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A Field Study of Different Soil Profiles

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Jørgen Vikelsøe
Marianne Thomsen
Elsebeth Johansen
Lars Carlsen
Department of Environmental Chemistry

Data sheet

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Abstract: Soils typical for Danish agriculture were investigated, an uncultured preserved area, two manured soils, an artificially fertilised soil and four soils exposed to different amounts of sludge. At each location two soil cores 50 cm in depth were taken, divided into sections of 10 cm each and analysed for nonylphenoles and phthalates by GC/HRMS. The results show that DEHP and occasionally DiNP were the most abundant phthalates. A close relationship was found between the concentrations and the method of dressing. The concentration levels were low and similar in all the soils with the exception of two soils exposed to high amounts of sludge. A time trend study suggested a downward movement for DEHP of about 20 cm in 2 years.

Keywords: Phtalates, nonylphenoles, nonylphenol-ethoxylate, soil, analysis, DEHP.

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

Miljøbutikken
Information and Books
Læderstræde 1
DK-1201 Copenhagen K
Denmark
Tel.: +45 33 37 92 92
Fax: +45 33 92 76 90

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Summary

The purpose of the investigation has been to evaluate the concentration, distribution and possible migration of nonylphenoles and phthalates in vertical profiles of soils cultivated by different fertilisation and dressing methods, representing a broad range of exposure to environmental pollutants.

The soils selected were typical for Danish agriculture. The individual soils had been cultivated by the same method for at least two years, assumed sufficient to have a significant impact on the soil concentrations of the substances studied. A prerequisite for comparable results is similar characteristics of the soils, i.e. texture as well as the content of humus, clay, silt and sand. Such data are found in the Danish Square Grid Database, used to select the locations.

All the soils are developed on morainic deposits since the last ice age and have hence a comparably high clay content. The sites were all located in a limited geographical region (Roskilde), leading to comparable contributions from deposition as shown in a previous part of the project.

Seven cultured soils were investigated. These were: Two soils ecologically cultured through 40 and 5 years respectively, an artificially fertilised soil, three soils amended with low, medium and high amounts of sludge, respectively, and finally a soil exposed to runoff from a sludge storage. The sludge originates from medium sized municipal city waste water treatment plants and a smaller rural plant, respectively. For comparison and as a background reference was included a soil in a preserved area not cultured for more than 50 years.

At each location two soil cores 50 cm in depth were taken, each profile being divided into 5 sub-samples of each 10 cm, representing the soil profiles. Further information on soil characteristics were obtained by visual inspection of the profiles on site, noting colour, texture and content of clay, sand and particles. This information is only qualitative, but represents the location more closely than the square grid database.

The samples were extracted in dichloromethane and analysed for nonylphenoles and phthalates by gaschromatopgraphy / high resolution mass spectrometry (GC/HR-MS).

The results show that DEHP was the most abundant phthalate in most samples, but high concentrations of DiNP occurred occasionally. Nonylphenoles seemed to occur in high concentrations only in the two soils exposed to high amounts of sludge.

A close relationship was found between the concentration levels in the profiles, and the method of dressing. The concentration levels were low and similar in the artificially fertilised soil and in the soils amended with low amounts of sludge as well as in the manured soils, and did not differ significantly from the level in the preserved soil. In contrast, much higher concentrations were found in the two soils exposed to high amounts of sludge.

In several soils, predominantly clayey in character, a distinct concentration profile was observed, characterised by a concentration maximum at a depth of 20-30 cm just below the ploughing layer. In other soils, sandy in character, no such maximum was seen.

In some profiles, detectable concentrations in the bottom depth were present, demonstrating that the sampling depth of 50 cm is not sufficient for a complete profile evaluation.

The time trend was investigated by revisiting the location amended with high amounts of sludge after the lapse of two years, reaching a sampling depth of 60 cm. This time, the profile maximum for the higher phthalates were found at a depth of 40-50 cm, suggesting a downward wandering of 10 cm / y. A relatively high concentration found in the bottom depth indicates that downward flow may pose a risk for the groundwater.

Resumé

Jordundersøgelsens formål har været at undersøge forekomst og fordeling af nonylphenoler og phthalater i dybdeprofiler fra forskelligt gødet, behandlet og dyrket jord, med store forskelle i belastning med miljøfremmede stoffer.

Der er udvalgt typiske danske landbrugsjorde, som hver især har været dyrket med samme metode i mindst to år, hvilket skønnes tilstrækkeligt til at have væsentligt indflydelse på koncentrationen af de undersøgte stoffer i jorden. En forudsætning for sammenlignelige resultater er ensartede karakteristika for jordene, d.v.s. tekstur samt indhold af humus, ler, silt og sand. Data herover findes i Danmarks Kvadratnetsundersøgelsers database, som blev anvendt ved udvælgelsen af lokaliteterne.

Alle jorde forekommer på moræneaflejringer fra sidste istid og er derfor ret lerholdige. Lokaliteterne var alle placeret i samme geografiske egn (Roskilde) hvilket ifølge tidligere undersøgelser i projektet fører til sammenlignelige bidrag fra deposition.

Syv opdyrkede jorde blev undersøgt. Disse er: To jorde gødet med husdyrgødning gennem henholdsvis 40 og 5 år, en handelsgødet jord, tre jorde gødede med forskellige mængder af slam, og endelig en jord udsat for afstrømning fra et slamdepot. Slammet produceres henholdsvis på mellemstore rensningsanlæg i byzone og et mindre anlæg i landzone. Til sammenligning og som baggrundsreference valgtes en udyrket naturgrund, der har henligget fredet i over 50 år.

Hvert sted blev udtaget to borekærner af 50 cm dybde, som hver blev delt i fem delprøver hver 10 cm høje, repræsenterende en jordprofil. Yderligere information om jordbundsforholdene blev indhentet ved at inspicere profilerne visuelt ved prøvetagningen, og iagttage farve, tekstur og indhold af ler, sand og partikler. Denne information er kun kvalitativ, men repræsenterer stedet bedre end kvadratnets databasen.

Prøverne blev ekstraheret med dichlormethan, og analyseret for nonylphenoler og phthalater med massespektrometri/højtopløsende gaschromatografi (GC/HR-MS).

Resultaterne viste, at DEHP gennemgående var det i højest koncentration forekommende phthalat, men høj koncentration af DiNP forekom lejlighedsvis. Nonylphenoler forekom kun i høj koncentration i de to jorde udsat for høje slammængder.

Der fandtes en tæt sammenhæng mellem koncentrationsniveauerne i profilerne og gødningsmetoden. Koncentrationsniveauerne i den handelsgødede jord og i jordene gødet med lave slammængder samt i de to økologisk dyrkede jorde var af samme størrelsesorden, og afveg ikke væsentligt fra niveauet i den fredede jord. Derimod fandtes betydelig højere koncentrationer i de to jorde udsat for høje slammængder.

I adskillige jorde, fortrinsvis lerede, fandtes en karakteristisk koncentrationsprofil kendetegnet ved et koncentrations maksimum i 20-30 cm dybde, netop under pløjelaget. I andre jorde, af sandet karakter, fandtes ikke et sådant maksimum.

Nogle profiler udviste kendelige koncentrationer i det nederste lag, hvilket viser at prøvedybden på 50 cm ikke er tilstrækkelig til en fuldstændig profil evaluering.

Tidsafhængigheden blev undersøgt ved at genbesøge den højt slamgødede jord efter 2 års førløb, ned til en prøvetagnings dybde på 60 cm. Denne gang fandtes profil-maksimum for de højere phthalater i 45-50 cm's dybde, hvilket antyder en vandring nedad på 10 cm / år. En forholdsvis høj koncentration i bunddybden tyder på, at nedsivning muligvis kan udgøre en risiko for grundvandet.

1 Introduction

In recent years an increasingly intense debate in the news media as well as in the scientific literature concerning the possible role of environmental chemicals such as pesticides, detergents, plasticizers and other industrial chemicals, has developed.

The emission of such compounds into the environment leads to the risk of human exposure. Some phthalates and nonylphenoles has been recognised as possibly oestrogen, making them harmful to male reproduction, and possibly playing a role for the development of breast cancer in humans (*Toppari et. al. 1995*).

Several Danish investigations of phthalates in waste water and sewage sludge have been carried out, confirming the omni-presence of phthalates (*Grüttner et. al. 1995, Grüttner et. al. 1996, Jepsen & Grüttner 1997, Kjølholt et. al. 1997, Vikelsøe et. al. 1998*). These substances tend to be concentrated in the sewage sludge from the waste water by processes in the waste water treatment plants. For this reason, the use of sewage sludge in agriculture could lead to the introduction of these compounds into the human food chain.

But other possible sources for phthalates and nonylphenoles in agriculture exists. Thus phthalates are found in deposition and artificial fertiliser. Further, phthalates are used as emulsifying agents in pesticide spray solutions, and even manure contain phthalates.

The sources, abundance, distribution and fate of phthalates and nonylphenoles in agricultural soils is the aim of the present study. A number of differently dressed and fertilised soils are investigated. The vertical distribution of these substances in soil depth profiles has not previously been studied.

The sources of the phthalates have been addressed in a number of studies. Thus, phthalates has been found in household waste water, probably from washing of plastics containing softeners (*Vikelsøe 1995, Jepsen & Grüttner 1997*).

The emission of phthalates in the waste water from an array of industries and institutions, as well as deposition has been investigated previously (*Vikelsøe et. al. 1998*). The present project is a continuation, being a part of a larger scheme addressing pollutants in the technosphere, the atmospheric, the terrestrial and the aquatic (fjord and lake) environments. At a later stage of the project series, it is planned to extend the study from phthalates and nonylphenoles to a number of other environmental pollutants.

The investigations are carried out in a limited geographical region, leading to many advantages, thus the contribution from deposition can be addressed concerted, as shown by *Vikelsøe et. al. (1998*). The series of investigations are carried out near the city of Roskilde, which makes a representative Danish provincial city of average size. The city is situated near a fjord, which is a prerequisite for the fjord study.

The analytical methods used has been developed specially for the present study as an extension and improvement of the methods used in the previous source study (*Vikelsøe et. al. 1998*).

2 Analytical methods

General precautions

A general problem for analysis of phthalates is a high blank, which masks the phthalates in the samples thus elevating the limits of determination. This is particularly problematic for samples in low concentrations. Furthermore, the use of a complicated procedure increases the risk of contamination since the main cause for this is contact with contaminated glassware and chemicals. To reduce the contamination from glass as far as possible, exclusively new glassware, heat-treated at 450°C, was used. The heat treatment is necessary, since even new glassware in most cases is contaminated with material amounts of DBP as shown in a previous part of the project (*Vikelsøe et. al. 1998*). To reduce the blank even further, the extraction was carried out *only once* using only a single bottle, and the only other glassware in contact with the samples were pasteur pipettes, 20 ml vials, and the injection vials and inserts for the autosampler. Because of the application of high-resolution mass spectrometry for the analysis, no interferences from other substances prevail, making it possible to analyse un-cleaned samples with good results.

2.1 Sampling

(The experimental plan regarding the sampling is described in Section 5.1) The soil samples were taken by means of a drill made of stainless steel with a length of 50 cm and 10 cm diameter, which was hammered into the ground. A longitudinal slot on the side of the drill tube makes it possible to insert a stainless steel blade into the core to remove core specimens. The core was divided on site into 5 core-sections each 10 cm long, the *primary samples*, which were transferred to cleaned glass sampling bottles. The primary samples were inspected visually, and the colour, texture and content of roots, pebbles, clay and sand was noted. After labelling, the samples were immediately transported to the laboratory, frozen, and stored at -20°C until analysed.

2.2 Extraction

After thawing at room temperature, two sub-samples of 50 g from each primary sample (core section) were weighed accurately into 250 ml wide-necked Pyrex bottles. To avoid the risk of contamination and evaporation, no mixing of the primary samples was carried out before the sub-samples were taken. A volume of 0.1 ml extraction spike solution (Table 1) was added directly to each bottle which were subsequently shaken and left for 15 min to equilibrate the extraction spikes with the soil and the glass surfaces. The spikes are used for calculation of the extraction recovery and the final results. A volume of 100 ml dichloromethane was added, and the bottle was closed by a screw-lid covered by aluminium-foil. The sample was extracted by shaking for 1 hour in a shaking apparatus (Heidolph Unimax 2010 at 200 shakes/min). It was left overnight, and subsequently shaken the next day for 1 hour.

The bottle was left until the phases were separated. A sub-extract of about 10 ml of the solvent phase was transferred to a 20 ml glass vial by means of a pasteur pipette. This approximate pipetting of the sub-extract does not impair precision, since the results are calculated in relation to the spikes already present. Thus, the use of volumetric pipettes, which are difficult to decontaminate completely, is avoided. The solvent was removed by careful evaporation under N_2, the sample re-dissolved in a volume of 1 ml syringe spike solution, Table 2, and analysed directly by high-resolution GC/MS. If necessary, the sample was diluted appropriately with syringe spike solution.

Table 1 Extraction spike solution

Substance	Acronym	Label	µg/ml
Dibutylphthalate	D_4-DBP		
Benzylbutylphthalate	D_4-BBP	D_4	10
Bis(2-ethylhexyl)-phthalate	D_4-DEHP		
Solvent	Ethanol		

Table 2 Syringe spike solution

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

Standard solutions

Standard solutions are used for quantification and identification, (Table 3) analysed by GC/MS for about every 5 samples). They are called external, since they are analysed separately from the samples.

Table 3 Phthalate standard solutions for GC/MS

Substance	Acronym	µg/ml low	µg/ml high	Type	Ref
Nonylphenol	NP	0.01	0.1		1
Nonylphenol diethoxylate	NPDE	0.05	0.5		1
Dibutylphthalate	DBP	0.01	0.1		1
Dipentylphthalate	DPP	0.01	0.1		1
Benzylbutylphthalate	BBP	0.01	0.1	Ana	2
Di-(2ethylhexyl)-phthalate	DEHP	0.01	0.1		3
Di-(n-octyl)-phthalate	DnOP	0.01	0.1		3
Di-(n-nonyl)-phthalate	DnNP	0.01	0.1		3
Di-("iso"-nonyl)-phthalate	DiNP	0.01	0.1		3
D_4-Dibutylphthalate	D_4-DBP				1
D_4-Benzylbutylphthalate	D_4-BBP	0.1	0.1	Esp	2
D_4-Bis-(2ethylhexyl)-phthalate	D_4-DEHP				3
D_4-Di-(n-octyl)-phthalate	D_4-DnOP	0.1	0.1	Ssp	4
Solvent for standard	n-Hexane				

The Type column refers to: Ana = Analyte, Esp = Extraction spike, Ssp = Syringe spike
The Ref columns indicates the spikes used for calculation of the results for each analyte, thus DBP and DPP are calculated from D_4-DBP (Ref 1), BBP from D_4-BBP (Ref 2) etc.

Blanks	Empty bottles were extracted for blank (empty laboratory blanks). A blank was made every day (about 1 blank for 6 samples). During laboratory work, great care was taken to ensure that the blanks are diluted and treated in any way as a sample, using the same batches of solvents etc.
Moisture determination	The moisture content in each sample was determined by drying about 10 g of sample at 120°C for 20 hours. The dry-matter content was used to calculate the final results for both sub-samples.

2.3 Gaschromatography

Gaschromatograph	Hewlett-Packard 5890 series II gas chromatograph
Injection:	CTC autosampler. 2 µl split/splitless 270°C, purge closed 40 sec.
Pre-column:	Chrompack Retention Gap. Fused silica, 2.5 m x 0.32 mm i.Ø,
Column:	J&W Scientific DB5-MS. Fused silica, 30 m x 0.252 mm i.Ø, crosslinked phenyl-methyl silicone 0.25 µm film thickness
Carrier gas:	Helium, pressure 120 Kpa
Temperature program:	40 sec at 80°C, 10°C /min to 290°C, 15 min at 290°C

2.4 Mass spectrometry

Instrument:	Kratos Concept 1S high resolution mass spectrometer
Resolution:	10.000 (10% valley definition)
Ionisation:	Electron impact 45 - 55 EV depending on tuning, ion source 270°C
Interface:	290°C direct to ion source
Calibration gas:	Perfluoro-kerosene (PFK)
Scan:	0.6 sec per scan (about 0.1 sec per ion) in Selected Ion Monitoring (SIM) mode (Table 4).

Table 4 Masses for high resolution MS- analysis

Substance	**Mass**
Nonylphenoles	135.0809
Unlabelled phthalates	149.0239
D_4-labelled phthalates (spikes).	153.0490
Lock mass	130.9920

(The lock mass is a mass in the PFK-spectrum used to compensate for random variations in the magnetic field of the instrument).

In Fig. 1 is shown mass tracks (ion chromatograms) from the GC/MS analysis of the external standard, and in Fig. 2 from a soil sample. The 3 mass tracks correspond to (from top) nonylphenoles, labelled phthalates (spikes) and native phthalates.

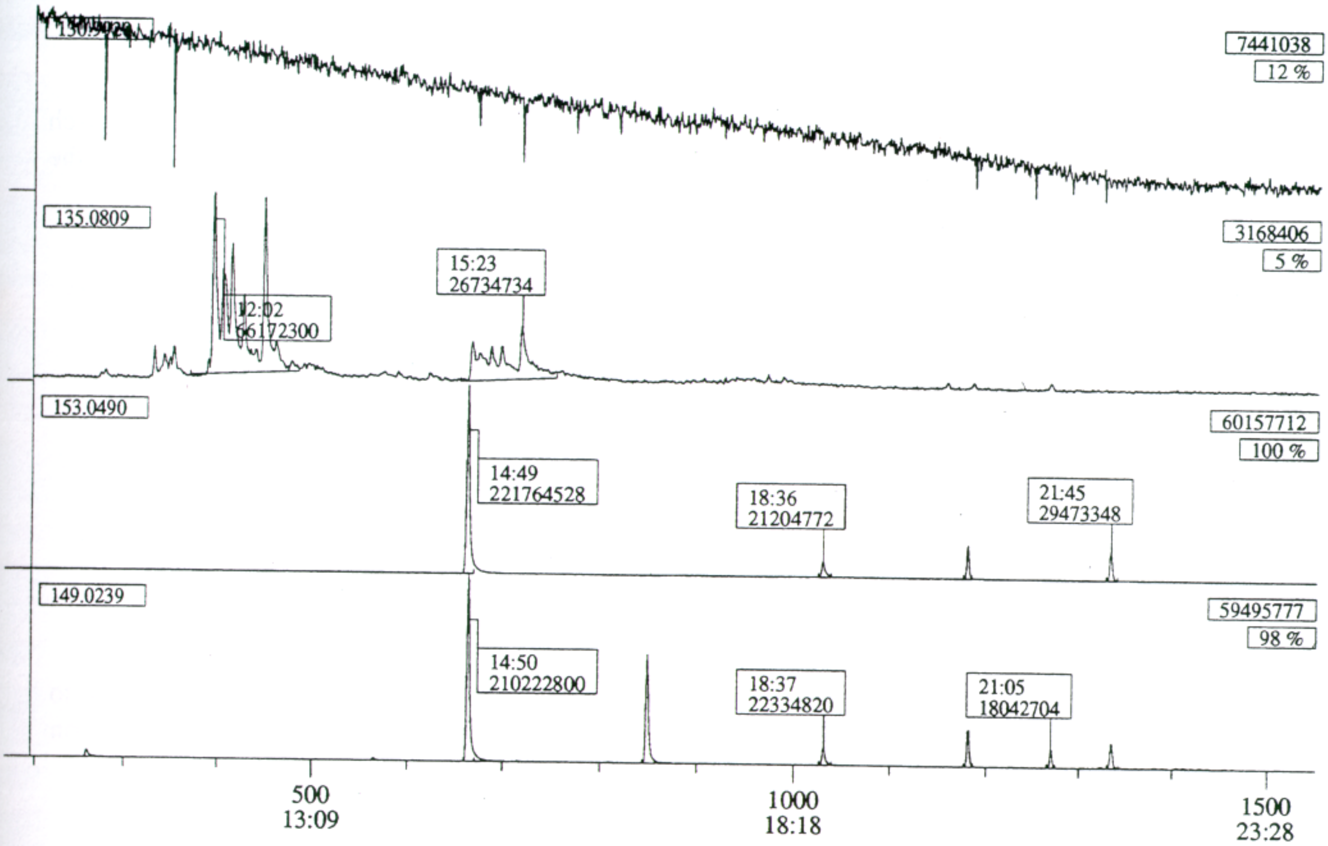

Fig. 1 GC/MS analysis of the high level external standard. Mass tracks for labelled and native phthalates, and nonylphenoles.

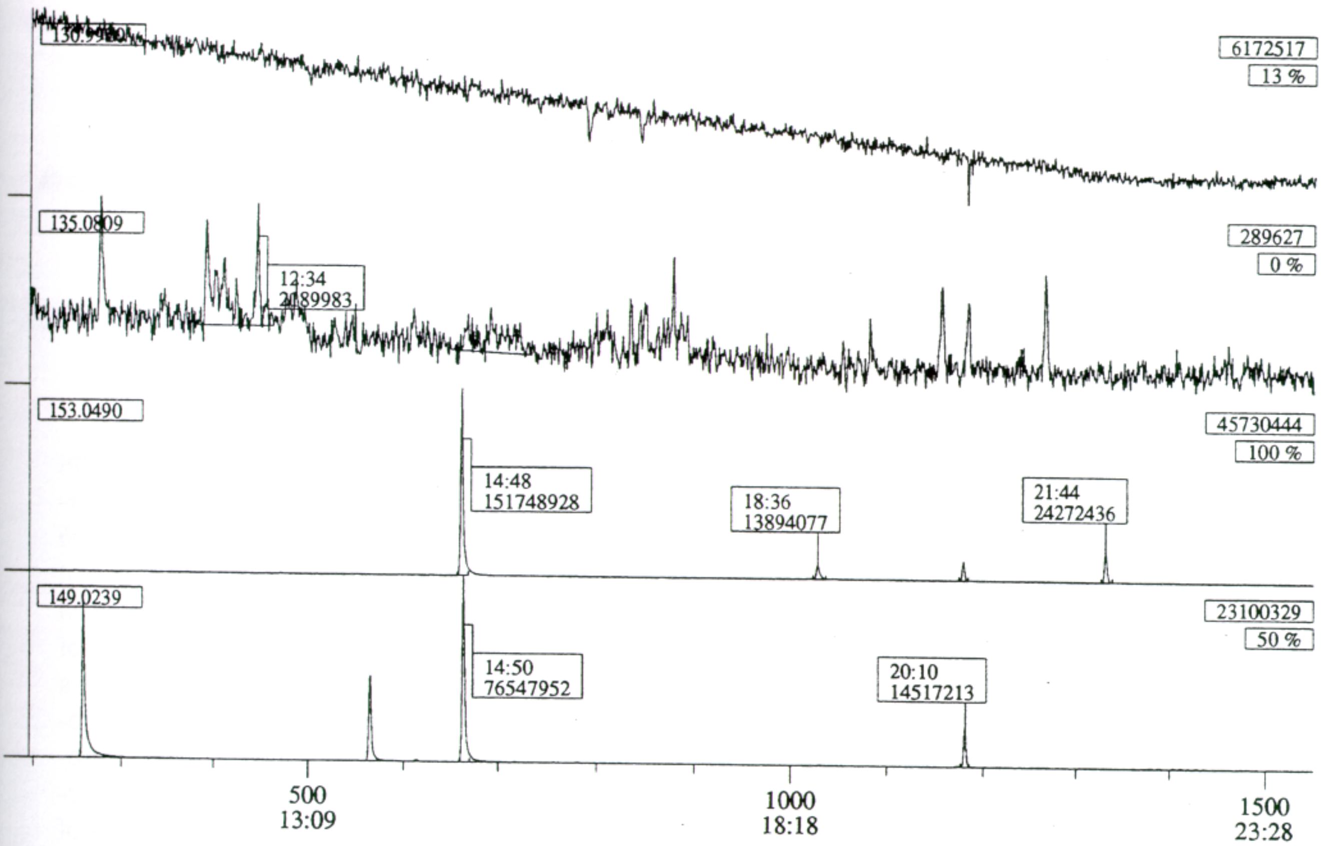

Fig. 2 GC/MS analysis of a soil sample (NERI no 6-917-1). Mass tracks for labelled and native phthalates, and nonylphenoles.

