about 3 orders of magnitude lower (i.e. 10^{-3}) than ΣPAH in sludge and 4 orders of magnitude lower than ΣPAH in as well sediment as sludge, occupying a middle position.

ΣPAE and ΣNPE are almost a order of magnitude higher in sludge compared to ΣPAH, whereas in sediment those substances occur 1 order of magnitude lower. It is tempting to interpret this observation − in analogy with the PBDEs − as a rise in the level in sludge in the recent years. However, since NPEs are degraded in the environment (Jones & Westmoreland, 1998) this is not quite as persistent as the halogenated substances, which could explain the lower occurrence in sediment. Also, as mentioned above, the higher solubility in water of NPEs may impede sedimentation.

A further consideration to take into account is the improvement in the wastewater treatment technology. The current WWTP at Bjergmarken went into operation in 1993, replacing an older, lesser efficient plant located near the harbour. The pollution of the old plant is probably still found in the sediment.

Sludge/environment ratios Figure 9 show the ratios of all substance sums in soil and sediment in relation to sludge in a logarithmic bar graph.

The positive bars in Figure 9 indicate that an accumulation of PCBs and PCNs have occurred at the high amended soil location.

It is evident that a large variation between the ratios for the different substances exists, which means that the substances occur in different patterns in the environment compared to sludge. As seen, the soil concentrations exceed the sludge for ΣPCB and ΣPCN, indicating that these substances are the most persistent of the ones investigated. A substance build-up may have taken place during the years of heavy sludge amendment; i.e. the substances are supplied to the soil faster than they are removed or degraded. In addition, the concentrations in the sludge were probably higher in the past. As mentioned, PCBs were banned in Denmark in 1977, which must have implied a substantial reduction of the occurrence in sludge. This view is supported by the sediment core data, discussed in a later section. Unfortunately, the exact reduction in sludge concentrations is unknown because data is lacking for old sludge.
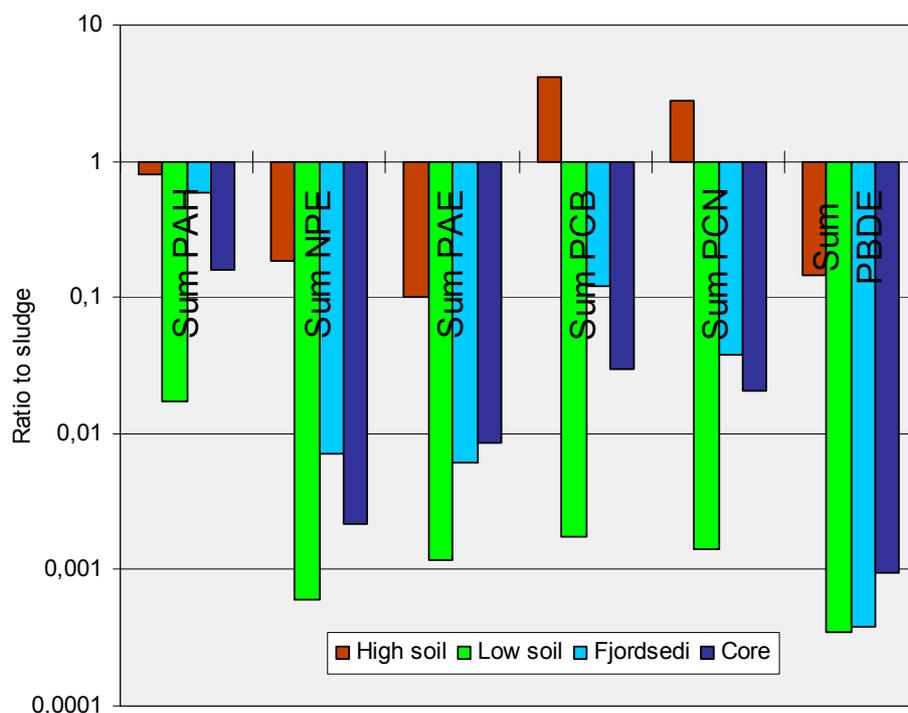
Figure 9   Ratios of substance sums measured on each location divided by substance sums measured in sludge.

In all other cases, the concentrations are considerable lower in soil and sediment. Thus PBDEs display a very low ratio of 0.001 (i.e. occurs in about 1000 times lower concentrations in sediment compared to sludge). A straightforward explanation for this may be that these recent chemicals have not yet reached the sediment. They may never do so because of the improved wastewater cleaning technology introduced in recent years, making the outlet water discharged into the fjord much cleaner than previously. This improvement took place just in the period when PBDEs was being introduced. The low sludge amended soil display about the same ratio as the sediment. In contrast, PBDEs ratio for the high sludge soil is about 0.1, on level with NPEs and PAEs. In addition, the PBDEs ratio could be explained if these compounds be lesser persistent than the PCBs in the environment.

For PAHs the ratios are small, probably because deposition is a significant source as well as sludge. This is particularly pronounced for the fjord sediment having a ratio close to 1. Furthermore, since PAHs are produced unintentionally during combustion e.g. for heating of buildings, the emission must have been more constant over the years than that of the synthetic chemicals.

5.2 Geographical distribution

The abundance and geographical distribution of the individual components in the different matrices are addressed in this chapter. Each group of substances is treated in its own subsection.

In the following figures, the mean and standard deviation of selected results from soil, sludge and sediment are given for all components. The mean and standard deviation are calculated from all samples and depths at the selected location.

The geographical distribution of the substances is further shown for the individual locations in 3-dimensional plots in relation to location, giving a view of the distribution in the environment of soil and sediment, respectively.

5.2.1 PAHs and nitro-PAHs

Figure 10 shows the mean abundance of PAHs in high sludge amended soil at Bistrup (left), and low sludge amended soil at Sundbylille and Ejby (right), respectively. Figure 11 shows the abundance in fjordsediment as mean of samples taken at Roskilde Vig, Bredning and at Isefjord (left), and further the mean of all depths of the sediment core taken at Roskilde Vig (right). Figure 12 shows the occurrence in sludge.

Figures 13 and 14 show the concentration means at the individual locations in 3-dimensional bar graphs. This gives a better view of the geographical distribution than Figures 10 and 11, but does not show the levels as precisely, especially the low levels.
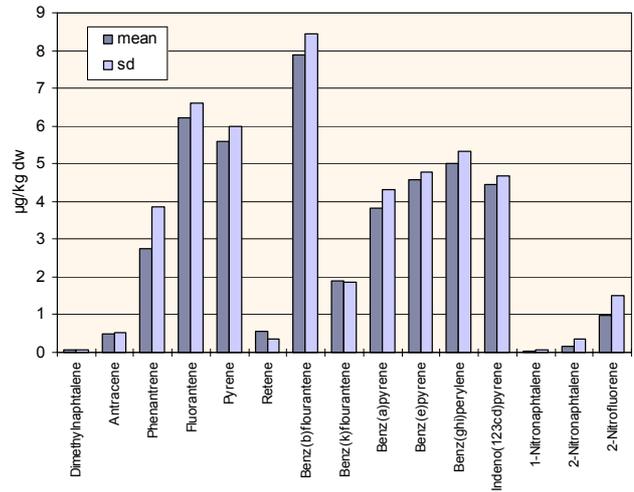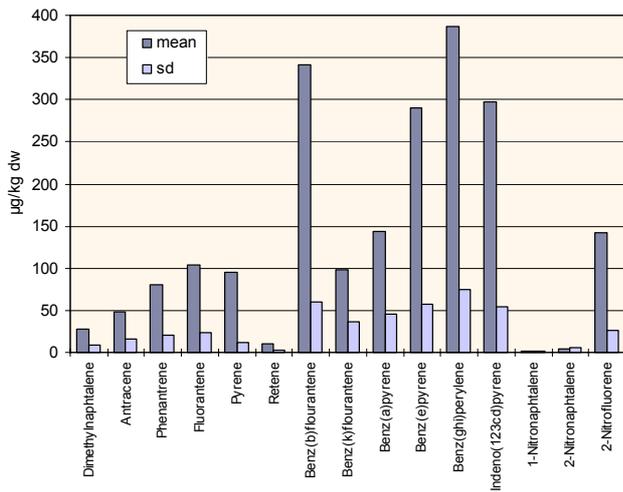
Figure 10   Abundance of PAHs soil, left high sludge amended, right low sludge amended. Mean and standard deviation (sd).
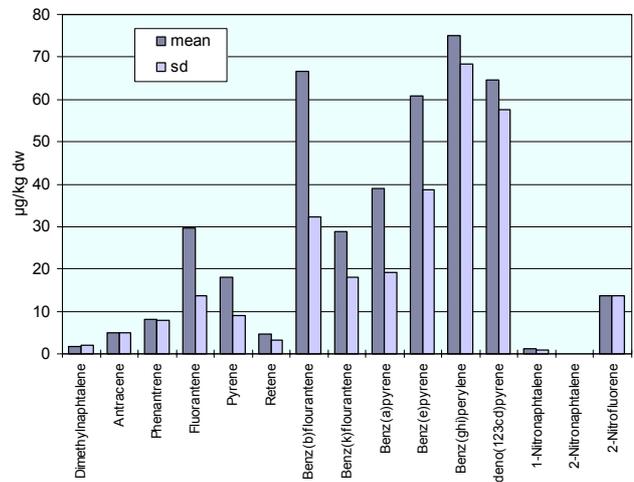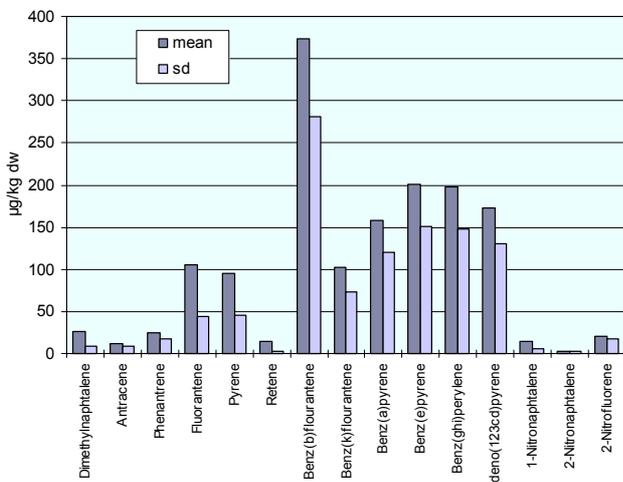
Figure 11   Abundance of PAHs in fjord sediment, left Roskilde Vig, Bredning and Isefjord, right sediment core. Mean and standard deviation (sd).
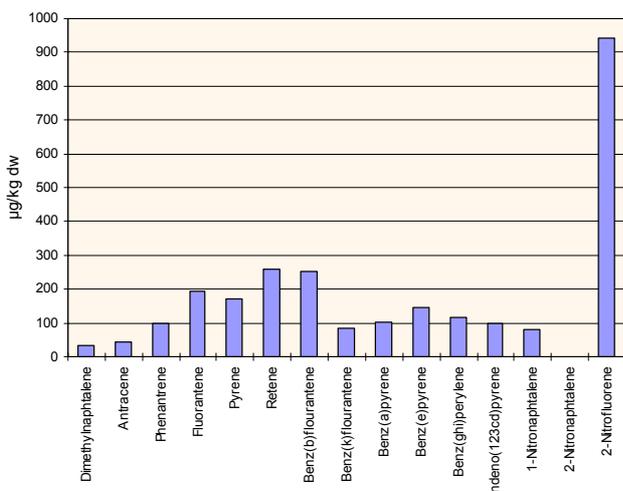
Figure 12   Abundance of PAHs in sludge.
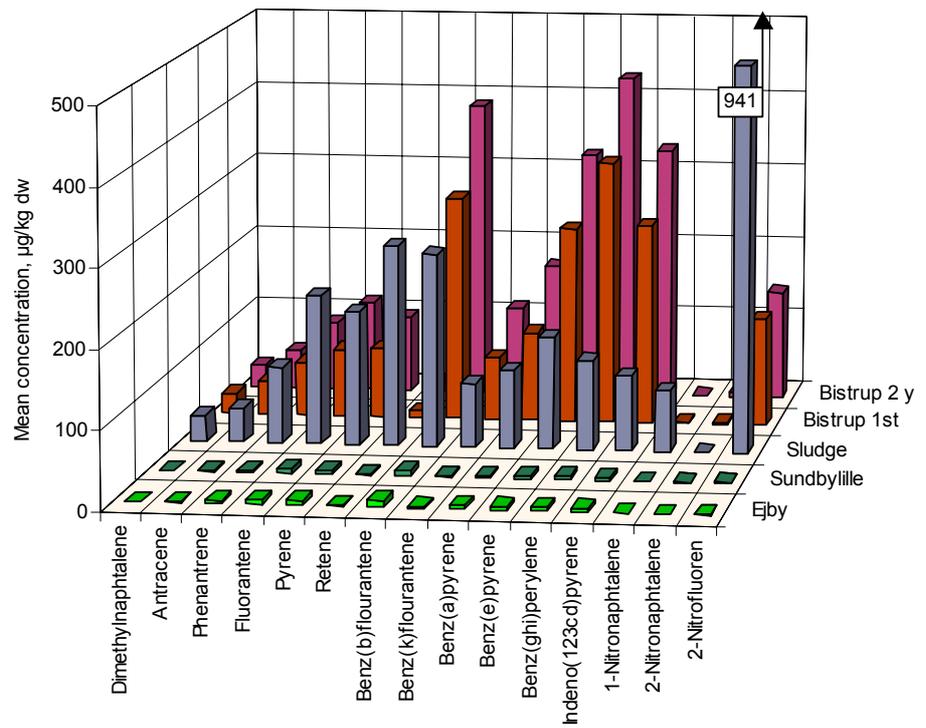
Figure 13   Concentrations of PAHs in soil and sludge. Means of soil locations.
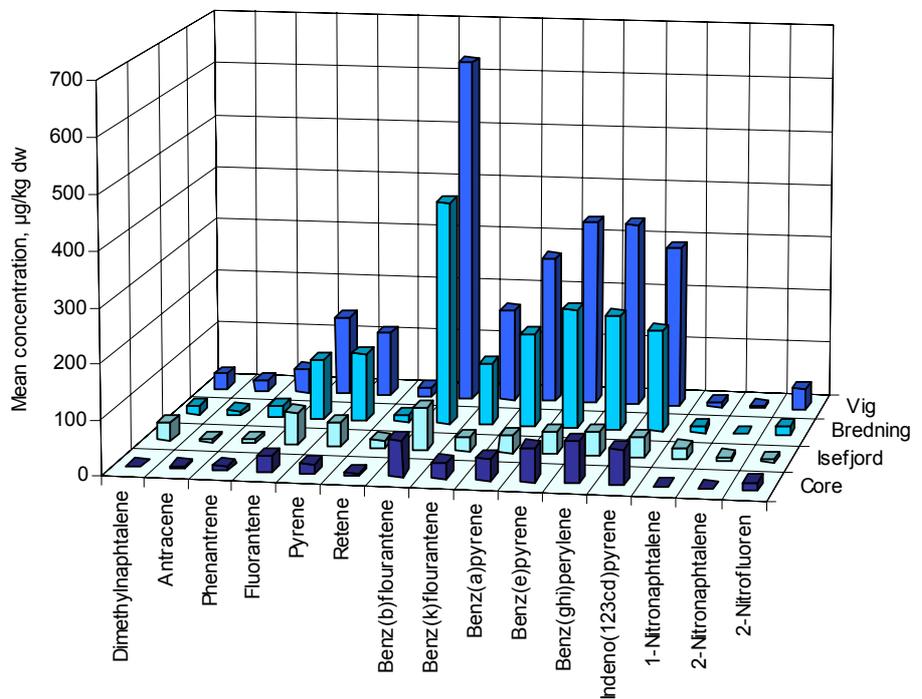
Figure 14   Concentrations of PAHs in fjord sediment, means of locations.

Soil	It is remarkable (Figures 10 and 12) that the higher PAHs (from benz[b]-fluorantene and up) occur in higher abundance in the highly sludge amended soils at Bistrup than in sludge, demonstrating that under these heavy sludge load circumstances PAHs behaves persistent. A concentration build-up might have been taking place during the many years of sludge amendment. In addition, there may have been higher PAHs concentrations in the past in the sludge produced at the former, now closed, smaller WWTP. There is no visible difference between Bistrup 1 and 2, sampled with an interval of about 2 years, as all PAHs seem to occur in the same concentrations (Figure 13).

The levels in the low amended soils are significantly lower (Figure 10). It is further observed (Figure 13 and Table 10) that the soils at Sundbylille and Ejby display similar component patterns and levels, in spite of the fact that Sundbylille has been amended with low amounts of sludge, whereas the preserved area of Ejby has not. This points to deposition as the source of PAHs in these locations, and further indicates that low amounts of sludge do not lead to concentration build-up of PAHs in the soil.

Sediment	The highest levels in the Bredning and particularly in the Vig are considerably higher than in sludge, demonstration a concentration build-up for PAHs in fjord sediment (Figures 11, 12 and 14, cf. also Figure 9). The level in sediment from Isefjord is considerably lower. A neat descending concentration gradient of all components is observed from the Vig (about 2 km from the WWTP outlet) through the Bredning (about 6 km from the outlet) to Isefjord, a neighbour fjord regarded as being lesser polluted (Figure 14). The mean concentration in the sediment core is on level with Isefjord. The core reflects the historical development in the pollution of Roskilde Fjord; this will be addressed in a later section.

| *Component pattern*	The generally most abundant PAH components in soil/sediment are benz[b]-fluorantene and benz(g,h,i)-perylene, and also indeno(1,2,3-cd)-pyrene occur in substantial concentrations, particularly in the sediment core (Figure 11). The patterns of the lower PAH components from dimethylnaphthalene up to benz[a]pyrene are similar in both matrices, whereas the patterns of the higher ones from benz[e]pyrene and up are dominated by higher abundance in soil, particularly for 2-nitrofluorene. In high-amended soil and in sediment, particularly in the core, the higher PAHs occur in higher abundance than the lower ones, whereas the reverse is true for sludge. This indicates a higher persistence of the higher PAHs in the environment than the lower ones, which can be understood in terms of their higher chemical stability, lower water solubility and lower vapour pressure. Further differences between soil/sediment and sludge are the higher abundance of benz[b]-fluorantene in soil and sediment, and the higher abundance of retene in sludge (Figures 10-12). An extraordinary feature of the sludge component pattern is the extremely high abundance of 2-nitrofluorene, which stands out as the PAH component occurring in the highest concentration. This is worrying, since this compound is recognized as highly carcinogenic (Beije & Möller, 1988). The higher occurrence in sludge relative to the other matrixes - particularly sediment - suggests that this compound is degraded more readily than the other PAHs. However, it must be stressed that this result is based on only a single sludge sample. Furthermore, the specificity of the analysis may be lower than that of the other PAHs due to the lack of labelled spikes for nitro-PAHs, which at the time of analysis were not commercially available.

5.2.2 NPEs and PAEs
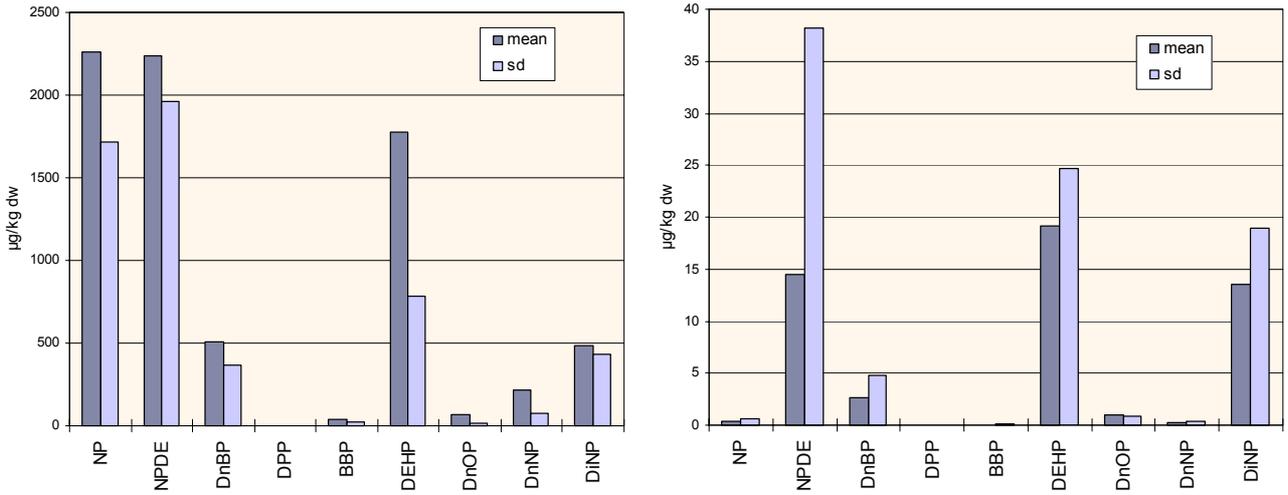
Figure 15 Abundance of NPEs and PAEs in high- (left) and low-amended soil (right), mean and standard deviation (sd).
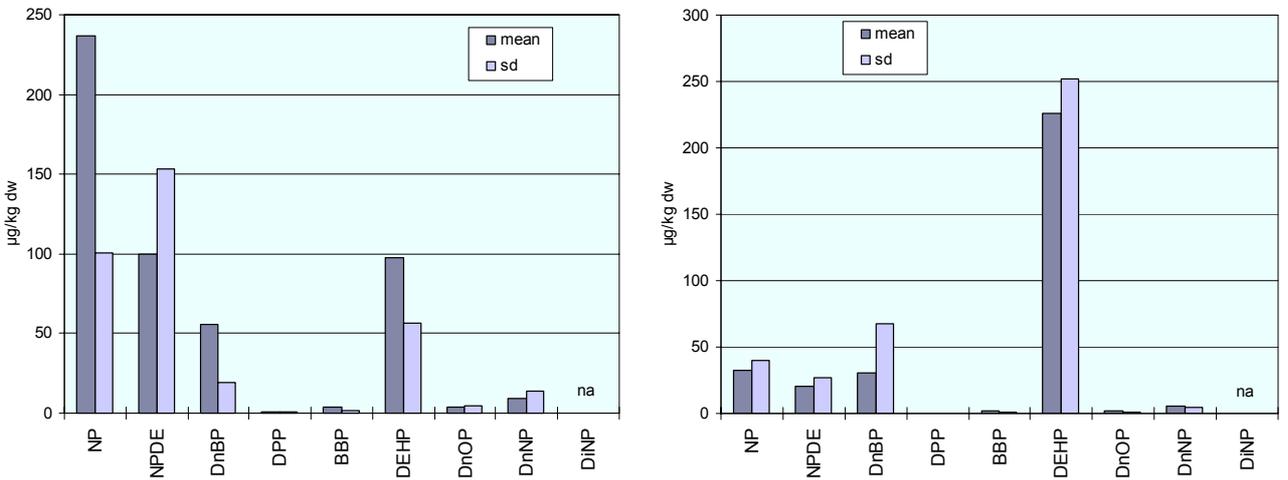

Figure 16 Abundance of NPEs and PAEs in fjord sediment (mean of Roskilde Vig, Bredning and Isefjord) (left) and core (right), mean and standard deviation (sd).
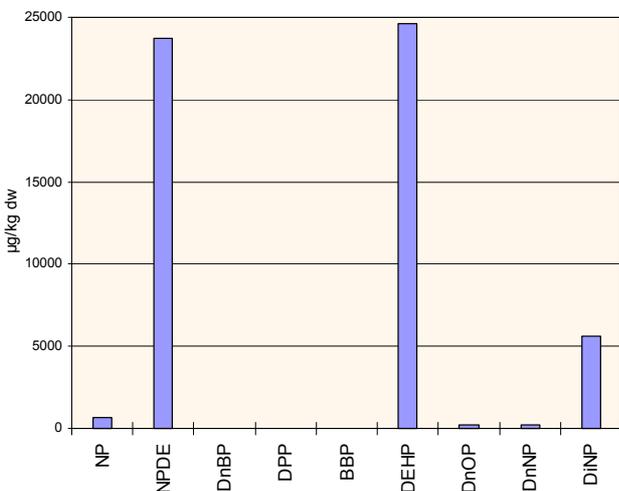

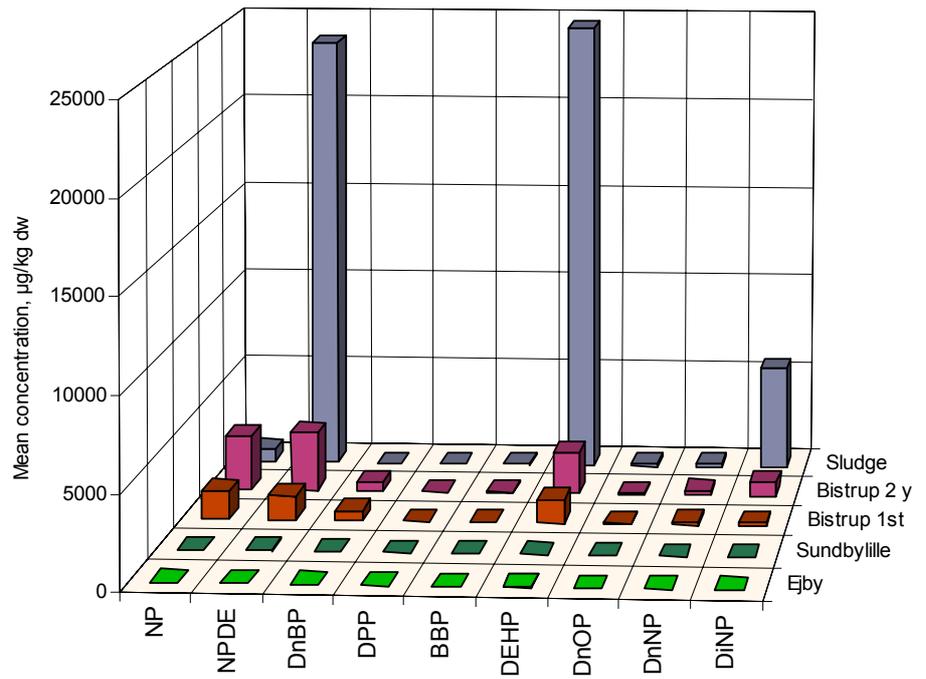**Figure 17** Abundance of NPEs and PAEs in sludge.