2.5 Calculations

Response factors

The extraction spikes are used as reference for the analytes. For each analyte a response factor is calculated from the GC/MS analysis of the external standard according to formula 1:

$$R_i = \frac{C_{es}}{C_{is}} \cdot \frac{A_{is}}{A_{es}} \qquad (1)$$

where:

R_i = Response factor for analyte "i"
C_{is} = Concentration of analyte "i" in the external standard
C_{es} = Concentration of the corresponding extraction spike
A_{is} = Area for the analyte "i" for the external standard
A_{es} = Area of the corresponding 1) extraction spike

Analyte concentrations

The concentrations in the unknown samples are calculated in relation to the areas of extraction spikes and analytes, compensating for extraction losses and blanks, according to formula 2:

$$C_{ip} = \left(D \cdot V_u \cdot \frac{C_{eu} \cdot A_{iu}}{R_i \cdot A_{eu}} - C_b \right) \cdot \frac{1}{M_p} \qquad (2)$$

where:

C_{ip} = Concentration of analyte "i" in sample
D = Dilution factor (x dilution)
V_u = Volume of syringe spike
C_{eu} = Concentration of corresponding extraction spike in sample
A_{iu} = Area of analyte "i" in sample
R_i = Response factor for analyte "i" (calculated above)
A_{eu} = Area for corresponding extraction spike in the sample
C_b = Average of corresponding blanks, each calculated according to first term inside parenthesis
M_p = Dry weight of sample extracted

Results presentation

Note that the blank average is subtracted before division with the amount of sample M_p, i.e. in the unit µg/sample. By subtraction the blank average from very low concentrations, negative differences may arise. *Such results are shown as blank spaces in the results tables*. During the use of results e.g. for the calculations of averages, sums and mass flows, *such numbers are set to zero*. From a statistical point of view, the inclusion of negative result in sums and averages would be more correct, but from a chemical viewpoint negative concentrations have no meaning. The procedure adopted here, i.e. setting the negative differences to zero, introduces a slight positive bias for the averages containing such results. Occasionally, a result will turn out as a positive number below the limit of determination as calculated in the following

.

Of course such results are highly uncertain, but are nevertheless included in the calculation of sums, averages and mass flows. *Such average results are shown in parenthesis in the results tables.*

Limits of determination

The limit of determination is calculated for each substance from the variances of the difference between sample and blank, equal to the sum of the variance of the average of blanks and the MS variance (calculated by the software of the mass spectrometer from the signal to noise ratio and response factor of the corresponding standard), according to formula 3. The first term inside the square-root is the variance of the mean of blanks. The formula refer to the 1 σ (sigma) level of significance. This low significance level was chosen in order to retain as many low-level data as possible, since a major objective of the investigation is to compare low levels (and not to check limit values).

$$LD = \sqrt{\frac{VarB}{n} + VarMS} \qquad (3)$$

where:

LD	=	Limit of determination (single determination, 1 σ level)
VarB	=	Variance of the blank
n	=	multiplicity of blank determination (e.g. 10 or 2)
VarMS	=	Variance of MS (calculated from signal to noise ratio and response factor by the MS software)

As can be seen, the LD can be reduced by increasing n, the number of blanks in the average subtracted.

The LD for quadruple determination average is 1/2 of LD for single determination

Recovery

The recovery for extraction spike “e” is calculated according to formula 4:

$$R_e\% = 100 \cdot \frac{A_{eu} \cdot C_{su}}{A_{su} \cdot C_{eu}} \cdot \frac{A_{ss} \cdot C_{es}}{A_{es} \cdot C_{ss}} \qquad (4)$$

where:

$R_e\%$	=	Recovery % of extraction spike “e” in sample
A_{eu}	=	Area of extraction spike “e” for sample
C_{eu}	=	Nominal (added) concentration of extraction spike “e” in sample
A_{su}	=	Area of syringe spike for sample
C_{su}	=	Concentration of syringe spike in the sample
A_{es}	=	Area of extraction spike “e” for standard
C_{es}	=	Concentration of extraction spike “e” in standard
A_{ss}	=	Area of syringe spike for standard
C_{ss}	=	Concentration of syringe spike in standard

2.6 Blanks and limits of determination

Blanks

In Table 5 the statistics for the blanks for the soil samples are shown. The table contains sections for undiluted and 10 times diluted blanks, showing the mean, standard deviation, coefficient of variation and standard deviation of the mean. This latter is used in the calculation of the limit of determination. The number of blanks, n, belongs to the same analytical series from which the blank mean is subtracted during the calculation of result. The means and the standard deviations shown in Table 5 are pooled from two such analytical series. According to the calculations section, the blank average subtracted from the sample result is given in µg/sample. This can immediately be compared with the blanks found in the previous part of the project (*Vikelsøe et. al. 1998*). To facilitate comparison with the results, the blanks have also been calculated in Table 5 in the unit µg/kg by assigning a fictitious sample weight of 0.05 kg (close to the average actually used for soil samples) to the blanks.

Table 5 Statistics for blanks for soil samples

Statistics	n	Unit	NP	NPDE	DBP	DPP	BBP	DEHP	DnOP	DnNP	DiNP
						Undiluted blanks					
Mean	10	µg/sample	0.06	0.15	0.42	0.002	0.016	0.29	0.041	0.005	0.50
Mean	10	µg/kg	1.1	3.1	8.4	0.03	0.31	5.8	0.82	0.10	10
Std.dev.	10	µg/kg	0.69	5.8	4.6	0.07	0.53	3.2	0.37	0.29	7.2
CV	10	%	63	190	55	200	170	56	45	300	73
Std M	10	µg/kg	0.22	1.8	1.5	0.02	0.17	1.0	0.12	0.09	2.3
						Blanks diluted 10 x					
Mean	2	µg/sample	1.4	1.4	3.4	0.009	0.095	1.5	0.153	0.039	2.5
Mean	2	µg/kg	27	28	69	0.17	1.9	29	3.1	0.78	49
Std.dev.	2	µg/kg	6.6	5.1	50	0.28	1.1	1.7	1.2	1.6	21
CV	2	%	24	18	73	160	58	6	41	200	42
Std M	2	µg/kg	4.7	3.6	35	0.20	0.78	1.2	0.88	1.1	15

D = dilution factor CV = coefficient of variation Std M = standard deviation of the mean

It is observed from Table 5 that the mean blanks for the diluted samples are higher than for the undiluted ones. This is due to unavoidable contamination of equipment and solutions used during the dilution process. Nevertheless, the blanks of the present project (in µg/sample) are on the same or lower level compared with the lowest blank of previous part of the project, the deposition measurements (*Vikelsøe et. al. 1998*).

For the samples of artificial fertiliser, manure and sludge, blanks were specially prepared and analysed. In Table 6, the mean and standard deviation of the blanks for these measurements are given.

Table 6 Blanks for fertiliser, manure and sludge

Fertiliser	D	n	NP	NPDE	DBP	DPP	BBP	DEHP	DnOP	DnNP	DiNP
					Mean, µg/kg						
Artificial	1	2	67.7	60.4	13.0	0	0.8	30.9	0.3	0	7.0
Manure	1	2	289	479	11.6	4.1	5.2	31.5	3.2	9.7	37.2
Sludge	10	4	705	3580	262	22.9	37.6	433	23.8	17.2	505
Sludge	100	2	2410	3050	693	53.9	82.5	1550	33.0	56.1	2060
					Standard deviation, µg/kg						
Artificial	1	2	23.1	17.5	2.4	0	0.04	5.4	0.5	0	0.01
Manure	1	2	109	250	6.2	5.7	7.3	3.1	4.5	6.8	18.9
Sludge	10	4	6.0	1460	65.8	0	14.5	282	19.8	34.4	59.1
Sludge	100	2	945	4310	242	76.3	117	660	46.6	79.4	1150

D = dilution factor

Limits of determination

In Table 7 the limits of determination (LD) for single determinations are shown in units of µg/kg for undiluted and diluted samples. All soil samples were undiluted except the highly concentrated samples at location 7 and 8, for which dilution was necessary to avoid saturation of the MS-signal. The LDs in Table 7 are calculated according to formula 3 from the variation of the blanks in Tables 5 and 6, and the MS variation (not shown). The latter is calculated from the average of all corresponding MS-runs.

Table 7 Limits of determinations for single determinations, µg/kg

Sample	D	NP	NPDE	DBP	DPP	BBP	DEHP	DnOP	DnNP	DiNP
Soil locations 1-6	1	0.2	2	1.5	0.02	0.2	1	0.1	0.1	2
Soil locations 7&8	10	6	8	40	0.2	0.8	1	0.9	1	10
Artificial fertiliser	1	2	2	0.2	0.007	0.02	0.4	0.04	0.04	0.3
Manure	1	20	50	1	1	2	0.6	0.9	1.4	4.
Sludge	10	120	900	40	8	10	70	10	10	60
Sludge	100	700	3000	170	50	80	500	30	60	800

D = dilution factor

As observed from Table 7, the limit of determination for DEHP for the samples of soil, manure and artificial fertiliser is about 1 µg/kg. Comparing the soil samples (first two rows) of Table 7 with the standard deviation of the mean of blanks (StdM) in Table 5, it is seen that in most cases the LD is only slightly above StdM. This indicates that the blank is playing the major role for the LD compared to the MS signal to noise ratio. As seen from Table 7, the limits of determination increases with the dilution factor, but not proportionally. Of course, for highly concentrated samples which must be diluted to avoid signal saturation, detection is not the main problem.

3 Samples

Criteria for selection

To ensure comparable, representative and relevant results, the following criteria were adopted for the selection of soils:

- Typical for Danish agriculture with respect to soil and methods
- Encompass a broad range of dressing/fertilisation and cultivating methods, comprising high and low level sludge, organic manure, artificial fertiliser and an uncultivated area for background reference.
- Known history including known characteristics of dressing/fertiliser.
- Be exposed for a time sufficient to allow the dressing/fertilisation method to have a significant impact on the xenobiotics studied in the soil. This condition is assumed to be reached when the same method has been in operation for at least two years.
- Identical or similar and known soil characteristics, i.e. the content of humus, clay, silt and sand. This criterion is necessary since soil differences will blur the picture of different dressing/fertilisation and cultivating methods.
- Similar and known atmospheric deposition. It is more likely that the depositions at different locations are comparable within a small region.

Discussion

In practice, it is not possible to fulfil all these criteria completely at every single location selected. Thus, the amount applied of sludge, manure and artificial fertiliser is only known approximately, and their content of xenobiotics may have changed over the years in an unknown way. Furthermore, quantitative data of soil characteristics is only known from the Danish Square Grid Database, which may deviate substantially - especially in a morainic landscape - from those in the sampling cores because of the distance between the database sampling points and the sampling positions on the locations. This distance is even not known precisely, since the exact grid point sampling positions are not found in the database - only the grid mesh number. Finally, it could perhaps be expected that significant differences between deposition rates at the locations might exist. This item is further discussed in Chapter 7, where it is concluded that a single sampling station is sufficient to yield a reasonable representative estimate of the deposition of nonylphenoles and phthalates in the whole region.

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. Thus, the deposition of nonylphenoles and phthalates were measured in a meteorological station (Lille Valby) as well as in small rivers in the region. This is of importance for evaluation of the infiltration. Furthermore, sludge from the municipal waste water treatment plant in this city is used in several of the soil sites, and has been extensively investigated. These studies has been published in another part of the project concentrating on sources of nonylphenoles and phthalates (*Vikelsøe et. al. 1998*). Finally, sediment and water of the nearby Roskilde fjord is being investigated in a separate study, for which the present soil investigation is of importance in evaluating the run-off into the fjord, in a concerted effort to map the sources and distribution of xenobiotics in the area.

3.1 Locations

Eight locations were selected according to the above criteria, listed in order of expected increasing load.

1. Preserved natural area not cultured for 50 - 100 years, cattle grazing (Ejby). Sampled 5 Oct. 1996.

2. Ecologically cultured for 40 years (Ledreborg).
   Sampled 5 Oct. 1996.

3. Manured sustainable in ecologically culture for 5 years, formerly conventionally cultured (Kirke Såby). Sampled 5 Oct. 1996.

4. Conventionally cultured using artificial fertiliser (Ågerup).
   Sampled 5 Oct. 1996.

5. Sludge amended, medium amounts, cultured (Jyllinge).
   Sampled 26 Sep. 1996

6. Sludge amended, low amounts, cultured (Sundbylille).
   Sampled 26 Sep. 1996.

7. Sludge amended with high amounts for 25 years, changed to artificial fertiliser 6 years before first sampling, cattle grazing (Bistrup).
   Sampled 25 Oct. 1996 and again 4 Nov. 1998.

8. Meadow in run-off zone from sludge storage, cattle grazing (Bistrup).
   Sampled 25 Oct. 1996.

9. Deposition sampling station (Lille Valby). Sampled monthly
   from 30 Oct. 1996 to 7 Nov. 1997.

The samples were taken as described in the methods section. At each *location* two cores were drilled with depths of 50 cm at two *positions* at a distance of 5 to 10 meters. Each core was divided into five primary samples for different depth, giving in total ten primary samples. These primary sample were each divided into two sub-samples which were all analysed, leading to four measurements for each depth at each location. Location 7 was sampled twice, with an interval of two years, to study the change over time. During the second sampling, a depth of 60 cm was reached.

The location of the sampling sites for soil and deposition is shown in the map Fig. 3

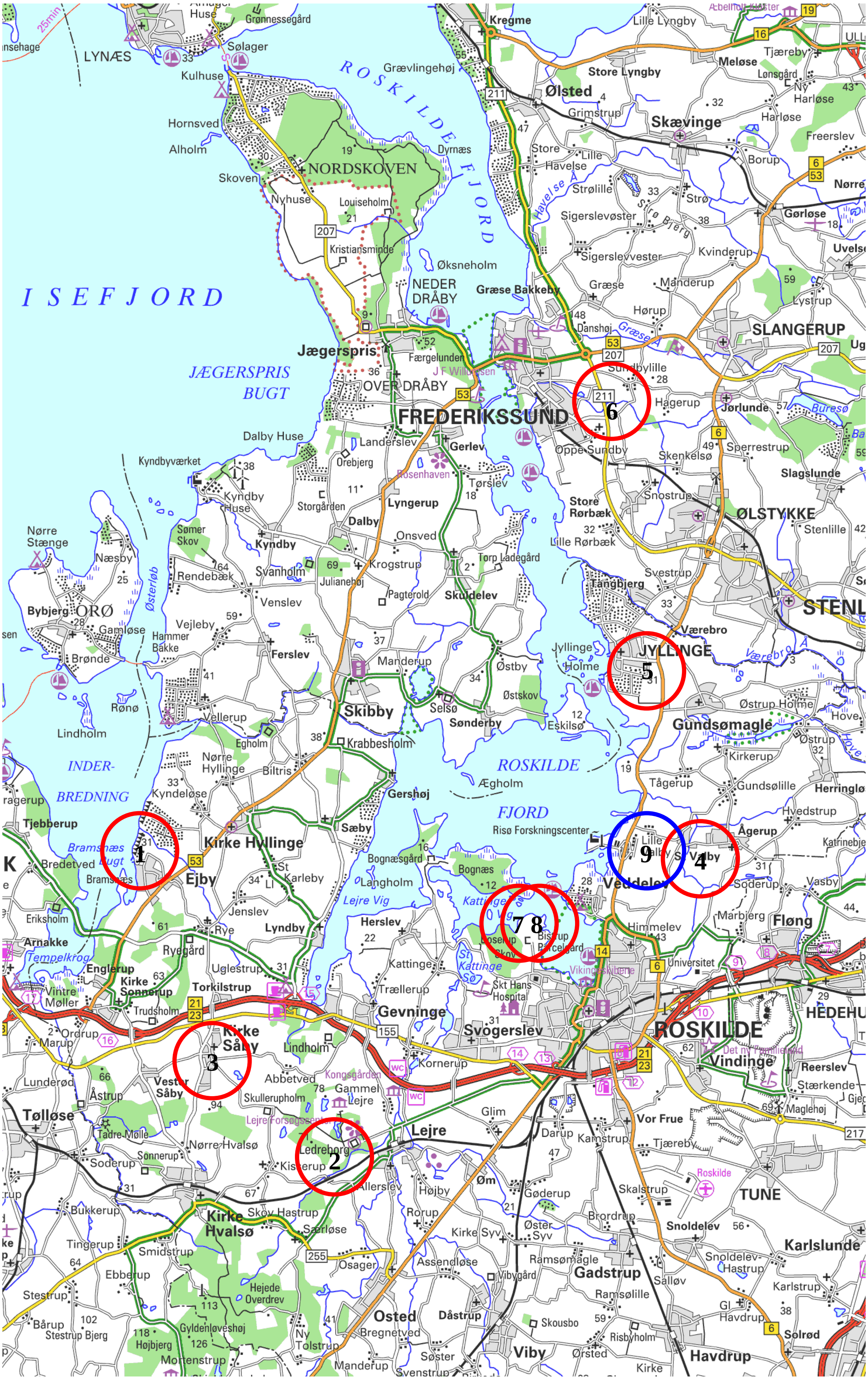

Fig. 3 Map in scale 1/200,000 showing the sampling locations for soil and deposition

3.2 Use and agriculture

Location 1 is a preserved natural area neither cultivated, dressed nor fertilised for more than 50 years, used for cattle grazing. The location was selected as a background reference in relation to the dressed and cultured soils, and to evaluate the contribution from the deposition, since this was the expected main source of pollution in the area. It is evident that the soil characteristics at this site deviates from the cultured sites, since it is reportedly neither ploughed nor has any lime been applied as pH regulation. Hence, such soil will gradually become more acidic, leading to a elution of the clay and thus a very low clay content, as described in the preceding section. However, some artificial fertiliser has been used to improve grass growth.

Location 2 had been ecologically ("biodynamically") cultured for 40 years, making this location unique. The location was selected as a reference for comparison with the sludge dressed soils.

Location 3 was formerly conventionally cultured, but had changed to ecological culture and manuring 5 years before sampling. The Danish legal minimum time limit before the products may be sold with the label "ecological" is 3 years. All manure used is produced by own livestock feeding on locally grown crops (sustainable manuring). Hence, indirect contamination of the manure through the livestock from imported contaminated fodder is presumably minimal. However, 25% of imported fodder is allowed for ecological agriculture according to regulation. The location was included to test whether any substances from the previous form of agriculture remained.

Location 4 was conventionally cultured using artificial fertiliser. About 330 kg of 27% calcium ammonium nitrate and 365 kg of NPK 25/3/9 per ha was applied in 1995.

Location 5 was dressed with medium amounts of sludge, 0.9 t dw/ha in 1993 and 4 t dw/ha in 1995, produced at a small rural municipal waste water treatment plant (Jyllinge WTP). This sludge load is close to the amount recommended by Danish agricultural consultants (4 t/ha dw every third year).
The location was included as typical for sludge amendment, and as a basis for comparison with soils dressed with high amounts of sludge.

Location 6 was regularly cultured and dressed with about 0.7 t dw/ha/y of sludge (low amounts) from an urban plant (Frederikssund WTP). It was intended to find a site in the region cultured and dressed with sludge from Roskilde WTP, but unfortunately this was not possible. The location was chosen as an alternative, since Frederikssund WTP and Roskilde WTP are both urban plants of comparable size. Furthermore, the location had received large amount of cows manure.

Location 7 received through a period of about 25 years all the sludge from Roskilde older WTP at the harbour, in operation until the new WTP at Bjergmarken was built in 1993. The sludge load amounts to about 17 t dw/ha/y (see further in Chapter 5.4). Six years before the first samples were taken, the dressing method was changed to artificial fertiliser. The site would give an impression of the persistence of nonylphenoles and phthalates in a highly sludge loaded environment.

Time trend and persistence

To yield further information of the persistence and movements of the substances in the soil over time, location 7 was revisited after two years and sampled a second time.

By comparing locations 5, 6 and 7, it was intended to get an impression of the effects of sludge dressing, either light, medium or heavy. Specifically, it was hoped to get an idea of the possible benefits if a general reduction of the organic contaminants in sludge was introduced.

Location 8

is a meadow situated near location 7 on a slope between Roskilde Fjord and a higher located sludge storage facility, which has been in use for many years and contains large amounts of sludge. The storage facility receives 15 - 20 t (3 - 4 t dw) of sludge from Roskilde WTP (Bjergmarken) every day. The surface run-off from the sludge storage passes location 8 and runs further into the fjord. The location was included to evaluate the pollution from sludge storage facilities of the nearby environment and the fjord.

pH balance

For all the cultured soils at locations 2 to 7 - in contrast to the preserved area at location 1 and the meadow at location 8 - lime had been applied at regular intervals to avoid acidification of the soil, thus sustaining the pH balance (*Petersen, 1994*).

3.3 Soil characteristics

Importance of soil type

As mentioned previously, it is of major importance that the soils from all sites conform to similar characteristics if the results are to be compared, and valid conclusions regarding the concentrations, distribution and transportation of xenobiotics on the different sites are to be drawn. Thus, the texture (the distribution of particle size) is of crucial significance for the hydrological resistance and water accumulation capacity, and hence for the evaporation and infiltration, which in turn influences as well diffusive as advective transportation of xenobiotics through the soil. Furthermore, the content of organic and inorganic substances (such as humus and clay) is significant for the sorption to the soil, which in turn exerts influence on the distribution between solid and liquid phase. These aspects have been investigated in other parts of the project (*Thomsen & Carlsen 1998*, *Sørensen et. al. 1999a*).

Selection criteria

The soil characteristics considered for selection of locations to ensure comparable soils were:

- texture
- content of humic substances,
- content of clay
- content of silt
- content of sand

Morainic landscape

All the soils included in the present investigation seem to be developed on moraines deposited during the last ice age. Such soils are characterised by high clay contents. The high hydrological resistance of clay leads to low infiltration rates, in comparison to the more sandy soils typically found in the western part of Denmark (Jutland).

Database information

The relevant information was drawn from the nearest grid-point in the Danish Square Grid Database (Danmarks Kvadratnetsundersøgelser 1996), which contains quantitative data, shown in Table 8.

Table 8 Soil characteristics from the nearest grid-points in Danish Square Grid Database

Depth, cm	Humus %	Clay %	Silt %	Fine sand %	Coarse sand %
Locations 1, 7 & 8 (gridpoint no 8)					
0-25	2.0	9.9	9.3	51.1	27.7
25-50	1.4	10.2	9.1	49.7	27.7
50-75	0.8	7.7	8.2	49.1	31.2
75-100	0.7	7.2	7.3	52.0	29.4
Location 2 (gridpoint no 13)					
0-25	2.2	16.8	12.7	66.2	2.2
25-50	0.6	16.3	12.6	39.6	19.5
50-75	0.9	11.4	11.4	39.5	16.5
75-100	0.1	8.7	13.8	34.8	17.4
Location 3 (gridpoint no 11)					
0-25	1.4	4.7	4.8	58.8	30.4
25-50	0.6	9.2	6.3	65.0	18.9
50-75	0.3	13.3	11.7	53.4	20.1
75-100	0.2	14.6	11.5	57.4	14.6
Location 4 (gridpoint no 4)					
0-25	2.3	8.3	11.8	51.0	26.7
25-50	1.6	9.0	14.2	49.8	25.4
50-75	0.8	13.6	13.3	46.9	25.4
75-100	0.6	16.7	14.2	48.0	20.5
Location 5 (gridpoint no 3)					
0-25	2.4	10.9	11.2	51.4	24.2
25-50	1.7	10.3	10.9	50.8	26.4
50-75	1.0	18.7	13.1	43.7	23.6
75-100	0.7	14.0	11.8	46.8	23.8
Location 6 (gridpoint no 1)					
0-25	1.8	11.2	10.9	49.7	24.3
25-50	1.2	11.3	11.5	49.7	23.9
50-75	1.2	12.8	10.5	54.9	18.4
75-100	1.0	15.1	7.7	54.3	17.2

As seen in Table 8, the content of humus in the top layer 0-25 cm for all the locations are in a narrow range, with the exception of location 3, where the humus content is significantly lower. This soil also has the highest clay content, and a heavier texture than the others. For all locations, the humus content reaches the minimum in the bottom layer. This tendency is more pronounced for the locations 2 and 3, the ecologically cultured soils, than for the others. Of course, it cannot be concluded that the tendency is due to the culturing.

Database grid-points

Unfortunately, the exact positions of the sampling points used for the database are unpublished, as previously remarked. It is known that a sample is taken inside each grid mesh as further explained in Appendix A. Hence, the precise distances between the grid-point samples and the sampling positions of the present project cannot be deduced. For example, the locations 1, 7 and 8 belong to the same database grid-point (no. 8), even if location 1 is far from locations 7 and 8, which are close together (map Fig. 3). Further, even these close locations are very different, since location 7 is a cultured field, whereas location 8 is a meadow.

Visual inspection

Since the soil characteristics may vary considerably within short distances - especially in a morainic landscape - a substantial mismatch could very well exist between the data in the grid-points, and the soil characteristics at the actual locations. Hence, it is important to check the grid point data with the actual cores sampled. For this reason, qualitative supplementary data of soil characteristics were collected by visual inspection of each core on location, noting the texture, colour and content of clay, sand, pebbles, roots and larger particles. These notes are given in Appendix A, and shown in short form in Figs. 4a-12a.

4 Results and discussion

The results for the content of nonylphenoles and phthalates are given in tables and figures in this chapter, which also contains a discussion of the soil results. The complete results of all single determinations are given in tables in Appendix B, which also contain recovery. The results are further illustrated as figures in Appendix C, which also show mean and standard deviation for each depth and substance.

In addition to the soils, nonylphenoles and phthalates were measured in deposition, sludge, manure and artificial fertiliser, with the aim of making a budget for mass flows from sources. These results are presented and discussed in Chapter 5.

4.1 Concentration in soils

The soil concentrations measured are given in Table 9. Each location has its own section of the table, showing the average of the four measurements for each depth and substance. The results are given in μg/kg dry weight (parts per trillion, ppt), corrected for laboratory recovery, blank subtracted.

Limit of determination

Results below the limit of determination (< LD) are shown as ***blank spaces*** in the Table 9, provided all 4 corresponding single determinations are non-detects (i.e. < 0 after subtraction of the blank). In case 1 to 3 of the corresponding 4 single determinations are non-detects, the average is calculated setting the non-detects to zero. Such uncertain results are shown in parenthesis. The limits of determination are given in Table 9 for quadruple determinations on the 1 σ level of significance, calculated according to formula 4 in Chapter 2.5 on analytical calculations.

Rounding and truncation

The numbers are rounded to 2 significant digits. Numbers above 100 are truncated to 2 significant digits by substituting zeroes in place of the non-significant digits.

Outliers

Outliers, which are deviating results as defined in Appendix D on statistics, are excluded from the averages in Table 9 (they are shown in Appendix B). Of the total of 1440 single substance measurements carried out for the soil samples, 14 outliers were found, all of them high values of either DEHP, DnNP or DiNP. All such results were carefully rechecked, without finding any evident analytical errors. They might be caused by “hot spots” (e.g. lumps of sludge) in the soil, but the fact that they occur for only three substances, and in some cases in samples far below the ploughing layer, where no lumps of sludge are present, makes that unlikely. Furthermore, these substances were abundant in the blank, suggesting a laboratory cause. However, in the about 36 laboratory blanks analysed during the project, no outliers were found.

Legend to Table 9 Average of quadruple determinations, corrected for extraction recovery, blank subtracted. Blank space = All 4 single determinations non detects. Averages below average-LD are shown in ( ).

Table 9 Concentrations of nonylphenoles and phthalates in soil, average of quadruples, µg/kg dw

Depth, cm	NP	NPDE	DBP	DPP	BBP	DEHP	DnOP	DnNP	DiNP
Location 1, preserved, uncultivated for more than 50 years									
0-10	1	7	2	0.02	0.3	8	2	0.2	17
10-20	0.7	3	(0.5)		(0.04)	6	0.5		7
20-30	0.5	3	8		(0.07)	27	0.4		5
30-40	0.1					4	0.2		3
40-50	(0.01)	(0.5)	(0.4)	0.02	(0.04)		3		6
Location 2, ecologically cultured for 40 years									
0-10	0.2	2.6	2.7	0.07	0.5	16	14	1.6	18
10-20	0.6	3.0	1.6		(0.06)	15	0.6	0.2	4
20-30	1.6	6.3	2.7			32	0.5		15
30-40	(0.003)	(1.3)	(0.5)		(0.04)	14	2	0.3	34
40-50			(0.5)		(0.03)	20	4	0.7	26
Location 3, manured for 5 years, cultured									
0-10	0.3	9.0	1.3	0.03	0.7	16	2	0.7	13
10-20	0.6	2.0		0.01	0.1	18	0.5		3
20-30						8	0.4		4
30-40	0.5	(0.9)				18	1		8
40-50	3.5	2.6	1.3	0.3	1	1	2	1.7	7
Location 4, conventionally cultured, artificially fertilised,									
0-10	0.6	6.5	2.1	0.03	0.1	9	2		35
10-20	0.4	3.1	(0.6)		(0.03)	12	0.8	0.1	5
20-30	0.1	1.6		0.01	(0.04)	9	0.6	0.1	4
30-40		6.8	1.9	0.03	(0.07)	15	0.6	0.3	8
40-50	(0.04)	(0.3)	1.1	0.02	(0.01)	20	3	0.2	34
Location 5, sludge amended, medium amounts, cultivated									
0-10			(0.5)	0.03	0.3	18	5	0.6	16
10-20	0.2	7.6	(0.5)			13			8
20-30		5.6				9			3
30-40		2.6	(0.3)			6	0.7		16
40-50			(0.1)		(0.01)	15	1.1		1
Location 6, sludge amended, low amounts, cultivated									
0-10	(0.03)	71	2.2			22	0.7	0.7	4
10-20		6.3	2.3	0.04	(0.04)	18	0.6	0.8	3
20-30		2.0	1.6			17	0.5	0.5	4
30-40			(0.7)	0.01		23	0.3	0.1	3
40-50		(0.8)	1.8	0.02		21	1	0.2	9
Location 7, heavily amended with sludge, changed to artificial fertiliser6 y before sampling									
0-10	1100	620	350	4.0	25	990	49	160	130
10-20	1600	1140	280	0.20	28	1700	66	200	220
20-30	1900	1600	350	1.8	25	1400	56	200	200
30-40	2000	1090	450	0.52	25	880	50	180	96
40-50	630	1400	760	4.5	41	590	40	120	93
Location 7, sampled 2 years later									
0-10	800	610	230	0,8	21	1400	50	120	410
10-20	1000	730	240	1,1	23	1700	59	160	540
20-30	2300	2100	290	1,3	27	1800	77	210	670
30-40	4900	3900	680	0,7	36	3400	110	290	910
40-50	3200	3800	830	1,2	51	1200	42	210	280
50-60	440	630	530	0,8	7	550	8	84	63
Location 8, meadow in run-off zone from sludge storage									
0-10	160	530	39	1.7	29	670	28	30	110
10-20	14	34	4			76	1	5	16
20-30	(0.03)	2	1			9			5
30-40	0.1	1	10			26	3		7
40-50	3	8	1	0.01	0.3	5	2		1
Limits of determination for averages of quadruple determination (1 σ level of significance)									
	0.1	1	1	0.01	0.1	0.5	0.1	0.1	1

4.2 Discussion

Abundance

As can be seen from Table 9, DEHP generally is the most abundant phthalate. However, also DiNP occasionally occurs in high concentrations. DPP and BBP always occur in very low concentrations. DBP, DnOP and DnNP also occur in rather low concentrations compared to the other phthalates, and are substantial only in the heavily sludge amended soil location 7. NP and NPDE only occur in substantial concentrations in the highly sludge exposed locations 7 and 8.

Reference area

The preserved area location 1 shows the generally lowest concentrations of all the sites for most substances in the upper and the two lowermost layers. The substances found in this location are assumed to come mainly from the deposition, but also the manure from the cattle grazing in the area is a source as discussed in Chapter 5. It is surprising that such low concentration of DBP is found, especially in the upper layer, since this - as well as DEHP - is abundant in the deposition (Chapter 5, Table 10).
A possible explanation for this might be removal by evaporation of the rather volatile DBP from the soil surface. However, in the intermediate layers, substantial concentrations of DBP and DEHP are found, supporting that the deposition is a major source. Also, DBP is more soluble than the other phthalates, which might enhance the elution from the top layer. This problem is further addressed in the following section on concentration profiles. Another surprising finding is the high content of NPDE. Among the sources considered, this substance is found in substantial amounts only in artificial fertiliser. It cannot be excluded that this is the source of the NPDE.

Concentration levels

Overall it can be observed that low levels, with only minor differences, are found at site 1 to 6, whereas site 7 and 8 display much higher levels.

It is noteworthy that the artificially fertilised soil at location 4 and the low sludge amended soils at the locations 5 & 6 do not differ significantly from the unfertilised soil in the preserved area at location 1 or the two ecologically cultured soils at locations 2 & 3. This indicates that at low sludge loads, the biodegradation, elution or other removal mechanisms have been able to keep pace with the influx of phthalates and nonylphenoles.

In contrast, very high concentrations of nonylphenoles and phthalates were found in the high sludge amended soil location 7 throughout the profile, in spite of the fact that the application of sludge ceased 6 years before sampling. This comparatively long period of time is thus obviously insufficient to break down these high amounts of xenobiotics. The maximum concentrations of NP, DBP and DEHP exceed the recommended Danish soil quality criteria of 10 µg/kg, 100 µg/kg and 1000 µg/kg, respectively (*Jensen et. al. 1997*).

Time trend

Location 7 was revisited after 2 years. In the intervening period, it had not been dressed with sludge, but had been artificially fertilised. As can be seen, the concentrations found in the second sampling are on the same level or higher than those found in the first sampling. This is surprising, since lower concentrations were expected, but may be due to local concentration variation with the positions, which are difficult to find again.

In any case, the results show that the breakdown is modest. This is addressed in a parallel investigation (*Sørensen et. al. 1999b*).

It is noteworthy that the maximum concentrations for DEHP and the other higher phthalates occur deeper for the second sampling, indicating a downward transportation of these substances. This aspect is further discussed in the next section on soil profiles.

4.3 Variation of concentration with depth

An important question is the variation with depth of the concentrations of the substances. To illustrate this, the average concentrations (in Table 9) are shown as bar graphs in Figs. 4 to 12.

The figures come in two types, a and b, both showing the results for a particular location.

Depth profiles

The a-type figure shows depth by depth the average concentrations of all substances, colour coded according to substance (arranged in the same sequence as in Table 9). For each depth, the qualitative information of texture from the visual inspection of the sample cores is given in short form (the cores at location 6 were not inspected). A more complete description of the soil characteristics and texture is found in Appendix A; This type of figure is intended to give an impression of the general concentration of the substances and soil texture at each depth.

In figures of the a-type, the profile for a particular substance may be difficult to visualise, because the substance is shown mixed with the other substances.

Concentration profiles

In the figures of the b-type, the data are displayed to enhance the profiles. The concentrations of a particular substance are shown for all depths, colour coded according to depth, displaying a concentration profile. These profiles are arranged substance by substance.

To improve readability and facilitate comparison, the figures of both types for a particular location are shown on the same page, drawn to the same vertical scale.

Note that the figures for the locations 1-5 are drawn to the same scale, whereas the figures for locations 6-8 are drawn to larger scales. The depths in the figures are abbreviated, e.g. 0-10 cm to 10 cm etc.

Fig. 4a Depth profile for location 1, preserved area not cultured for more than 50 years. Average concentrations for each depth of quadruple determinations.

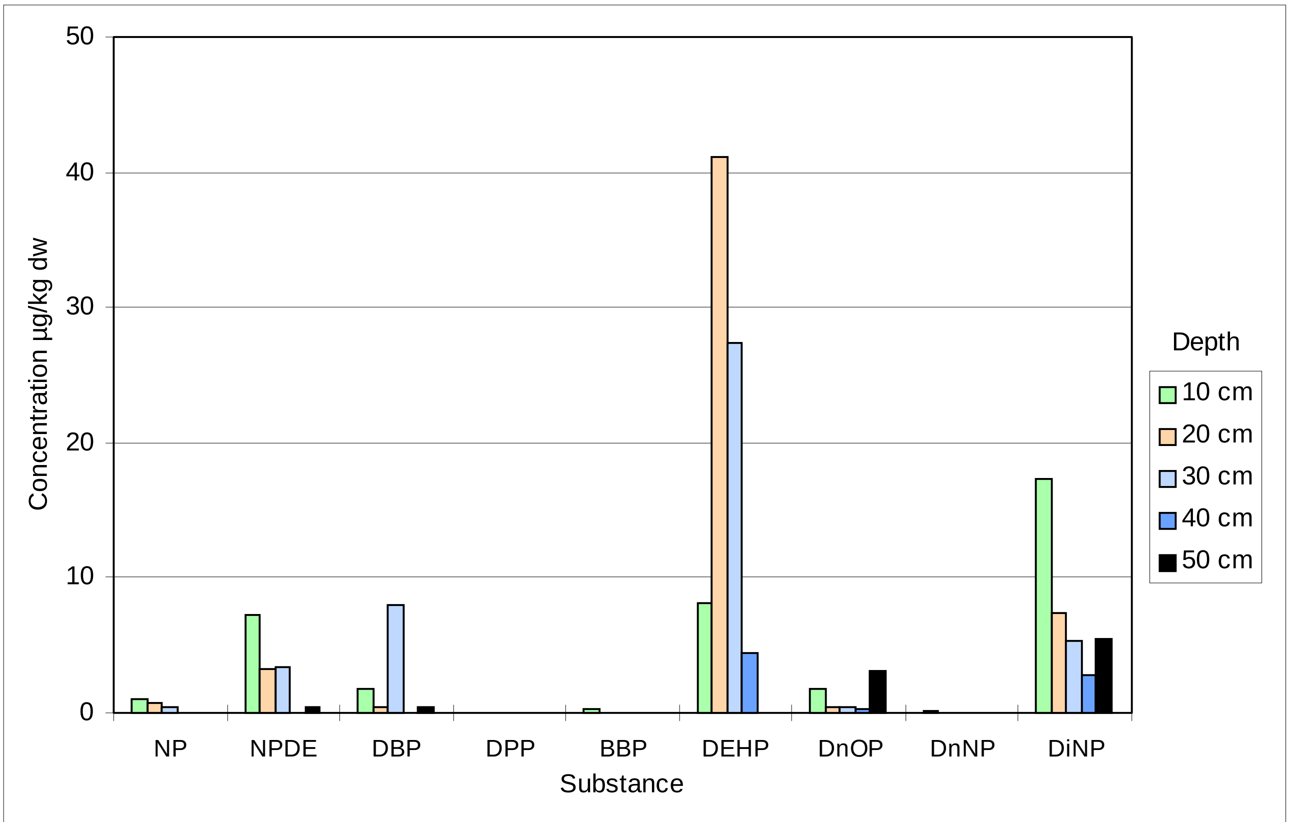

Fig. 4b Concentration profiles for location 1, preserved area not cultured for more than 50 years. Average concentrations of quadruple determinations for each depth.

Fig. 5a Depth profile for location 2, ecologically cultured for 40 years. Average concentrations for each depth of quadruple determinations.

Fig. 5b Concentration profiles for location 2, ecologically cultured for 40 years. Average concentrations of quadruple determinations for each depth.

Fig. 6a Depth profile for location 3, manured sustainable for 5 years. Average concentrations for each depth of quadruple determinations.

Fig. 6b Concentration profiles for location 3, manured sustainable for 5 years. Average concentrations of quadruple determinations for each depth.

Fig. 7a Depth profile for location 4, conventionally cultured using artificial fertiliser. Average concentrations for each depth of quadruple determinations.

Fig. 7b Concentration profiles for location 4, conventionally cultured using artificial fertiliser. Average concentrations of quadruple determinations for each depth.

Fig. 8a Depth profile for location 5, sludge amended with medium amounts. Average concentrations for each depth of quadruple determinations.

Fig. 8b Concentration profiles for location 5, sludge amended with medium amounts. Average concentrations of quadruple determinations for each depth.

Fig. 9a Depth profile for location 6, sludge amended with low amounts. Average concentrations for each depth of quadruple determinations.

Fig. 9b Concentration profiles for location 6, sludge amended with low amounts. Average concentrations of quadruple determinations for each depth.

Fig. 10a Depth profile for location 7, heavily sludge amended, changed to artificial fertiliser 5 years before sampling. Average concentrations for each depth of quadruple determinations.

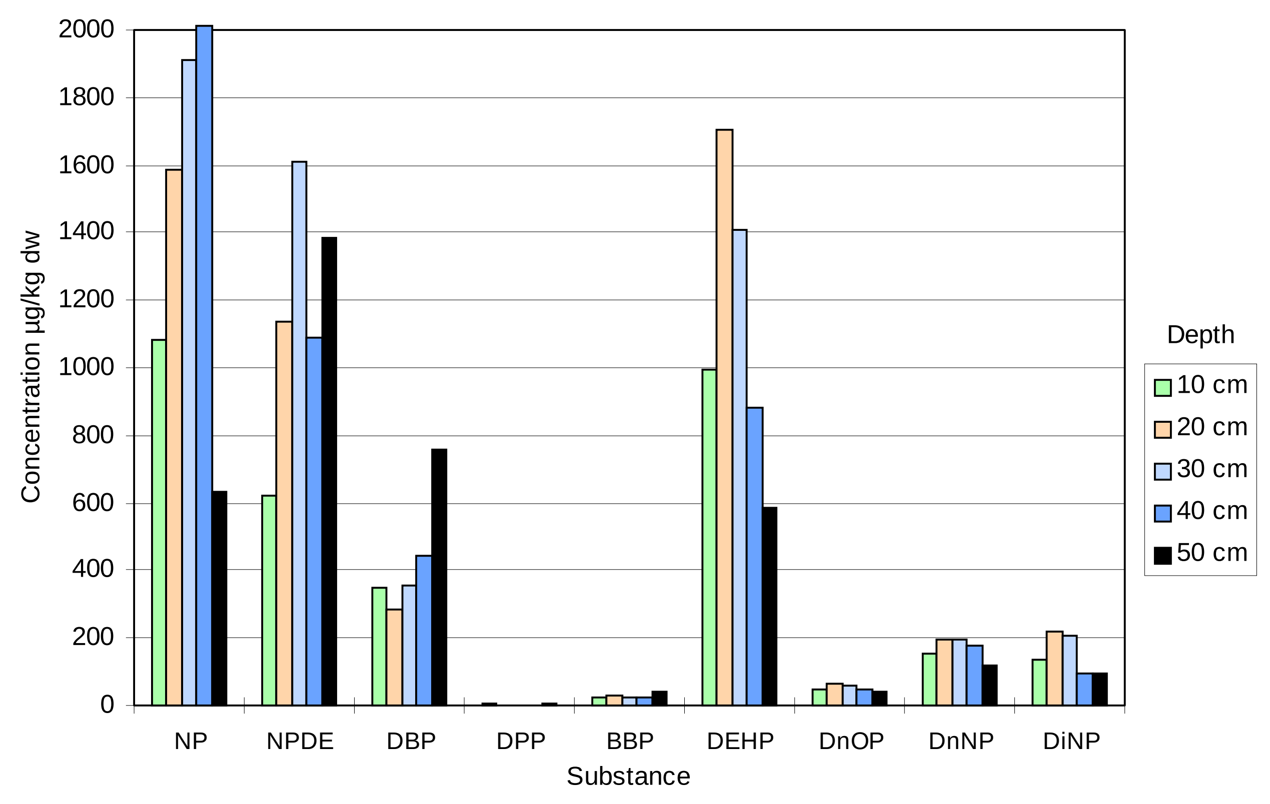

Fig. 10b Concentration profiles for location 7, heavily sludge amended, sampled 1996, changed to artificial fertiliser 1991. Average concentrations of quadruple determinations for each depth.

Fig. 11a Depth profile for location 7 sampled 2 years later, heavily sludge amended. Average concentrations for each depth of quadruple determinations.

Fig. 11b Concentration profiles for location 7 sampled 2 years later, heavily sludge amended. Average concentrations of quadruple determinations for each depth.

Fig. 12a Depth profile for location 8, meadow exposed to run-off from sludge storage. Average concentrations for each depth of quadruple determinations.