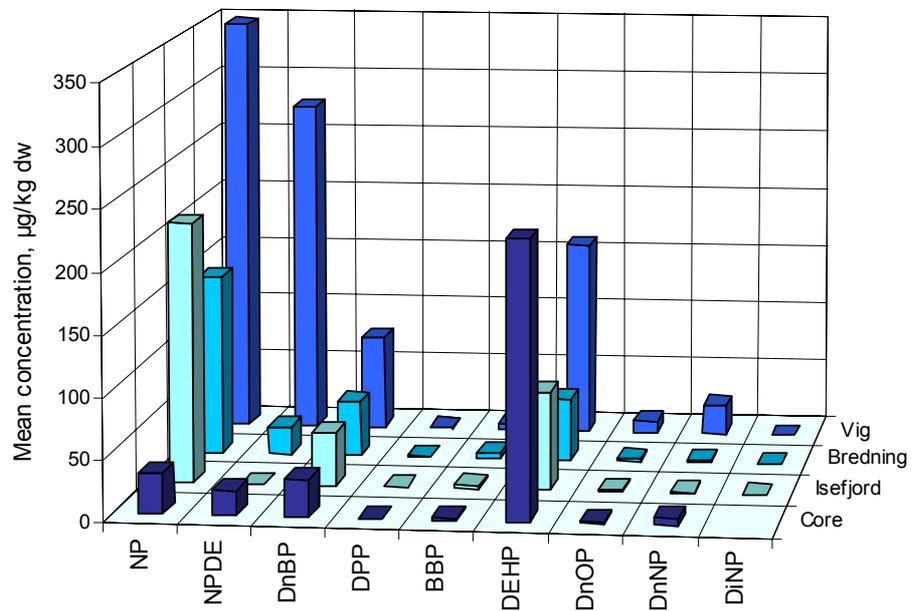**Figure 18** Concentrations of NPEs and PAEs, means of soil locations.

Figure 19 Concentrations of NPEs and PAEs, means of sediment locations.

The results of NPEs and PAEs in soil, sludge and sediment have been compiled from the previous studies (Vikelsøe et al. 1999; 2001). The subset of results selected here corresponds to the samples analysed for PAHs, PCBs etc. in order to make the results comparable.

Levels in sludge and soil

As noted from Figures 15-17, the concentrations are ten times lower in the highly sludge amended Bistrup soil than in sludge, and are vanishing small at Ejby and Sundbylille in comparison, being further 100 times lower, see also Figure 9.

Levels in sediment

The low occurrence of NPDE in sediment seen in Figure 16 is probably caused by chemical or biological hydrolysis to NP in water (Jones & Westmoreland, 1998), and in general by higher solubilities of NPEs compared to the other compounds (OECD, 1997). In sludge, very small concentrations of DnBP occur, indicating another source for this substance in the environment, probably atmospheric deposition.

Component pattern

As noted from Figure 15, a prominent difference between the pattern in high-amended and low-amended soils is the low abundance of NP the latter. The pattern for sludge is roughly similar with that of the highly sludge amended soil from Bistrup, apart from a much lower NP concentration in sludge. This is also seen from Figure 18. The patterns of sediment in Figure 19 display an interesting variation. The Bredning and Isefjord agree well, apart from the fact that NPDE is not detected in Isefjord, in spite of a considerable concentration in the Bredning. In the core, much lower amounts of NPEs were found, DEHP being the dominant component. This reflects the higher age of the sediment core, which contains a considerable portion of layers originating before NPEs were widely used.

In the following section on PCBs, it is concluded that the PCB-pattern in environmental samples is very constant, due to the high persistence of PCBs. The larger variation in the pattern of NPEs and PAEs reflects their lesser persistence and higher chemical and biological turnover in the environment, but may also reflect a larger historical variation in the use of these softeners and detergents.
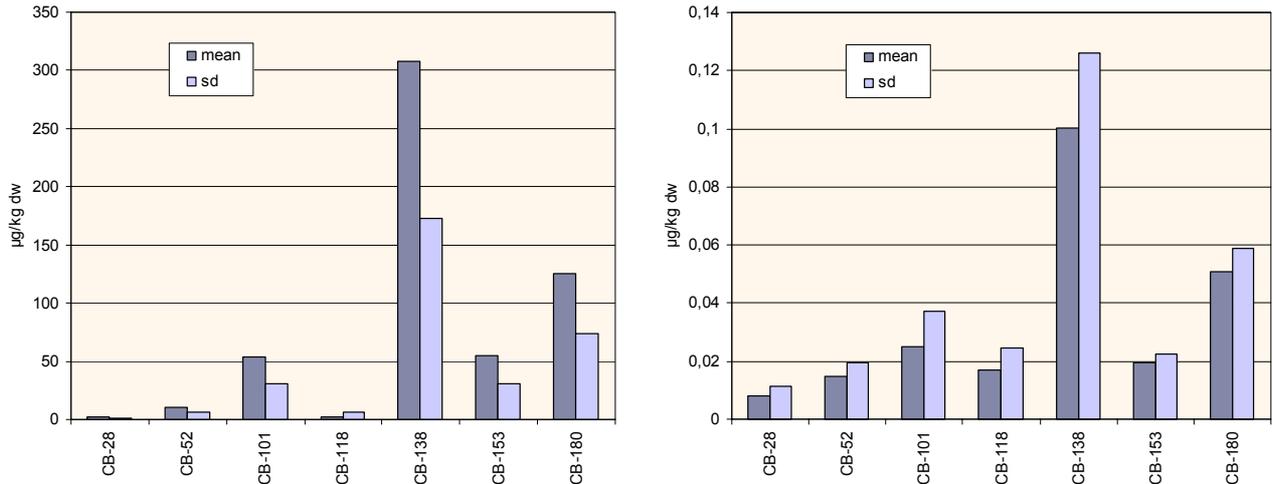
5.2.3 PCBs

Figure 20 Abundance of PCBs in high- (left) and low-amended soil (right), mean and standard deviation (sd).
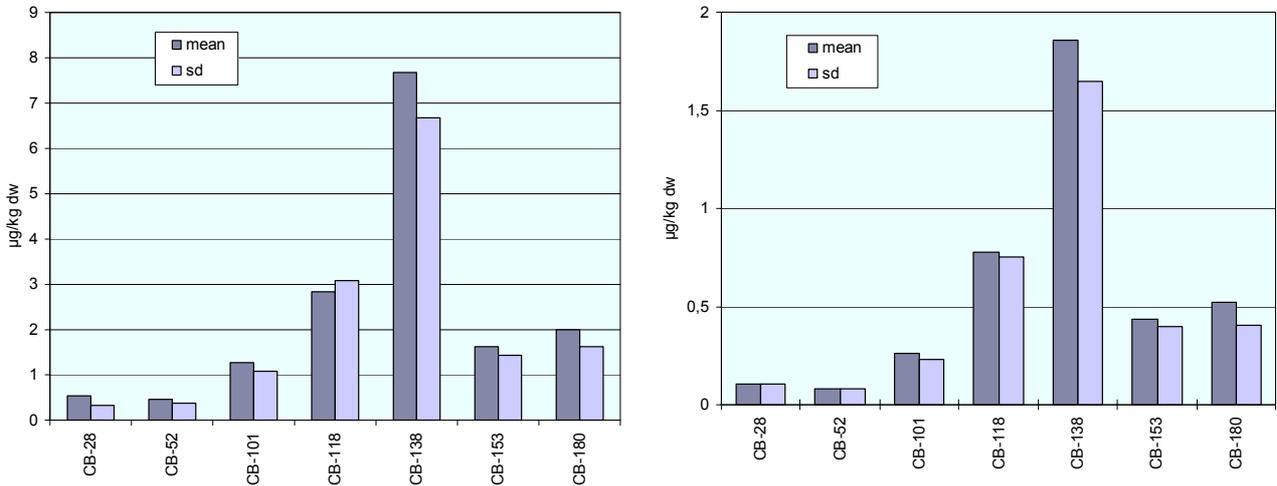

Figure 21 Abundance of PCBs in fjord sediment (Roskilde Vig, Bredning & Isefjord) (left) and sediment core (right), mean and standard deviation (sd).
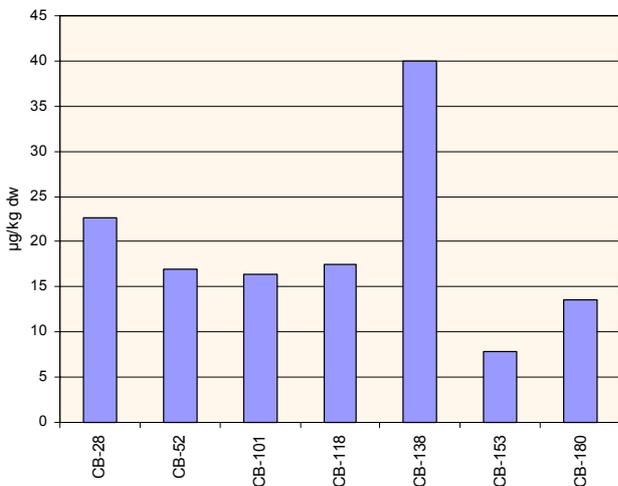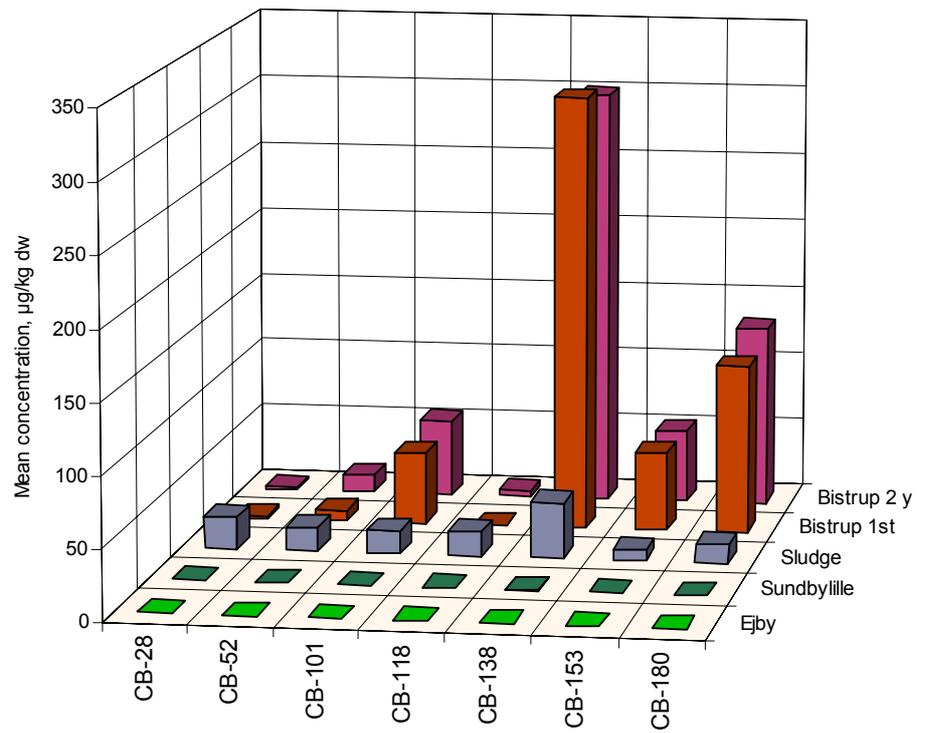

Figure 22 Abundance of PCBs in sludge.

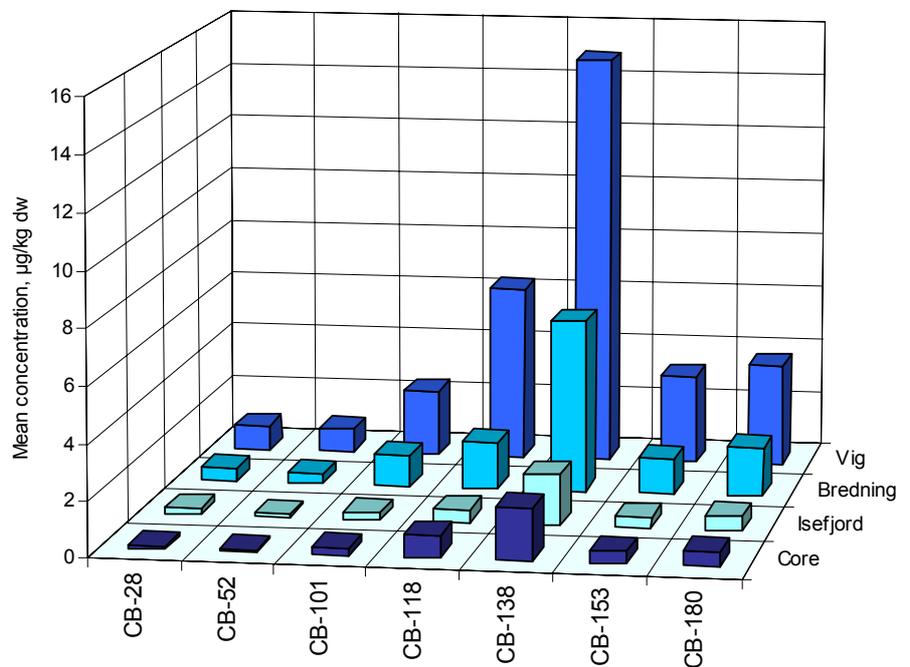**Figure 23**   Concentrations of PCBs, means of soil locations and sludge.

Figure 24   Concentrations of PCBs, means of sediment locations.

Levels in sludge and soil

It is noteworthy, as seen in Figures 20-22, that the abundance in the highly sludge amended soils from Bistrup are about eight times higher than in sludge. This indicates without question that a build up of PCBs have taken place during the many years of heavy sludge amendment at this location, to a level which still is high because of the extreme persistence of these compounds. The high concentration found in the present time may further have been enhanced by a higher concentration in sludge in the past, particularly before and some years after 1977, when PCBs were banned in Denmark. Figure 23 shows the high and almost identical concentrations of the two high-amended soils from Bistrup, taken with 2 years interval. The mean levels at the low-amended soils are roughly 3000 times lower (Figure 20). Inspection of Table 10 further reveals that the level in the preserved no-sludge soil at Ejby is considerably below the level at low-sludge soil at Sundbylille. These findings strongly suggest that sludge amendment, and not deposition, is the source of PCB-contamination at Sundbylille.

Levels in sediment

In contrast to the PAHs having similar soil and sediment abundance, the abundance of PCBs are about forty times lower in fjord sediment than in high-amended soil (Figures 20-22). The mean level in fjord sediment is only four times lower than in sludge, indicating that the PCBs are extremely persistent on the fjord-bottom. It also is reasonable to assume that in the past - before the ban - the amount of PCBs discharged into the fjord may have been substantially higher. Figure 24 shows a monotonously decreasing gradient from Roskilde Vig to Isefjord, as was also the case for PAH. Almost the same levels are found in the sediment core and in Isefjord.

Congener pattern

CB-138 is the most abundant congener in all matrixes. The congener patterns are similar for all diagrams, but in soil and sediment a higher occurrence of the higher PCBs from CB-138 and up is found, and lower occurrence of the lower ones compared to sludge, which shows a more equal component pattern. The higher persistence, lower solubility and lower volatility of the higher PCBs can explain this difference, as was the case for PAHs also. For unknown reasons, a low abundance of CB-28 and CB-118 is found in Bistrup soil compared to the other samples. The very constant congener pattern found in the environmental samples is an attribute of the high persistence of PCBs, and further reflects that the distribution in the environment has reached a constant state, perhaps many years ago.
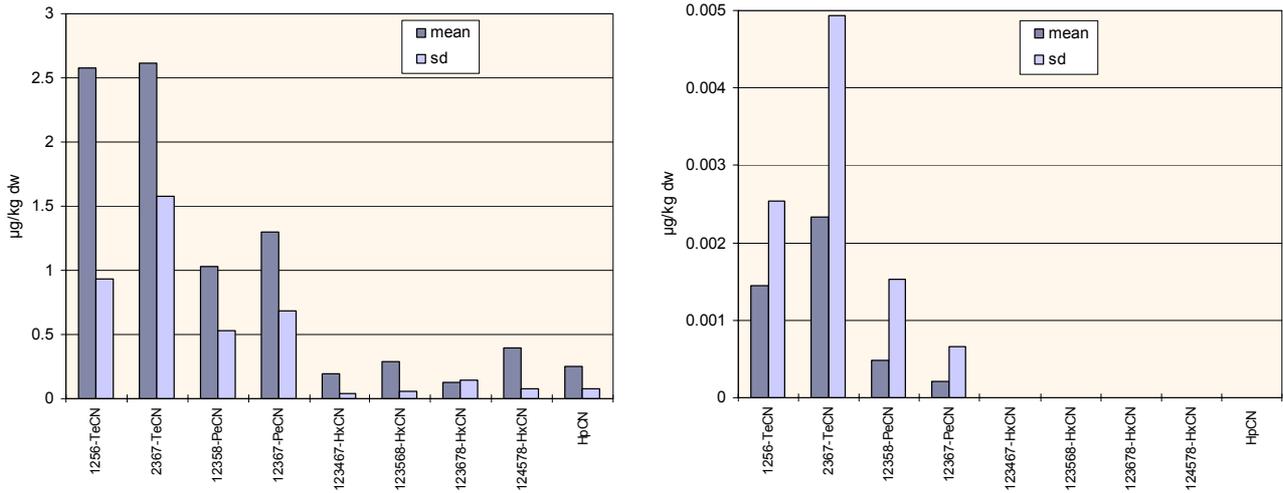
5.2.4 PCNs

Figure 25 Abundance of PCNs in high- (left) and low-amended soil (right), mean and standard deviation (sd).
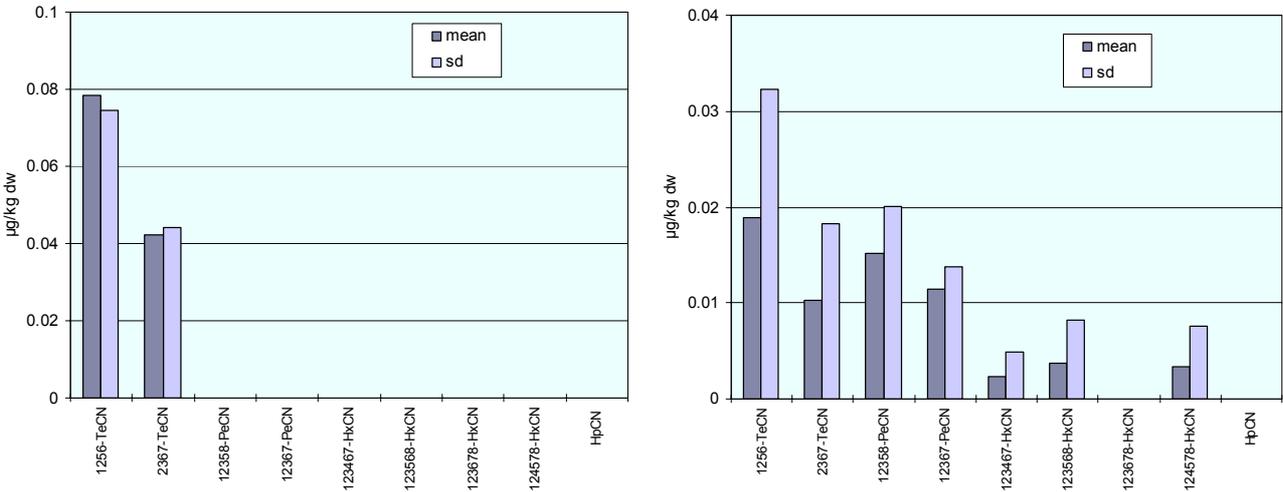

Figure 26 Abundance of PCNs in fjord sediment (Roskilde Vig, Bredning & Isefjord) (left) and sediment core (right), mean and standard deviation (sd).
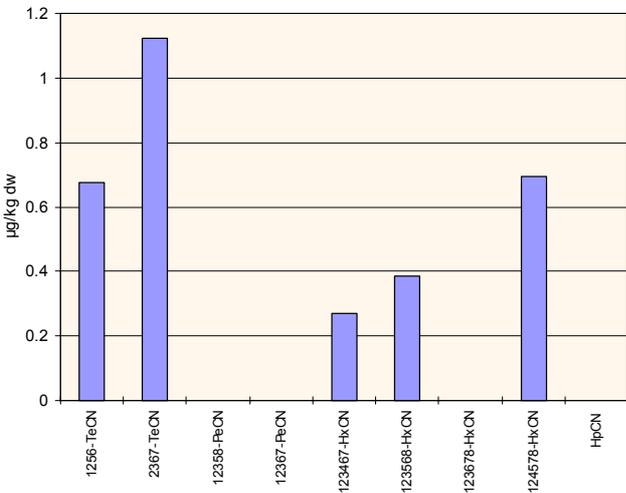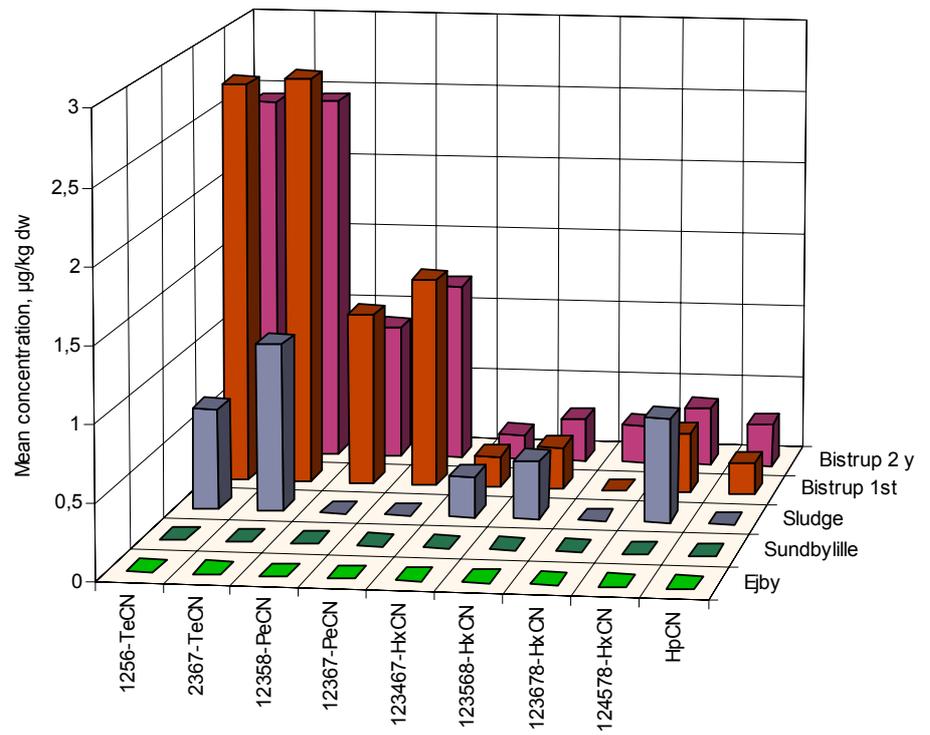

Figure 27 Abundance of PCNs in sludge.

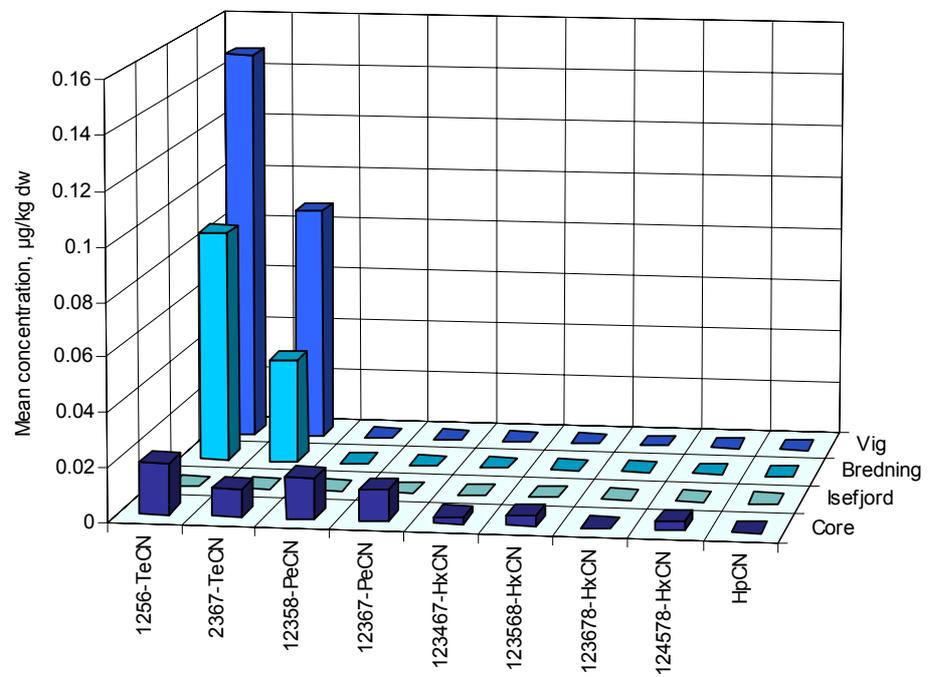**Figure 28**   Concentrations of PCNs, means of soil locations and sludge.