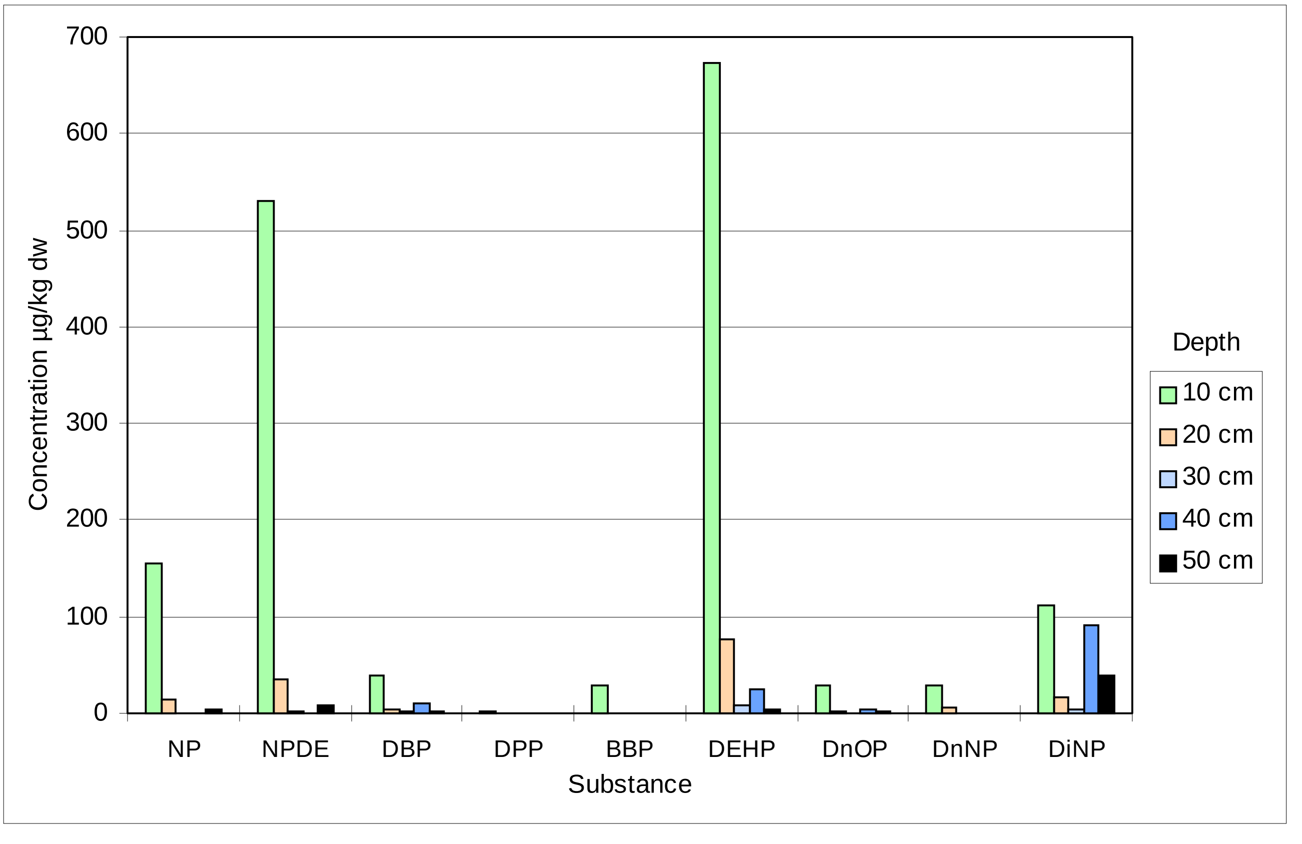

Fig. 12b Concentration profiles for location 8, meadow exposed to run-off from sludge storage. Average concentrations of quadruple determinations for each depth.

4.4 Concentration profiles

Profile types

For all locations, with the exception of location 7, DEHP is the only statistically significant concentration profile. In the soil profiles at the locations 1, 2, and 7 (first sampling), a distinct concentration profile is observed, characterised by a maximum for DEHP occurring in a depth of 20-30 cm (Figs. 4, 5 & 10). For location 7, such a profile is also visible for DnOP, DnNP and DiNP. In contrast, the locations 3, 4, 5 and 6 display a DEHP-concentration profile without such a pronounced maximum.

Influence of clay

These concentration profiles are to a certain extent reflected in the texture of the soil layers. Thus location 1 is characterised by a clayey texture in the depth of 0-20 cm, followed by more sandy layers below. The DEHP-concentration increases sharply in the clayey layers until a depth of 20 cm, then declines abruptly in the lower sandy layers. The concentration of DEHP seems to follow the clay content. This is also the case for location 2, since here the DEHP concentration profile also rises sharply in the clay layers until the maximum at a depth of 20 cm, but then declines gently in the clayey layers below.

In these cases, a concentrating of DEHP seems to occur in the clayey layers, probably brought about by binding to the clay minerals, or perhaps more likely to organic substances residing in the clay.

Influence of sand

In contrast, DEHP occur in low concentrations in the sandy layers. The same tendency apply for the soils in the locations 3 to 6, which are sandy in character. In these cases, low concentration profiles of DEHP without pronounced maximum are found. DEHP seems to be eluted from sand.

High sludge amendment

Location 7 is an exception to this tendency, however. This location is comparatively sandy in character, but nevertheless displays a pronounced DEHP maximum. The discrepancy between this location and the others might be due to the exceptional conditions prevailing here, caused by the considerably higher concentration level. Thus, the soil concentrations of DEHP and the higher phthalates are above the solubilities in water about 20 µg/l, (*Thomsen & Carlsen 1998*). Hence, the saturated water phase of the soil contains only a small fraction of the bulk concentration. This will impede the downward transportation.

Furthermore, the load of bacteria in the sludge applied to the field is particularly high for this location. These bacteria from the WTP have a high DEHP degradation capacity, leading to a high degradation rate in the ploughing zone, in turn leading to lower concentration in the top layer. This process probably depletes the top layer in addition to elution. The sludge bacteria are in the course of some months replaced by normal soil bacteria with lower DEHP degradation capability. The bacteria *per se* have not been studied in the present investigation, however.

For location 7, statistically significant concentration profiles occur for other substances as well, as previously mentioned. Thus DBP displays a marked concentration profile, rising until a maximum is reached in the bottom layer. This profile is probably brought about by the higher solubility and mobility of DBP, promoting the elution of this substance to the bottom layer. The same profile is seen for BBP, but is in this case not statistically significant. Also for NP and NPDE, profiles with pronounced maxima are found, occurring at a depth of 30-40 cm, i.e. intermediate between DBP and the higher phthalates (Fig. 10a).

Bottom layers

In the profiles at the locations 2, 4, 5, 6 and in particular 7, measurable concentrations were found in the bottom layer, showing that the profile depth of 50 cm was not fully sufficient for a complete evaluation of the transport and fate of xenobiotics in deeper soil layers.

Time trend study

Location 7 was sampled a second time 25 months after the first one, 8 years after the cessation of sludge amendment, to investigate changes over time. For the above reason, the sampling was deeper this time, reaching 60 cm. As seen in Fig. 11, the concentration profiles for DEHP, DnNP and DiNP still contain pronounced maxima, but now occurring at a depth of 30-40 cm, i.e. about 20 cm deeper than found in the first sampling. This suggests a downward movement for these substances of 10 cm/y. Furthermore, the shape of the DEHP profile has changed, rising gently until maximum, then again falling abruptly.

Remarkably, for the profiles of DBP, NP and NPDE, the shape and position of maxima have not changed significantly since the first sampling. The maxima for NP and NPDE again occur at a depth of about 30-40 cm, and that of DBP at a depth of 40-50 cm.

Groundwater risk

As seen from Fig 11a, the concentrations of NP, NPDE, DBP and DEHP in the bottom layer (50-60 cm) at location 7 (second sampling) are all about 500 µg/kg. Although this is considerably lower than the maxima of the profiles, it is still very high compared to the maxima of the other locations.

Because of this finding, it cannot at present be excluded that a risk of groundwater contamination may exist. Hence, it is recommended to take deeper profiles in future studies, if possible combined with appropriate groundwater samples.

Meadow in runoff zone

The profile from location 8, the meadow located in the runoff zone from the sludge storage, differs markedly from all the other profiles. It is characterised by a high concentration in the upper layers, followed by much lower concentrations in the layers below (Figs. 12 a & b). This indicates that this profile is more dominated by surface runoff than by downward transportation. This finding may be due to a minimal downward water flow caused by the high groundwater level in the meadow near the fjord. Furthermore, no ploughing, and hence no vertical mixing, takes place at this location.

5 Sources and mass budget

An important question is whether a relationship exists between the nonylphenoles and phthalates found in the soils and the amount carried into the soils by different sources. To make such a mass budget possible, special investigations of nonylphenoles and phthalates in sources has been carried out. The known sources are the deposition, the sludge and the artificial fertiliser applied, but also the manure from the cattle feeding on the areas might contain xenobiotics from secondary sources. These secondary sources are taken into consideration by investigation of the manure. In the following, the results of these investigations are shown.

5.1 Concentration in fertiliser, manure and sludge

In Table 10 the results for the artificial fertiliser, manure and sludge are shown. The data for sludge from Frederikssund WTP has kindly been supplied by the municipal authorities in that city (Frederikssund 1996).

Table 10 Concentration of nonylphenoles and phthalates in fertiliser, cows manure and sludge.

Sampled at	**Sample**	**D**	**NP**	**NPDE**	**DBP**	**DPP**	**BBP**	**DEHP**	**DnOP**	**DnNP**	**DiNP**
Concentrations, mg/kg dw											
	Artificial		0.03	0.96	0.09	0.001	0.04	1.1	0.04	0.10	0.11
Location 1	Manure F		0.5		0.02		0.02	0.03			0.004
Location 8	Manure F		0.1		0.01	0.001	0.01	0.03	0.001	0.001	
Jyllinge WTP	Sludge F			0.7	0.08		0.04	29	0.23	0.19	6.7
Frd.sund WTP	Sludge F		na	8.9	2.7	na	0.12	21	0.45	na	na
Bjergmark. WTP	Sludge F		0.7	24	(0.01)		0.03	25	0.19	0.21	5.6
Bjergmark. WTP	Sludge S*		1.5	5.2			0.01	8.7	0.01	0.05	2.1
Bistrup DS1	Sludge S	0-1	1.2	3.3	0.2		(0.005)	9.4	0.03	0.08	2.1
Bistrup DS1	Sludge S	1-2	1.0	4.8	0.1		0.02	15	0.09	0.13	3.4
Bistrup DS1	Sludge S	2-3	0.5	1.5	0.1		(0.001)	6.5	0.04	0.06	1.5
Bistrup DS1	Sludge S	3-4	0.7		0.2		0.01	3.1	0.04	0.12	0.37
Bistrup DS1	Sludge S	4-5	430	26	0.7	0.01	0.06	5.9	0.15	0.48	2.4
Bistrup DS2	Sludge S	0-1	18	3.9	0.2		0.02	8.2	0.06	0.08	1.5
Bistrup DS2	Sludge S	1-2	10	11	0.4		0.05	20	0.10	0.12	3.1
Bistrup DS2	Sludge S	2-3	0.4	1.7	0.1	0.004	0.02	4.2	0.02	0.04	0.41
Bistrup DS2	Sludge S	3-4	(0.02)		0.06			(0.003)			
Bistrup DS2	Sludge S	4-5			0.04		(0.001)				
Bistrup DSP	Sludge S	0-1	1.3	5.1	0.1	0.004	0.05	14	0.21	0.31	5.5
Bistrup WS1	Sludge S	0-1	130	89	2.6		0.37	117	1.8	2.0	23
Bistrup WS2	Sludge S	0-1	75		0.82		0.08	15	0.39	1.5	5.4
Limits of determination for average of duplicates, mg/kg dw (1 σ level of significance)											
	Artificial		0.001	0.001	0.0001	0.00001	0.00002	0.0003	0.00003	0.00003	0.0002
	Manure		0.02	0.04	0.001	0.001	0.001	0.0005	0.001	0.001	0.004
	Sludge		0.06	0.4	0.02	0.004	0.006	0.04	0.005	0.006	0.06

Average of duplicates. Blank space = Not detected. Uncertain results below limit of determination in ( ).
D = Depth in dm F = Fresh S = stored * = stored 1 year, the other storing times unknown.
DS1 = Dry store position 1 DSP = Dry store pool WS1 = Wet store position 1
Frd.sund = Frederikssund, information supplied by the municipal authorities.

5.2 Discussion

Artificial fertiliser

Note that in Table 10 the unit is *mg/kg dry weight*. As seen, much higher levels of in particular of NPDE and DEHP, but also of DBP, are found in the artificial fertiliser than in the manure, but lower levels of NP. Compared to sludge, the levels of these substances are much lower, except for DBP, for which the artificial fertiliser has about the same content.

Manure

Albeit the cattle reportedly feed on product grown on the location, it may be exposed to phthalates from secondary sources, for example through imported fodder (25% allowed in ecological agriculture), from the drinking water if delivered through plastic hoses, or from plastic feeding or drinking jars. It is not possible to find and investigate all these secondary sources, nor is it necessary, since it is the amount excreted in the manure which is of importance for the soil. Furthermore, the secondary sources do not contaminate the fields directly. Thus, by investigating the manure, these sources are taken into consideration. The most abundant substances found in manure is NP, followed by DBP, BBP and DEHP. It is noteworthy that the concentrations in the manure from the two locations are very low and very close together, although the cattle at Bistrup feed at a highly contaminated site, whereas the cattle at Ejby feed at the unfertilised preserved area. This lack of difference is surprising, since *a priori* a higher content in the manure from the contaminated site was expected. However, a number of possible explanations could apply. For example, if the substances from the sludge did not contaminate the grass, the difference between the two locations would disappear. Being highly hydrophobic, phthalates are only with difficulty taken up by the grass-roots. A recent study thus found a very small uptake of DEHP by plants (*Grøn et. al 1999*). However, even in the absence of root uptake, wind-borne dust and evaporation might transport the substances from the surface layer to the grass. Hence, another explanation might be that the xenobiotics are transported to the grass and subsequently ingested by the cattle, but then removed from their digestive tract either by uptake into the blood circulation, or by chemical degradation in their digestive tract, for example by hydrolysis. The presence of NP shows that the cattle do ingest xenobiotics, and remarkably, since no NPDE is detected, this substance is probably hydrolysed to NP during digestion. This view agree with studies on composting, which demonstrates that the higher nonylphenol-ethoxylates are hydrolysed (or oxidatively hydrolysed) stepwise into the lower ones (*Jones & Westmoreland 1998*). Another study show that as well NPE as DEHP are degraded during composting, albeit DEHP significantly slower than NPE (*Petersen, 1998*). This being the case, it is likely that phthalates to a certain extent might be hydrolysed also during digestion. The cattle may receive the DBP and DEHP from deposition on the grass, but also recycling of substances from manure to grass to cattle, especially of NP, may play a role. The BBP content, of the same order of magnitude as the DBP and DEHP content, is difficult to explain. Possibly, some use of artificial fertiliser may be responsible.

Sludge

The concentrations in the fresh sludge from the two WTPs Jyllinge and Bjergmarken (the former is located in a rural area, the latter is cleaning the wastewater from Roskilde) are very close together, except for NPDE for which the concentration in the sludge from Bjergmarken is considerably higher. The concentrations of the sample profiles taken at the dry sludge store Bistrup at two positions show an appreciable variation, as well between positions as between depths. This store receives the sludge from the WTP at Bjergmarken, and the sludge for agricultural use is taken from here. Hence, the different layers and positions differ from each other, reflecting the variation between individual charges of sludge, which furthermore has random positions and widely different ages. The dry store pool is made from a large amount of homogenised sludge and used in the laboratory as a reference sludge sample for analytical quality control. As seen the concentrations in the pool are within the range for the individual dry store samples for all substances. In contrast, the concentration in the wet store seems to be substantially higher. The concentrations in the fresh sludge are generally higher than - or in the higher end of - the dry store range. As noted, NPDE is more abundant than NP in the fresh sludge from Bjergmarken, whereas the reverse is true for the stored sludge. The NP-concentration is exceptionally high in the bottom layer of the dry store position 1 (DS1, 430 mg/kg). Most likely, NPDE is converted to NP during storage. Finally, comparing the 1 year old sludge with the fresh sludge from Bjergmarken reveals that the concentrations of all substances - with the exception of NP, which has increased - has decreased considerably. For example, BBP, DEHP and DiNP has decreased to about a third. The increase of NP again indicates a conversion of NPDE into NP.

Other studies

The results for sewage sludge agree well with other Danish studies on sewage sludge. Thus Grüttner *et. al.* 1995 reported 0.9-189 mg/kg DEHP in sewage sludge from three plants, (*Kjølholt et. al. 1995*) 18-120 mg/kg in three plants, (*Krogh et. al. 1996*) 14-23 mg/kg DEHP in two plants, (*Boutrup et. al. 1998*) 9-61 mg/kg in six plants,. The results for manure in the present study are somewhat lower than reported in another study (*Stenvang, 1998*), which found from 0-0.5 mg/kg DEHP with an average of 0.2 mg/kg in cows manure.

Taken together, the data in Table 10 demonstrates an appreciable variation in concentrations in the stored sludge. This indicates that deducing the concentration of xenobiotics in WTPs by measurements of stored sludge is problematic, and that the results from such measurements should be interpreted with caution. In contrast, the results for the fresh sludge seem more consistent, and these results are consequently used in the following mass flow calculations, although they represent the conditions at a single instant of time.

5.3 Deposition

The deposition was sampled at Lille Valby meteorological station in bulk, as described by *Vikelsøe et. al. 1998*, which also contains a more complete discussion of the analytical method and results. Whereas the bulk sampling method is known to yield good estimates of the wet deposition, a known drawback of the method is a certain underestimation of the dry deposition. Further, the bulk method does not measure gaseous air concentrations well, but these seem to play a minor role for phthalates (*Ligocki et. al. 1985*).

The deposition study at Lille Valby continued for a year, from November 1996 to October 1997. In Table 11 the results given in µg/m^2/y as averages of each half year periods and the total average. The average has been calculated from the monthly depositions of phthalates in µg/m^2/month, not taking the precipitation (rainfall) into account. This approach has been used because of the important finding of the previous project, that the deposition of phthalates was independent of the rainfall (*Vikelsøe et. al. 1998*). Some of the very few other studies on deposition of phthalates were carried out in Denmark in northern Zealand (Ganløse and Blovstrød, located to the north-east of Lille Valby at distances of 14 km and 25 km, respectively) (*Kjølholt et. al. 1996*) and in Jutland (Ulfborg near the west coast, and Højbjerg to the south of the city of Århus on the east coast) (*Boutrup et. al. 1998*). The phthalate results selected from these studies are shown for comparison in the lower section of Table 11.

Discussion

As observed in Table 11, the most abundant substances found in the deposition are NP, DBP, DEHP and some BBP, the others being insubstantial in comparison. There is a good agreement between the two studies, in spite of the distance between the sampling stations, although the concentration of DEHP of the present study is somewhat lower. However, this may be due to different analytical methods and laboratories.

Table 11 Deposition of phthalates in Denmark, µg/m^2/y

Station	Sampling period		n	NP	NPDE	DBP	DPP	BBP	DEHP	DnNP	DnOP	DiNP
Northern Zealand, Present study												
Lille Valby	Nov. 96	Apr. 97	8	7.9		120		19	210		23	na
Lille Valby	May 97	Oct. 97	10	110	0.7	290	0.2	15	250	5.1	4.0	33
Lille Valby	Nov. 96	Oct. 97	18	61	0.3	210	0.1	17	230	2.6	13	17
Northern Zealand, Kjølholt & Juhl 1996												
Blovstrød	Nov. 95	14 d	1	na	na	230	na	15	420	na		na
Blovstrød	Feb. 95	14 d	1	na	na	300	na	13	390	na		na
Blovstrød	Apr. 96	14 d	1	na	na	<100	na	17	1000	na		na
Ganløse	Nov. 95	14 d	1	na	na	270	na	13	480	na		na
Ganløse	Feb. 95	14 d	1	na	na	330	na	12	390	na		na
Ganløse	Apr. 96	14 d	1	na	na	<200	na	14	590	na		na
Jutland, Boutrup et. al 1998												
Ulfborg	Jan 98	Mar 98	2	<30	<30	565	na	11	403	na	<7	na
Århus Højbjerg	Jan 98	Mar 98	2	<30	<30	664	na	46	157	na	<7	na

na = not analysed. Blank space = not detected

With the exception of a single high value at Blovstrød in April of 1000 µg/m^2/y, there is no substantial difference between the stations Blovstrød and Ganløse. The distance between these stations (11 km) is comparable to the distance from Lille Valby to the most distant soil sampling location (location 1, 17 km). Also the study in Jutland agree with the present, although the DBP results seem somewhat higher. It could perhaps *a priori* be expected that significant differences between deposition rates at this distance might exist, such as those found for deposition of PAHs (*Poulsen et. al. 1995*), but it seems that such local differences are not found for nonylphenoles and phthalates. This is in agreement with the important finding of the previous project, that the deposition of nonylphenoles and phthalates are largely independent of the wind speed and direction. Thus, during sampling periods with low wind, the deposition rate were comparable with more windy periods. Furthermore, in the windy periods, the direction of the wind did not influence the deposition significantly (*Vikelsøe et. al. 1998*).

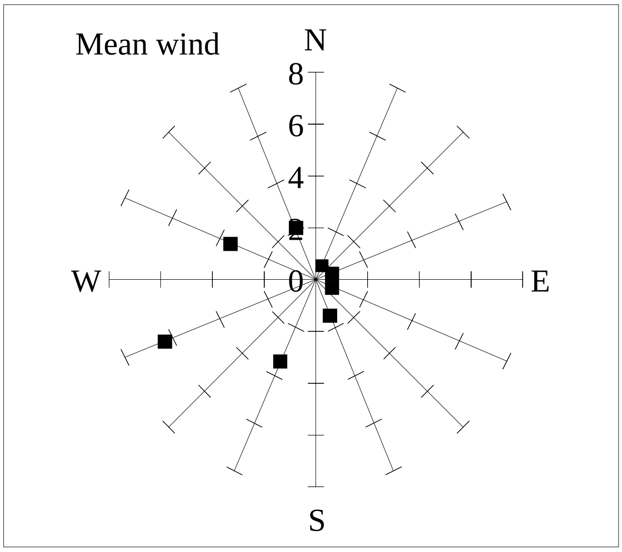

Fig. 13 Wind intensity diagram for Lille Valby for the period November 1996 to April 1997. Average wind speed in units of 1000 km per month, shown as distance from centre.

This indicates that point sources and other local differences play a minor role. Accordingly, the deposition is approximately distributed evenly over the soil sampling region. That being the case, a single deposition sampling station will suffice to represent the deposition of nonylphenoles and phthalates in the region with good approximation.

Fig. 13 is a wind rosette diagram for Lille Valby, covering the period from November 1996 to April 1997. The wind intensity in each sector is calculated by summing the product of wind speed and time. The average wind speeds and directions thus calculated are shown in Fig. 13 in units of 1000 km per month, which is the average deposition sampling period.

As seen from Fig. 13, the wind is predominantly in the WSW sector, blowing from the rural areas in the central Zealand. The maximum monthly wind length of about 6000 km is much longer than the extension of geographical region for the soil samples.

5.4 Mass flow budget for sources

The contributions from the sources and the amounts carried annually into the soil are considered in this section. The mass flow is defined as the amount of substance annually entering a surface area of 1 m^2, calculated as shown in the following for each location, source and substance, making a mass flow budget.

Mass flow calculation

The mass flow from dressing are calculated from the measured concentrations (given in Table 10) and the average annual amount of dressing applied to 1 m^2 of surface area. The amount of manure and artificial fertiliser applied is based on the owners information. For cattle grazing at locations 1 and 8, the amount of manure is estimated from the number of animals per hectare (average 1.4), assuming an annual production of 10 t ww per animal (*Plantedirektoratet, 1994*) and 30% dry matter content (average of all manure samples). The concentrations measured in the manure from Ejby (Table 10) are used for the calculations in locations 3, 5 and 6, for which the manure has not been analysed. Location 5 received 30 t/ha sludge (3% dm) in 1993 and 20 t/ha (20% dm) in 1995 produced at Jyllinge WTP as reported by the owner, amounting to an average sludge load of 1.6 t dw/ha/y. At location 6, 10 t/ha sludge (20% dm) from Frederikssund WTP was applied in 1993 as reported by the owner, corresponding to an average of 0.7 t dw/ha/y. The high sludge loaded location 7 received all the sludge produced at Roskilde older WTP through a period of 25 years. The sludge load is in this case estimated from the number of personal equivalents (80000 p.e.) and the area of the field (100 ha) assuming a daily production of 60 g dw sludge per p.e. (*Hvitved-Jacobsen et. al. 1994*), amounting to maximum 17 t dw/ha/y.

For the runoff zone from the sludge store location 8, is has not been possible to calculate a mass flow, since the amount and concentration of the runoff could not be measured because of technical difficulties. Furthermore, even if these quantities were known, the transport into that area would still be exceedingly difficult to describe precisely.

The deposition at Lille Valby given in Table 11 is used for the mass flow calculations at all locations.

Legend to Table 12

In Table 12, the mass flows for each source and substance as well as the sum for each location are summarised. The mass flows are given in $mg/m^2/y$ and the amounts of dressing applied in kg dry weight per hectare per year (kg dw/ha/y). To facilitate the comparison and readability of mass flows and their sums, 4 decimal places are used (breaking the rule of displaying only 2 significant digits in result tables).

Discussion of sources

As observed from Table 12, all the sources contribute considerably less than 1 mg of substance per m^2 per year, with the exceptions of the sludge amended locations for which the flow of NP, NPDE, DEHP and DiNP ranges from about 1 mg to about 40 mg. At the manured locations, the manure dominates the NP-flow, whereas the contribution of NPDE and phthalates from this source is insubstantial. At all locations, the deposition contributes more DBP than any other source, and dominates the DEHP-flow for the non-sludge locations 1 to 4, whereas the sludge dominates the DEHP-flow at the sludge amended locations 5 to 7. A similar pattern as for DEHP is found for the higher phthalates and for NPDE as well. In contrast, sludge seem to be lesser important source for NP and DBP, but comparable with the deposition. The sludge load at location 5 is close to the amount recommended by Danish agricultural consultants (20 t/ha ww every third year ≈ 1.3 t dw/ha/y).

The sludge load at location 7 is considerably above the maximum allowed in Danish agriculture, which at present is 10 t dw/ha/y, but will be reduced to 7 t dw/t/y from the year 2000 (*Miljø- og Energiministeriet, 1996*).

Table 12 Annual mass flow from individual sources, mg/m²/y

Source	Load 1)	NP	NPDE	DBP	DPP	BBP	DEHP	DnOP	DnNP	DiNP
				Location 1, Preserved						
Deposition 2)		0.0607	0.0003	0.2061	0.0001	0.0171	0.2281	0.0026	0.0131	0.0169
Manure	4351	0.1970	0.0000	0.0085	0.0000	0.0104	0.0128	0.0001	0.0000	0.0017
Artificial	430	0.0012	0.0415	0.0040	0.0000	0.0017	0.0490	0.0017	0.0043	0.0048
Sum		0.2589	0.0418	0.2186	0.0001	0.0291	0.2900	0.0044	0.0174	0.0234
				Location 2, Ecological						
Deposition		0.0607	0.0003	0.2061	0.0001	0.0171	0.2281	0.0026	0.0131	0.0169
Artificial	770	0.0021	0.0743	0.0072	0.0000	0.0031	0.0878	0.0031	0.0076	0.0086
Sum		0.0628	0.0746	0.2133	0.0001	0.0201	0.3159	0.0057	0.0208	0.0255
				Location 3, Manured						
Deposition		0.0607	0.0003	0.2061	0.0001	0.0171	0.2281	0.0026	0.0131	0.0169
Artificial	315	0.0009	0.0304	0.0030	0.0000	0.0012	0.0359	0.0013	0.0031	0.0035
Manure	6400	0.2898	0.0000	0.0125	0.0000	0.0153	0.0189	0.0001	0.0000	0.0025
Sum		0.3514	0.0307	0.2215	0.0001	0.0336	0.2829	0.0040	0.0163	0.0229
				Location 4, Conventional						
Deposition		0.0607	0.0003	0.2061	0.0001	0.0171	0.2281	0.0026	0.0131	0.0169
Artificial	695	0.0019	0.0671	0.0065	0.0000	0.0028	0.0792	0.0028	0.0069	0.0078
Sum		0.0626	0.0674	0.2126	0.0001	0.0198	0.3073	0.0054	0.0200	0.0246
				Location 5, Medium sludge						
Deposition		0.0607	0.0003	0.2061	0.0001	0.0171	0.2281	0.0026	0.0131	0.0169
Artificial	439	0.0060	0.0423	0.0041	0.0000	0.0017	0.0500	0.0018	0.0044	0.0049
Manure	2200	0.0996	0.0000	0.0043	0.0000	0.0052	0.0065	0.0000	0.0000	0.0009
Sludge Jyllinge	4300	0.0000	0.2881	0.0347	0.0000	0.0153	12.5483	0.0997	0.0829	2.8813
Sum		0.1616	0.3308	0.2492	0.0001	0.0394	12.8329	0.1041	0.1004	2.9039
				Location 6, Low sludge						
Deposition		0.0607	0.0003	0.2061	0.0001	0.0171	0.2281	0.0026	0.0131	0.0169
Artificial	120	0.0003	0.0116	0.0011	0.0000	0.0005	0.0137	0.0005	0.0012	0.0013
Manure	27000	1.2227	0.0000	0.0527	0.0000	0.0644	0.0797	0.0005	0.0000	0.0107
Sludge Frd.sund	667	na	*0.5933	0.1800	0.0000	0.0080	1.4000	0.0300	na	na
Sum		1.2838	0.6053	0.4399	0.0001	0.0899	1.7215	0.0336	0.0143	0.0289
				Location 7, High sludge						
Deposition		0.0607	0.0003	0.2061	0.0001	0.0171	0.2281	0.0026	0.0131	0.0169
Artificial	430	0.0012	0.0415	0.0040	0.0000	0.0017	0.0490	0.0017	0.0043	0.0048
Sludge Bjergm.	17520	1.1827	41.5626	0.0150	0.0000	0.0494	43.1654	0.3292	0.3749	9.8566
Sum		1.2446	41.6044	0.2250	0.0001	0.0682	43.4425	0.3336	0.3923	9.8783

1) Average loads in kg dw/ha/y   2) Average of Nov. 1996 to Nov. 1997   * Sum of NP and NPDE
na = Not analysed   0.0000 = Not analytically detected

5.5 Source flows versus content in soil

In the following, the rate of substances entering the soil (the mass flow) is compared to the actual content in the soil.

To compare the amount in the soil with the mass flow, the amount must refer to the same surface area as the mass flow. Hence, the amount below 1 m^2 of soil is calculated. This corresponds to the content in a square box of soil with side lengths of 1 m and 0.5 m depth. The weight of soil in this volume of 0.5 m^3 is 430 kg dry weight, assuming a density of 0.86 kg dw per litre (average of 4 soil densities). Multiplication with the average concentrations over all depths for each location and substance yields the *accumulated content* for the location, given in mg/m^2 in the lower section of Table 13.

To facilitate the comparison, an excerpt of the sums of mass flows from Table 12 are given in the upper section of Table 13.

Table 13 Mass flow from sources into soil, and accumulated content in soil, for each location

Loc.	Use	NP	NPDE	DBP	DPP	BBP	DEHP	DnOP	DnNP	DiNP
				Mass flow into soil, mg/m²/y						
1	Preserved	0.26	0.042	0.22	0.0001	0.029	0.29	0.004	0.017	0.023
2	Ecological	0.06	0.075	0.21	0.0001	0.020	0.32	0.006	0.021	0.025
3	Manured	0.35	0.031	0.22	0.0001	0.034	0.28	0.004	0.016	0.023
4	Conventional	0.06	0.067	0.21	0.0001	0.020	0.31	0.005	0.020	0.025
5	Medium sludge	0.16	0.33	0.25	0.0001	0.039	13	0.10	0.10	2.9
6	Low sludge	1.3	0.61	0.44	0.0001	0.090	1.7	0.034	0.014	0.029
7	High sludge	1.2	42	0.23	0.0001	0.068	43	0.33	0.39	9.9
				Accumulated content in soil, mg/m²						
1	Preserved	0.20	1.2	0.91	0.004	0.04	7.0	0.52	0.02	8.7
2	Ecological	0.20	1.1	0.68	0.006	0.05	11	1.9	0.24	27
3	Manured	0.42	1.3	0.23	0.03	0.16	5.3	0.52	0.20	3.0
4	Conventional	0.10	1.6	0.49	0.007	0.02	17	0.65	0.06	9.5
5	Medium sludge	0.02	1.4	0.12	0.003	0.02	5.3	0.58	0.05	8.4
6	Low sludge	0.003	6.9	0.74	0.006	0.003	16	0.26	0.20	2.0
7	High sludge 1 samp.	620	500	190	0.95	12	480	22	72	64
7	High sludge 2 samp.	1100	1000	240	0.5	14	860	30	93	250
8	Runoff	15	49	4.8	0.14	2.5	68	3.0	3.0	31

Mass flow into soil

As observed from the upper section of Table 13, the mass flow of DEHP into the non-sludge amended locations 1 to 4 are low and almost identical, rising substantially for the sludge amended locations 5-7. A similar pattern is observed for the higher phthalates and for NPDE as well. For DBP, DPP and BBP the difference between the mass flows for the locations is much lesser.

Accumulated content

In the lower section of Table 13 it is observed that the accumulated content of DEHP in the investigated depth are within a factor of 3 for the “normally” cultured locations 1 to 6, ranging from 5 to 17 mg/m^2 without any obvious connection between content and the type of agriculture. The accumulated DEHP-content is much higher for locations 7 and 8, and a similar pattern is observed for the other phthalates and nonylphenoles as well. It is further observed that for locations 1 to 6, the accumulated content of NPDE is much higher than that of NP, whereas the reverse is true for the mass flows. This is surprising, since the data in the sludge store (Table 10) as previously discussed indicates a degradation of NPDE into NP. Since the substances in the sources have had lesser time to degrade, the NPDE/NP ratios in the sources ought to be higher than in the soils. Perhaps NP is more mobile than NPDE, thus being removed faster, this could also explain the high NP concentration found in the bottom of the sludge store (Table 10). Alternatively, some substantial sources of NPDE might have been overlooked. For location 7 the accumulated content of NP and NPDE are nearly identical, whereas the mass flow for NPDE is considerably higher than for NP, in better agreement with expectations.

Flow/content ratios

An important issue is whether the content found in the soils can be explained reasonably well by the contribution from the sources. It should *a priori* be expected that soils exposed to high mass flows would accumulate higher content of xenobiotics than lesser exposed soils. One way to compare the mass flow from sources with the content in the soil, is to calculate the ratio between mass flow and accumulated content in the soil. This ratio indicates the actual rate of accumulation for the substances in the investigated depth of the soil. The ratio has the dimension of y^{-1}. If steady-state conditions prevailed, the ratio would be proportional to the degradation rate, because it is proportional to the amount carried into the soil per time unit, which during steady state conditions is equal to the amount degraded or transported away (according to the law of mass-conservation). The reciprocal ratio, which has the dimension of years, correspond to the time it theoretically would take to fill the soil from the sources to the accumulated content (provided no degradation or transportation took place, which is not realistic, of course). In Table 14 the flow/content ratios are shown. Since the mass flows into the runoff zone location 8 are unknown, the corresponding ratios cannot be calculated.

Table 14 Ratios between mass flow into soil / accumulated content in soil, y^{-1}

Loc.	Use	NP	NPDE	DBP	DPP	BBP	DEHP	DnOP	DnNP	DiNP
1	Preserved	1.3	0.03	0.24	0.03	0.74	0.04	0.008	1.0	0.003
2	Ecological	0.31	0.07	0.31	0.02	0.38	0.03	0.003	0.09	0.001
3	Manured	0.83	0.02	0.97	0.003	0.21	0.05	0.008	0.08	0.008
4	Conventional	0.62	0.04	0.44	0.02	0.80	0.02	0.008	0.33	0.003
5	Medium sludge	8.6	0.24	2.1	0.04	1.6	2.4	0.18	2.0	0.35
6	Low sludge	470	0.09	0.59	0.02	28	0.11	0.13	0.07	0.01
7	High sludge 1 samp.	0.002	0.08	0.001	0.0004	0.006	0.09	0.01	0.005	0.15
7	High sludge 2 samp.	0.001	0.04	0.001	0.0002	0.005	0.05	0.01	0.004	0.04

Discussion

As seen, the ratios for DEHP for the non-sludge locations 1 to 4 range from 0.02 to 0.05, and the sludge amended locations 6-8 from 0.05 to 0.11 with the exception of location 5 with a ratio of 2.4. A ratio of 0.1 means that the soil receives 10 percent of the accumulated content every year, thus it will theoretically take 10 years for the mass flow of DEHP to build up the accumulated content, even in the absence of degradation or transportation. Hence, it must be concluded that in the most cases, the mass flows of DEHP are grossly underestimated. The same remarks apply for the higher phthalates and for NPDE as well. This could be because the present size of the flows from the sources investigated has been underestimated, e.g. because of underestimated amounts of sludge manure and fertiliser, unrepresentative samples, analytical uncertainties etc.

A second explanation might be that in the past the source flows may have been larger, since it is the accumulated amount from many years of source contribution that is found in the soils today. For example, the fertiliser or the deposition may have contained larger amounts of phthalates.

A third possibility is that sources exist (or have existed in the past) that have been overlooked in the present investigation (e.g. irrigation through plastic hoses). For NP, DBP and BBP much higher ratios are found for all locations (with the exception of the high sludge amended location 7), in better agreement with expectations. The high ratios for NP might be due to a low accumulated content, which in turn might be due to washing out of NP, as mentioned previously.

Degradation rate

In the literature, a degradation rate half-live of 23 days for DEHP in soil was estimated by *Howard et. al. 1991*. Even if assuming an initial concentration corresponding to pure sludge, this effective degradation rate operating for several years would lead to a concentration far below the actual concentrations found in all the soils. In contrast, newer Danish studies on sludge amended soil indicate degradation rates for DEHP corresponding to half-lives in excess of 140 *days (Henriksen et. al. 1998, Roslev et. al. 1998*). This degradation thus seems to agree considerable better with the findings of the present project.
The degradation is addressed in the parallel mathematical modelling project (Sørensen *et. al.* 1999b), in which the degradation rate for DEHP at location 7 has been estimated.

6 Conclusions

It can be concluded that a modest application of sludge for soil amendment apparently does not give rise to elevated concentrations of nonylphenoles and phthalates, compared to the manured or artificially fertilised soils. Further, the concentrations are very close to those found in a not cultivated preserved soil.

Phthalates were detected in the preserved soil not cultivated for more than 50 years, thus other sources than dressing must be present. The most likely source in this case is atmospheric deposition. However, the atmospheric deposition measured in the present study is not sufficient to account for the amounts or composition observed in the soil.

Even 8 years after the amendment with high amounts of sludge had ceased, very significant concentrations of nonylphenoles and phthalates still remained in the soil of the location. The concentrations in this case far exceed the level expected from the aerobic degradation rate found in laboratory experiments, and exceed the Danish soil quality criteria for some of the compounds (*Jensen et. al. 1997*).

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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-DBP	DBP deuterium-labelled in ring
D_4-DEHP	DEHP deuterium-labelled in ring
D_4-DnOP	DnOP deuterium-labelled in ring
DBP	Di(n-butyl)phthalate
DEHP	Di(2-ethylhexyl)phthalate
DiNP	Di("iso"-nonyl)phthalate (technical mixture of isomeric dinonylphthalates)
DnNP	Di(n-nonyl)phthalate
DnOP	Di(n-octyl)phthalate
DPP	Dipentylphthalate
DSGD	Danish Square Grid Database, Danmarks kvadratnetsundersøgelser, Database for soil characteristics covering Denmark
dm %	Content of dry matter in weight percent of total
dw	Dry weight
GC	Gaschromatography
GC/MS	GC combined with MS
ha	Hectare (10.000 m^2)
HRMS	High resolution MS (high ability of MS to discriminate between masses)
LD	Limit of determination, concentration below which the result is uncertain
mg/kg dw	Milligram per kg dry weight (Parts Per Million, ppm)
µg/kg dw	Microgram per kg dry weight (Parts Per Billion, ppb)
MS	Mass spectrometry
nd	Not detected, non-detect
non-detect	Result < 0 after subtraction of the blank
NP	Nonylphenol
NPDE	Nonylphenol-diethoxylate
NPE	Nonylphenol-ethoxylates
p.e.	Personal equivalent
PFK	Perfluoro kerosene (calibration gas for HRMS)
Phthalate	Di ester of phthalic acid (1,2-benzene dicarboxylic acid)
SIM	Selected ion monitoring (MS operating mode)
Spike	Labelled substance added during the analytical procedure for quality control
WTP	Wastewater treatment plant
ww	Wet weight

Appendix A. Soil characteristics

The information about the soil characteristics on the selected locations are drawn as well from the Danish Square Grid Database (DSGD) as from visual inspections of the sample cores carried out during the sampling session on the locations.

1 Data from the Danish Square Grid Database

The available data from the DSGD are the basis for selection of locations before sampling as well as a basis for a quantitative comparison of the soil types in the locations.

The DSGD data are in general based on determination of the texture in the surface soil, comprising one sample per 60 - 90 ha, taken in the ploughing layer ranging from the surface to a depth of about 25 cm. The grid-points used for classification of deeper soil layers are more scattered, based one sampled profile per 200 - 600 ha. The data from the square grid are of course not valid everywhere in each grid mesh, since the soil characteristics in a typical moraine landscape, i.e. the majority of the Danish cultured land, may be prone to a substantial variation (Petersen, 1994), possible within shorter distances than the average mesh width.

In contrast to the profile depth of 50 cm sampled in the present investigation, the DSGD covers the depth until 100 cm. In the database, the content of humus, clay, silt and fine and coarse sand as well as the content of nitrate and ammonium are given in 4 depth ranges, each comprising 25 cm.

The data from DSGD are shown in table 1, omitting nitrate and ammonium, which is considered not relevant for the present investigation. The DSGD grid point numbers are shown in parenthesis for the corresponding locations. The locations 1 and 7 share a common nearest grid point, hence the data for these locations are identical.

Table 1 Soil data from Danish Square Grid Database (DSGD)

Depth cm	**Humus %**	**Clay %**	**Silt %**	**Fine sand %**	**Coarse sand %**	**Soil description**
			Location 1, 7 & 8 (DSGD Gridpoint No 8)			
0-25	2.0	9.9	9.3	51.1	27.7	Fine sand-mixed clayey
25-50	1.4	10.2	9.1	49.7	27.7	Fine sand-mixed clayey
50-75	0.8	7.7	8.2	49.1	31.2	Fine clay-mixed sandy
75-100	0.7	7.2	7.3	52.0	29.4	Fine clay-mixed sandy
			Location 2 (DSGD Gridpoint No 13)			
0-25	2.2	16.8	12.7	66.2	2.2	Clay
25-50	0.6	16.3	12.6	39.6	19.5	Special soil type
50-75	0.9	11.4	11.4	39.5	16.5	Special soil type
75-100	0.1	8.7	13.8	34.8	17.4	Special soil type
			Location 3 (DSGD Gridpoint No 11)			
0-25	1.4	4.7	4.8	58.8	30.4	Fine sandy
25-50	0.6	9.2	6.3	65.0	18.9	Fine clay-mixed sandy
50-75	0.3	13.3	11.7	53.4	20.1	Fine sand-mixed clayey
75-100	0.2	14.6	11.5	57.4	14.6	Fine sand-mixed clayey
			Location 4 (DSGD Gridpoint No 4)			
0-25	2.3	8.3	11.8	51.0	26.7	Fine clay-mixed sandy
25-50	1.6	9.0	14.2	49.8	25.4	Fine clay-mixed sandy
50-75	0.8	13.6	13.3	46.9	25.4	Fine sand-mixed clayey
75-100	0.6	16.7	14.2	48.0	20.5	Clay
			Location 5 (DSGD Gridpoint No 3)			
0-25	2.4	10.9	11.2	51.4	24.2	Fine sand-mixed clayey
25-50	1.7	10.3	10.9	50.8	26.4	Fine sand-mixed clayey
50-75	1.0	18.7	13.1	43.7	23.6	Clay
75-100	0.7	14.0	11.8	46.8	23.8	Fine sand-mixed clayey
			Location 6 (DSGD Gridpoint No 1)			
0-25	1.8	11.2	10.9	49.7	24.3	Fine sand-mixed clayey
25-50	1.2	11.3	11.5	49.7	23.9	Fine sand-mixed clayey
50-75	1.2	12.8	10.5	54.9	18.4	Fine sand-mixed clayey
75-100	1.0	15.1	7.7	54.3	17.2	Clay

The content of humus in the topsoil layers ranging from the surface to a depth of 25 cm, are within a narrow range for all locations with the exception of location 2 (organically manured through 40 years), which is significantly lower. The average is 2.1 %.

The humus content in the next layers ranging from a depth of 25 to 50 cm corresponding to the bottom layers in the sampled profile cores, are lower compared to the top layer at all locations, and more so for the organically manured soils at locations 2 and 3.

In all cases, the humus content reaches the minimum in the bottom layer, the locations 2 and 3 displaying the lowest content.

The soil organically manured through 40 years at location 2 displays the highest clay content and a heavier texture than the others. It is classified as a special soil type according to DSGD.

2 Soil types and soil horizons

Soil types

The locations of the present investigation are all typical for the Eastern part of Denmark, developed on morainic deposits from the last ice age. Such morainic landscapes are characterised by a high content of clay, and soils of the types *Cambisols* and *Luvisols* are predominantly found. The Cambisols represent the least degree of elution (washing out of organic matter and minerals), whereas Luvisols represent intermediate elution. In landscapes containing sandy moraines and melting water deposits, soils of the *Podsol* type are found, representing the highest degree of elution (Petersen, 1994). These soils are typical for western Jutland located in the western part of Denmark

On basis of the degree of the elution of clay minerals from the upper layers, all the soils of the present investigation can be classified as ***Luvisols*** *or* ***Cambisols*** or as a ***transition*** between these soil types.

Luvisols

An important difference between these soil types is caused by the state of acidification. Thus, in the more acidic Luvisol an elution of clay from the upper layers has occurred, due to the greater solubility of clay minerals in acidic environment. This gives rise to the development of a layer depleted of clay, the so-called *E-horizon*, often accompanied by an underlying layer rich in clay minerals, *the B-horizon*.

To designate the soil as a Luvisol requires that the clay content in the B-horizon is at least 20% relative, as well as 3% absolute higher than in the overlying E-horizon (Petersen, 1994).

Cambisols

Soils with a lesser pronounced elution of clay minerals will formally be designated as Cambisols. It is characteristic for these soils that no substantial transport of clay minerals, humic substances or sesquioxides of Al or Fe or oxides of Si from the overlying layers into the B-horizon has occurred. In Cambisols a *Cambric B-horizon* is often found, characterised by weathering processes, which often results in the formation of sesquioxides giving rise to red or yellow colours (Petersen, 1994).

Soil horizons

Horizontal layers in the soil with similar chemical composition are called horizons. Their designations and positions in relation to the depth is:

- Ap-horizon Ploughing zone, organic matter
- E-horizon Depleted of clay
- B-horizon Underlying layer rich in clay
- C-horizon Morainic clay without organic matter

The Ap-horizon will typically extend from the surface to a depth of 25 cm. In contrast, the underlying E, B and C horizons may lack well-defined visible borders, and the vertical extension of the layers may vary considerably (*Petersen, 1994*).

The Ap- horizon consists of the ploughed primarily organic topsoil layer containing mould and humus.

The E- and B-horizons has been described above.

The C-horizon is the deepest inorganic layer often containing morainic clay. It represents the basis on which the soil is formed, and does not itself belong to the soil. The C-horizon begins at a depth so large that the influence of the soil-forming factors is insignificant. The presence of bluish or greyish colours indicates a history of periodic reducing conditions, often due to poor drainage. In some cases reddish dots or stripes from Fe-oxides may occur in the greyish background colour. The red or yellow coloration in the B-horizon may also, but much lesser pronounced, be found in the C-horizon (*Petersen, 1994*).