Figure 29   Concentrations of PCNs, means of sediment locations.

| *Levels in sludge and soil*	PCNs are newly recognised as persistent environmental pollutants (Crookes & Howe, 1993). As previously noted, the levels found in the present study are much lower than those of PCBs. The present results for sludge agree with a Swedish study (Nylund et al., 1992). In spite of the low levels, these compounds display the same tendency of higher abundance in sludge-amended soils compared to sludge, attesting to their high persistence. This may indicate concentration build-up. Alternatively, the discharges probably have been larger in the past when the PCNs were in use. They are also found as by-products in technical PCB-preparations (Yamashita et al., 2000), which may have been a further source during the PCB-epoch. The level in highly sludge-amended soil from Bistrup is about four times higher than in sludge (Figures 25-27), whereas the concentrations in soil from Sundbylille is about 500 times lower, vanishing low in comparison. The concentration in Bistrup 2 (second sampling, Figure 28) is somewhat lower than Bistrup 1 (first sampling), possible indicating a decreasing tendency. In the preserved soil from Ejby no PCNs were found.
	These findings taken together suggest that sludge for PCNs is the source of soil contamination, as was the case for PCBs.
Levels in sediment	The mean abundance in fjord sediment is about 15 times lower than in sludge, and in the sediment core it is about 40 times lower. In sediment from the lesser-polluted Isefjord no PCNs were found. This points to wastewater from Roskilde as the source. The low level in sediment agrees with the Swedish study by Nylund et al. (1992), which failed to detect PCNs in sediment from the Baltic Sea.
	PCNs were phased out many years ago (Crookes & Howe, 1993) as were the PCBs, and have probably reached the final distribution in the environment. Hence, the concentrations are at present expected to be slowly decreasing is soil, sludge and sediment.
Congener pattern	The most prominent congeners found in soil, sludge and sediment are the TeCNs (Figures 33 & 34). In contrast to PCBs, the lower congeners are more prevailing in the environmental samples than in sludge, which has a higher proportion of HxCNs. This is surprising, since the higher PCN-congeners probably are more persistent than the lower ones. This difference may probably be ascribed to a different component pattern of PCNs in the past, when it was in use, compared to the present pattern in sludge. The missing PeCN in sludge supports this view. Alternatively, the higher congeners may have been dechlorinated to the lower ones during the long stay in the environment.
	In Roskilde Vig and Bredning only TeCNs were found, whereas the core contains also the higher congeners in a more equal distribution (Figure 29). This suggests that those were more abundant in the past.

48

5.2.5 PBDEs
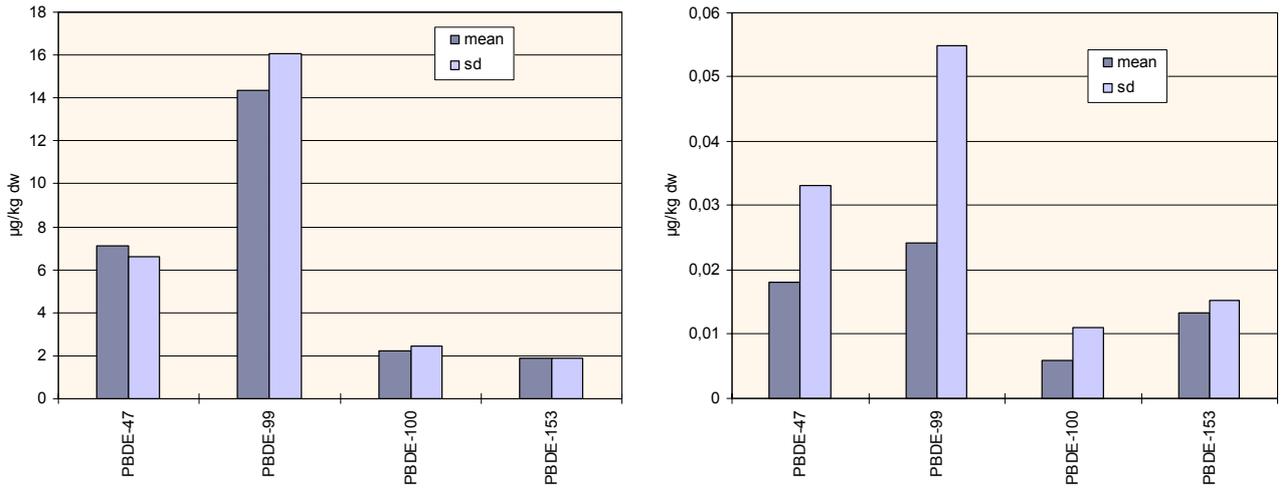
Figure 30   Abundance of PBDEs in high- (left) and low-amended soil (right), mean and standard deviation (sd).
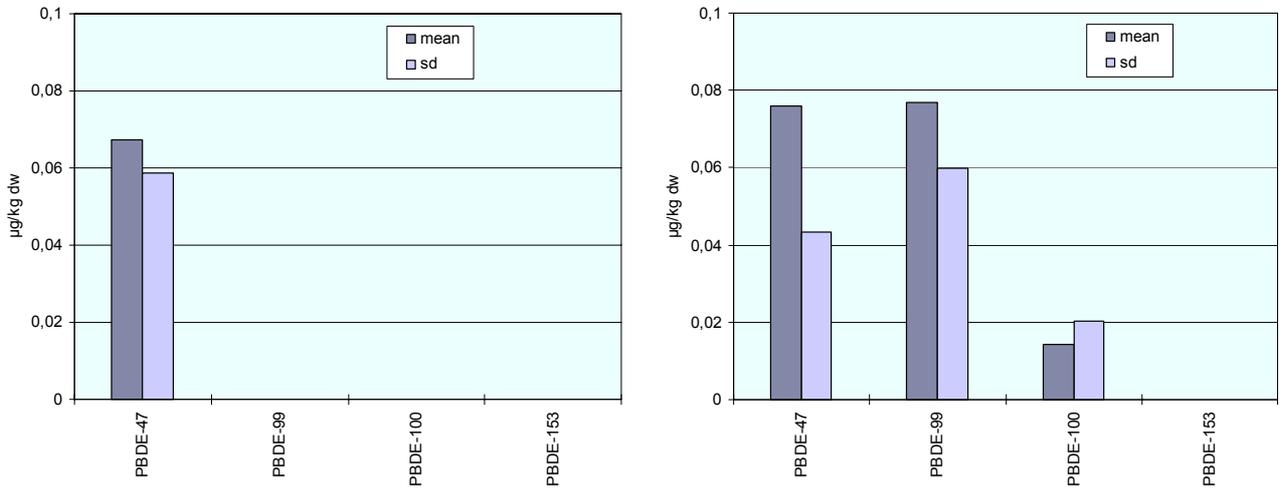

Figure 31   Abundance of PBDEs in fjord sediment (Roskilde Vig, Bredning & Isefjord) (left) and sediment core (right), mean and standard deviation (sd).
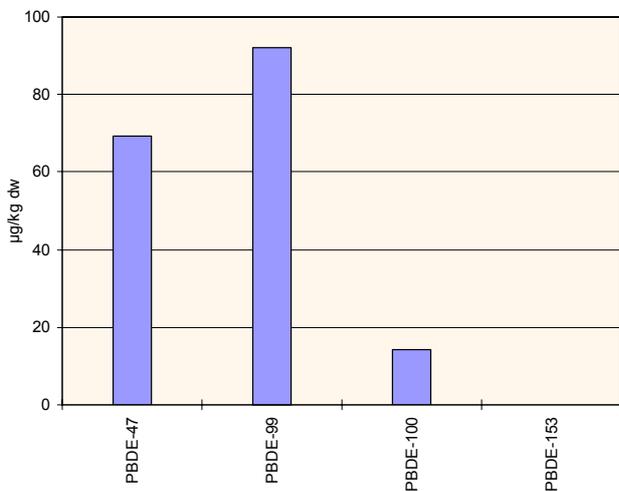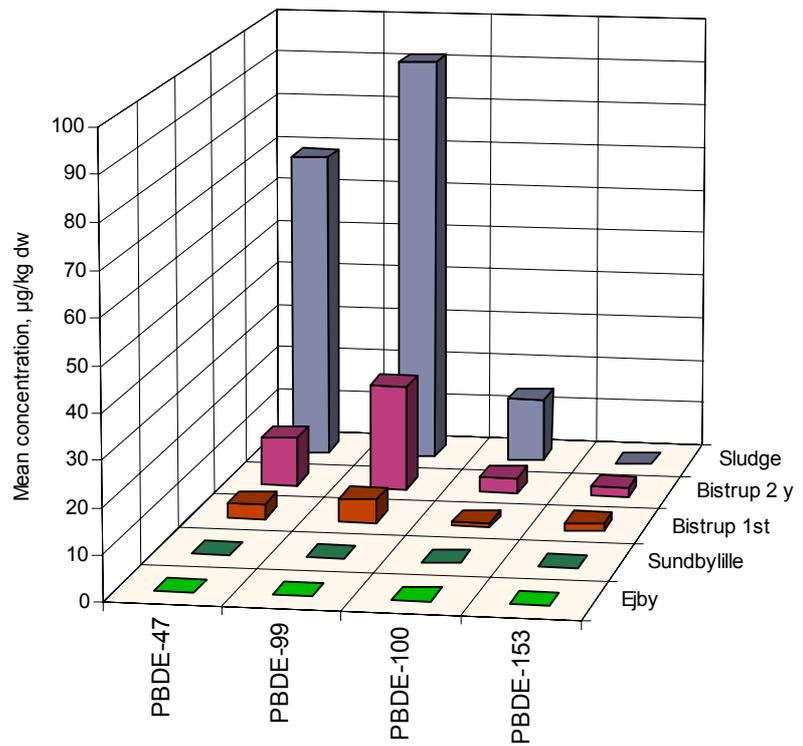

Figure 32   Abundance of PBDEs in sludge.

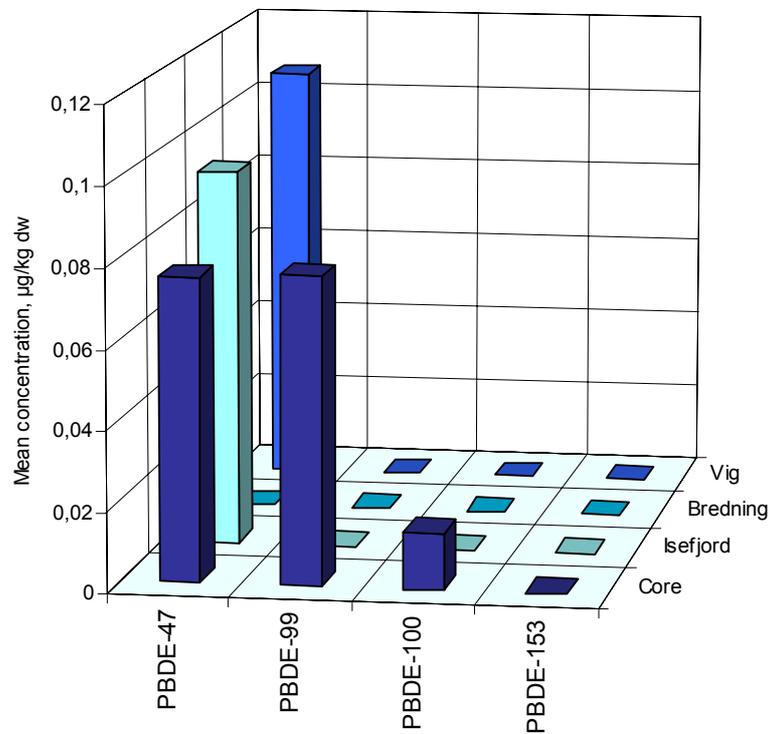**Figure 33**   Concentrations of PBDEs, means of soil locations and sludge.

Figure 34   Concentrations of PBDEs, means of sediment locations.

| *Levels in sludge and soil* | Remarkably (Figures 30 & 32), the PBDEs occur in considerable lower concentrations in the highly sludge amended Bistrup soils than in sludge, contrary to the findings for PCBs and PCNs. The current consumption of penta-BDEs (PBDE-99 & -100) is assumed to be low (European Commission, 2001), conflicting somewhat with the present data. |

Most probably the difference between PBDEs and PCBs arise because of a temporal increase in the concentration of PBDEs in sludge over the years. Hence, the steady state environmental distribution for PBDEs in the soil was not yet reached when the samples were taken, and has probably not yet been reached. Remarkably, the first sampling of high-amended soil (Bistrup 1st) display a substantial lower PBDE-concentration than the second one after 2 years (Bistrup 2y, Figure 33), suggesting an increasing PBDE-level. However, this difference might also be explained by spatial variations of concentrations in the high-amended field, which over the years received many batches of sludge in random places. The exact positions of Bistrup 1 and 2 are a few meters apart. In contrast, PCBs and PCNs were phased out many years ago, resulting in the present situation that their concentrations are slowly decreasing everywhere. In the low-amended soils much lower levels were found. However, a higher amount was found in the low-sludge soil from Sundbylille than in preserved no-sludge soil from Ejby (Table 10), a difference also found for PCBs.

Taken together, these findings suggest that sludge and not deposition is the main source of soil contamination in the case of sludge amended soils. However, in the case of the preserved soil (Ejby) that has not been subjected to sludge amendment deposition most probably plays the dominant role. This is an important conclusion, since the flame-retardants probably are emitted into the atmosphere from fire-protected plastics (such as computer cabinets, TV sets etc.), either though simple evaporation when heated during use, or during fires. The reasons why PBDEs occur in sludge are at present unknown. The compounds have been found in indoor air in rooms with computer cabinets. Presumably they contaminate the walls and floors in the buildings, and perhaps also the clothes, hair and skin of people. The compounds are then carried into the sewer system by washing.

| *Levels in sediment* | In the sediments the concentrations were on level with the low-amended soils (Figure 31). This also contrasts with the case for PCBs, and is probably also for sediment attributable to the comparatively recent use of PBDEs, which has not allowed a sufficient time to build up a significant concentration in sediment, and to the recent improvements in wastewater cleaning technology. |

An alternative explanation could be that PBDEs are not so persistent as PCBs and PCNs, which would impede or prevent the concentration build-up in soil and sediment. However, the PBDE-persistence is not known with great accuracy, and the explanations do not exclude each other.

| *Congener pattern* | In sludge, soil and sediment core PBDE-99 is the most abundant congener, followed by PBDE-47, PBDE-100 and PBDE-153. However, in the preserved soil of Ejby PBDE-153 was found in higher concentration than the lower congeners, indicating a higher persistence of PBDE-153, which allow a small concentration build-up in this very low contaminated environment (Table 10). |

Remarkably, in sediment from Roskilde Vig, Bredning and Isefjord only PBDE-47 was found (Figure 34) in concentrations on level with low amended soil. This is surprising, since it is mainly the higher congeners – particularly deca-BDE – that are currently in use. This discrepancy might be explained by a higher mobility in the environment (vapour pressure, solubility in water etc.) of the lower congeners, which will be the fastest to reach the environment. And as previously remarked, the wastewater cleaning technology of today may prevent the higher PBDEs in current use to reach the sediment in substantial amounts.

The lower congeners are also the most abundant in biota, which is worrying since these are expected to be the most toxic ones. According to an alternative, highly controversial explanation, the higher PBDEs might be debrominated to the lower ones in the environment. However, it is not, possible to draw any conclusions regarding this from the present study, since it does not include the deca-BDEs. But, as remarked previously, the occurrence of PBDE-153 in the preserved Ejby soil points to a relatively high stability of that congener.

5.2.6 Overall geographical distribution

The geographical distribution is summarised in the following figures, giving an overview of the abundance in sludge and in the environment, and illustrates the conclusions reached in the preceding paragraphs.

In Figure 35, the distribution of all substance sums in all locations is shown in a 3-dimensional plot. The most prominent features in the figure are the high PAH-level in sediment with decreasing gradient from Vig to Isefjord, the high PCB-level in high-sludge Bistrup soil, and the high NPE/PAE level in sludge. Furthermore, the low levels of all compounds in preserved Ejby soil and in low-sludge Sundbylille soil.
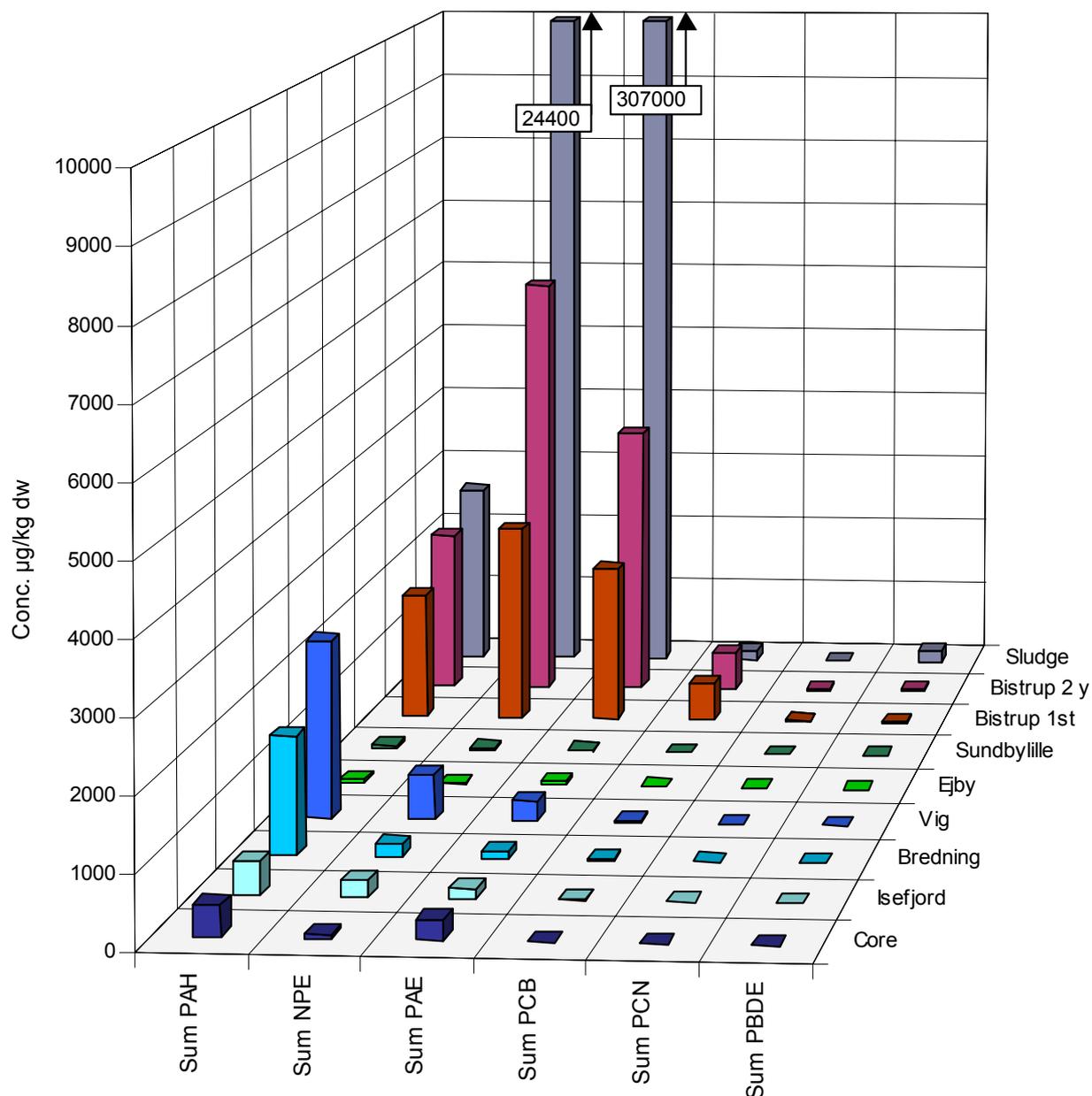

Figure 35 Geographical distribution overview of all compounds. Sums of substance groups, means of each location.

Figure 36 summarise the same data as Figure 35 in a logarithmic 2-dimensional bar graph, showing the substance concentrations − particularly the lower values − more clearly. The figure show of course the same features as Figure 35. But furthermore is seen that the PCBs in sediment follows the same pattern as the PAHs, and that the PCB-level in no-sludge Ejby soil is lower than in low-sludge Sundbylille soil. A further important observation is that the PBDE-levels in all environmental locations are lower than in sludge.
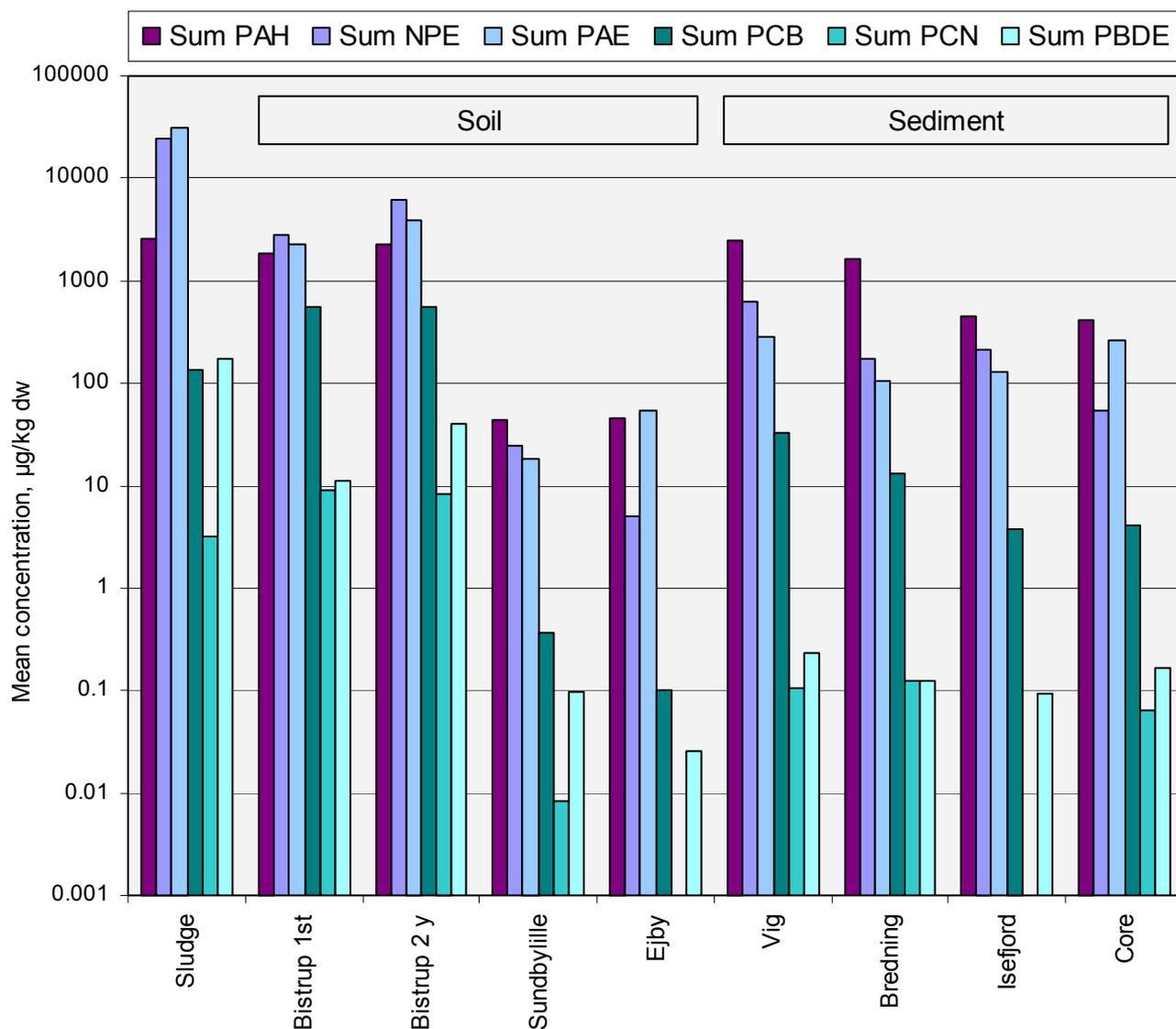

Figure 36 Geographical distribution overview of all compounds. Sums of substance groups, means of each location. Non-detected PCNs in Ejby and Isefjord are shown as blanks.

In Figure 37 the relative abundances for all substance sums are shown for each location, forming a substance profile. The relative abundance of each substance sum is calculated by division of the substance sums with the total substance sum for the location (i.e. the sum of sums), set to 100 %. Remarkably, the relative abundance of PAHs is highest in sediment, and lowest in sludge. A further noteworthy result is the lower relative abundance of PCBs is in sludge compared to the environmental matrixes, with the exception of Ejby where no sludge was applied. The PCNs follow a similar pattern. In contrast, higher relative abundances are found in sludge for NPEs, PAEs and PBDEs than in the environmental matrixes.
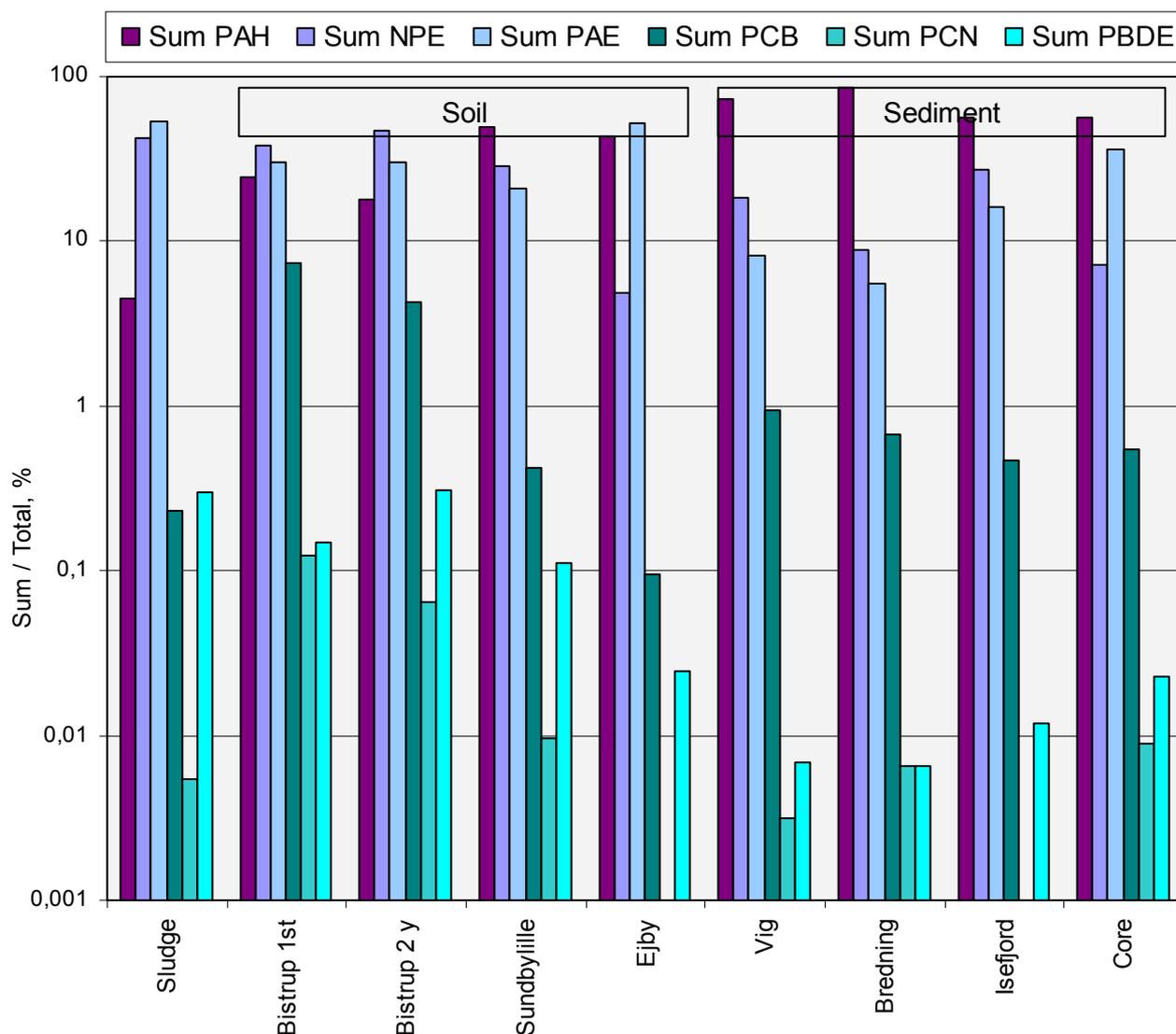

Figure 37 Geografical distribution of substance profiles. For each location the relative abundance of each substance has been calculated by normalising the sum by division with the total substance sum of that location, set to 100 %.