3 Field observations and characterisation of soils

As mentioned, in a moraine landscape considerable variations is soil characteristics within short distances may occur. Hence, because of the distance between the grid points and the sampling positions, a precise correlation between the DSGD data and the samples cannot be expected. For this reason, the data were complemented with visual inspection of the soil cores during sampling, which yielded valuable additional qualitative information. Thus, the humus content may be derived from the characteristic colour, and the content of sand and clay from the texture of the individual soil layers.

The present investigation comprises morainic soils mainly of the types Luvisols, Cambisols or a transition between these, as mentioned previously. In the following, the soils type at each location is characterised on basis of the DSGD data combined with the field observations of the soil profile.

Table 2 Qualitative field observation data for profile 1

Depth cm	**Texture**	**Colour**	**Horizons**
0-10	Clayey soil, grass, roots	Dark brown	Ap
0-20	Clayey soil, some roots	Dark brown	Ap
20-30	Sand, clay, gravel, some large angular stones, sticky	Dark brown	
30-40	Stones, gravel, sand and clay, large stones, lose	Dark brown	
40-50	Stones, gravel, sand and clay, large angular stones	Dark brown	

The soil contains much gravel, and thus seem more coarse-grained in texture than the other soils. The soil seem surprisingly clayey, considering that it is located in a preserved area not cultured. Hence an acidification process (podzolation) should be expected, which would lead to dispergation and elution of clay minerals.

The observed lack of the expected elution of clay may be due to the use of a certain amount of artificial fertiliser, which to some extent may have neutralised the acidification. This is not allowed on a preserved area, but probably the authorities has given dispensation from the preservation rules.

Table 3 Qualitative field observation data for profile 2

Depth cm	Texture	Colour	Horizons
0-10	Clayey soil, roots	Dark brown	Ap
0-20	Clayey soil, some roots.	Dark brown	Ap
20-30	Clayey soil, pebbles	Dark brown, orange coating	Cambric C
30-40	Clayey soil, pebbles	Dark-light brown, orange red coating	
40-50	Clayey soil, large angular stones	Light brown-yellow, orange spots	

This location is unique since it has been ecologically cultured for 40 years without any use of artificial fertilisers or other artificial substances. The observed texture differs from the other locations as it seems more heavy, wet and sticky, but does not differ substantially in porosity. Nevertheless the texture is lose with an organic look. The yellow and orange spots observed in the 20-30 cm layer indicates the presence of a Cambric C-horizon. The upper layers seem considerably more clayey than the other locations, hence no material elution of clay seem to have occurred.

The DSGD data confirm the observations, since the clay content in the upper layer 0-25 cm is the highest of all locations. The 3 lower layers are described as a special soil type.

The soil type is not comparable with any of the other locations, probably due to a more varied culturing, and as a consequence of the yearlong use of ecological methods.

The soil is characterised as belonging to a special type.

Table 4 Qualitative field observation data for profile 3

Depth cm	Texture	Colour	Horizons
0-10	Loose clay-mixed sandy soil, roots	Light brown	Ap
0-20	Clay-mixed sandy soil, gravel	Light brown	Ap
20-30	Clayey, sandy soil, gravel	Light brown	E
30-40	Clayey sandy soil, stones and gravel	Light brown	
40-50	Clayey, sandy soil, gravel, large angular stones	Light brown	Argic B

The colour observed throughout the profile depth is uniformly light brown. The soil texture is very loose and sandy in the upper 25 cm, followed by layers with increasing clayey character.

The DSGD data indicate a lower content of humus compared to the other locations, in agreement with the observed light colour. Further, these data indicate a very low clay content in the ploughing zone, which only amounts to about the half of the average clay content of that zone in the other locations. The clay content tend to increase with depth, in agreement with the qualitative observations, making the clay content in the lower layers rise to a level even comparable with the clay-rich locations 4 and 5. The rise in clay content from the 25-50 cm zone to the 50-75 cm zone amounts to 4.1% absolute and 44.6% relative. This indicates the presence of an E-horizon (elution layer) in the 25-50 cm zone followed by an Argic B-horizon in the 50-75 cm zone. The rise is too small to characterise the soil as a Luvisol.

The soil is characterised as a *transition between a Luvisol and a Cambisol.*

The light colour may be caused by the relatively high content of sand and does not necessarily indicate a low content of organic matter. However, the uniformity of the colour throughout the profile may be due to the combined effects of a decreasing content humus accompanied by the increasing clay content with depth. An increasing clay or humus content will in general make the colour darker, whereas a high sand content in a humus-rich soil will result in a light colour.

Table 5 Qualitative field observation data for profile 4

Depth cm	**Texture**	**Colour**	**Horizons**
0-10	Loose sand-mixed clayey soil (loam), some roots, dry	Dark brown	Ap
0-20	Loose sand-mixed clayey soil (loam), a little roots, dry	Dark brown, no substantial colour change	Ap
20-30	Sand-mixed clayey soil, pebbles, traces of roots, dry	Dark brown	
30-40	Clayey sticky soil, some pebbles of varying size.	Dark brown	Beginning C
40-50	Large angular stones	Dark brown	Beginning C

The soil appears well drained. No signs on periodic reducing conditions appear on the uppermost 50 cm of the profile. The 2 lower soil layers (30-50 cm) indicates beginning C-horizontal features, since the texture at this depth is morainic in character. However, no substantial change in colour is observed throughout the profile depth, indicating the C-horizon is below the profile depth of 50 cm. The stickiness increases with depth, and the uniform dark colour may be caused by an increasing clay content accompanied by a decreasing humus content.

The DSGD data indicates that a partial elution of clay and humus from the 25-50 cm zone to the 50-75 cm zone has occurred.

To characterise the soil as a Luvisol requires a relative increase the clay content of 20% from the E to the B-horizon, which is not indicated by the DSGD data in Table 1. The high content of clay in the 50 to 100 cm zone as well as the presence of large edgy stones indicates the C-horizon located in this depth.

The soil is characterised as a *transition type between Luvisols and Cambisols.*

Table 6 Qualitative field observation data for profile 5

Depth cm	Texture	Colour	Horizons
0-10	Clay-mixed sandy soil, roots	Dark-light brown*	Ap
0-20	Loose clay-mixed sandy soil, some roots	Dark-light brown*	Ap
20-30	Sandy soil, some clay, pebbles	Dark-light brown*	E
30-40	Very sandy soil, pebbles	Dark-light brown*	E
40-50	Sandy soil, larger stones	Light brown	B

* A somewhat lighter colour than the dark brown of 4 & 7, probably caused by a higher sand content

This profile is more sandy and loose in texture compared to the profiles at locations 4 and 7. The observed qualitative data indicate the presence of an elution horizon (E-horizon).

According to the DSGD data, the clay content is approximately constant in the upper 50 cm, but then increase by 8.4% absolute and 81.6% relatively from the 25-50 cm zone to the 50-75 cm zone. This increase in clay content agree with the existence of an Argic B-horizon, supporting the qualitative finding.

The soil can be characterised as a *Luvisol*, from which the sampled profile contains the Ap horizon (the ploughing layer) and the E-horizon.

Table 7 Qualitative field observation data for profile 7

Depth cm	Texture	Colour	Horizons
0-10	Porous topsoil, sand and clay, some roots	Dark brown	Ap
0-20	Loose sand-mixed clayey soil (loam), some roots, dry	Dark brown, no substantial colour change	Ap
20-30	Sand-mixed clayey soil, pebbles, a little roots, dry	Dark brown with smooth transition to next layer	
30-40	Clayey sticky soil, some pebbles	Light brownish grey	Cambric B
40-50	Clayey sticky soil, gravel, sand, large angular stones	Light brownish grey, orange spots	Cambric B

The observed greyish coloration as well as the orange spots in the lower 30 to 50 cm of the profile indicate a history of periodic reducing conditions, probably caused by poor drainage. The root-zone clearly extends to a depth of 30 cm. The colours and the lack of organic material observed in this depth indicate the existence of a Cambric B-horizon.

According to the DSGD data, the clay content decreases from the 25-50 cm zone, which includes the B-horizon, to the lower layers, indicating a Cambisol. The decreasing clay content, however, is not quite in agreement with the observed increasing stickiness with depth.

Based on the above data, the soil type is characterised as being close to a *Cambisol with clay elution*, but to a lesser extent than in profile 4.

4 Conclusion

From the qualitative observed data on the sampled soil profile, it can generally be concluded that the drilling core depth of 50 cm does not contain all soil horizons.

Profile 5 is a Luvisol, characterised by a pronounced clay elution. The profiles 4 and 7 can be characterised as Luvisols or transition types having characteristics close to Luvisol. The profiles 2 and 7 are apparently closest in character to Cambisols of all profiles.

In all profiles, a general trend in the DSGD data is a decreasing humus content with depth, and a maximal clay content in a depth of about 50 cm.

Appendix B. Tables of results

In this appendix the results from all soil samples are given in tables. In the top of each page, a short preamble is shown, describing the location. In most cases the name given corresponds to the name of the nearest town, village or other named location on the map of Denmark in scale 1/25000 published by the Geodetic Institute of Denmark. The dressing and culturing methods are also given, as well as the annual amounts per hectare of artificial fertiliser, manure and sludge.

Each table contains data from one location and comprises two sections, one for each sample profile corresponding to the positions.

The NERI numbers given are sample identification numbers used in the QA system.

The results are given in μg/kg dry weight.

All results are corrected for extraction recovery, and blanks are subtracted. The recovery for each of the 3 Deuterium-labelled extraction spikes are given in % of the amount added.

The wet weight analysed of each sub-sample (member of double determination) are given in g. One common value for dry matter content is given in % for corresponding sub-samples, used to calculate the dry weight in g for both sub-samples from the wet weight.

Results not detected (i.e. negative after subtraction of the blank) are shown as blanks spaces.

The results are to rounded to 2 significant digits, or in case it is below 1, to 1 digit. Large numbers are truncated by substituting zeroes instead of the non-significant digits.

Outliers, which are deviation results as defined in Appendix D on statistics, are marked with *.

Table 1 Results for Location No.1

Location No:	1
Location name:	Ejby
Methods:	Preserved
Art. fertiliser:	210 kg N-24, 220 kg N-32 /ha 1995
Remarks:	Not cultured for 50-100 y
Use:	Cattle grazing
Sampled:	5 Oct. 1996

Position No	1									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-8621	6-8622	6-8631	6-8632	6-8641	6-8642	6-8651	6-8652	6-8661	6-8662
NP	1.7	1.6	1.3	0.5	0.7	1.2	0.2	0.1		
NPDE	17	4.5	7.2	1.6		14				
DBP	1.9	0.6	1.8		0.04	32				
DPP	0.1									0.1
BBP	0.6					0.3				0.1
DEHP	16	8.1	* 150	12	5.1	78	5.5	4.2		
DnOP	1.8	1.5	0.7	0.6	0.3	0.5	0.4	0.4		5.9
DnNP	0.8									
DiNP	17	26	16	10	2.4	8.2	5.6	5.7	4.7	* 130
D_4DBP %	150	156	76	86	79	74	74	86	150	144
D_4BBP %	98	97	88	97	88	82	84	91	99	93
D_4DEHP %	58	64	58	66	60	53	54	56	53	50
DM, %	89.2	89.2	92.9	92.9	93.2	93.2	92.1	92.1	94.3	94.3
WW, g	50.29	50.07	50.02	50.03	50.12	50.12	50.02	50.18	50.10	50.39
DW, g	44.86	44.66	46.47	46.48	46.71	46.71	46.07	46.22	47.24	47.52
Position No	2									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-8671	6-8672	6-8681	6-8682	6-8691	6-8692	6-8701	6-8702	6-8711	6-8712
NP	0.9		0.6	0.5	0.1					0.02
NPDE	7.7		4.2						1.9	
DBP	2.3	2.4								1.6
DPP										
BBP	0.5	0.2	0.16							
DEHP	5.0	3.3	4.3	1.2	22	4.4	2.1	5.9		
DnOP	1.9	2.1	0.5	0.2	0.3	0.5		0.2	0.1	6.5
DnNP										
DiNP	13	12	1.90	1.0	2.8	7.6	0.1	0.04	6.4	* 140
D_4DBP %	109	116	78	75	73	73	115	106	102	128
D_4BBP %	81	88	93	87	83	82	92	90	85	83
D_4DEHP %	45	49	65	63	61	62	67	68	51	48
DM, %	87.2	87.2	89.6	89.6	90.7	90.7	91.5	91.5	93.0	93.0
WW, g	50.27	50.14	50.14	50.26	50.50	50.42	50.37	50.12	50.07	50.06
DW, g	43.84	43.72	44.93	45.03	45.80	45.73	46.09	45.86	46.57	46.56

* Outlier

Table 2 Results for Location No. 2

Location No: 2
Location name: Ledreborg
Methods: Biodynamic culturing since 40 years
Use: Agriculture
Art. fertiliser: 200 kg urea, 300 kg NPK, 270 kg N-28 /ha 1995
Sampled: 5 Oct. 1996

Position No	1									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-8821	6-8822	6-8831	6-8832	6-8841	6-8842	6-8851	6-8852	6-8861	6-8862
NP	0.01	0.2		0.5	2.0	0.2				
NPDE		6.5	4.6	4.5	8.5	2.6	1.1	0.2		
DBP	0.6	4.3		6.2		2.8		1.8	1.0	1.0
DPP	0.1									
BBP	0.8	0.4					0.1			
DEHP	10	22	* 140	17	85	15	11	3.6	38	4.4
DnOP	5.9	5.8	0.5	0.5	1.1	0.8	2.7	0.3	2.1	3.7
DnNP	1.1						1.1		0.2	
DiNP	6.5	15	2.4	3.8	14	7.9	88	3.8		19
D_4DBP %	95	80	73	63	89	85	97	106	100	106
D_4BBP %	62	54	68	63	90	80	97	104	81	80
D_4DEHP %	37	36	52	49	58	48	62	71	60	54
DM, %	86.4	86.4	85.9	85.9	90.6	90.6	92.8	92.8	93.4	93.4
WW, g	50.04	50.24	50.11	50.92	50.11	50.50	50.14	50.51	50.18	50.26
DW, g	43.23	43.41	43.04	43.74	45.40	45.75	46.53	46.87	46.87	46.94
Position No	2									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-8871	6-8872	6-8881	6-8882	6-8891	6-8892	6-8901	6-8902	6-8911	6-8912
NP		0.7	1.3	0.5	1.9	2.1	0.01			
NPDE	2.0	1.8		2.8	14			3.7		
DBP	5.7	0.3	0.2		8.0					
DPP		0.1								
BBP	0.3	0.5	0.2						0.1	
DEHP	14	16	13	16	13	15	6.1	35	33	5.2
DnOP	5.8	38	0.7	0.5				6.9	8.4	3.1
DnNP		5.3	0.6						1.9	0.9
DiNP	21	* 720	5.7	5.1	24	16	9.4	* 190	77	9.5
D_4DBP %	99	93	82	84	50	56	71	65	116	127
D_4BBP %	65	62	80	82	69	100	120	108	84	97
D_4DEHP %	36	40	54	56	34	37	54	51	52	68
DM, %	87.7	87.7	86.7	86.7	87.6	87.6	90.9	90.9	92.8	92.8
WW, g	50.12	50.07	50.17	50.66	50.16	50.05	50.16	50.03	50.19	50.04
DW, g	43.96	43.91	43.50	43.92	43.94	43.84	45.60	45.48	46.58	46.44

* Outlier

Table 3 Results for Location No. 3

Location No: 3
Location name: Kirke Såby
Methods: Ecological culturing since 1991, formerly conventional
Use: Agriculture
Art. fertiliser: 315 kg N-20 /ha 1995
Manuring: Pig, 32 t ww (6.4 t dw) /ha 1994
Sampled: 5 Oct 1996

Position No	**1**									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-8721	6-8722	6-8731	6-8732	6-8741	6-8742	6-8751	6-8752	6-8761	6-8762
NP	0.5	0.6	0.2	0.7			1.2	0.4	0.5	0.7
NPDE	15	13								
DBP	0.5	2.5							3.2	1.3
DPP	0.1									
BBP	0.8	0.4	0.3							
DEHP	19	11	16	9.9	7.8	12	14	12	0.1	0.8
DnOP	1.1	0.5	0.5	0.3	0.5	0.4	1.8	1.2	0.5	
DnNP	1.8									
DiNP	10	11	1.1	0.6	4.2	4.2	18	11	10	16
D_4DBP %	111	102	86	80	85	85	76	79	98	114
D_4BBP %	78	66	92	83	86	86	74	84	89	98
D_4DEHP %	50	49	55	53	54	50	48	57	59	61
DM, %	88.7	88.7	88.8	88.8	88.9	88.9	91.1	91.1	92.8	92.8
WW, g	50.11	50.36	50.25	50.60	50.12	50.02	50.00	50.02	50.11	50.28
DW, g	44.45	44.67	44.62	44.93	44.56	44.47	45.55	45.57	46.50	46.66
Position No	**2**									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-8771	6-8772	6-8781	6-8782	6-8791	6-8792	6-8802	6-8801	6-8811	6-8812
NP	0.1	0.1	1.2	0.1			0.4	0.2	7.6	5.2
NPDE	6.7	1.9	8.0				0.8	2.8	6.8	3.7
DBP	2.3								0.7	
DPP	0.0002		0.04						1.1	0.2
BBP	1.1	0.6	0.2						3.2	1.0
DEHP	20	14	39	6.6	7.4	5.8	45	3.1	2.6	0.9
DnOP	3.4	3.4	1.1	0.2	0.4	0.2	0.5		5.5	2.7
DnNP	1.0								5.0	1.8
DiNP	17	12	9.9	1.7	3.2	4.6	5.6			
D_4DBP %	113	118	84	84	83	96	106	95	147	136
D_4BBP %	77	67	89	97	87	93	94	94	107	100
D_4DEHP %	41	38	57	56	52	54	56	49	82	76
DM, %	91.0	91.0	90.6	90.6	92.6	92.6	93.4	93.4	95.0	95.0
WW, g	50.02	50.05	50.42	50.19	50.03	50.03	50.23	50.15	50.16	50.13
DW, g	45.52	45.55	45.68	45.47	46.33	46.33	46.91	46.84	47.65	47.62

Table 4 Results for Location No. 4

Location No:	4
Location name:	Ågerup
Methods:	Conventional culturing
Use:	Agriculture
Art. fertiliser	330 kg Ca-NH_4-NO_3 , 365 kg NPK /ha 1995
Sampled:	5 Oct. 1996

Position No	1									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-8521	6-8522	6-8531	6-8532	6-8541	6-8542	6-8551	6-8552	6-8561	6-8562
NP	1.0	1.5	1.4	0.2	0.3				0.2	
NPDE	7.2	13	8.7		1.0	0.4			0.5	0.9
DBP	1.0	2.5					1.5		1.3	1.3
DPP	0.1	0.02					0.1		0.01	0.04
BBP	0.3	0.2	0.1	0.1		0.1	0.3		0.02	
DEHP	* 110	17	16	11	11	16	22	5.0	8.0	66
DnOP	3.2	1.2	1.1	1.5	0.9	0.8	1.5	0.3	0.6	3.7
DnNP			0.2	0.2	0.03	0.2	0.9			
DiNP	45	17	4.6	13	3.5	2.7	23	2.6	19	68
D_4DBP %	160	155	102	84	89	85	85	85	131	189
D_4BBP %	94	96	82	77	87	87	83	90	111	123
D_4DEHP %	52	51	65	60	68	71	67	69	77	81
DM, %	90.5	90.5	91.2	91.2	93.6	93.6	94.8	94.8	95.0	95.0
WW, g	50.10	50.04	50.28	50.04	50.23	50.19	50.30	50.30	50.12	50.07
DW, g	45.34	45.29	45.86	45.64	47.02	46.98	47.68	47.68	47.61	47.57
Position No	2									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-8571	6-8572	6-8581	6-8582	6-8591	6-8592	6-8601	6-8602	6-8611	6-8612
NP				0.1	0.1					
NPDE	2.6	3.2	0.8	2.8	3.3	1.5	27			
DBP	2.4	2.5		2.3			6.2		1.4	0.4
DPP		0.02			0.03				0.02	0.01
BBP		0.05			0.08					
DEHP	7.9	2.6	7.8	13	4.1	5.1	* 460	18	5.1	
DnOP	0.6	3.0	0.3	0.4	0.4	0.5	0.3	0.4	9.4	
DnNP					0.1		0.5		0.8	
DiNP	22	55	1.0	3.1	2.2	7.1	2.2	3.4	* 130	16
D_4DBP %	143	128	92	78	84	72	83	101	129	161
D_4BBP %	93	88	96	89	98	86	91	107	93	109
D_4DEHP %	52	53	59	72	79	72	89	78	70	76
DM, %	91.6	91.6	93.2	93.2	93.9	93.9	94.5	94.5	93.9	93.9
WW, g	50.00	50.08	50.05	50.10	50.12	50.00	50.16	50.07	50.03	50.01
DW, g	45.80	45.87	46.65	46.69	47.06	46.95	47.40	47.32	46.98	46.96

* Outlier

Table 5 Results for Location No. 5

Location No: 5
Location name: Jyllinge
Methods: Medium sludge amended
Use: Agriculture
Art. fertiliser: 920 kg urea, 530 kg NPK, 200 kg Ca-NH_4-NO_3 , 100 kg KCl /ha 1993-1996
Manuring: Mink, 22 t ww (2.2 t dw) /ha 1994
Sludge: 0.9 t dw/ha 1993, 4 t dw/ha 1996, Jyllinge WTP
Sampled: 26 Sep. 1996

Position No	1									
Depth, dm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-9161	6-9162	6-9171	6-9172	6-9181	6-9182	6-9191	6-9192	6-9201	6-9202
NP										0.001
NPDE			5.3	4.1	5.5		4.1			
DBP	0.5	0.7								
DPP		0.03								
BBP	0.1	0.2								
DEHP	13	15	12	11	4.1	6.0	1.2	9.7	27	4.9
DnOP	1.3	10							1.4	1.2
DnNP		1.1								
DiNP		* 230	15	6.5	4.6	3.3	3.5	5.2	1.0	2.0
D_4DBP %	127	133	87	89	94	100	95	111	103	110
D_4BBP %	85	80	108	94	116	117	114	116	90	97
D_4DEHP %	77	70	55	51	64	59	72	69	79	79
DM, %	94.9	94.9	91.9	91.9	93.4	93.4	94.1	94.1	96.2	96.2
WW, g	50.14	50.21	50.26	50.06	50.10	50.06	50.33	50.11	50.12	50.05
DW, g	47.58	47.65	46.19	46.01	46.79	46.76	47.36	47.15	48.22	48.15
Position No	2									
Depth, dm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-9111	6-9112	6-9121	6-9122	6-9131	6-9132	6-9141	6-9142	6-9151	6-9152
NP			0.7	0.2						
NPDE			11	9.7	13	3.9	2.1	4.1		
DBP	0.7			2.2				1.4		0.2
DPP	0.1									
BBP	0.6	0.3							0.003	
DEHP	13	33	16	13	13	12	4.9	7.9	26	4.1
DnOP	4.2	4.0					2.3	0.5	1.3	0.6
DnNP	0.9	0.3								
DiNP	10	36	5.0	7.0	2.5		40	14	1.4	0.6
D_4DBP %	126	120	83	82	93	98	92	96	112	99
D_4BBP %	72	80	126	111	125	129	117	124	95	91
D_4DEHP %	57	64	60	47	61	64	73	72	81	70
DM, %	92.5	92.5	90.5	90.5	91.7	91.7	92.9	92.9	94.8	94.8
WW, g	50.07	50.06	50.01	50.16	50.42	50.14	50.31	50.31	50.11	50.16
DW, g	46.31	46.31	45.26	45.39	46.24	45.98	46.74	46.74	47.50	47.55