5.3 Analysis of correlation

The previous section contained qualitative observations of the distribution of the investigated substances in the environment. This chapter addresses the important aspect of the statistical significance of the differences in substance distribution in the matrixes studied.

5.3.1 Correlations between locations

Correlation analysis

An analysis of correlation was performed by calculating the (normal parametric) coefficients of correlation between locations ("locational correlations"), comprising different selections of substances or averages of substances ("substance profiles"). That is, between the columns of Table 10. The statistical significance of the correlation coefficients may be determined by calculating t according to formula (Hald, 1973).

$$t = \frac{r}{\sqrt{1-r^2}} \sqrt{f} \qquad (1)$$

The test-variable t is t-distributed. From t and the degrees of freedom $f = n - 2$ is possible to calculate the level of significance p, making use of the t-distribution. An alternative method, used in the present investigation, is to calculate a critical value (r_{crit}) above which correlation coefficients are significant different from 0. From given f and p the critical value of t (t_{crit}) is found using the t-distribution. r_{crit} is then calculated from t_{crit} by Equation 2, which is derived from Equation 1 solved for r.

$$r_{crit} = \frac{t_{crit}}{\sqrt{f + t_{crit}^2}} \qquad (2)$$

In the following tables, as well r_{crit} as p are shown in footers. The level of significance used is $p < 0.05$ or $p < 0.01$, respectively, or both. Only correlation coefficients significant different from 0 on the $p < 0.05$ level are given, those only weakly significant ($0.05 < p < 0.01$) in *italics*, those highly significant ($p < 0.01$) in normal writing. To enhance the significant correlations, non-significant correlation coefficients are not shown in the tables, but indicated as blank spaces.

Similarity of profiles

A significant correlation between two samples indicates a similarity between the relative occurrences (i.e. the distribution) of the substances. In other words, that the "substance profiles" at the locations are similar, displaying a similar pattern. The absolute concentration level of a sample does not affect the outcome of this type of correlation analysis, only the relative mutual concentrations within one sample compared to the other.

All substances

In Table 11 the correlation coefficients for complete data comprising all substances are given ("full substance profile"). That is, the full columns in Table 10 excluding substance sums. In the table only correlation coefficients > 0.25 (r_{crit}) which are significantly ($p < 0.05$) different from 0 are given.

Table 11   Correlation between locations for complete substance sets ("full substance profiles").

Complete data set	Roskilde	Bistrup 1st	Bistrup 2 y	Sund-bylille	Ejby	Vig	Bred-ning	Ise fjord	Core
Matrix	*Sludge*	*Soil*	*Soil*	*Soil*	*Soil*	*Sedi*	*Sedi*	*Sedi*	*Sedi*
Sludge	1								
Bistrup1	0.71	1							
Bistrup2	0.77	0.97	1						
Sundbylille	0.82	0.64	0.70	1					
Ejby	0.65	0.47	0.47	0.54	1				
Vig		0.54	0.49	0.57	0.48	1			
Bredning		*0.30*		0.37	0.42	0.95	1		
Isefjord		0.70	0.63		0.42	0.65	0.60	1	
Core	0.63	0.61	0.51	0.50	0.96	0.56	0.50	0.51	1

$n = 43$, $p < 0.05 \approx r_{crit} = 0.25$, $p < 0.01 \approx r_{crit} = 0.35$, blank space = not significant.

As seen from Table 11, the distribution of substances ("substance profile") in sludge is highly correlated with the profiles in all soils, and also with those the sediment core, but not with sediment in Roskilde Vig, Bredning and Isefjord.

The substance profiles in highly sludge-amended soil at Bistrup 1st sampling and 2 years after are extremely significantly intercorrelated, and those in all soils are highly intercorrelated. Also those of the low sludge-amended soils are significantly correlated, and - not surprising - more so with each other than with those of the high-amended soils.

All sediment substance profiles are highly intercorrelated, in particular Roskilde Vig and Bredning.

The substance profiles of the soils are in most cases significantly correlated with those of the sediment. Roskilde Vig show a somewhat higher correlation with the soil than the Bredning, perhaps expected because of the closeness to the WWTP outlet. Remarkably, Isefjord is highly correlated with the high-amended soils, in spite of the fact that the concentrations the latter place are significantly higher, and the Isefjord is hydraulically unrelated to Roskilde. Also, the sediment core is highly significant correlated with Ejby. Those are exceptions without any straightforward explanation, but do reflect the ubiquitous and long lasting character of the substance profile. Furthermore, it is a warning that these correlation coefficients should not be over-interpreted, since random significant correlations may occur.

In conclusion, this correlation analysis demonstrates that substance profiles occurring in the different matrixes are similar in general, and in most cases more so in related matrixes.

The correlation between the different types of matrixes is an important issue. To investigate this the data for similar locations are averaged, arranging the data in five matrixes:

- Sludge
- Highs amended soil: mean of Bistrup 1 & 2
- Low and not amended soil: mean of Sundbylille & Ejby
- Sediment: mean of Vig, Bredning & Isefjord
- Core of sediment mean of all core depths

The preceding correlation analysis shows that the matrix-locations are highly intercorrelated, making is meaningful to pool them in the above scheme. A correlation analysis is performed on this data set, and the correlation coefficients significantly (p<0.05) different from 0 given in Table 12, leading to a matrix-oriented version of the correlation analysis.

Table 12   Correlation between matrixes, complete substance set.

Complete set	Sludge	High soil	Low soil	Sediment	Core
Sludge	1				
High soil	0.76	1			
Low soil	0.82	0.64	1		
Sediment		0.47	0.54	1	
Core	0.63	0.55	0.83	0.57	1

n = 43, p < 0.05 ≈ r_{crit} = 0.25, p < 0.01 ≈ r_{crit} = 0.35, blank space = not significant.

This analysis – although simplified – reaches the same conclusions as the previous, more complete one. But it does not include the correlations within matrixes. A lower correlation between high soil and sludge is found, compared to low soil and sludge. This may reflect the historical development in the sludge substance profile, since the high soil field probably still contains compounds from the sludge produced many years ago.

The correlation between locations for substance sums is now investigated. After all, the substance sums reflect a most important aspect of the full substance profile, namely the distribution between the amounts in the groups of substances. This analysis neglects the internal group component pattern, since the summation average out the internal variations. The analysis is carried out as the previous one using substance sums in stead of the full substance sets on the same matrix-means. A major drawback of this simplification is the low number of sums, resulting in only 4 degrees of freedom in the correlation coefficients, which leads to a low sensitivity of the statistical tests. The result of the analysis is shown in Table 13. Only correlation coefficients significantly (p < 0.05) different from 0 are shown.

Table 13   Correlation between matrixes for all substance sums.

All Σsubst	Sludge	High soil	Low soil	Sediment	Core
Sludge	1				
High soil	*0.86*	1			
Low soil			1		
Sediment			*0.78*	1	
Core			0.97	*0.85*	1

n = 6, p < 0.05 ≈ r_{crit} = 0.73, p < 0.01 ≈ r_{crit} = 0.88, blank space = not significant.

As seen from Table 13, the substance sums of sludge are now only significantly correlated with the high-amended soil, as one would expect. Furthermore, in contrast to correlations on the full substance set, the soils are not intercorrelated. The low-amended soil is still correlated with sediment and core. All significant correlations occurring in Table 13 are also found in Table 12.

Substance groups   The correlations between locations for complete substance set as well as for the sums gives a general overview of the substance distribution, but gives no indication of the correlation for substance groups. This is addressed in the following, where locational correlations for each substance group, comprising all its individual substances, are given.

For the PAHs (Table 14) no significant correlations were found between sludge and the environmental locations. Surprisingly, sludge is not significantly correlated with the high-amended soils at Bistrup. In contrast, the environmental locations are all highly intercorrelated.

Table 14   Correlations between locations for PAHs.

PAHs	Sludge	Bistrup 1st	Bistrup 2 years	Sund-bylille	Ejby	Vig	Bred-ning	Isefjord	Core
Matrix	Sludge	Soil	Soil	Soil	Soil	Sedi	Sedi	Sedi	Sedi
Sludge	1								
Bistrup 1st		1							
Bistrup 2y		1.00	1						
Sundbylille		0.71	0.73	1					
Ejby		0.73	0.76	0.97	1				
Vig		0.86	0.89	0.80	0.83	1			
Bredning		0.83	0.87	0.84	0.87	0.99	1		
Isefjord		0.61	0.64	0.88	0.85	0.80	0.84	1	
Core		0.96	0.98	0.76	0.79	0.91	0.89	0.70	1

n = 15, p = 0.05 ≈ r_{crit} = 0.44, p = 0.01 ≈ r_{crit} = 0.59, blank space = not significant.

It was attempted to carry out an analysis for NPEs and PAEs together, but this yielded sporadic results. This is hardly surprising, since after all, the PAEs and NPEs belongs to different substance groups. It is not possible to carry out this type of correlation analysis for NPEs alone because of 0 degrees of freedom. Hence, the analysis was done for PAEs alone (Table 15). Significant correlations were found between sludge and the environmental locations, and between most of the environmental locations. However, the preserved Ejby soil is not correlated with the sediments, and the sediment in the Bredning is not correlated with most soils.

Table 15   Correlations between locations for PAEs.

PAEs	Bjerg-marken	Bistrup 1st	Bistrup 2 years	Sund-bylille	Ejby	Vig	Bred-ning	Isefjord	Core
Matrix	*Sludge*	*Soil*	*Soil*	*Soil*	*Soil*	*Sedi*	*Sedi*	*Sedi*	*Sedi*
Sludge	1								
Bistrup 1st	0.89	1							
Bistrup 2 y	0.98	0.93	1						
Sundbylille	0.97	*0.88*	0.99	1					
Ejby	*0.87*		0.90	0.95	1				
Vig	*0.83*	0.99	*0.87*	*0.80*		1			
Bredning		0.90				0.93	1		
Isefjord	*0.81*	0.98	*0.86*	*0.80*		0.99	0.96	1	
Core	0.96	0.96	0.94	0.90		0.94	*0.78*	0.92	1

n = 6, p = 0.05 ≈ r$_{crit}$ = 0.73, p = 0.01 ≈ r$_{crit}$ = 0.88, blank space = not significant.

For PCBs (Table 16) all locations are highly intercorrelated, particularly the environmental ones, attesting to the high persistence and constant congener profile of PCBs in the environment. The correlation with sludge is weaker, attributable to the higher occurrence of the lower PCBs in that matrix (see Figure 23). This may reflect that the historical development has lowered the occurrence of the higher PCBs in sludge, which still are found in the environment.

Table 16   Correlations between locations for PCBs.

PCBs	Bjerg-marken	Bistrup 1st	Bistrup 2 years	Sundby-lille	Ejby	Vig	Bred-ning	Isefjord	Core
Matrix	*Sludge*	*Soil*	*Soil*	*Soil*	*Soil*	*Sedi*	*Sedi*	*Sedi*	*Sedi*
Sludge	1								
Bistrup 1st	*0.73*	1							
Bistrup 2 y	*0.72*	1.00	1						
Sundbylille	*0.73*	0.98	0.99	1					
Ejby	*0.75*	0.98	0.98	0.96	1				
Vig	*0.78*	0.88	0.87	0.89	0.84	1			
Bredning	*0.81*	0.95	0.94	0.95	0.92	0.98	1		
Isefjord	0.83	0.95	0.94	0.94	0.93	0.97	1.00	1	
Core	*0.76*	0.88	0.88	0.90	0.85	1.00	0.98	0.98	1

n = 7, p = 0.05 ≈ r crit = 0.67, p = 0.01 ≈ r crit = 0.83, blank space = not significant.

For the PCNs (Table 17) sludge is highly correlated with the sludge-amended soils, and with the sediment in Roskilde Fjord. It is not correlated with the no-sludge soil Ejby, or with the sediment in neighbour fjord Isefjord, where no PCNs were found. Ejby is not correlated with Sundbylille, no doubt because the latter is sludge amended whereas Ejby is not. This important finding points to sludge as the source for PCNs in soil. The sediment from Roskilde Vig and Bredning are highly correlated due to their unique profile (see Figure 29).

Table 17 Correlations between locations for PCNs.

PCNs	Bjerg-marken	Bistrup 1st	Bistrup 2 years	Sundby lille	Ejby	Vig	Bred-ning	Isefjord	Core
Matrix	*Sludge*	*Soil*	*Soil*	*Soil*	*Soil*	*Sedi*	*Sedi*	*Sedi*	*Sedi*
Sludge	1								
Bistrup 1st	*0.62*	1							
Bistrup 2 y	*0.63*	0.99	1						
Sundbylille	*0.74*	0.90	0.91	1					
Ejby		*0.59*	*0.61*		1				
Vig	*0.66*	0.86	0.89	0.78	0.84	1			
Bredning	*0.59*	0.82	0.85	*0.70*	0.90	0.99	1		
Isefjord	u	u	u	u	u	u	u	1	
Core		0.84	0.80		*0.63*	*0.67*	*0.68*	u	1

n = 9, p = 0.05 ≈ r_{crit} = 0.58, p = 0.01 ≈ r_{crit} = 0.75, u = undefined, blank space = not significant.

For the PBDEs (Table 18), the low number of congeners makes the statistical tests insensitive, but even so, some significant correlations were found. The sludge and sludge-amended soils are highly intercorrelated. It is noteworthy that the no-sludge soil at Ejby is not correlated with the amended soils, indicating that sludge-amendment is responsible for the PBDEs found at the amended locations. In contrast to soil, the correlations of PBDE involving sediment locations seem to be more sporadic. Thus, the core is highly correlated with sludge, and Roskilde Vig with Isefjord.

Table 18 Correlations between locations for PBDEs.

PBDEs	Bjerg-marken	Bistrup 1st	Bistrup 2 years	Sundby-lille	Ejby	Vig	Bred-ning	Ise-fjord	Core
Matrix	*Sludge*	*Soil*	*Soil*	*Soil*	*Soil*	*Sedi*	*Sedi*	*Sedi*	*Sedi*
Sludge	1								
Bistrup 1st	*0.94*	1							
Bistrup 2 y	*0.94*	*0.97*	1						
Sundbylille	0.99	*0.97*	*0.97*	1					
Ejby					1				
Vig						1			
Bredning	u	u	u	u	u	u	1		
Isefjord						1.00	u	1	
Core	0.98			*0.96*			u		1

n = 4, p = 0.05 ≈ r_{crit} = 0.90, p = 0.01 ≈ r_{crit} = 0.98, u = undefined, blank space = not significant.

The following conclusions can be drawn from the between locations correlation analysis:

- substance profiles occurring in the different matrixes are similar in general, and in most cases more so in related matrixes.

- The distribution of the full set of substances in sludge is highly correlated with those in all sludge amended soil locations, but not with those in the sediment locations.

- The substance distributions of all soils are highly intercorrelated, as are those of sediments.

- For the individual substance groups, the correlation between the environmental matrixes are generally higher than between those of sludge and the matrixes. This is particularly pronounced for PAHs.

5.3.2 Correlations between substances

The distribution in the environment of the different substances is an important issue, which is addressed is this section. In stead of investigating if the substance distributions (profiles) in different locations are correlated, the question is reversed, asking if the distribution of a particular substance in the environment (i.e. all locations) is similar to (i.e. correlated with) that of another substance ("substance correlations"). This type of correlation analysis can be carried out for all substances or groups of substances, and may comprise all locations or subsets of locations or matrixes.

The analysis of correlation is performed by calculating the coefficients of correlation between the rows in Table 10. Because of the large number of substances and combination of locations, this leads to an enormous number of correlation coefficients. Thus 44 substances lead to 946 correlation coefficients.

To handle this wealth of data and bring it on a form possible to overview, it is necessary to use some form of simplification. For instance, the many correlation coefficients of the complete correlation table can be summarised by counting the number of significant correlations in relation to the number of correlation coefficients in suitably grouped sections of the table. Also, performing the correlation analysis on the substance sums instead of on the complete data set reduces the correlation table to manageable dimensions. Both methods are used in the following.

Substance sums all locations An analysis of correlations was performed on substance sums for all locations (Table 19), and a further one excluding sludge (Table 20). Only correlation coefficients significant ($p < 0.05$) different from 0 are shown, those highly significant ($p < 0.01$) in normal writing, those only moderately significant ($0.05 < p < 0.01$) in *italics*.

Table 19   Correlations between substance sums for all matrixes

All locs	ΣPAH	ΣNPE	ΣPAE	ΣPCB	ΣPCN	ΣPBDE
ΣPAH	1					
ΣNPE	0.79	1				
ΣPAE	*0.58*	0.99	1			
ΣPCB				1		
ΣPCN				0.99	1	
ΣPBDE		1.00	0.99			1

n = 9, p = 0.05 ≈ r_crit = 0.58, p = 0.01 ≈ r_crit = 0.75, blank space = not significant.

As seen from Table 19, including all matrixes highly significant correlations are found for sums of NPEs/PAEs, PCBs/PCNs, PBDEs/PAEs and PBDEs/NPEs. In contrast, PCBs and PCNs are not correlated with the others.

Performing the analysis on environmental matrixes only by omitting sludge (Table 20), it is found that the substance sums of NPEs, PAEs, PCBs, PCNs, and PBDEs highly intercorrelated. These are synthetic chemicals, whereas the non-synthetic PAHs are only correlated with NPEs, and only weakly so. This is an important conclusion. All significant correlations in Table 19 are also found in Table 20. Some are extremely significant, for example NPEs/PAEs, which may be due to a common source in washing water. Also PCBs/PCNs are extremely significant, probably because PCNs occurs as an impurity in technical PCB-preparations, and because of parallel usage. PBDEs are higher correlated with NPEs/PAE than with PCBs/PCNs. This may be due to parallel recent histories in the use of PBDEs/NPEs/PAEs, whereas PCBs were phased out long since.

Table 20   Correlations between substance sums for all environmental matrixes (i.e. exc. sludge).

Soil & sedi	ΣPAH	ΣNPE	ΣPAE	ΣPCB	ΣPCN	ΣPBDE
ΣPAH	1					
ΣNPE	*0.62*	1				
ΣPAE		0.99	1			
ΣPCB		0.91	0.95	1		
ΣPCN		0.89	0.93	1.00	1	
ΣPBDE		0.98	0.96	0.84	0.81	1

n = 8, p = 0.05 ≈ r_crit = 0.62, p = 0.01 ≈ r_crit = 0.79, blank space = not significant.

Comparing Tables 19 and 20, it is further seen that excluding sludge yields a clearer picture of the correlation between the substance sums. This indicates that sludge is different from soil and sediment, expected since sludge is a source rather than an environmental matrix. Particularly the lack of correlation between PCBs and PCNs and the other substances in Table 19 stands out. The reason is probably the lower relative abundant of PCBs and PCNs in sludge compared to soil and sediment, see Figure 37. The

difference probably arises because the substance profile in wastewater sludge adjusts quickly to changes in input conditions, such as the phasing out of PCBs. In contrast, the environmental matrixes accumulate these persistent chemicals. The special character of sludge is in concordance with the locational correlation analysis, which generally showed somewhat higher correlations within the environmental matrixes than between sludge and the matrixes. For the above reasons, sludge is excluded in the following analysis of correlation. After all, it is the distribution in the environment which is the primary aim of the present study.

Full data set exc. sludge A correlation analysis is performed on the full set of data excluding sludge (and excluding sums). Between the 44 compounds 946 correlation coefficients exist (excluding the diagonal), 597 of which turned out to be significant ($p > 0.05$) different from 0.

The result of this is summarised in Table 21, which shows the number of significant correlations as percent of the number of correlations in each group. For example, between the 12 PAHs there are 66 correlation coefficients, of which 61 are significant ($p < 0.05$) different from zero. This gives a score for the within PAH-correlation of 61/66, or 92 %. Also, between the 7 PCBs and the 12 PAHs there are 84 correlation coefficients, of which 39 are significant different from zero, giving a score of 39/84, or 46 %. In contrast to the correlation coefficient tables having 1's in the diagonal, the diagonal in Table 21 gives a score for the within-group correlation, shown in boldface.

Table 21 Summary of correlations between substances for environmental locations. % significant correlations.

Soil & sediment	PAHs	NO$_2$-PAHs	NPEs	PAEs	PCBs	PCNs	PBDE
z	12	3	2	7	7	9	4
PAHs	**92**						
NO$_2$PAH	*22*	**0**					
NPEs	*42*	*33*	**100**				
PAEs	*46*	*38*	86	**90**			
PCBs	*46*	*29*	86	88	**71**		
PCNs	*31*	*33*	100	94	83	**86**	
PBDEs	*33*	*33*	100	89	86	100	**100**

$n = 8$ (number of locations), $p = 0.05 \approx r_{crit} = 0.62$,
z = number of substances in group
Total number of significant correlations = 456
Total number of correlation coefficients = 946

As seen from Table 21, high within group correlation scores (> 70%) are found for all substance groups, except NO$_2$PAH. Furthermore, the correlation scores in Table 21 roughly follow the correlation between the sums of substances in Table 20. Thus, the correlation between substance sums gives the same general picture of the distribution in the environment as the more complete analysis of correlations between all individual substances. All substance groups other than PAH are highly intercorrelated in the environmental samples, according to as well Table 20 as 21. On the

other hand, in both tables the PAHs and NO_2-PAHs stands out as generally poorly correlated with the other groups, as the scores are all below 50%. This is illustrated in Figure 38, which show the sums of substances for all locations normalised with the maximum sum occurrence for each substance group (set to 100%).

The normalised substance distributions would result in the same correlation coefficients as the un-normalised ones given in Table 13. Figure 38 is analogous to Figure 37 in the previous chapter. It is clearly seen from Figure 38 that PAHs stands out by a disproportionately high abundance in sediment, which explain the lack of correlation between PAHs and the other substances. As already mentioned, this is a surprising finding. For some reason PAHs seems to be ubiquitously abundant in sediment. A possible explanation for this might be that the PAHs – being only semipersistent – are degraded faster in an oxidising environment such as soil, but are preserved for longer periods in the oxygen deficient conditions prevailing in the sediment. Another factor may be photodegradation, which is prevented in sediment. These factors contribute to a slower degradation in sediment compared to soil, conserving PAHs for prolonged periods on the fjord-bottom.

Diesel exhaust from ships might contribute to the high PAH-level in sediment. However, against this speaks that NO_2-PAHs, characteristic for diesel exhaust, are not particularly abundant in sediment.

Also NPEs, PAEs and PCBs are comparatively abundant in sediment, but without coming any close to PAHs.
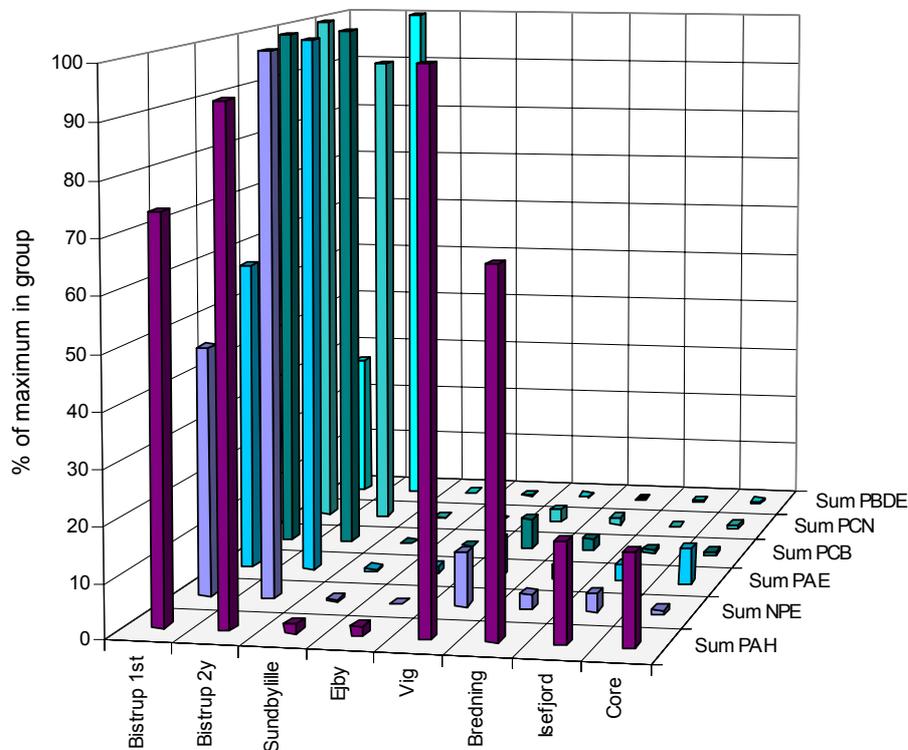
Figure 38   Distribution of substance sums in the environment, normalised by setting maximum in each substance group to 100%.

Soil, substance sums

The substance correlations in soil is now investigated in the same way as the analysis of all environmental locations done in the preceding paragraph. Correlations between substance sums are shown in Table 22 and the summary of correlations between all substances in Table 23.

Table 22 Correlations between substance sums for all soil locations.

Soil	ΣPAH	ΣNPE	ΣPAE	ΣCB	ΣPCN	ΣPBDE
ΣPAH	1					
ΣNPE	*0.95*	1				
ΣPAE	*0.98*	0.99	1			
ΣPCB	0.99		*0.93*	1		
ΣPCN	*0.97*		*0.91*	1.00	1	
ΣPBDE		0.98	*0.95*			1

n = 4, p = 0.05 ≈ r $_{crit}$ = 0.90, p = 0.01 ≈ r $_{crit}$ = 0.98, blank space = not significant.

Soil, all substances

The summary of the correlation analysis for soil on all substances (Table 23), roughly draws the same picture as Table 21. As observed, PAHs correlates with all the others substances except PBDEs. NPEs are highly correlated with PAEs, PAHs and PBDEs, as also was the case in the previous correlation analysis. PAEs, PCBs and PCNs are highly intercorrelated, but none of those are significantly correlated with PBDEs.

Table 23 Summary of significant substance correlations for soil, %.

Soil	PAHs	NO$_2$-PAHs	NPEs	PAEs	PCBs	PCNs	PBDEs
z	12	3	2	7	7	9	4
PAHs	**100**						
NO$_2$PAHs	56	*33*					
NPEs	92	50	**100**				
PAEs	71	57	71	*48*			
PCBs	86	62	*36*	65	**71**		
PCNs	88	59	*22*	57	75	**78**	
PBDEs	*38*	*33*	100	*43*	*43*	*31*	**50**

n = 4 (number of locations), p = 0.05 ≈ r crit = 0.90
z = number of substances in group
Total number of correlation coefficients = 946
of which significant > zero, 636

Taken together, the correlation in soil alone compared to all locations in the preceding paragraph is characterised by a higher correlation between PAHs and the other substances, which on the other hand seem lesser intercorrelated in soil.

The substance correlations in sediment are shown in Tables 24 & 25, according to the same scheme as used for soil.

Table 24   Correlations between substance sums for sediment.

Sediment	ΣPAH	ΣNPE	ΣPAE	ΣPCB	ΣPCN	ΣPBDE
ΣPAH	1					
ΣNPE		1				
ΣPAE			1			
ΣPCB	*0.96*	*0.93*		1		
ΣPCN	*0.95*			*0.96*	1	
ΣPBDE						1

n = 4, p = 0.05 ≈ r_{crit} = 0.90, p = 0.01 ≈ r_{crit} = 0.98, blank space = not significant.

Table 25   Summary of significant substance correlations for sediment.

Sediment	PAHs	NO$_2$-PAHs	NPEs	PAEs	PCBs	PCNs	PBDEs
z	12	3	2	6	7	9	4
PAHs	**61**						
NO$_2$PAHs	*22*	**0**					
NPEs	*13*	*17*	**0**				
PAEs	*22*	*11*	*33*	**13**			
PCBs	74	*29*	*43*	*52*	**100**		
PCNs	*17*	*7*	*6*	*7*	*22*	**31**	
PBDEs	*0*	*0*	*0*	*0*	*0*	*28*	**17**

n = 4 (number of locations), p = 0.05 ≈ r crit = 0.90
z = number of substances in group
Total number of correlation coefficients = 903
of which significant > zero, 254

As seen from Tables 24 & 25, only few and sporadic occurring significant correlations were found in sediment. Furthermore, the two tables do not agree. Consequently, the substance correlations in sediment do not draw a consistent picture. The explanation for this may be the widespread geography of the fjord sediment locations, which furthermore involves the sediment core having a much higher mean age than the other sediment samples, and Isefjord, which is a hydraulic separate entity. Also the much higher occurrence of PAHs than the other substances in sediment may contribute to the disagreement. In addition, the low number of degree of freedom leads to an insensitive test.

Conclusions, substances   The following general conclusions can be drawn from the substance correlation analysis:

- Sludge must be taken out to make the substance correlation analysis consistent. This is due to a low relative abundance of PCBs and PCNs in sludge compared to soil and sediment.

- For all environmental locations (soil and sediment) taken together, all substance groups – except PAHs – are intercorrelated. That is, synthetic chemicals are intercorrelated, whereas the non-synthetic PAHs are not correlated with most the other substances. The poor correlation of PAHs is caused by a disproportionately high abundance in sediment.

- In soil alone, PAHs are correlated with the other substances. PAEs, PCBs and PCNs are highly intercorrelated, but none of those are correlated with PBDEs, which stands apart.

- For sediment alone, the substance correlation analysis does not form a consistent picture.

5.4 Vertical distribution

An important question is the variation with depth of the concentration of substances. For soil, this attests to the downward migration in the soil, promoted by as well advective as by diffusive transport mechanisms. For sediment, the depth distribution also relates to the age of the different layers. These aspects have been described for NPEs and PAEs in soil and sediment in the previous investigation (Vikelsøe et al., 1999 & 2001). In the present study, the large number of substances precludes a thoroughly treatise of each single compound. Hence, a more general approach is needed. Also, mathematical modelling of the fate in soil and sediment of each single compound, or class of compounds, is beyond the limits of the present investigation.

In this section, the vertical distribution in soil and sediment will be addressed for all substance groups and all substances.

5.4.1 Depth profiles in soil

The variation with depth are illustrated in the following figures, which show occurrence of all substances at all locations and depths, arranged in substance groups. Each figure shows the vertical distribution for a particular substance group at a specific location. For each substance, the mean concentrations are shown colour coded according to depth.

The PAH-concentrations at the two sampling sessions at Bistrup with 2 years interval (Figures 39 & 40) are nearly identical. The concentrations seem to be essentially independent of depth for all PAHs.
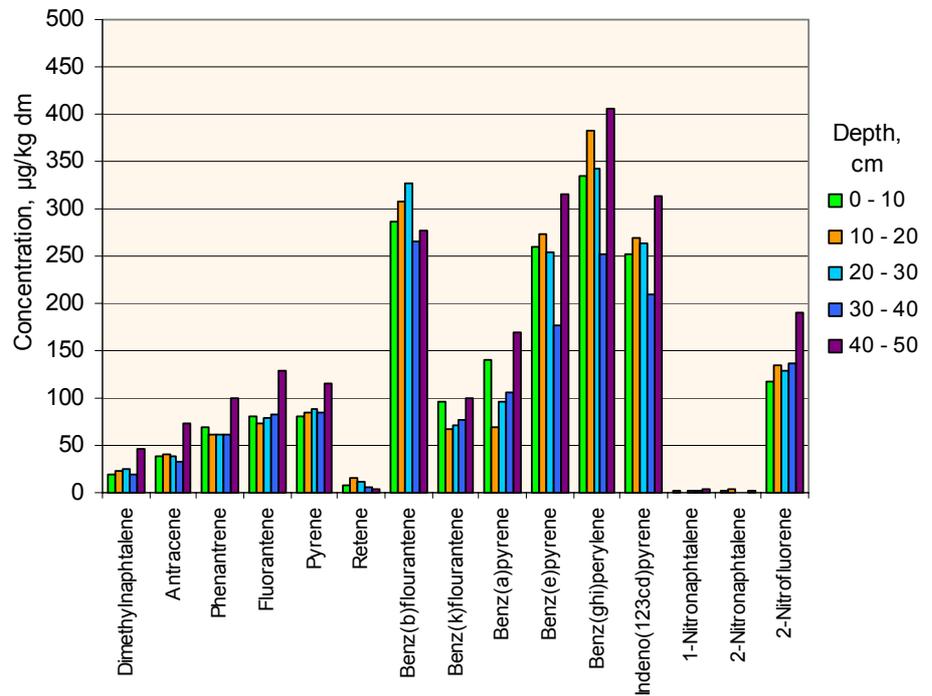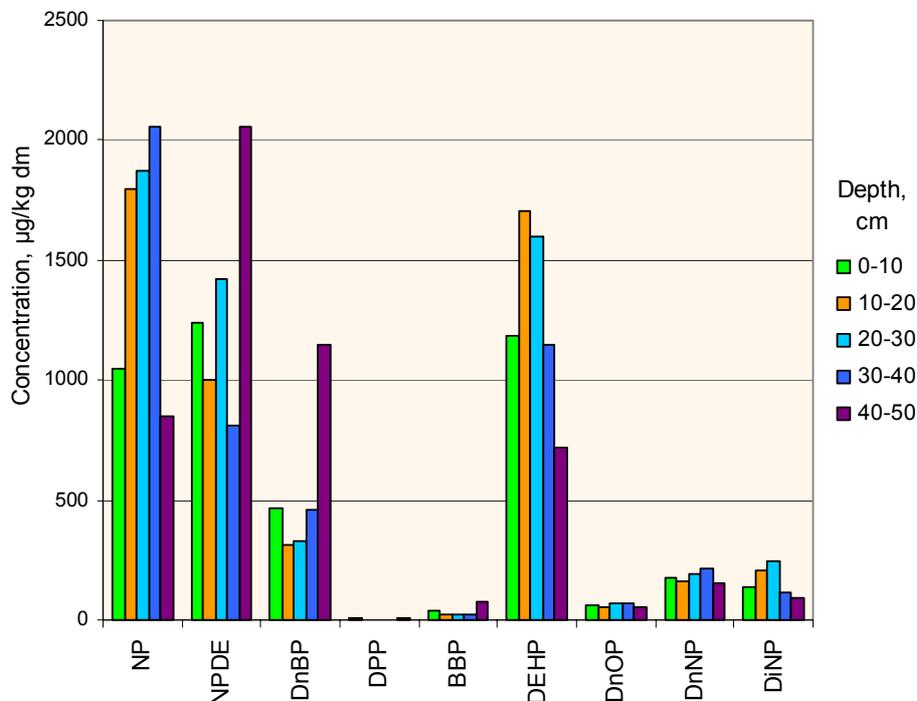

Figure 39 Depth profiles for PAHs in soil location Bistrup, 1st sampling (high sludge).
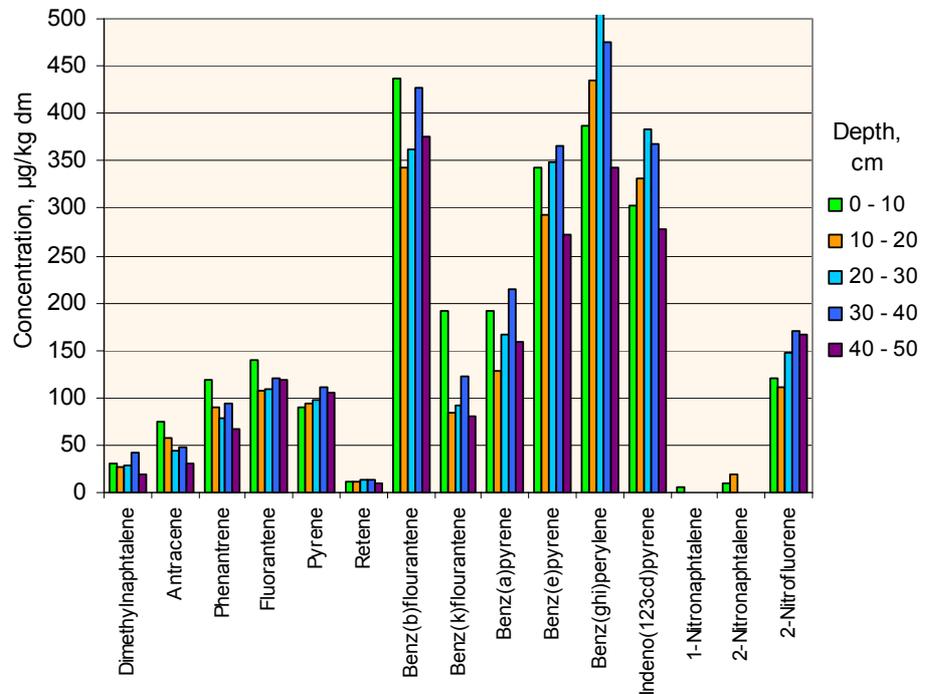
Figure 40 Depth profiles for PAHs in soil location Bistrup, 2 years after (high sludge).

PAHs, low-sludge soil

The maximum concentration (Figures 41 & 42) is found in upper layer (0-10 cm) at both locations for all PAHs, no-sludge Ejby having the higher concentration. This points to deposition as a significant PAH-source. In the next layer (10-20 cm), the locations are nearly identical.
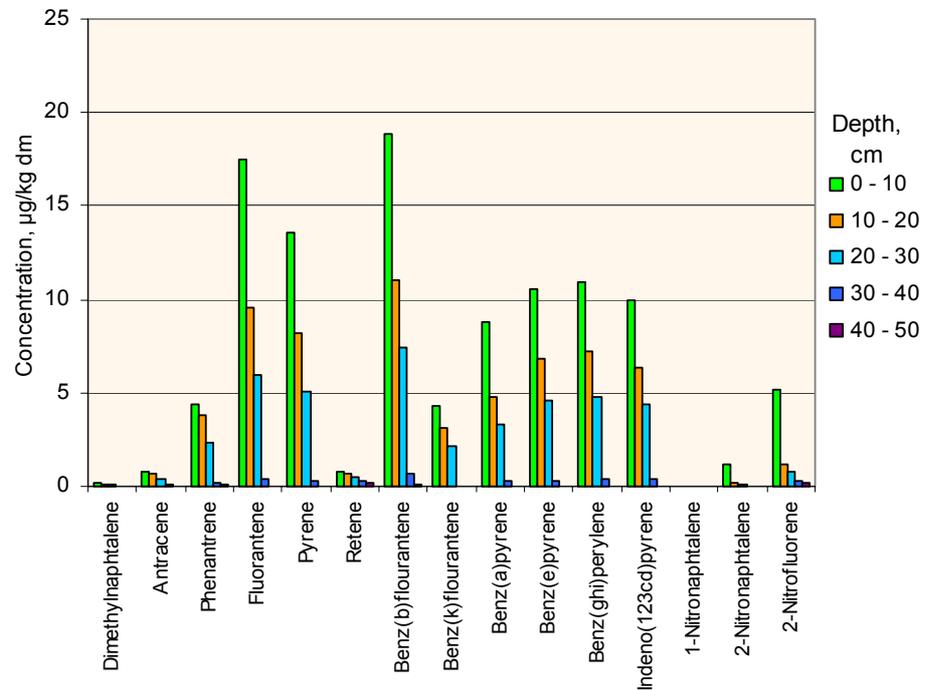
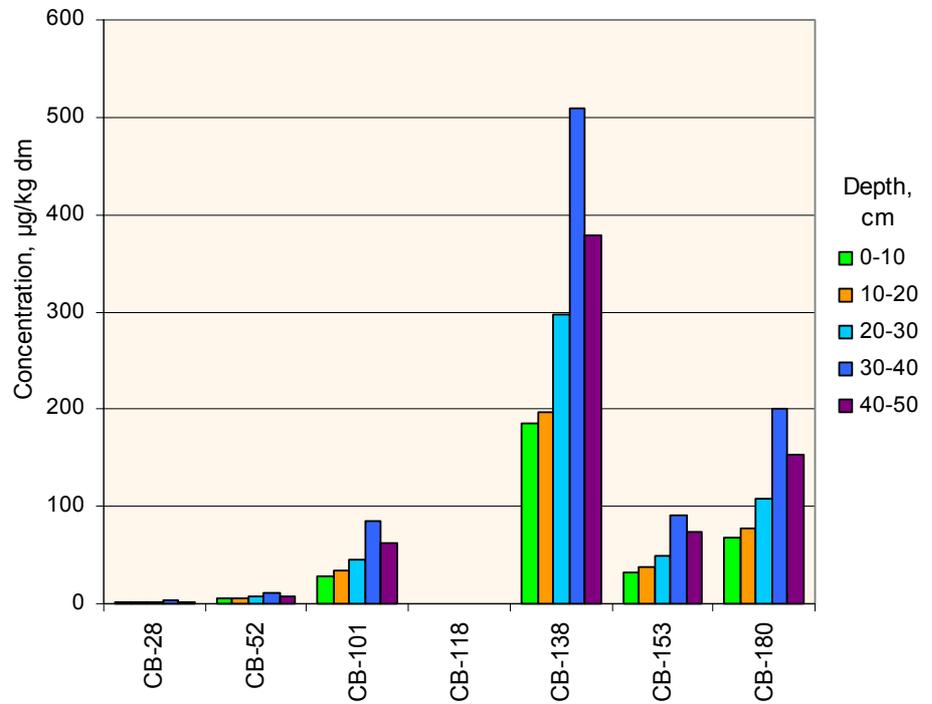**Figure 41** Depth profiles for PAHs in soil location Sundbylille (cultured field, low sludge).
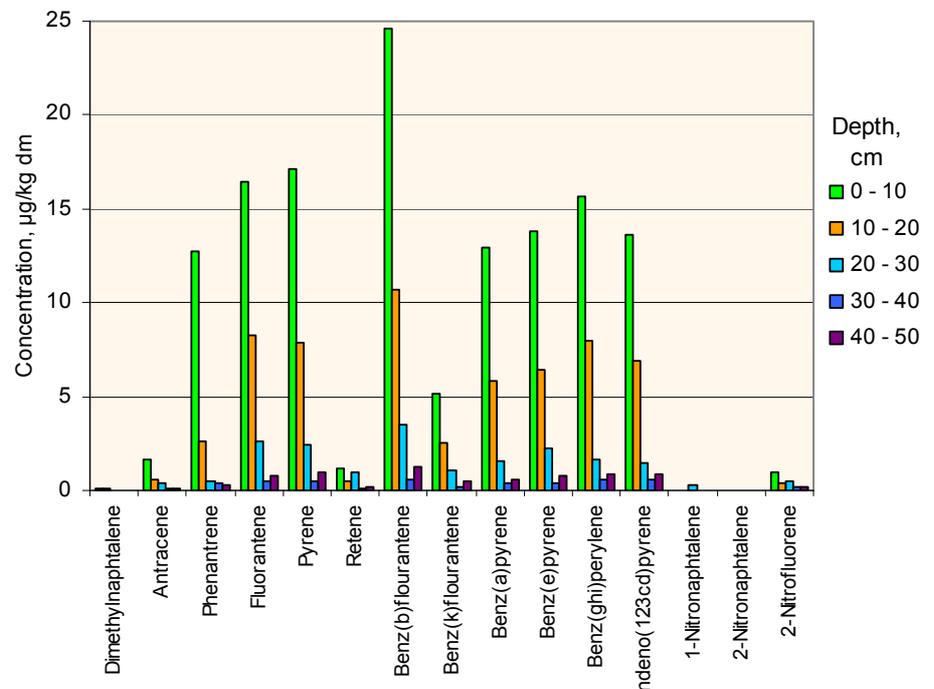
Figure 42 Depth profiles for PAHs in soil location Ejby (preserved area, no sludge).

The concentrations at Bistrup 2nd sampling are considerable higher than 1st sampling (Figures 43 & 44). The maximum concentrations of 2nd sampling occur 20 cm deeper than in the 1st, which could indicate a downward migration. However, this might also be caused by irregularities in the sludge amendment of the field, which over the years received many batches of sludge in random places.

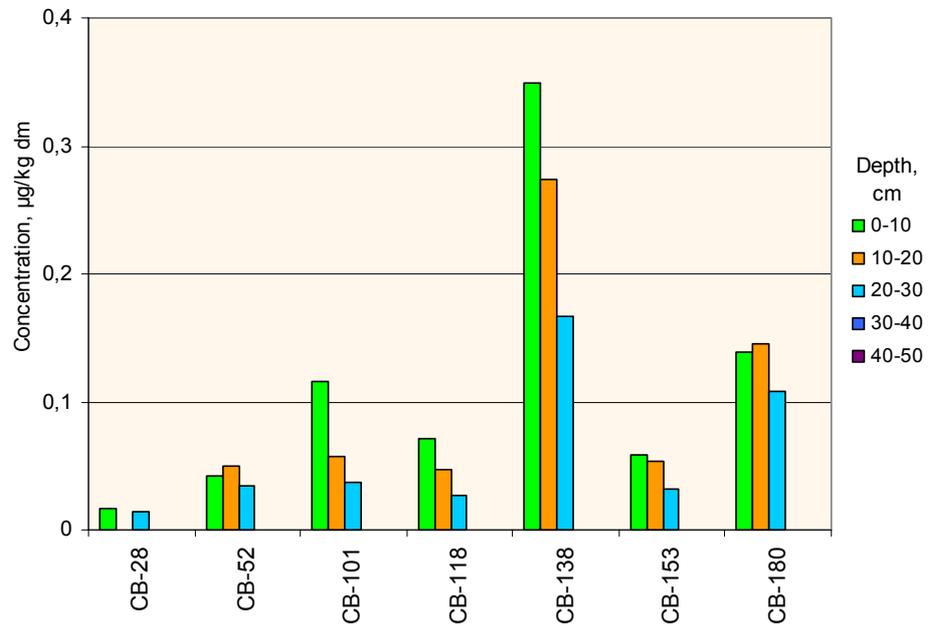**Figure 43**   Depth profile for NPEs & PAEs in soil location Bistrup, 1st sampling (high sludge).
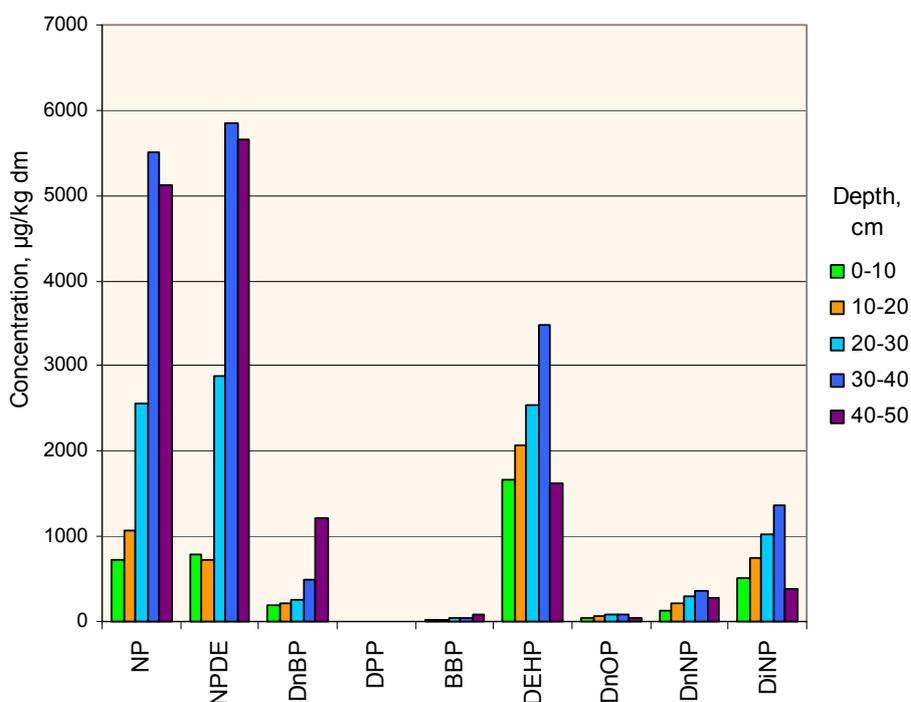
Figure 44   Depth profiles for NPEs & PAEs in soil location Bistrup, 2 years after (high sludge).

A similar pattern is seen for PCBs and PBDEs mentioned in the following.