* Outlier

Table 6 Results for Location No. 6

Location No: 6
Location name: Sundbylille
Methods: Low sludge amended, manured
Use: Agriculture
Art. fertiliser: 120 kg Ca-NH_4-NO_3 27% /ha 1995
Manuring: Cattle, 90 t ww (27 t dw) /ha 1995
Sludge: 10 t ww (2t dw) /ha 1993, Frederikssund WTP
Sampled: 26 Sep. 1996

Position No	1									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-9061	6-9062	6-9071	6-9072	6-9081	6-9082	6-9091	6-9092	6-9101	6-9102
NP										
NPDE	129	116								
DBP	2.3	3.3	1.3	1.0	1.2	1.3		1.0	2.6	2.8
DPP				0.03				0.03		
BBP										
DEHP	27	21	21	10	11	9.7	0.05	7.5	0.1	
DnOP	0.7	1.3	0.3	0.5	0.7	0.6		0.7		1.6
DnNP	0.6	1.4	0.8	0.6						0.1
DiNP	2.7	9.7	2.8	2.7	6.5	5.1	1.6	6.7	2.3	8.8
D_4DBP %	91	63	92	92	98	85	113	135	141	116
D_4BBP %	86	63	80	84	89	99	117	124	121	127
D_4DEHP %	51	46	45	51	53	57	82	84	74	87
DM, %	91.5	91.5	89.2	89.2	89.9	89.9	95.0	95.0	94.4	94.4
WW, g	50.12	50.18	50.13	50.19	50.13	50.48	50.05	50.01	50.21	50.05
DW, g	45.86	45.91	44.72	44.77	45.07	45.38	47.55	47.51	47.40	47.25
Position No	2									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-9011	6-9012	6-9021	6-9022	6-9031	6-9032	6-9041	6-9042	6-9051	6-9052
NP		0.1								
NPDE	29	11		25	8.1				3.2	
DBP	1.3	1.9	4.8	2.1	2.0	1.9	0.8	1.0	0.8	1.0
DPP				0.1					0.1	
BBP				0.1						
DEHP	19	* 350	19	23	23	23	53	32	54	32
DnOP	0.3	0.6	0.3	1.1	0.4	0.3	0.2	0.2	1.5	0.9
DnNP	0.4	0.5	0.5	1.2	0.8	1.3	0.5		0.6	
DiNP	0.9	1.0	2.0	5.2	2.7	2.8	3.1	2.2	16	7.0
D_4DBP %	114	99	77	95	80	92	90	83	85	86
D_4BBP %	110	102	85	96	87	90	94	109	89	91
D_4DEHP %	87	106	65	66	67	76	91	104	97	102
DM, %	91.7	91.7	90.7	90.7	91.5	91.5	95.1	95.1	97.0	97.0
WW, g	50.23	50.40	50.05	50.47	50.41	50.09	50.25	50.26	50.01	50.51
DW, g	46.06	46.22	45.40	45.78	46.13	45.83	47.79	47.80	48.51	48.99

* Outlier

Table 7 Results for Location No. 7 (first sampling)

Location No: 7
Location name: Bistrup
Methods: High sludge dressing ceased 1991, since then art. fertilised
Use: Agriculture
Art. fertiliser: 210 kg N-24 + 220 kg N-32 /ha 1995
Sludge: 17 t dw /ha/y (average before 1991), Bjergmarken WTP
Sampled: 25 Oct 1996

Position No	1									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-9711	6-9712	6-9721	6-9722	6-9731	6-9732	6-9741	6-9742	6-9751	6-9752
NP	990	1300	1500	1300	1700	2200	1900	2000	460	380
NPDE			1200	1400	1300	3000	1600	1100	890	570
DBP	200	270	280	230	400	350	500	370	510	240
DPP	1.6	8.8			2.0	2.0			0.8	
BBP	7.5	15	31	33	20	27	29	17	8	4
DEHP	480	1120	1700	1700	1200	1300	680	550	530	380
DnOP	36	45	80	82	48	45	35	24	15	42
DnNP	99	160	240	220	200	190	150	120	92	79
DiNP	90	170	210	260	160	160	116	40	140	54
D_4DBP %	166	95	77	81	104	87	100	82	132	85
D_4BBP %	195	96	76	94	105	103	105	100	99	64
D_4DEHP %	167	88	66	69	78	82	82	79	98	68
DM, %	68.3	68.3	69.7	69.7	82.9	82.9	90.9	90.9	90.6	90.6
WW, g	50.30	50.05	50.46	50.11	50.25	50.10	50.55	50.20	50.34	50.02
DW, g	34.35	34.18	35.17	34.93	41.66	41.53	45.95	45.63	45.61	45.32
Position No	2									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-9761	6-9762	6-9771	6-9772	6-9781	6-9782	6-9791	6-9792	6-9801	6-9802
NP	810	1300	1900	1700	1900	1900	2400	1700	860	830
NPDE	910	1600	1004	1000	1000	1800	800	820	1800	2300
DBP	590	350	290	330	380	280	520	400	1040	1300
DPP	11	2.4		0.8	2.4	1.0	0.9	1.1	7.6	9.5
BBP	43	35	23	25	26	25	30	22	87	64
DEHP	770	1600	1800	1600	1600	1600	1200	1060	930	500
DnOP	61	56	53	47	67	65	64	75	64	39
DnNP	120	240	170	150	200	190	190	250	190	120
DiNP	100	180	270	140	210	280	105	120	85	95
D_4DBP %	115	89	85	75	69	62	46	48	93	226
D_4BBP %	151	104	91	96	66	59	50	60	97	154
D_4DEHP %	128	90	72	79	73	71	63	68	84	158
DM, %	68.8	68.8	74.2	74.2	75.2	75.2	71.7	71.7	72.8	72.8
WW, g	50.05	50.00	50.25	50.33	50.89	50.04	50.01	50.11	50.04	50.39
DW, g	34.43	34.40	37.29	37.34	38.27	37.63	35.86	35.93	36.43	36.68

Table 8 Results for Location No. 8

Location No: 8
Location name: Bistrup
Description: Meadow on slope between sludge store and Roskilde Fjord
Use: Cattle grazing
Sludge: Runoff/percolate from storage for Bjergmarken WTP
Sampled: 25 Oct. 1996

Position No	3									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-9531	6-9532	6-9541	6-9542	6-9551	6-9552	6-9561	6-9562	6-9571	6-9572
NP	150	51	11	9.3				0.3	3.7	2.1
NPDE	430	340	22	17	1.2				7.6	5.5
DBP	86		12	0.4	2.3	2.0	8.2	24	3.8	0.9
DPP	0.4	0.03								0.02
BBP	18	3.2							0.3	0.1
DEHP	460	320	43	49	5.2	4.5	4.0	78	6.3	2.5
DnOP	47	10						14	1.0	6.8
DnNP	4.9	35	2.9	3.0						
DiNP	251	63	12	13	4.6	3.8	3.4	* 345		* 156
D_4DBP %	57	56	76	88	107	91	62	58	43	63
D_4BBP %	57	78	76	84	101	93	57	57	41	53
D_4DEHP %	35	60	43	46	69	64	65	58	59	69
DM, %	66.7	66.7	87.6	87.6	97.4	97.4	91.6	91.6	90.2	90.2
WW, g	50.22	50.26	50.08	50.62	50.20	50.07	50.18	50.25	50.02	50.08
DW, g	33.50	33.52	43.87	44.34	48.89	48.77	45.96	46.03	45.12	45.17
Position No	4									
Depth, cm	0 - 10		10 - 20		20 - 30		30 - 40		40 - 50	
NERI No	6-9481	6-9482	6-9491	6-9492	6-9501	6-9502	6-9511	6-9512	6-9521	6-9522
NP	260	150	17	16		0.1			6.0	1.8
NPDE	950	400	43	55	1.0	7.1	1.4	2.4	14	4.1
DBP	52	16	0.7	3.4		0.2	2.1	7.1	1.1	0.1
DPP	0.5	5.7								
BBP	34	61							0.6	0.3
DEHP	450	1500	100	110	7.0	17	11	10	8.7	2.3
DnOP	24	32	2.4	1.8					0.6	0.7
DnNP	52	27	8.8	6.6						
DiNP	95	36	21	19	6.4	5.1	9.7	8.4	1.4	2.2
D_4DBP %	155	222	113	88	92	92	92	92	58	72
D_4BBP %	135	376	108	100	99	97	82	89	42	49
D_4DEHP %	86	195	47	48	56	59	63	63	64	70
DM, %	65.5	65.5	86.1	86.1	97.7	97.7	94.9	94.9	89.6	89.6
WW, g	50.36	50.06	50.49	50.57	50.73	50.14	50.13	50.57	50.07	50.68
DW, g	32.99	32.79	43.47	43.54	49.56	48.99	47.57	47.99	44.86	45.41

* Outlier

Table 9 Results for Location No. 7 (second sampling)

Location No: 7
Location name: Bistrup
Methods: High sludge dressing ceased 1991, since then art. fertilised
Use: Agriculture
Art. fertiliser: 210 kg N-24 + 220 kg N-32 /ha 1995
Sludge: Bjergmarken WTP
Sampled: 4 Nov. 1998 (second sampling)

Position No	1											
Depth, cm	0 -10		10 - 20		20 - 30		30 - 40		40 - 50		50 - 60	
NERI No	8-5931	8-5932	8-5941	8-5942	8-5951	8-5952	8-5961	8-5962	8-5971	8-5972	8-5981	8-5982
NP	610	840	960	1200	2200	2900	5600	5400	5000	5200	590	400
NPDE	560	1000	920	510	2800	3000	8200	3500	5000	6300	630	390
DBP	210	190	170	280	270	230	520	460	1100	1300	680	180
DPP	0.6	1.1	1.0	1.2	3.1		0.7		2.3	1.3		0.9
BBP	17	20	22	24	33	33	61	35	29	160	8.0	6.1
DEHP	1500	1800	1900	2300	2500	2600	3600	3300	2000	1300	750	320
DnOP	46	47	73	51	73	100	100	81	47	58		6.7
DnNP	140	130	210	210	290	290	370	370	* 1200	280	68	60
DiNP	440	590	680	800	920	1100	1200	1500	390	360	37	35
D_4DBP %	178	159	193	197	128	135	147	175	162	157	86	124
D_4BBP %	125	135	139	127	138	121	108	121	120	122	77	103
D_4DEHP %	101	92	97	92	106	98	106	105	96	82	69	82
DM %	62	62	61.6	61.6	60.3	60.3	60.9	60.9	62.8	62.8	78.3	78.3
WW, g	50.07	50.20	50.13	50.12	50.29	50.06	50.83	50.11	50.24	50.44	50.33	50.51
DW, g	31.04	31.12	30.88	30.87	30.32	30.19	30.96	30.52	31.55	31.68	39.41	39.55
Position No	2											
Depth, cm	0 -10		10 - 20		20 - 30		30 - 40		40 - 50		50 - 60	
NERI No	8-5871	8-5872	8-5881	8-5882	8-5891	8-5892	8-5901	8-5902	8-5911	8-5912	8-5921	8-5922
NP	730	1000	990	1000	2000	1900	3800	4700	1200	1100	410	370
NPDE	570	310	770	710	990	1800	580	3400	1900	2000	750	770
DBP	210	290	260	240	410	260	1200	600	510	390	570	670
DPP	0.7	0.8	0.9	1.5		2.0		2.2	0.8	0.4	1.4	0.8
BBP	22	23	21	23	22	20	25	24	11	8.2	7.9	6.1
DEHP	1000	1400	1300	1300	960	1300	5000	1500	800	650	410	730
DnOP	42	66	58	53	64	68	150	110	32	29	10	15
DnNP	100	120	120	100	120	160	220	210	140	210	64	140
DiNP	200	390	350	340	290	360	460	450	220	170	70	110
D_4DBP %	134	128	138	116	134	162	136	128	152	153	108	105
D_4BBP %	88	102	103	100	120	137	124	122	147	144	112	104
D_4DEHP %	89	95	86	80	92	101	85	84	99	98	88	85
DM %	65.4	65.4	63.6	63.6	67	67	62	62	70.5	70.5	77.2	77.2
WW, g	50.00	50.22	50.13	50.09	50.00	50.60	50.14	50.68	50.15	50.09	50.29	50.69
DW, g	32.70	32.84	31.88	31.86	33.50	33.90	31.09	31.42	35.36	35.31	38.82	39.13

* Outlier

Appendix C. Figures

In this appendix the complete results are shown in graphical form in the following figures.

The figures

Each figure refers to a particular location and substance, showing the concentration at all depths. The figures come in two types. One type shows the *mean concentrations* as dots for each depth as well as the corresponding standard deviations as plus/minus-bars. The other type of figure shows the individual *concentrations* as dot diagrams colour coded according to position.

Numbering

The figures are arranged and numbered according to:

Location. Substance. Type.

Units

All concentrations are given in:

μg/kg dry weight

corrected for extraction recovery, blank subtracted.

Scale

The scale is for each figure set to accommodate the maximal concentration as well as the standarddeviation-bars. Because of the large concentration span covered by the investigation, it is not possible to draw all figures to the same scale without rendering the lowest concentrations illegible. Hence, different scales are used. The minimum scale is set to 10 μg/kg, and corresponding figures of the two types are drawn to the same scale.

Figure texts

A short description of the location is given on each page. For a more detailed description is referred to Appendix A or Chapter 5 in the report.

Fig. 1.1.1

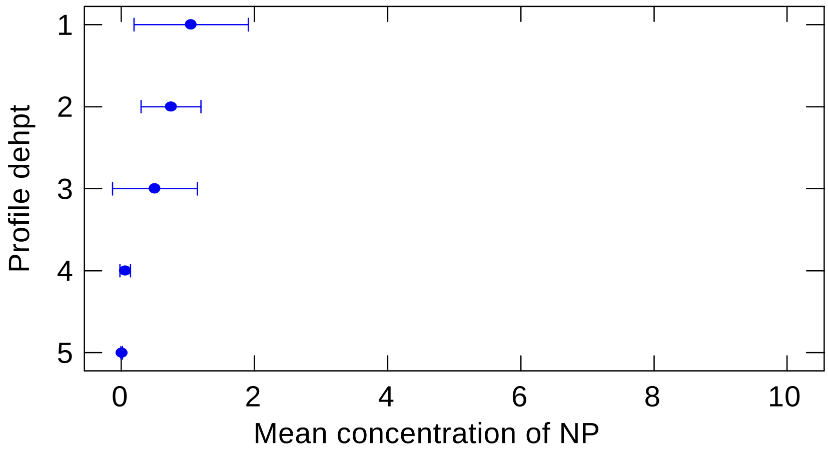


Fig. 1.1.2

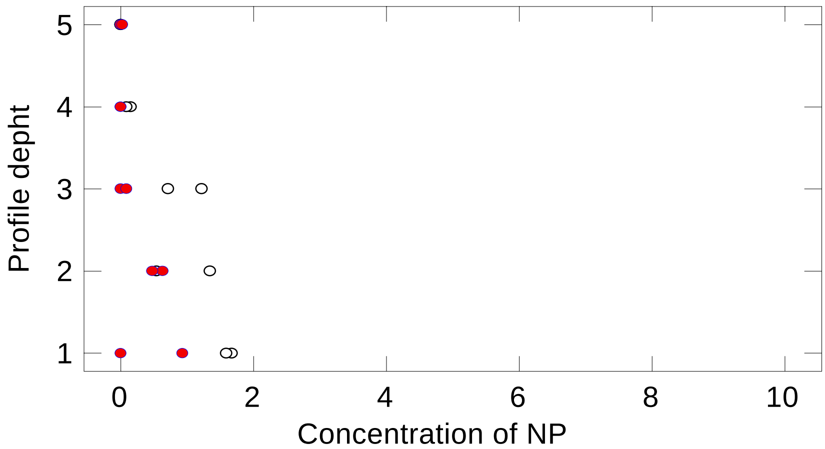


Fig. 1.2.1

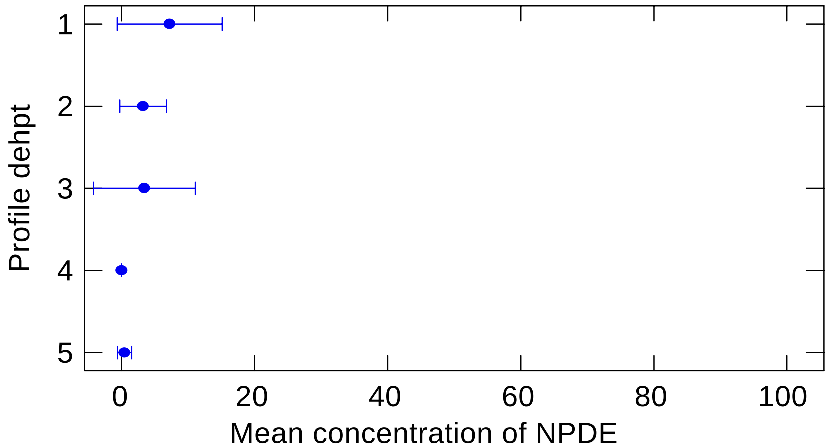
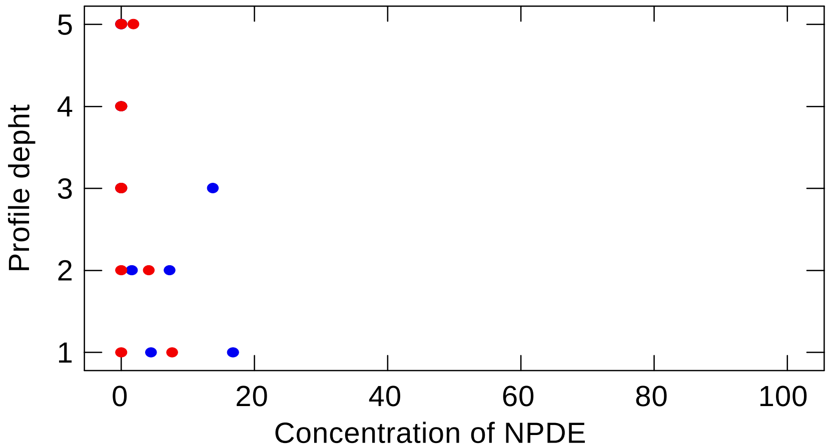


Fig. 1.2.2



Figs. 1.1 - 1.2 Location 1 preserved for more than 50 years. Profiles for NP and NPDE.

Fig. 1.3.1

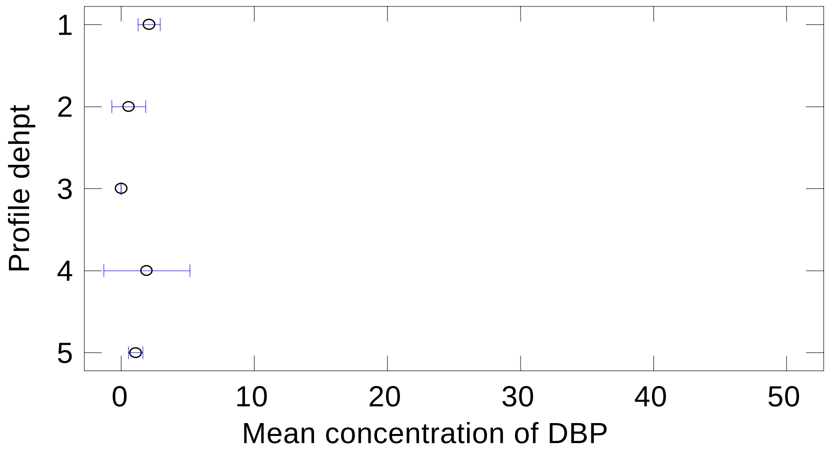


Fig. 1.3.2

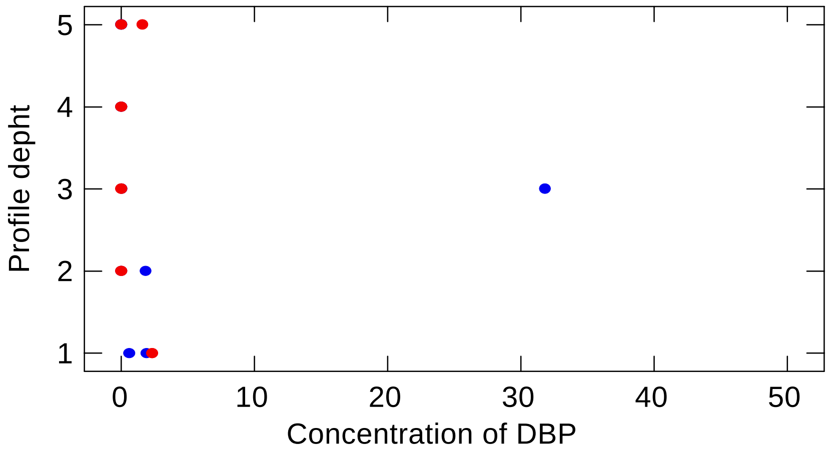


Fig. 1.4.1

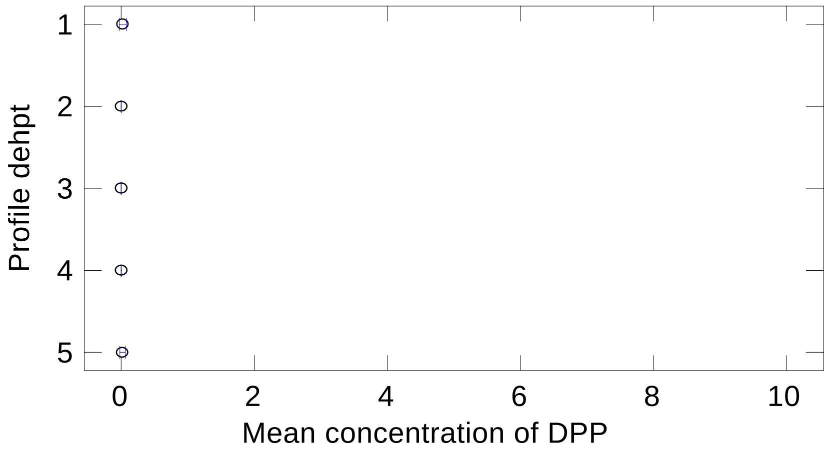
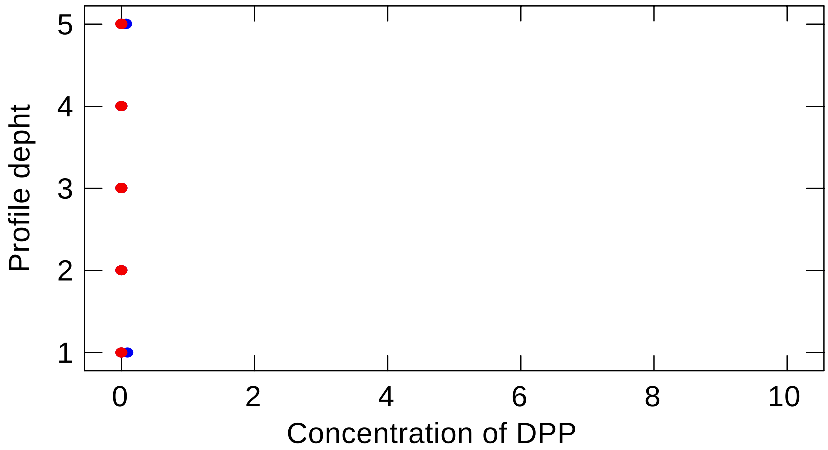


Fig. 1.4.2



Figs. 1.3 - 1.4 Location 1 preserved for more than 50 years. Profiles for DBP and DPP.