NPEs & PAEs, low sludge Very low levels occur at both locations (Figures 45 & 46), no-sludge Ejby having higher PAE-levels than low-sludge Sundbylille, whereas the reverse is seen for NPDE. Unlike the high sludge soils, the maximums occur in the uppermost layers.
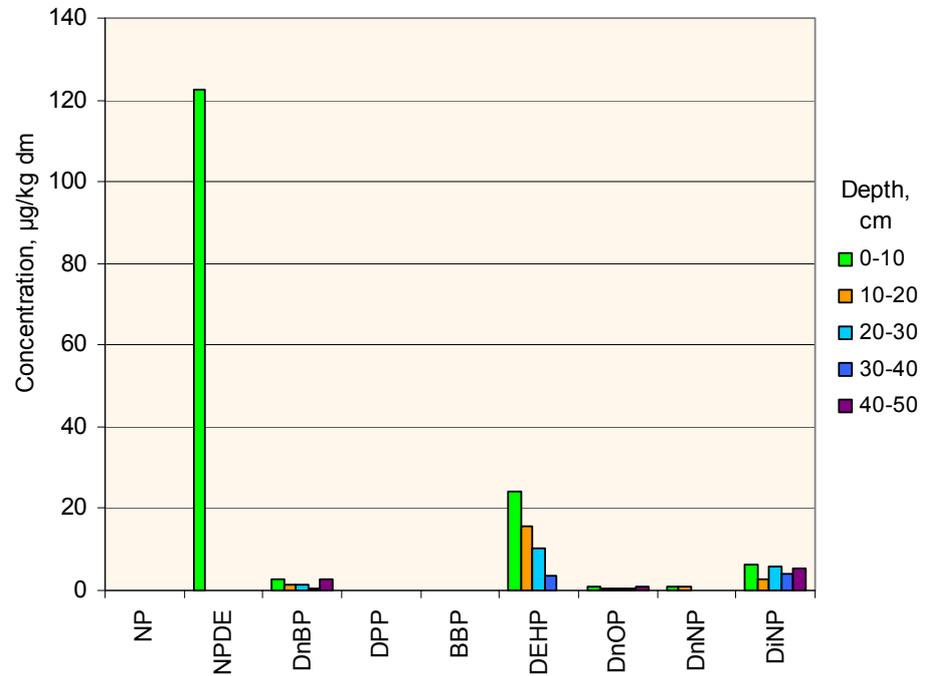
Figure 45 Depth profiles, NPEs & PAEs, soil location Sundbylille (cultured field, low sludge).
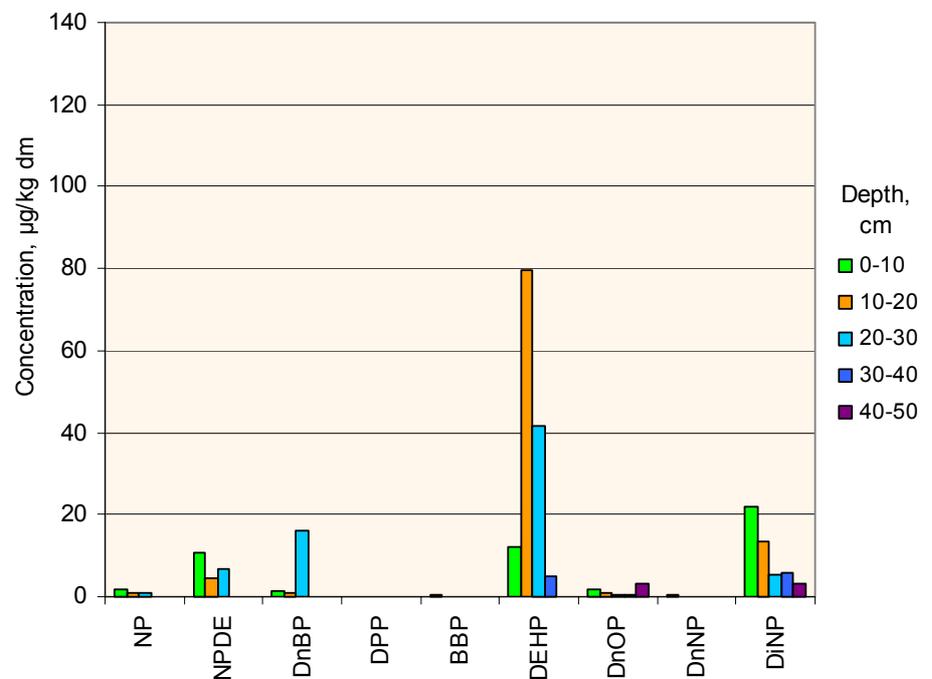
Figure 46 Depth profiles, NPEs & PAEs, soil location Ejby (no sludge).

PCBs, high sludge soil Concentration level are nearly the same for both samplings at Bistrup (Figures 47 & 48). Depth profiles are alike for all PCB-congeners in the same sampling, but maximum concentrations occur in the deepest layer for 2nd sampling. This is suggestive of a downward migration, but may as well be caused by irregularities in the sludge amendment, as remarked for DEHP.
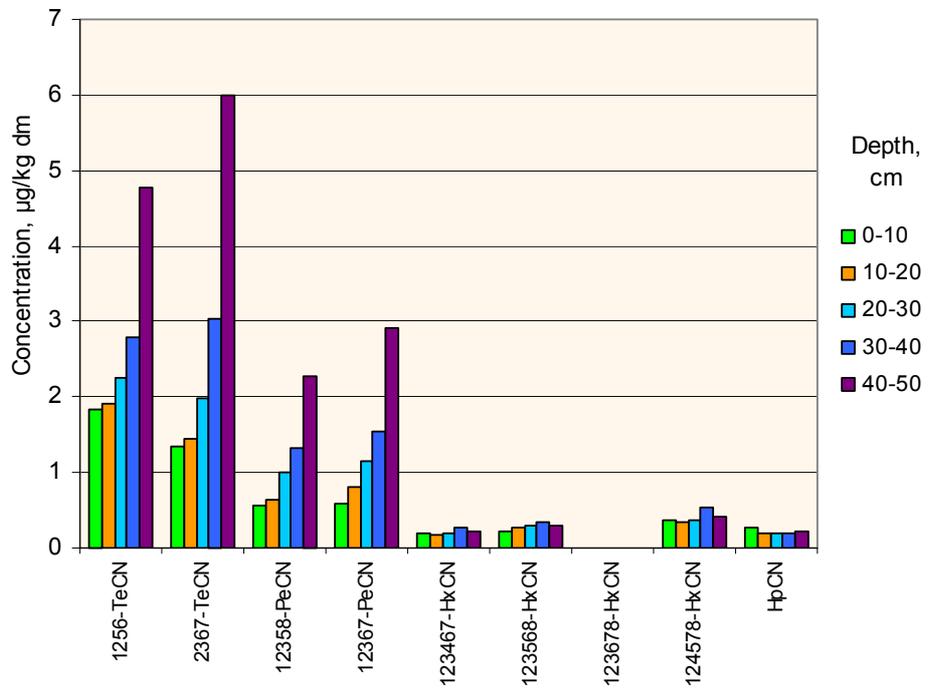

Figure 47 Depth profiles for PCBs in soil location Bistrup, 1st sampling (high sludge).
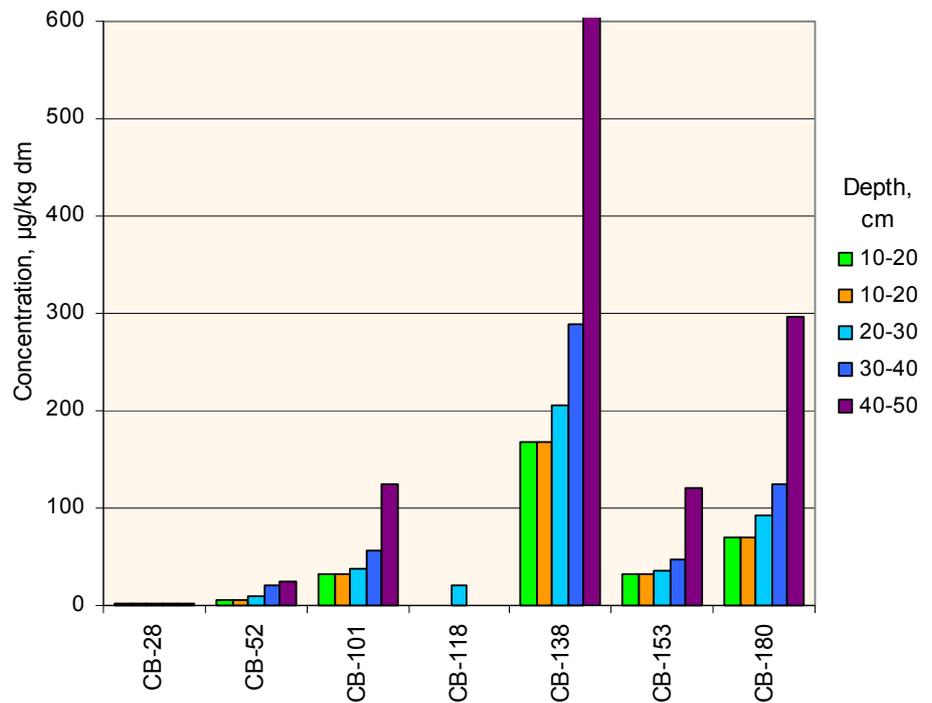
Figure 48 Depth profiles for PCBs in soil location Bistrup, 2 years after (high sludge).

74

PCBs in low sludge soils Considerably lower concentrations (Figures 49 & 50) occur in no-sludge soil from Ejby than in low-sludge soil from Sundbylille. In both soils, the maximum concentrations occur in the surface layer. CB-118 is found in the low-amended soil, contrary to the high-amended soils.
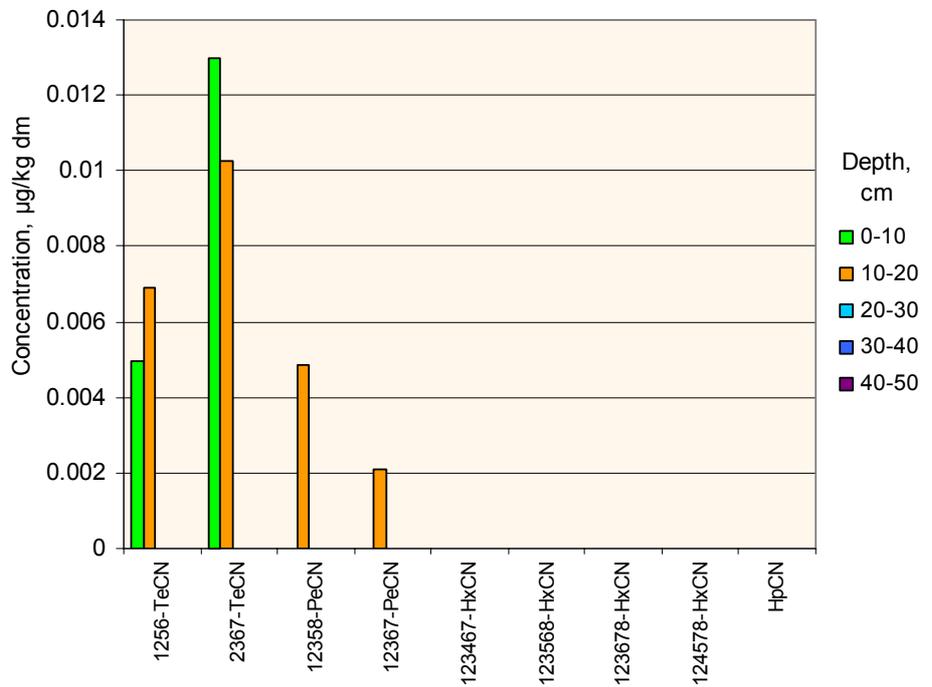

Figure 49 Depth profiles for PCBs in soil location Sundbylille (cultured field, low sludge).
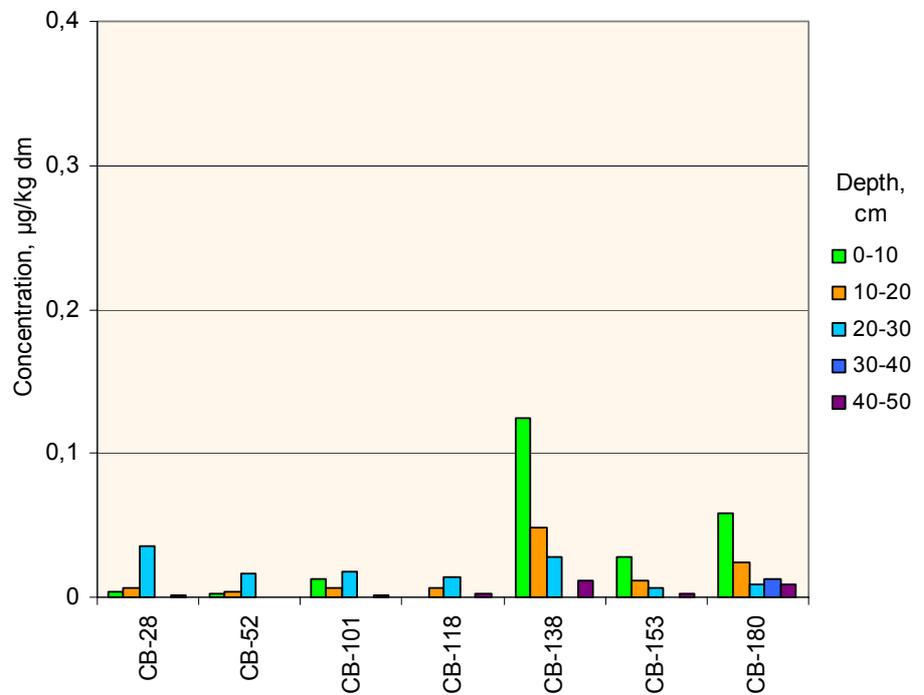
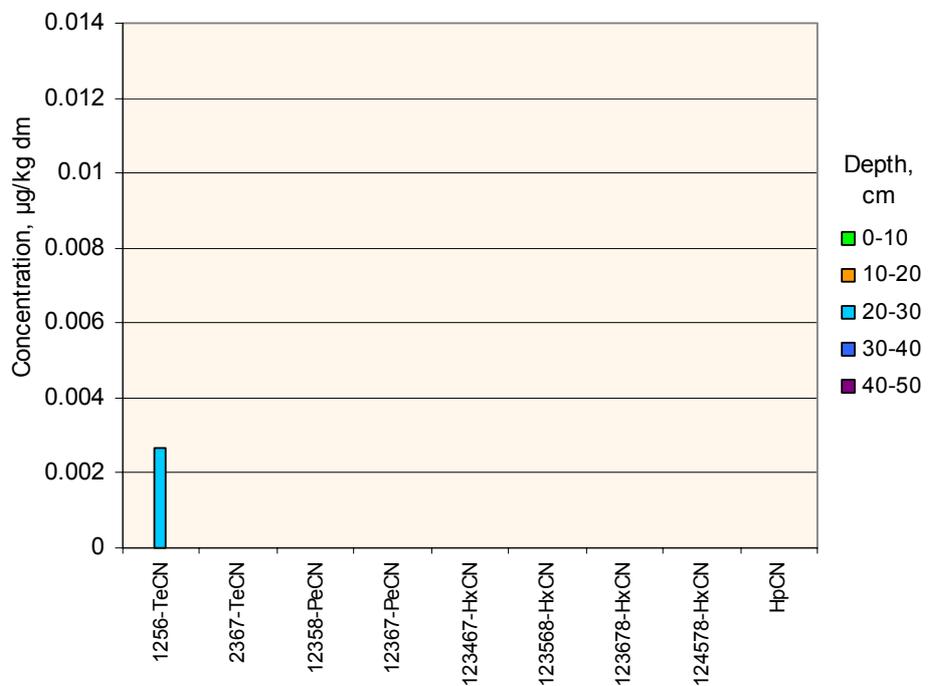**Figure 50** Depth profiles for PCBs in soil location Ejby (preserved area, no sludge).

PCNs in high sludge soil   Concentration levels (Figures 51 & 52) are nearly the same for both samplings at Bistrup, and the depth profiles are similar for all PCN-congeners, the maximum concentration occurring in the deepest layer. This was also the case for DEHP and PCBs.

Figure 51   Depth profiles for PCNs in soil location Bistrup, 1st sampling (high sludge).
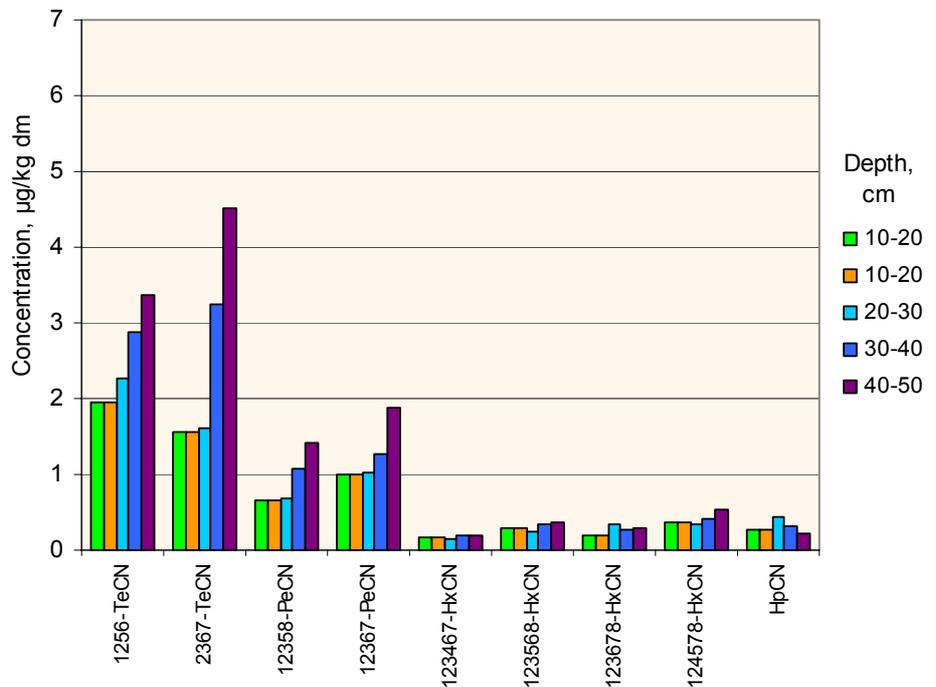
Figure 52   Depth profiles for PCNs in soil location Bistrup, 2 years after (high sludge).

PCNs occur (Figures 53 & 54) only in low-sludge soil of Sundbylille, in no-sludge Ejby soil almost no PCNs were found. In Sundbylille, the maximum occurs in the surface layers, unlike the high-amended soils.

Figure 53   Depth profiles for PCNs in soil location Sundbylille (cultured field, low sludge).

Figure 54   Depth profiles for PCNs in soil location Ejby (preserved area, no sludge).

Concentration levels are considerably higher in 2nd sampling at Bistrup, in spite of the almost equal levels found for PCBs, PCNs and PAHs. The depth profiles are similar for all PBDE-congeners in both samplings, but the concentration maximums occur 20 cm deeper in the 2nd sampling. Both effects might be caused by irregularities in the sludge amendment, as mentioned for PAEs, PCBs and PCNs.
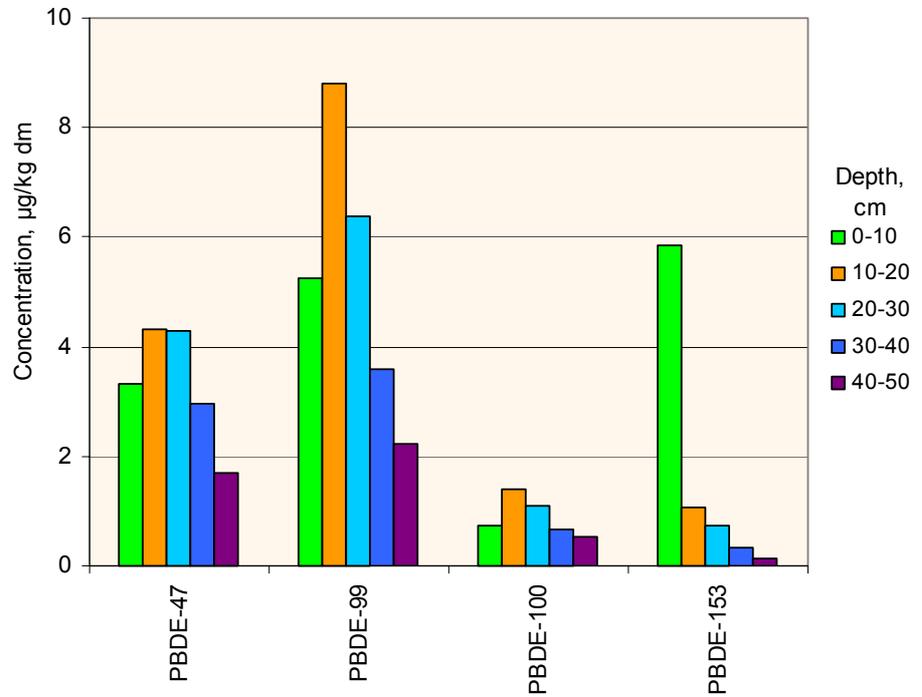

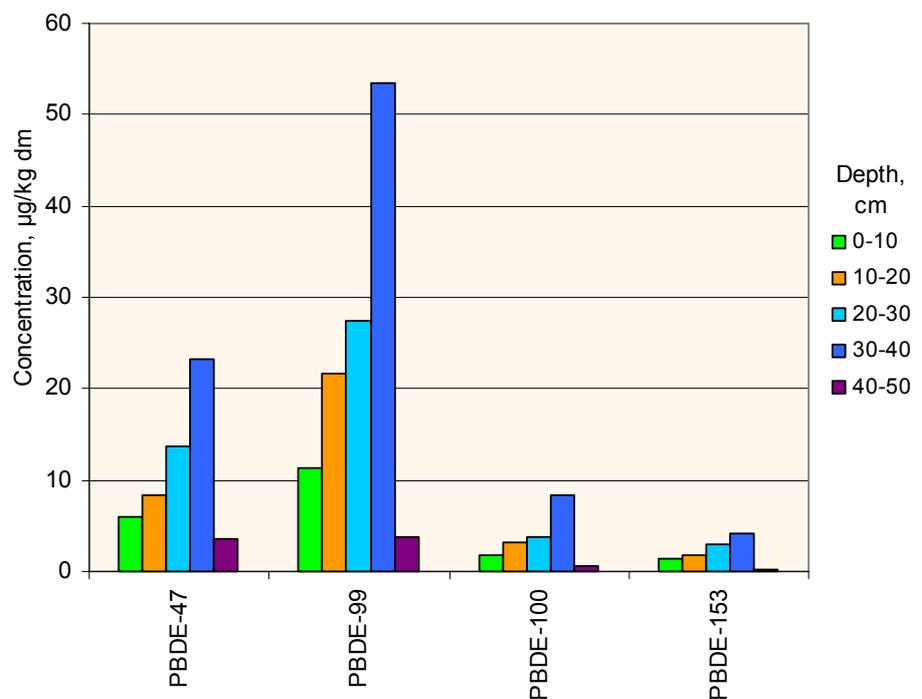**Figure 55** Depth profiles for PBDEs in soil location Bistrup, 1st sampling (high sludge).

Figure 56 Depth profiles for PBDEs in soil location Bistrup, 2 years after (high sludge).

PBDEs in low sludge soil   PBDEs occur only in low-sludge Sundbylille soil, in no-sludge Ejby soil only traces were found (of PBDE-153). In Sundbylille, the concentration maximums occur in the surface layer, unlike the high-amended soils, as was the case also for PCBs and PCNs.
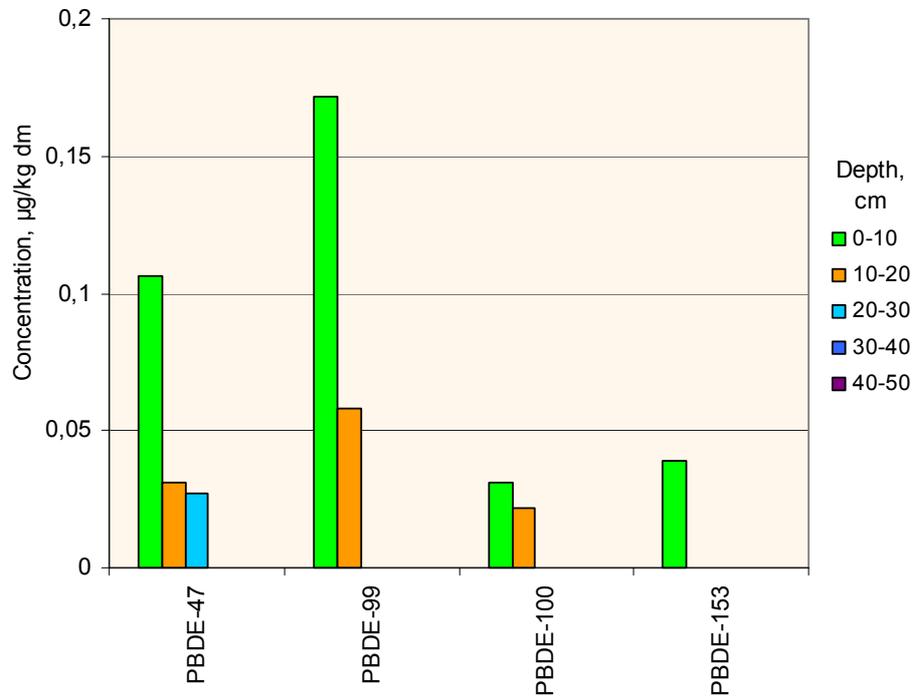

Figure 57   Depth profiles for PBDEs in soil location Sundbylille (cultured field, low sludge).
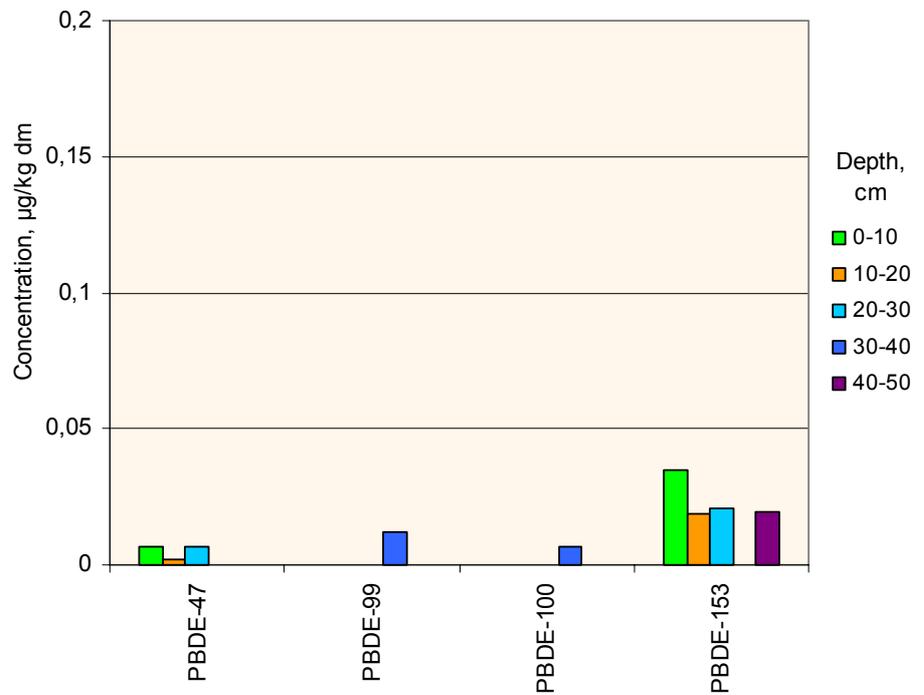

Figure 58   Depth profiles for PBDEs in soil location Ejby (preserved area, no sludge).

Discussion, high sludge soil   For many substance groups in the high sludge amended soil in Bistrup, a deeper maximum in the vertical distribution is seen at the second sampling performed 2 years after the first. Furthermore, a higher concentration is observed for the second sampling.

While the first observation might be interpreted as a downward migration (although perhaps somewhat larger than expected for these almost insoluble compounds), the second implies an increasing concentration during the years without sludge amendment, which obviously is impossible. A more likely interpretation of this situation would be that the difference in the two samplings at Bistrup rather be caused by spatial variations, in stead of the temporal variations intended during the planning of the samples. The spatial variations (as well horizontal as vertical) may be caused by irregularities in the sludge amendment (as mentioned previously), and the difference arises because the sampling positions had to be some meters apart in order not to disturb each other.

According to this view, the sampling positions happened to be chosen so as to have received very different sludge batches, perhaps produced with an interval of years. If this is the case, the difference in the samples reflects the historical development in the sludge during the period of amendment. Consequently, a large difference may be caused by an increase/decrease in the sludge batches during the period of amendment. Thus, the differences for PAHs, PCBs and PCNs are very small (see also Figure 36), indicating a constant concentration during the period, in agreement with the conclusions reached elsewhere. In contrast, for NPEs, PAEs and PBDEs a large increase from 1st to 2nd sampling at Bistrup is found, indicating a history of varying concentrations in the sludge. Most likely they are increasing (i.e. Bistrup 2nd sampling received the latest produced sludge) because of the recent introduction of PBDEs.

In any case, it must be stressed that the Bistrup location had received considerably larger amounts of sludge than is normal in Danish agriculture. Rather, the location has been used as a sludge-dumping site.

5.4.2 Depth profiles in sediment core

The distribution of substances in the fjord sediment core is an important clue to the historical development of the aquatic pollution with chemicals. This distribution does also depend on the diffusion and adsorbance characteristics of the substances and of the sediment, which may be very different for the individual substances, affecting pre- as well as post-sedimentation behaviour. In a previous investigation, this problem has been addressed for DEHP by development of a mathematical model (Vikelsøe et al. 2001). However, the development and application of models for all substances, or classes of substances, is outside the scope of the present investigation.

A tentative time scale for the layers of the sediment core are shown in Table 26 below, based on the sedimentation rate of 0.25 cm/year found by Madsen & Larsen (1979) using ^{210}Pb dating. This scale, which assumes constant sedimentation rate, probably underestimates the age of the oldest sediments, since compression takes place in the deeper layers.

Table 26   Tentative age of sediment core layers according to depth.

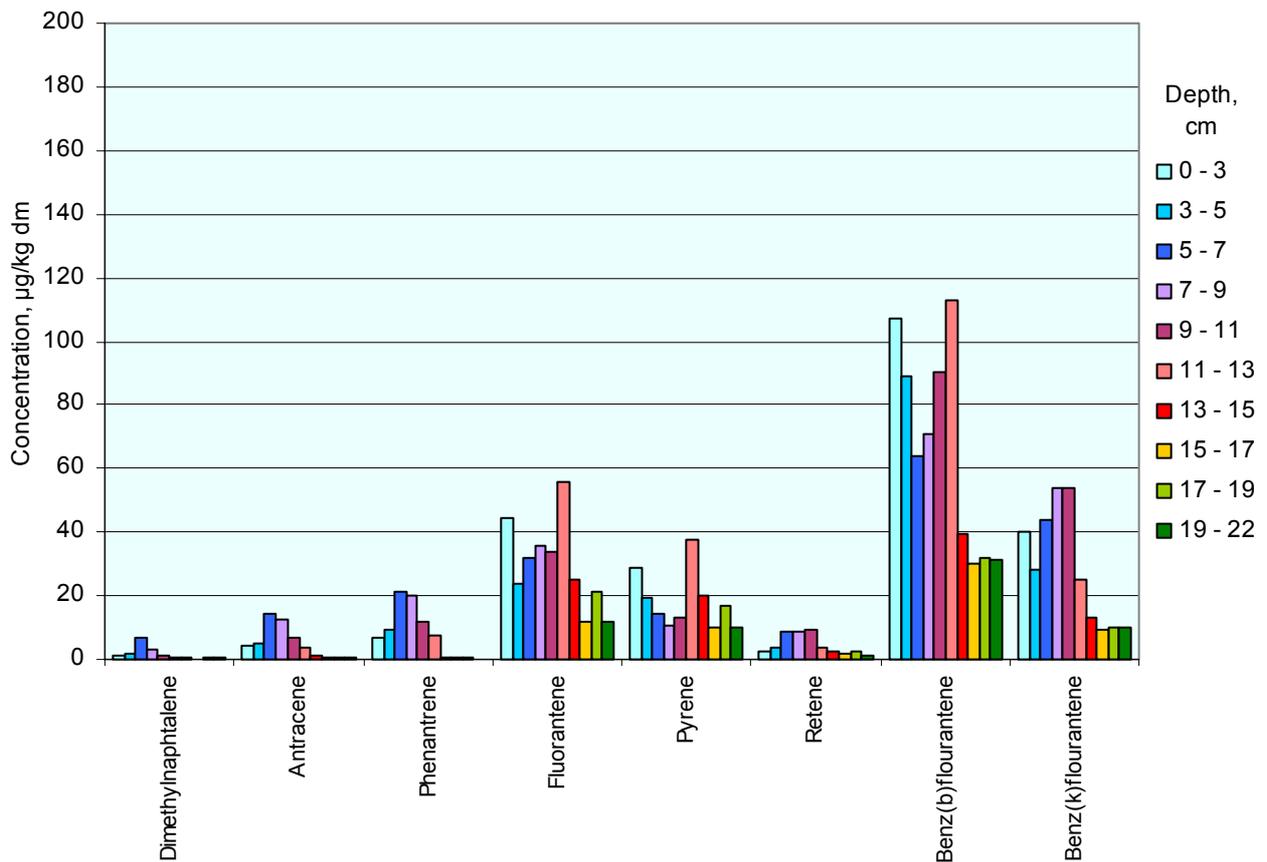| Layer	Depth, cm		Age, years		Mean age	Year
1	0	3	0	12	6	1990
2	3	5	12	20	16	1980
3	5	7	20	28	24	1972
4	7	9	28	36	32	1964
5	9	11	36	44	40	1956
6	11	13	44	52	48	1948
7	13	15	52	60	56	1940
8	15	17	60	68	64	1932
9	17	19	68	76	72	1924
10	19	22	76	88	82	1914

Figure 59   Depth profiles for PAHs (lower MWs) in sediment core from Roskilde Vig.
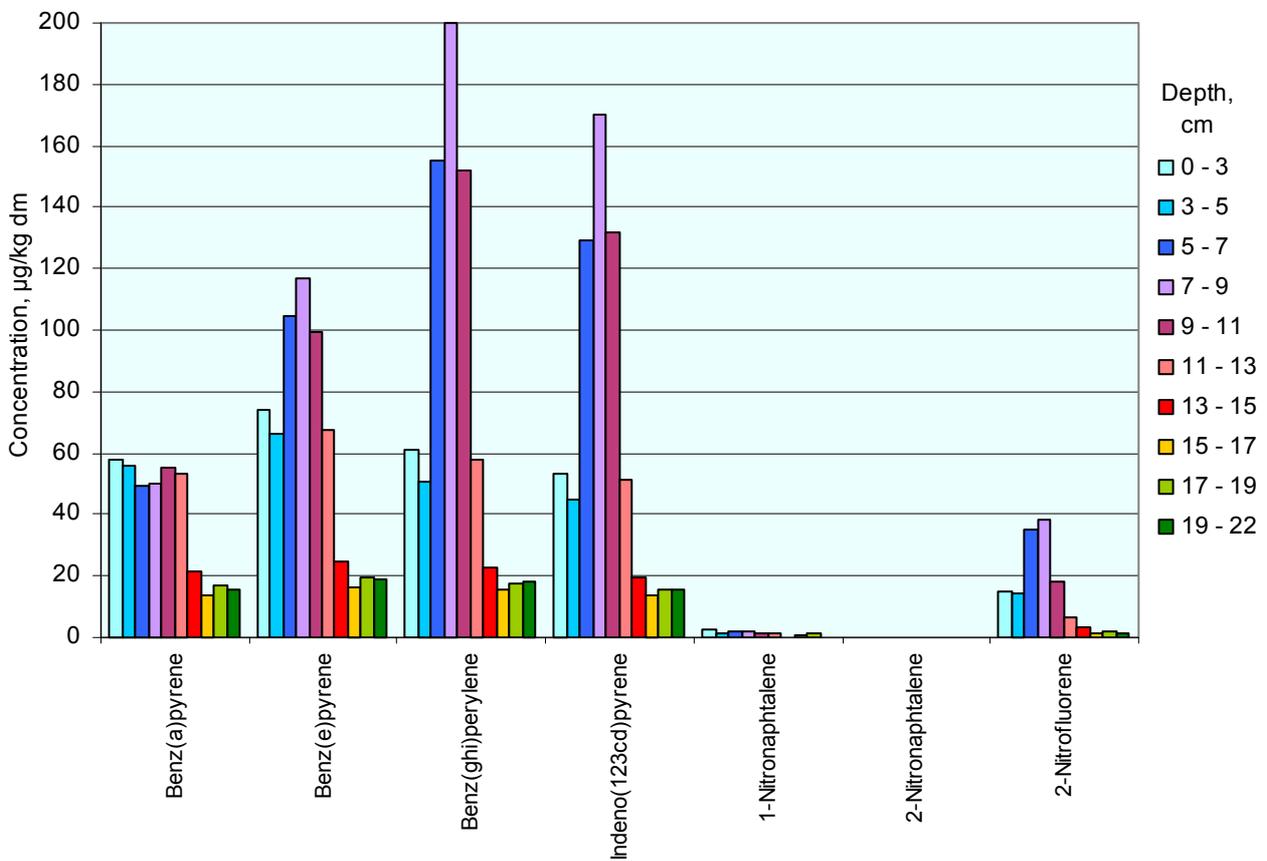

Figure 60   Depth profiles for PAHs (higher MWs) in sediment core from Roskilde Vig.
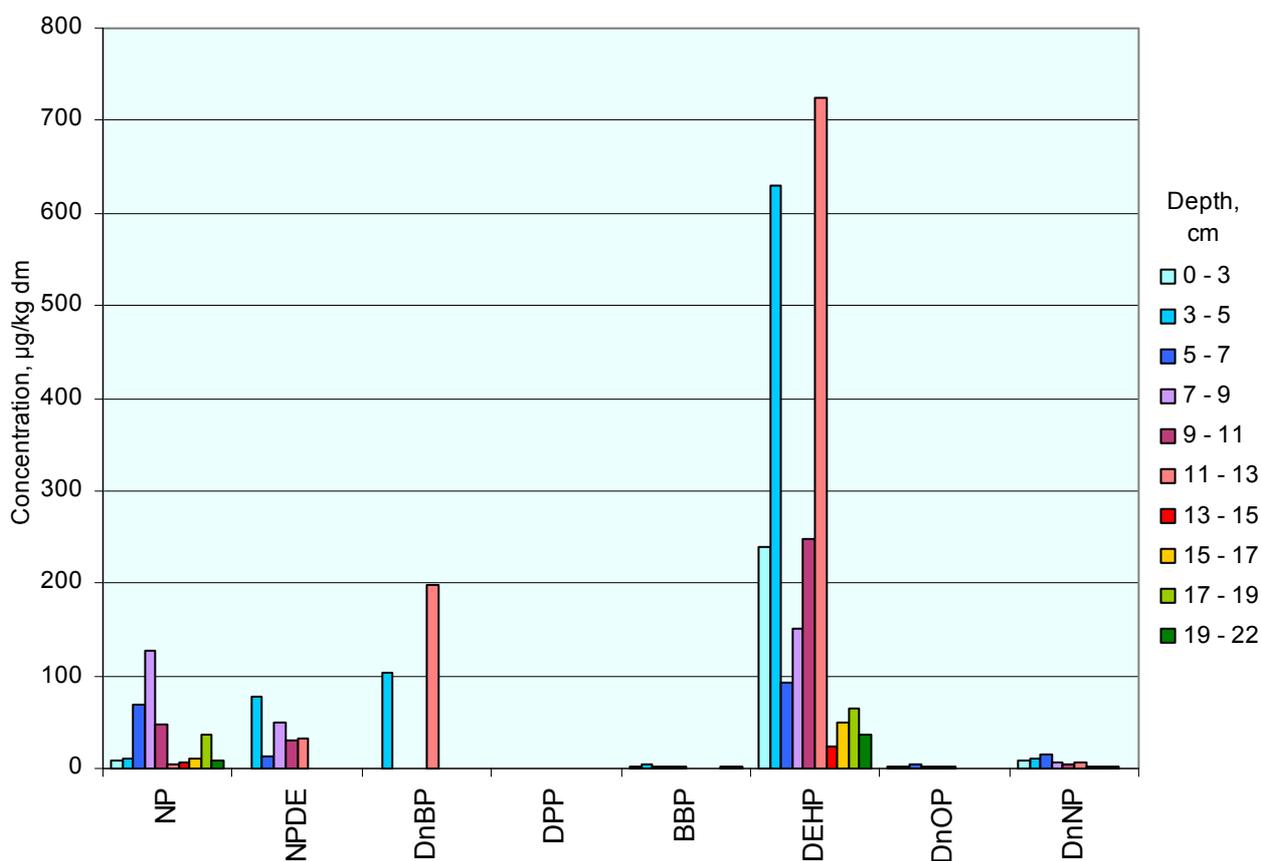
Figure 61   Depth profiles for NPEs and PAEs in sediment core from Roskilde Vig.

Non-halogen compounds   The PAH depth profiles fall in two classes (Figures 59 & 60). Fluoranthene, pyrene and particularly benz[b]fluoranthene are nearly congruent, characterised by two peaks (two peak profile) occurring at depths of 0-3 cm and 11-13 cm, respectively. In contrast, for most other PAHs a single peak occur at 3-9 cm. Benz[a]pyrene is a "square" transition form. Retene, generated during burning of spruce and fir, stands out by having the deepest occurring single peak profile of all PAHs (9-11 cm). For all PAHs a monotonous descent follows after the deepest peak until a low plateau is reached at a depth of 13 cm. Since PAHs mainly originate from combustion, it is unlikely that these different types of depth profiles are caused by a different emission pattern in the past compared with the present. This is discussed in a following section.

For DEHP (Figure 61) a very characteristic depth profile is observed. Three peaks occur at 3-5 cm, 11-13 cm and 17-19 cm, respectively. A very sharp minimum occurs between the upper peaks. The profile is roughly congruent with that of benz[b]fluoranthene, but with sharper peaks. The BBP profile, barely visible, is roughly similar to that of DEHP.

In the depth profile of NP two peaks occur at 7-9 cm and 17-19 cm, respectively, the largest peak-separation in the data. The upper peak coincide with higher PAHs (e.g. benz(g,h,i)perylene), and the lower peak with the lower DEHP peak.
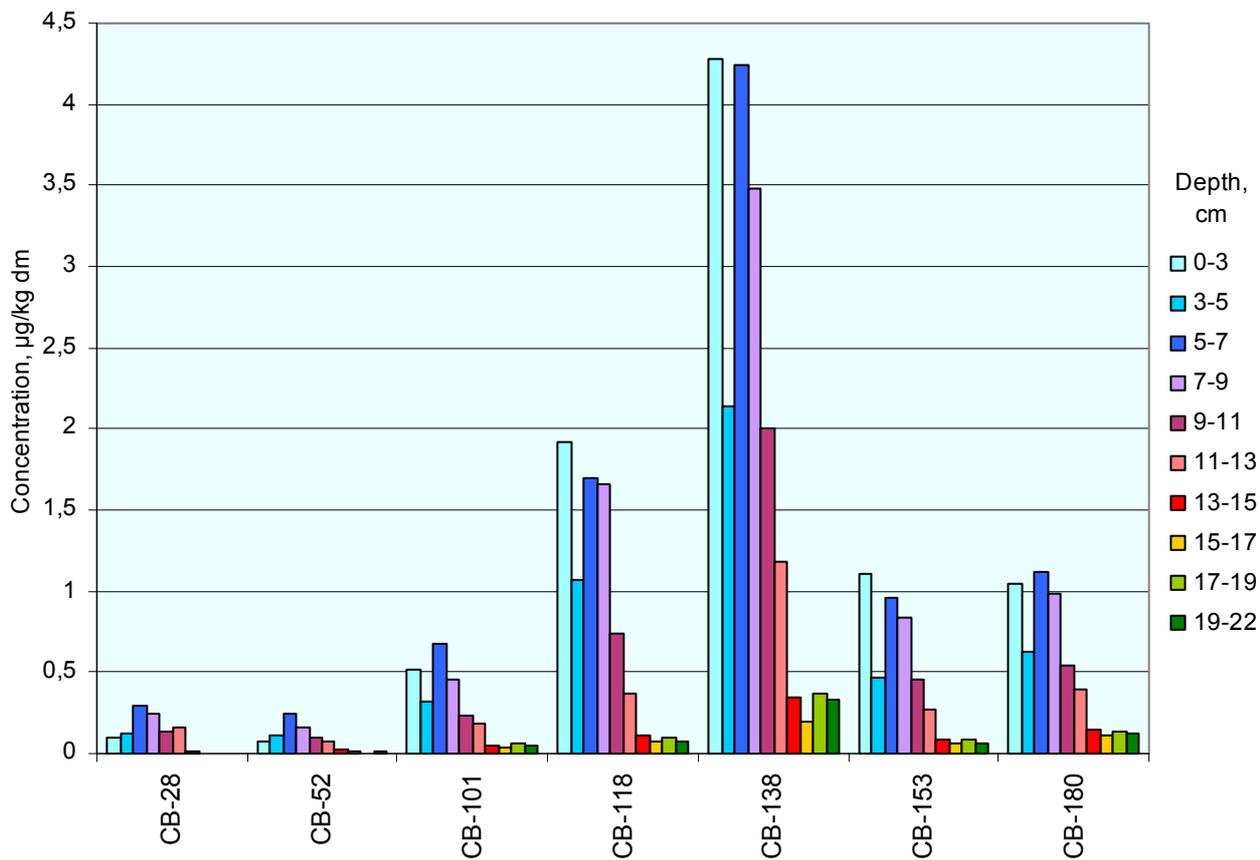
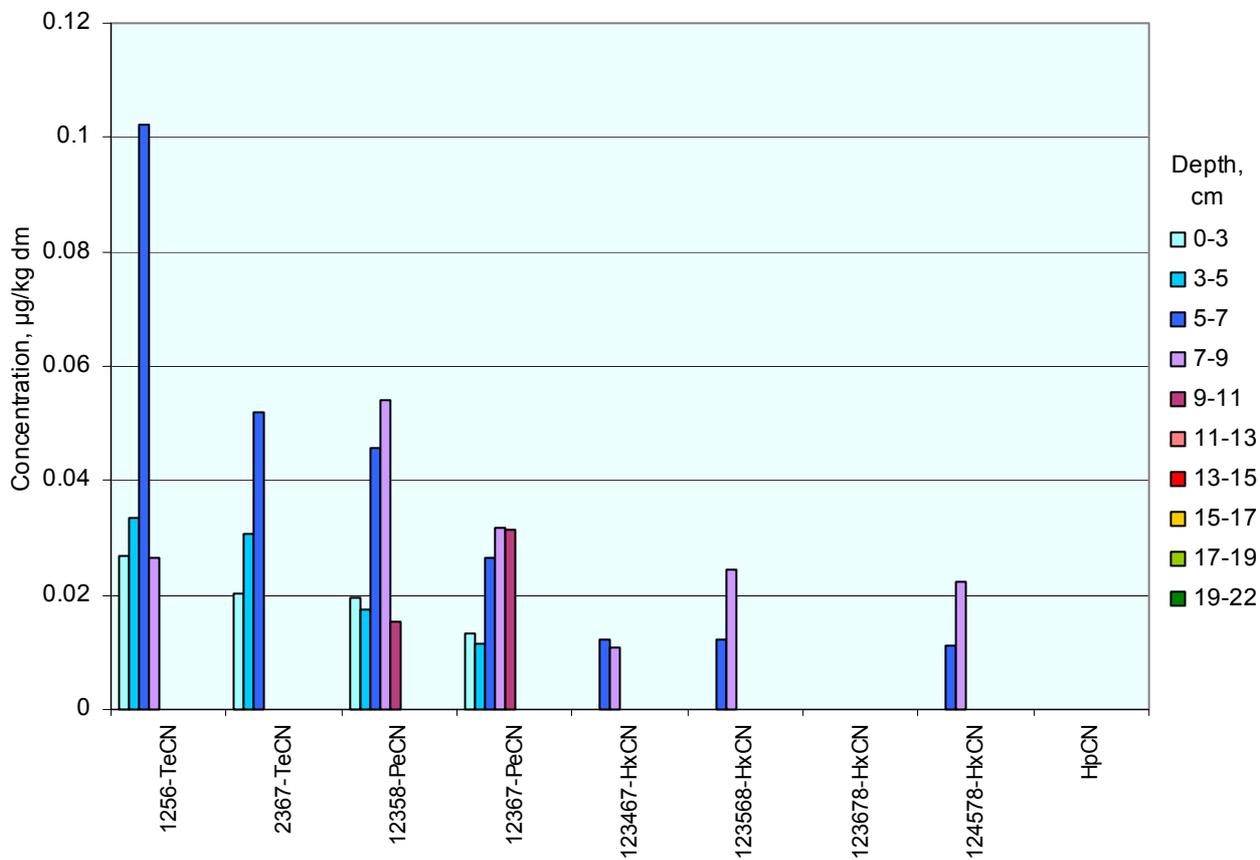**Figure 62**   Depth profiles for PCBs in sediment core from Roskilde Vig.

Figure 63   Depth profiles for PCNs in sediment core from Roskilde Vig.
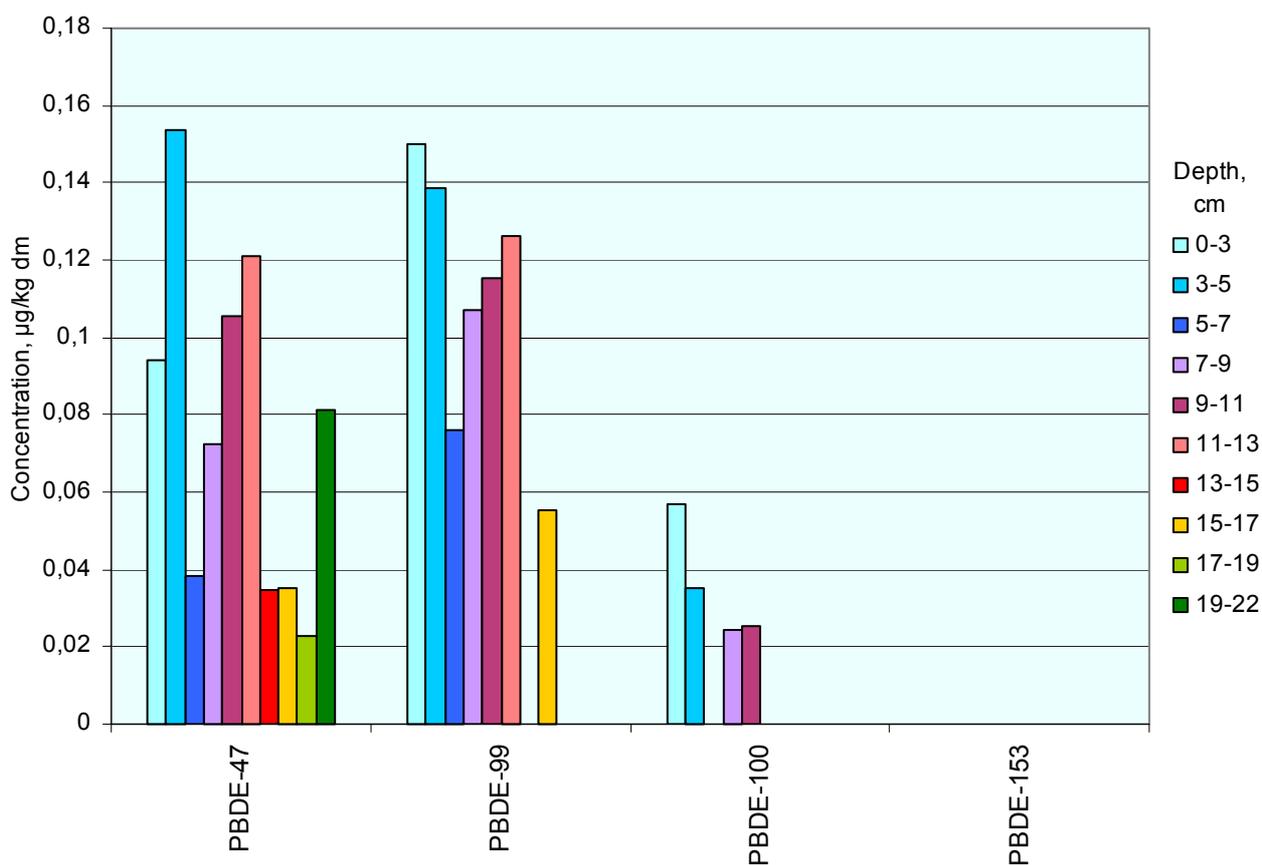
Figure 64   Depth profiles for PBDEs in sediment core from Roskilde Vig.

Halogenated compounds

The PCB depth profiles (Figure 62) are nearly congruent from CB-101 to CB-180, having two peaks (two peak profile) occurring at 0-3 cm and 5-7 cm, respectively. The deepest peak is followed by a monotonous descent until a low plateau is reached at 11 cm. In contrast, the lower MW PCBs CB-28 and CB-52 have single peak at 5-7 cm depth. The PCB profile pattern is reminiscent of the PAHs, but the deepest PCB-peaks occur at lesser depths than those for the PAHs. The PCN profiles (Figure 63) have many similarities with the PCBs, as the TeCNs with lower MW have single peak at 5-7 cm and the higher MW PeCNs two peaks at 0-3 cm and 7-9 cm, respectively. However, the minimum between peaks is much lesser pronounced, almost missing. The higher HxCNs and HpCNs show incomplete profiles because of too low concentrations.

A reasonable interpretation of these observations is that PCBs and PCNs have similar histories of pollution, leading to essentially congruent profiles from 3 cm and down. This may reflect that PCNs are by-products in technical PCB preparations, a view supported by the correlation analysis mentioned previously. It is noteworthy that the deeper PCB maximum occurs at a depth of 5-7 cm corresponding to year 1980, which coincides with the year 1977 when PCBs were banned in Denmark.

For the PBDEs (Figure 64) consistent depth profiles are found for PBDE-47 and PBDE-99, whereas the higher PBDEs are too close to detection limits. The profiles are two peak occurring at 0-5 cm and 11-13 cm, respectively, reminiscent of DEHP.

Peak depth overview	**PAHs**	
	Low MW:	Single peak 5-7 cm.
	Middle MW:	Two peaks 0-3 cm & 11-13 cm.
	High MW:	Single peak 7-9 cm.
	All:	Low plateau from 13 cm down
	NPEs	
	NP:	Two peaks 7-9 cm & 17-19 cm.
	PAEs	
	DEHP:	Three peaks 3-5 cm &11-13 cm, 17-19 cm.
	PCBs	
	Low MW:	Single peak 5-7 cm.
	Higher MW:	Two peaks 0-3cm & 5-7 cm.
	All:	Low plateau from 13 cm down.
	PCNs	
	TeCNs:	Single peak 5-7 cm.
	PeCNs:	Two peaks 0-3 cm & 7-9 cm.
	PBDEs	
	PBDE-47&99	Two peaks 0-5 cm & 11-13 cm.

Discussion, pollution history A general decreasing tendency of concentration with depth is observed for all substances. Hence, it is evident that old sediment layers contain lesser xenobiotics than newer ones. This reflects a history of increasing pollution, which would result in an increase in the concentration in the upper layers. For almost all substances a steep increase is observed from a depth of 11-13 cm and up. This corresponds to year 1948, from which an unprecedented economic development took place in the western world. This is reflected in the sediment layers since all high concentrations are post- World War II (1939-1945), whereas those below 13 cm (before 1940) form a low plateau. It is seen that for some PAHs, the pre- World War II levels was comparatively higher than for the other substance classes (compare for example benz[b]flourantene with CB-138), probably because PAHs are emitted mainly during fuel burning for heating. Apart from the general technical-economic development, the depth profile for this particular sediment core close to the harbour also reflects the local history pollution, mentioned below.

Degradation The general decrease with depth also reflects a degradation of the substances. This would mostly affect the deeper oldest layers, which have had more time to be degraded. However, the effect of degradation in deep sediment layers must not be overrated. For example, deep layers contain relatively high concentrations of PAHs, which under normal conditions are more readily degraded than e.g. PCBs. The oxygen-deficient conditions in the sediment may provide an explanation.

Two peak profiles It is remarkable that some, but not all, substances (e.g. middle MW PAHs, DEHP and higher MW PCBs) display an additional peak at 0-5 cm (year ≈ 1980-1990), leading to a characteristic "two peak" depth profile. This feature can hardly be ascribed to the general history of pollution, because it is very unlikely that the history is identical for all these compounds which have been introduced independently in the technosphere. Furthermore, many PAH-components and some PCB-congeners do not display the two peak

profile. For example, it is unlikely that PCB-congeners have separate and different general history, since all PCB-congeners in a technical preparation are emitted simultaneously during use, handling and disposal.

Local history

More likely, recent local activities may have created the upper (latest) peak by temporarily increasing the pollution in the fjord. Such activities exerts a significant influence in the vicinity the harbour. For instance, harbour cleaning and construction operations or sludge dumping in the fjord, which are known to have taken place. Unfortunately, it is difficult to obtain reliable information of the precise circumstances. The local pollution history furthermore involves introduction of wastewater cleaning, the improvement of the technology, the shifting outlet location, the specific local industrial activities, consumer behaviour, the ship traffic and the local air pollution. If the upper peak were due to a single recent high episode of, say, sludge dumping, one would expect that the uppermost part of all profiles should be alike. This does not agree with the varying depths for the upper peak for different substance classes. Rather, different activities have taken place over a span of years.

The core site

The site for the sediment core has been chosen close to the harbour and the WWTP outlet in order to reflect local activities. A further understanding of the depth profiles would require investigation of sediment cores from other, more undisturbed locations (such as Roskilde Bredning or Isefjord). In addition, such sites would be more representative of the general pollution history.

Bioturbation and mixing

One could imagine that two peak profiles might arise through disturbance of the sediment layers, caused by bioturbation or mechanical mixing. However, two reasons speak against this. First, the sediment core was very hard, almost as sandstone, showing horizontal layers without visible sign of disturbance. Second, bioturbation or mechanical shuffling of the layers would create similar or identical depth profiles all the compounds, in disagreement with the findings.

Physical properties

Pollution history alone does not seem to fully explain the two peak profiles. For example, this type of profile is most pronounced for substances in the intermediate molecular weight range, whereas many low MW substances display single peak profiles. This could point to a mechanism based on differences in solubility, adsorption, diffusion, chemical stability or other physical or chemical properties. Such properties would work in concert with the other factors influencing the depth profile. A more complete understanding of such effects would require a theoretical model for the behaviour of the substances in the sediment and the water.

6 Conclusions

General: The present study demonstrates that multianalysis of persistent environmental pollutants in a local environment may yield a cross-section of the chemical state of the area. It is possible to map the geographical and vertical occurrence of the most persistent compounds, revealing important clues regarding the sources, transport, fate and history of xenobiotics. This leads to wealth of findings from which a large number of conclusions can be drawn, the most important of which are summarised below.

Overall abundances : The concentration span is very large as well between substances as between locations, ranging from 10000 - 0.001 μg/kg dm. The levels of the non-halogenated substances were of the same order of magnitude and considerably higher than those of halogenated ones. PCBs were the most abundant organohalogen even if it was banned in Denmark 1977. Nitro-fluorene (carcinogenic) most abundant PAH in sludge, but not in soil and sediment.

Geographical distribution: In the high-sludge soils much higher levels than in low sludge soils, exceeding those in sludge for PCBs, PCNs and the higher PAHs. Hence, a substance build-up in the environment has taken place for these substances, or the concentration in sludge has decreased.

In low- and no-sludge soils non-halogen substances occur in comparable levels, pointing to other sources than sludge, and indicates that low sludge amendment do not cause concentration build-up in these cases. On the contrary, the organohalogens do build-up, even from low sludge amendment, whereas in the no-sludge soil, almost no organohalogens were found.

In sediment the highest PAH-level exceeds that in sludge, indicating a concentration build-up, or additional sources such as atmospheric deposition. For the other substances, the levels in sediment are considerable lower. For most substances decreasing concentrations are observed from Roskilde Vig (near Roskilde) through the Bredning (about 6 km N) to Isefjord (lesser-polluted neighbour fjord).

Component pattern: Higher components of PAHs, PCBs and PBDEs relatively more abundant in environment than in sludge indicating loss of the lower components in the environment, i.e. higher persistence of the higher components.

Correlation between locations: The pattern of substance distribution (substance profile) in sludge is highly correlated with those the soils, but not with those in the sediment. The substance profiles in all soils are highly intercorrelated, as are those in all sediments.

For substances in the individual substance groups, the correlation between the environmental matrixes (soil and sediment) are generally higher than between those of sludge and the environment. This is particularly pronounced for PAHs.

Correlation between substance: Sludge must be omitted to make the substance correlation analysis consistent. This is due to a low relative abundance of PCBs and PCNs in sludge compared to soil and sediment.

For environmental locations (soil and sediment), all groups of synthetic substances (NPEs, PAEs, PCBs, PCNs & PBDEs) are significantly intercorrelated, but are not correlated with non-synthetic PAHs. The poor correlation between synthetics and PAHs is caused by a disproportionately high PAH-abundance in sediment.

In soil alone, PAHs are correlated with the other substances. PAEs, PCBs and PCNs are highly intercorrelated, but none of those are correlated with PBDEs, which stands apart.

For sediment alone, the substance correlation analysis does not form a consistent picture.

Depth profiles in soil: In low/no sludge soil, all substances occur in surface layer 0–10 cm, PAEs 0–20 cm.

High sludge soil sampled 2 years after 1st sampling, depths of maximums for PCBs, PAEs & PBDEs cm deeper than 1st sampling, and the concentrations of NPEs, PAEs and PBDEs are higher.

The difference suggests a downward migration, but might also be caused by spatial variations due to irregular sludge amendment. That being correct, the difference reflects the historical development in the sludge, indicating comparative constant concentration of PAHs, PCBs and PCNs, but varying – probably increasing – concentrations of NPEs, PAEs and PBDEs.

Depth profiles in sediment core: All substances display a general decreasing tendency of concentration with depth, reflecting the history of pollution. This decrease also reflects a degradation of the substances, which mainly has affected the deeper (oldest) layers. For most substances a peak is found at a depth of 11-13 cm (year $\approx$ 1948). For PCBs and PCNs, the peak is found at 5-7cm ($\approx$ 1972). Below the peaks a steep decrease leads to a low plateau at 13 cm ($\approx$ 1940), indicating that the pollution was low before 1940 (World War II).

PCBs and PCNs do have essentially similar depth profiles from 3 cm and down, probably caused by parallel histories of pollution, reflecting that PCNs are by-products in technical PCB preparations.

Artefact peaks in depth profile caused by bioturbation or mechanical mixing of layers at the core site unlikely because of undisturbed horizontal layers in the core, which had a very hard texture.

Depth profiles for some compounds display an additional peak at 0-5 cm (year $\approx$ 1980-1990) forming "two peak profiles". Most likely, the upper peak was formed during local activities (sludge dumping).

The occurrence of the single peak or two peak profiles are dependant of molecular weight. This indicate that solubility, diffusion, adsorption, stability or other physical or chemical properties of the substances play a role for shaping the depth profiles.

7 References

Beije, B. & Möller, L. (1988). 2-Nitrofluorene and related compounds: prevalence and biological effects. Mutation Research *196*, 177-209.

Berger, W.H. & Heath, G.R. (1968). Vertical Mixing in Pelagic Sediments. Journal of Marine Research, *26*, 134 – 143.

Brinkman, U.A.,Th & Reymar, H.G.M. (1976). Polychlorinated naphthalenes. J Chromatography *127*, 203-243.

Crookes, M.J., Howe, P.D. (1993) Environmental hazard assessment: Halogenated naphthalenes. Department of Environment, London, UK.

EU Commision (2000). Risk assessment on penta-PBDE, 2000.

Flindt, M., Pedersen, C.B., Hansen, L.R. & Hedal S. (1998). Hydrografisk Modellering af Typeområdet Roskilde Fjord 1998. NOVA 2003 Årsrapport, Roskilde og Frederiksborg Amter.

Grüttner, H. & Jacobsen, B. N. (1994). Miljøfremmede stoffer i renseanlæg. Miljøstyrelsen, Miljøprojekt nr. 278.

Grüttner, H., Lindgaard-Jørgensen, P. & Vikelsøe, J. (1995): Måleprogram for phthalater på 3 danske renseanlæg. Miljøstyrelsen, Arbejdsrapport nr. 54.

Grüttner, H., Vikelsøe, J. & Pritzl, G. (1996). Miljøfremmede stoffer i spildevand og slam. Massestrømsanalyser for renseanlæg. Miljøstyrelsen, Miljøprojekt nr. 325.

Hald, A (1973) Statistiske metoder. Akademisk Forlag, Copenhagen, Denmark, 483.

Harremoës, P. & Malmgren-Hansen, A. (1990). Lærebog i Vandforurening. Polyteknisk Forlag.

Hedal, S., Hansen, L.R., Thingberg, C. & Jensen, K.B. (1999). Overvågning af Roskilde Fjord 1998. Roskilde Amt, Teknisk Forvaltning og Frederiksborg Amt, Teknik og Miljø.

Jones, F. W. & Westmoreland, D. J. (1998). Degradation of nonylphenol ethoxylates during composting of sludges from wool scour effluents. Environ. Sci. Technol. *32,* 2623 - 2627.

Larsen, S.H. (2000). DEPA. Personal communication.

Madsen, P.P. & Larsen, B. (1979). Bestemmelse af Akkumulations rater i marine sedimentations områder ved Pb-210 Datering. Vand, *5*, 2 - 6.

Miljøministeriet (1976). Bekendtgørelse om begrænsninger i indførslen og anvendelsen af PCB og PCT. Miljøministeriets bekendtgørelse nr. 18 af 15. januar 1976.

Miljø- og Energiministeriet (1996). Bekendtgørelse om anvendelse af affaldsprodukter til jordbrugsformål Nr. 823, 16. Sep.

Miljø- og Energiministeriet (2000). Bekendtgørelse om anvendelse af affaldsprodukter til jordbrugsformål Nr. 49, 20 Jan.

Nylund, K., Asplund, L., Jansson, B., Jonsson, P., Litzén, K. & Sellström, U. (1992). Analysis of some polyhalogenated organic pollutants in sediment and sewage sludge. Chemosphere *24*, 1721-1730.

OECD (1997). HPV programme / EU Existing Substances Regulation. Risk Assessment Report for Nonylphenol. National Centre for Ecotoxicity and Hazardous Substances, London, UK.

Remberg, M. (1999). Analysis of phthalate esters in Swedish lakes and rivers. Presented at Phthalate Esters Environmental Analysis Workshop, arr. ECPI, Kortrijk, Belgium, 4-5 Nov. 1999.

Roskilde County & Municipality (1994). Hydrografic investigation of Roskilde Fjord. Reports from Danish Hydraulic Institute and Water Consult.

Roskilde County (1999). Rambøll, Hydrometriske beregninger 1998 Roskilde Amt, Denmark.

Shang, D.Y, MacDonald, R.W. & Ikonomou, M.G. (1999). Persistence of Nonylphenol Ethoxylate Surfactants and Their Primary Degradation Products in Sediments from near a Municipal Outfall in the Strait of Georgia, British Columbia, Canada. Environmental Science and Technology, *33*, 1366 – 1372.

Sørensen, P.B., Fauser, P., Carlsen, L & Vikelsøe, J. (2000). Evaluation of Sub-Process Validity in the TGD in Relation to Hydrophobic Substances. Ministry of Environment and Energy, National Environmental Research Institute, Department of Environmental Chemistry, Research Report submitted for publication.

Thomsen, M. & Carlsen, L. (1998). Phthalater i miljøet, opløselighed, sorption og transport. Faglig rapport fra DMU nr. 249.

Thomsen, M., Carlsen, L. & Hvidt, S. (2000). Solubilities and Surface Activities of Phthalates Investigated by Surface Tension Measurements. Environmental Toxicology and Chemistry, in press.

Toppari, J., Larsen, J.C., Christiansen, P., Giwercman, A., Grandjean, P., Guilette Jr, L.J., Jégou, B., Jensen, T.K., Jouannet, P., Keiding, N., Leffers, H., McLachlan, J.A., Meyer, O., Müller, J., Meyts, E.R.-D., Scheike, T., Sharpe, R., Sumpter, J., & Skakkebæk, N.E. (1995): Male reproductive health and environmental chemicals with estrogenic effects. Miljøstyrelsen, Miljøprojekt nr. 292.

van der Velde, E.G., de Korte, G.A.L. Linders, S.H.M.A. & Hijman, W.C (1999) Method development for the analysis of phthalates in environmnetal samples with GC-MS. Presented at Phthalate Esters Environmental Analysis Workshop, arr. ECPI, Kortrijk, Belgium, 4-5 Nov. 1999.

Vikelsøe, J., Thomsen, M. & Johansen, E. (1998): Sources of phthalates and nonylphenoles in municipal waste water. NERI technical report No. 225.

Vikelsøe, J., Thomsen, M., Johansen, E. & Carlsen, L. (1999). Phthalates and Nonylphenols in Soil – A Field Study of Different Soil Profiles. Ministry of Environment and Energy, National Environmental Research Institute, Department of Environmental Chemistry, Technical Report No. 268.

Vikelsøe, J., Fauser, P., Sørensen, P. B. & Carlsen, L. (2001). Phthalates and Nonylphenols in Roskilde Fjord. A Field Study and Mathematical Modelling of Transport and Fate in Water and Sediment. The aquatic environment. NERI Technical Report No. 339

Yamashita, N., Kannan, K., Imagawa, T., Miyazaki, A. & Giesy, J.P. (2000). Concentrations and profiles of polychlorinated naphthalenes in eighteen technical polychlorinated biphenyl preparations. Environ. Sci. Technol *34*, 4236-4241.

8 Abbreviations

Analyte	Substance analysed
BBP	Butylbenzylphthalate
D	Deuterium (^{2}H, heavy isotope of hydrogen)
D_4-BBP	BBP deuterium-labelled in ring
D_4-DEHP	DEHP deuterium-labelled in ring
D_4-DnBP	DnBP deuterium-labelled in ring
D_4-DnOP	DnOP deuterium-labelled in ring
DEHP	Di(2-ethylhexyl)phthalate
DEPA	Danish Environmental Protection Agency
dm	Dry matter
DiNP	Di("iso"-nonyl)phthalate
DnBP	Di(n-butyl)phthalate
DnNP	Di(n-nonyl)phthalate
DnOP	Di(n-octyl)phthalate
DPP	Dipentylphthalate
GC	Gaschromatography
GC/MS	GC combined with MS
HpCN	Heptachloro-naphthalene
HRMS	High resolution MS (high ability of MS to discriminate between masses)
HxCN	Hexachloro-naphthalene
LD	Limit of determination, concentration below which the result is uncertain
µg/kg dw	Microgram per kg dry weight (Parts Per Billion, PPB)
m/z	mass/charge ratio for an ion analysed in MS
MS	Mass spectrometry
MW	Molecular weight
n	number of measurements

na	not analysed
nd	Not detected, non-detect
NERI	National Environmental Research Institute
NP	Nonylphenol
NPDE	Nonylphenol-diethoxylate
NPE(s)	Nonylphenol-ethoxylate(s)
p	Probability level, level of statistical significance
PAE(s)	Phthalic acid diester(s), Phthalate(s)
PAH(s)	Polyaromatic hydrocarbons(s)
PBDE(s)	Polybrominated diphenyl ether(s)
PCB(s)	Polychlorinated biphenyl(s)
PCN(s)	Polychlorinated naphtalenes(s)
PeCN(s)	Pentachloro-naphthalene(s)
PFK	Perfluoro kerosene (calibration gas for HR-MS)
Phthalate	Di ester of phthalic acid (1,2-benzene dicarboxylic acid)
r_{crit}	Critical value above which a correlation coefficient is significantly different from zero
RT	Retention time
sd	Standard deviation
t	Students t variable
SIM	Selected ion monitoring (MS operating mode)
Spike	Labelled substance added during the analytical procedure for quality control
Steady-state	Situation with constant conditions
TeCN(s)	Tetrachloro-naphthalene(s)
u	Undefined
WWTP	Wastewater treatment plant

9 Acknowledgements

National Environmental Research Institute

The National Environmental Research Institute, NERI, is a research institute of the Ministry of the Environment. In Danish, NERI is called *Danmarks Miljøundersøgelser (DMU)*.
NERI's tasks are primarily to conduct research, collect data, and give advice on problems related to the environment and nature.

Addresses:

National Environmental Research Institute
Frederiksborgvej 399
PO Box 358
DK-4000 Roskilde
Denmark
Tel: +45 46 30 12 00
Fax: +45 46 30 11 14

National Environmental Research Institute
Vejlsøvej 25
PO Box 314
DK-8600 Silkeborg
Denmark
Tel: +45 89 20 14 00
Fax: +45 89 20 14 14

National Environmental Research Institute
Grenåvej 12-14, Kalø
DK-8410 Rønde
Denmark
Tel: +45 89 20 17 00
Fax: +45 89 20 15 15

URL: http://www.dmu.dk

Management
Personnel and Economy Secretariat
Research and Development Section
Department of Policy Analysis
Department of Atmospheric Environment
Department of Marine Ecology
Department of Environmental Chemistry and Microbiology
Department of Arctic Environment
Project Manager for Quality Management and Analyses

Environmental Monitoring Co-ordination Section
Department of Terrestrial Ecology
Department of Freshwater Ecology
Project Manager for Surface Waters

Department of Landscape Ecology
Department of Coastal Zone Ecology

Publications:
NERI publishes professional reports, technical instructions, and the annual report. A R&D projects' catalogue is available in an electronic version on the World Wide Web.
Included in the annual report is a list of the publications from the current year.

NERI Technical Reports

Nr. 366: On the Fate of Xenobiotics. The Roskilde Region as Case Story. By Carlsen, L. et al. 66 pp., 75,- DKK

Nr. 367: Anskydning af vildt. Status for undersøgelser 2001. Af Noer, H. et al. 43 s., 60,00 kr.

Nr. 368: The Ramsar Sites of Disko, West Greenland. A Survey in July 2001. By Egevang, C. & Boertmann, D. 66 pp., 100,- DKK

Nr. 369: Typeinddeling og kvalitetselementer for marine områder i Danmark. Af Nielsen, K., Sømod, B. & Christiansen, T. 105 s. (elektronisk).

Nr. 370: Offshore Seabird Distributions during Summer and Autumn at West Greenland. Ship Based Surveys 1977 and 1992-2000. By Boertmann, D. & Mosbech, A. 57 pp. (electronic)

Nr. 371: Control of Pesticides 2000. Chemical Substances and Chemical Preparations. By Krongaard, T., Petersen, K.K. & Christoffersen, C. 28 pp., 50,00 DKK

Nr. 372: Det lysåbne landskab. Af Ellemannn, L., Ejrnæs, R., Reddersen, J. & Fredshavn, J. 110 s., 120,00 kr.

Nr. 373: Analytical Chemical Control of Phthalates in Toys. Analytical Chemical Control of Chemical Substances and Products. By Rastogi, S.C. & Worsøe, I.M. 27 pp., 75,00 DKK

Nr. 374: Atmosfærisk deposition 2000. NOVA 2003. Af Ellermann, T. et al. 88 s. (elektronisk primo december 2001)

Nr. 375: Marine områder 2000 – Miljøtilstand og udvikling. NOVA 2003. Af Henriksen, P. et al. (elektronisk primo december 2001)

Nr. 376: Landovervågningsoplande 2000. NOVA 2003. Af Grant, R. et al. (elektronisk primo december 2001)

Nr. 377: Søer 2000. NOVA 2003. Af Jensen, J.P. et al. (elektronisk primo december 2001)

Nr. 378: Vandløb og kilder. NOVA 2000. Af Bøgestrand, J. (red.) (elektronisk primo december 2001)

Nr. 379: Vandmiljø 2001. Tilstand og udvikling – faglig sammenfatning. Af Boutrup, S. et al. 62 s., 100,00 kr.

Nr. 380: Fosfor i jord og vand – udvikling, status og perspektiver. Kronvang, B. (red.) 88 s., 100,00 kr.

Nr. 381: Satellitsporing af kongeederfugl i Vestgrønland. Identifikation af raste- og overvintringsområder. Af Mosbech, A., Merkel, F., Flagstad, A. & Grøndahl, L. 42 s., 100,00 kr.

Nr. 382: Bystruktur og transportadfærd. Hvad siger Transportvaneundersøgelsen? Af Christensen, L. (i trykken)

Nr. 383: Pesticider 2 i overfladevand. Metodafprøvning. Af Nyeland, B. & Kvamm, B. 45 s. + Annex 1, 75,00 kr.

Nr. 384: Natural Resources in the Nanortalik Area. An Interview Study on Fishing, Hunting and Turism in the Area around the Nalunaq Gold Project. By Glahder, C.M. 81 pp., 125,00 kr.

Nr. 385: Natur og Miljø 2001. Påvirkninger og tilstand. Af Bach, H., Christensen, N. & Kristensen, P. 368 s., 200,00 kr.

Nr. 386: Pesticider 3 i overfladevand. Metodeafprøvning. Af Nyeland, B. & Kvamm, B. 94 s., 75,00 kr.

Nr. 387: Improving Fuel Statistics for Danish Aviation. By Winther, M. 56 pp., 75,00 DKK

2002

Nr. 388: Microorganisms as Indicators of Soil Health. By Nielsen, M.N. & Winding, A. 82 pp., 90,00 DKK

Nr. 389: Naturnær skovrejsning – et bæredygtigt alternativ? Af Aude, E. et al. 47 s. (elektronisk)

Nr. 390: Metoder til at vurdere referencetilstanden i kystvande – eksempel fra Randers Fjord. Vandrammedirektiv-projekt. Fase II. Af Nielsen, K. et al. 43 s. (elektronisk)

Nr. 391: Biologiske effekter af råstofindvinding på epifauna. Af Lisbjerg, D. et al. 54 s. (elektronisk)

Nr. 392: Næringssaltbegrænsning af makroalger i danske kystområder. Et samarbejdsprojekt mellem Ringkøbing Amt, Nordjyllands Amt, Viborg Amt, Århus Amt, Ribe Amt, Sønderjyllands Amt, Fyns Amt, Roskilde Universitetscenter og Danmarks Miljøundersøgelser. Af Krause-Jensen, D. et al. 112 s. (elektronisk)

Nr. 393: Vildtudbyttet i Danmark i jagtsæsonen2000/2001. Af Asferg, T. 34 s., 40,00 kr.

Nr. 394: Søerne i De Østlige Vejler. Af Jeppesen, E. et al. 90 s., 100,00 kr.

Nr. 395: Menneskelig færdsels effekt på rastende vandfugle i saltvandssøen. Af Laursen, K. & Rasmussen, L.M. 36 s., 50,00 kr.

Nr. 396: Miljøundersøgelser ved Maarmorilik 1999-2000. Af Møller, P. et al. 53 s. (elektronisk)

Nr. 397: Effekt af lystfiskeri på overvintrende troldænder i Store Kattinge Sø. Af Madsen, J. 23 s. (elektronisk)

Nr. 398: Danske duehøges populationsøkologi og forvandling. Af Drachmann, J. & Nielsen, J.T. 51 s., 75,00 kr.

Occurrence, sources, geographical distribution, transport and fate of
the persistent pollutants PAH, NPE, PAE, PCB, PCN and PBDE was
investigated in sludge, soil and sediment in a local environment.
Further investigated was the vertical distribution in cores of soils
and sediment.