Fig. 1.5.1

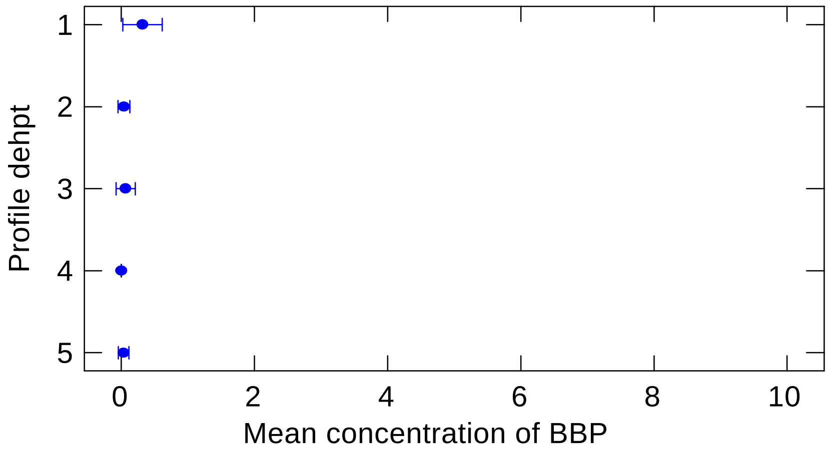


Fig. 1.5.2

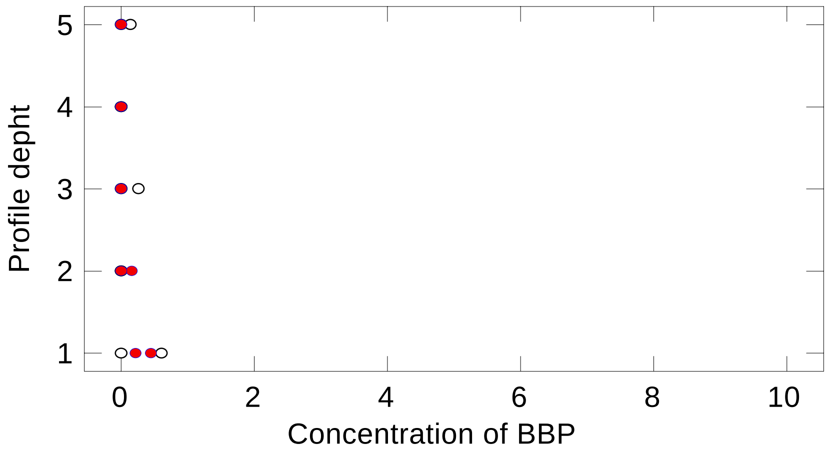


Fig. 1.6.1

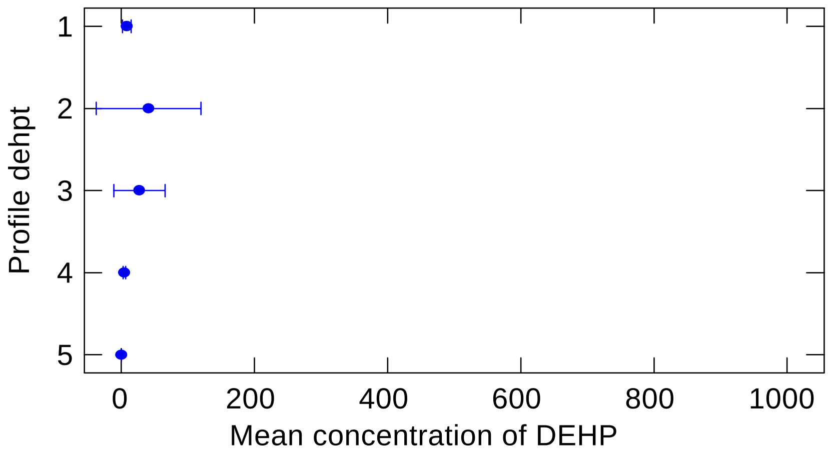
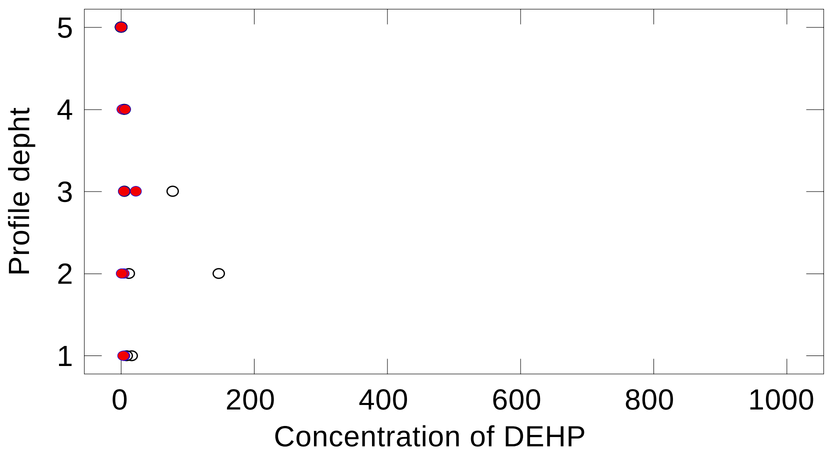


Fig. 1.6.2



Figs. 1.5 - 1.6 Location 1 preserved for more than 50 years. Profiles for BBP and DEHP.

Fig. 1.7.1

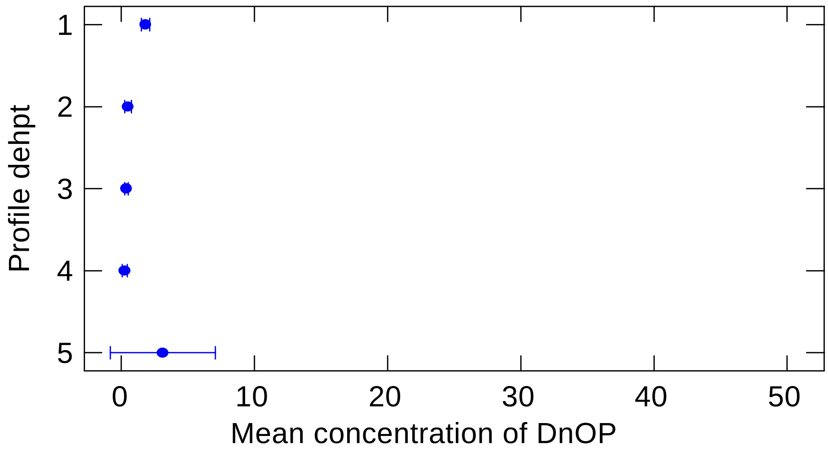


Fig. 1.7.2

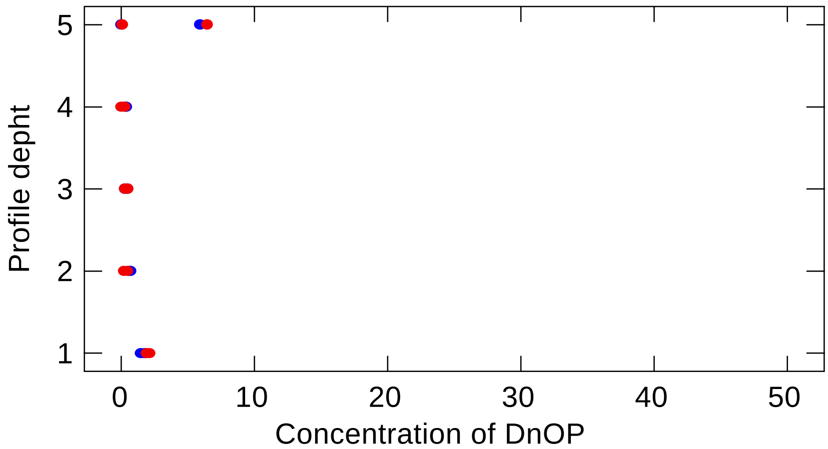


Fig. 1.8.1

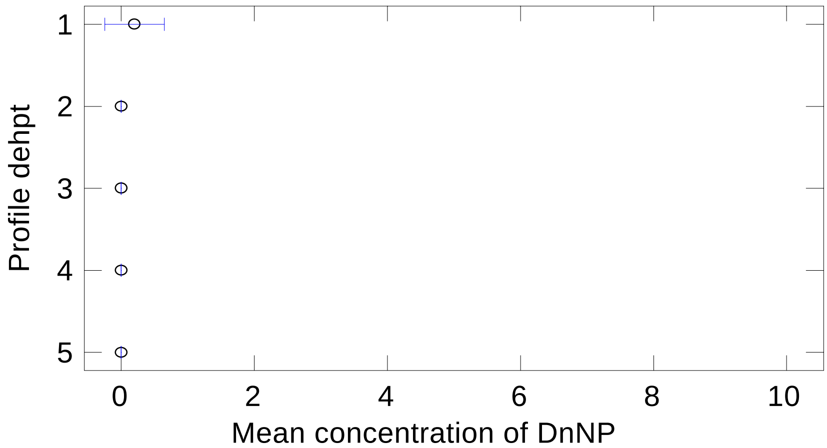
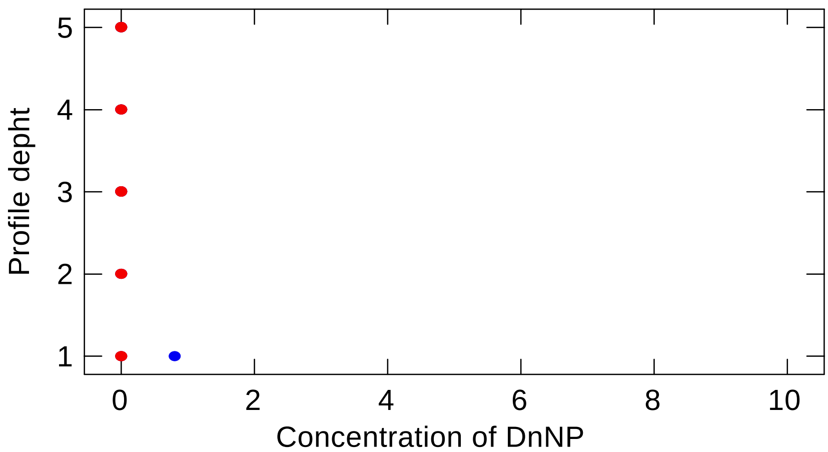


Fig. 1.8.2



Figs. 1.7 - 1.8 Location 1 preserved for more than 50 years. Profiles for DnOP and DnNP.

Fig. 1.9.1

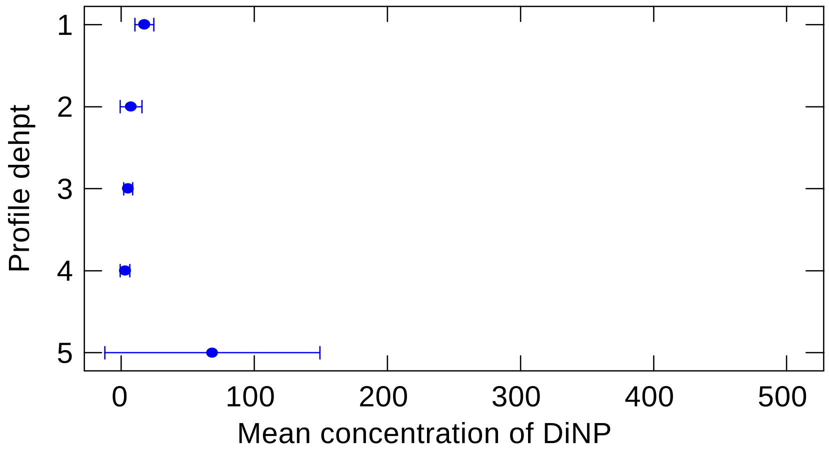


Fig. 1.9.2

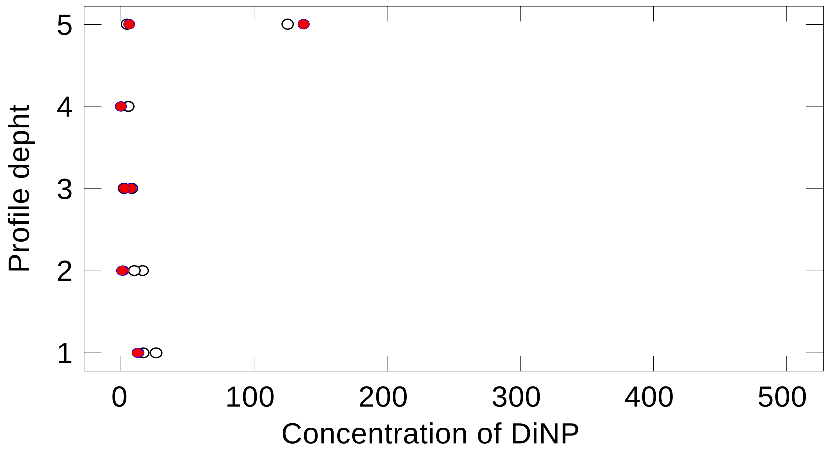


Fig. 1.9 Location 1 preserved for more than 50 years. Profile for DiNP.

Fig. 2.1.1

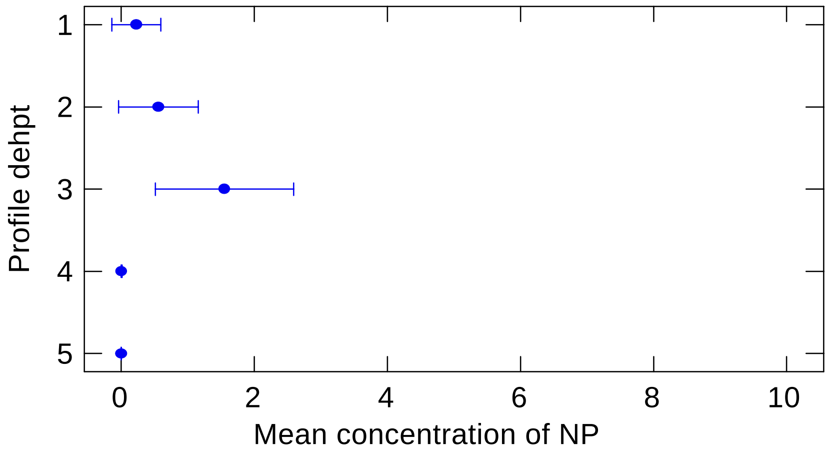


Fig. 2.1.2

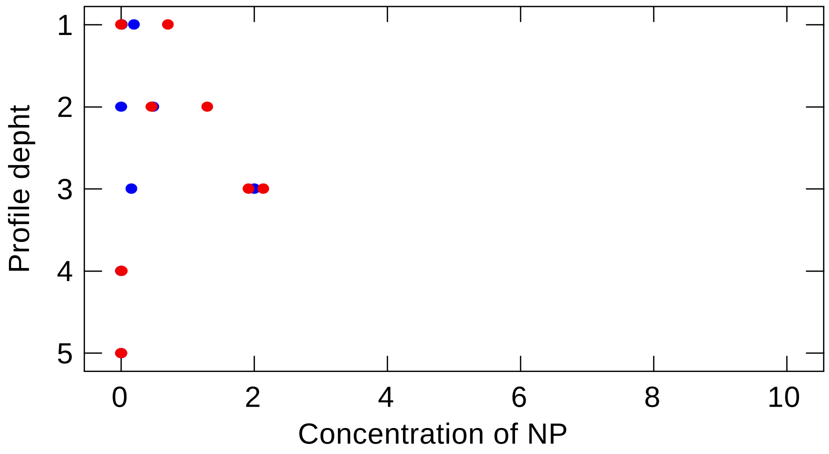


Fig. 2.2.1

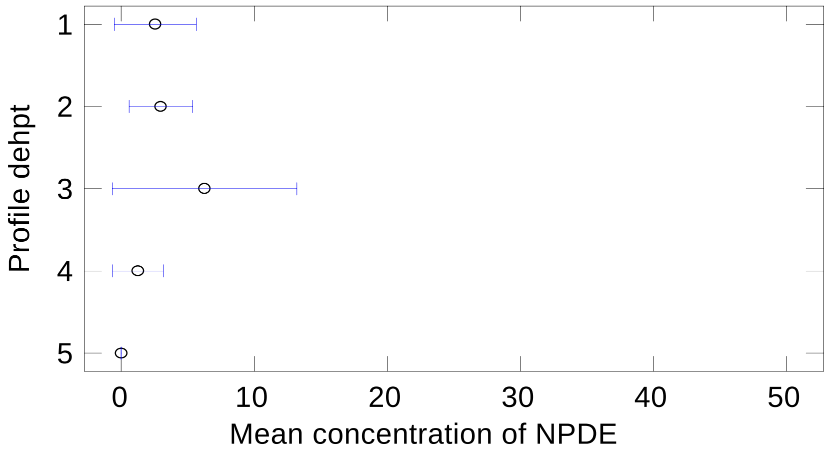
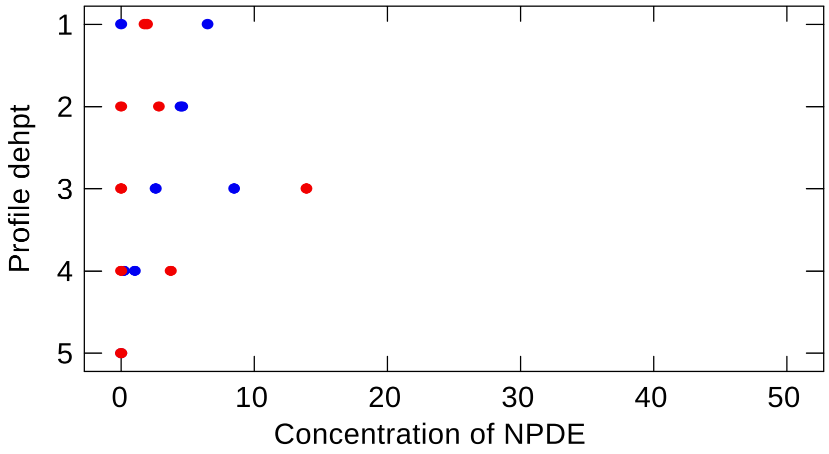
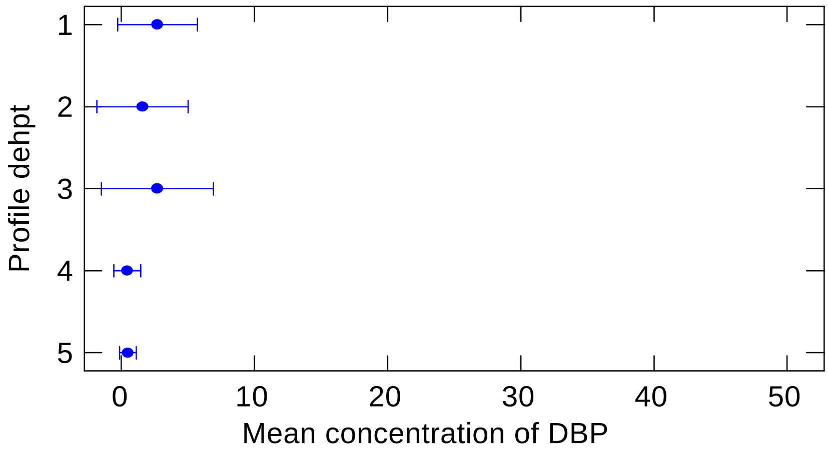


Fig. 2.2.2



Figs. 2.1 - 2.2 Location 2 organically manured for 40 years. Profiles of NP and NPDE.

Fig. 2.3.1



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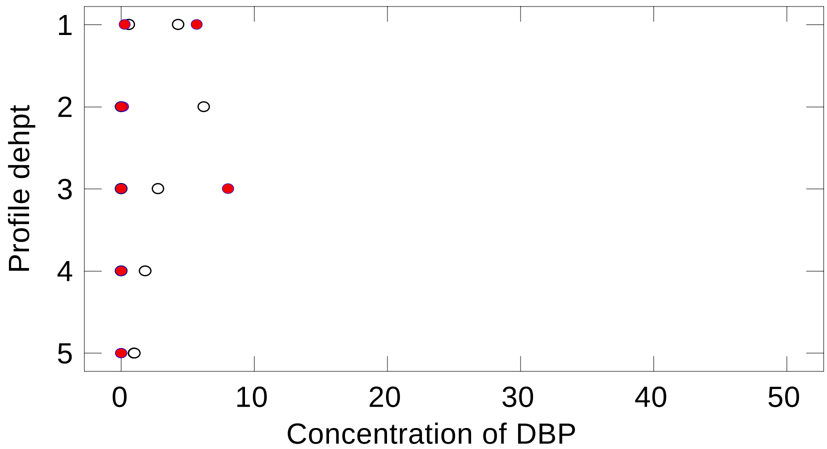
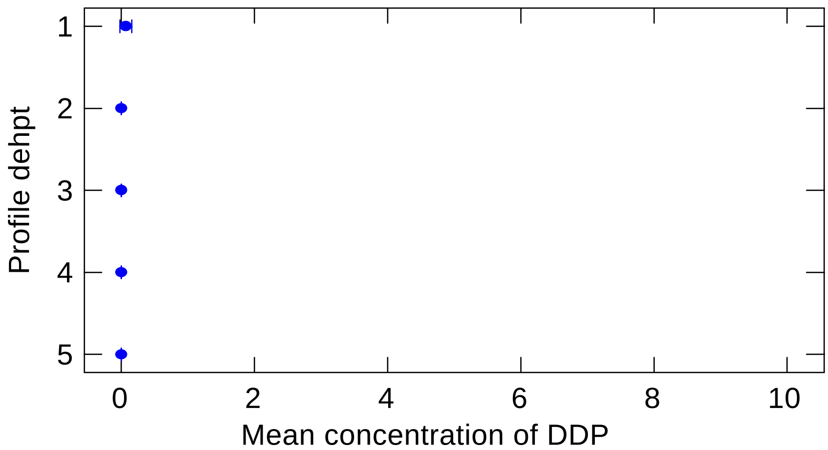


Fig. 2.4.1



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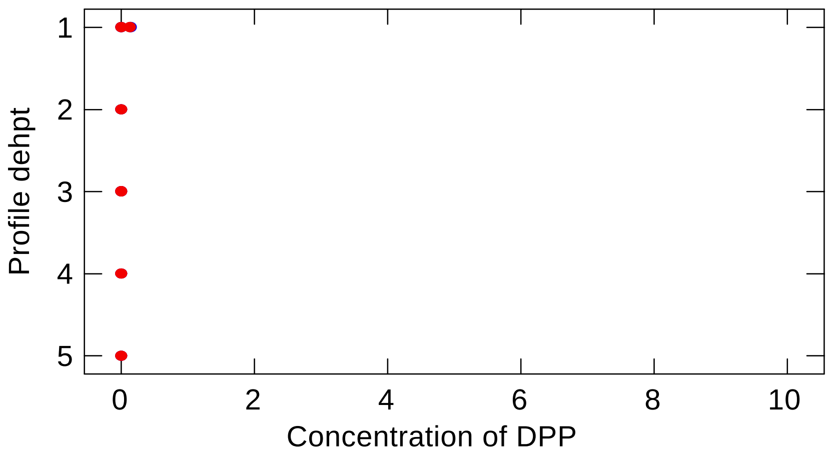
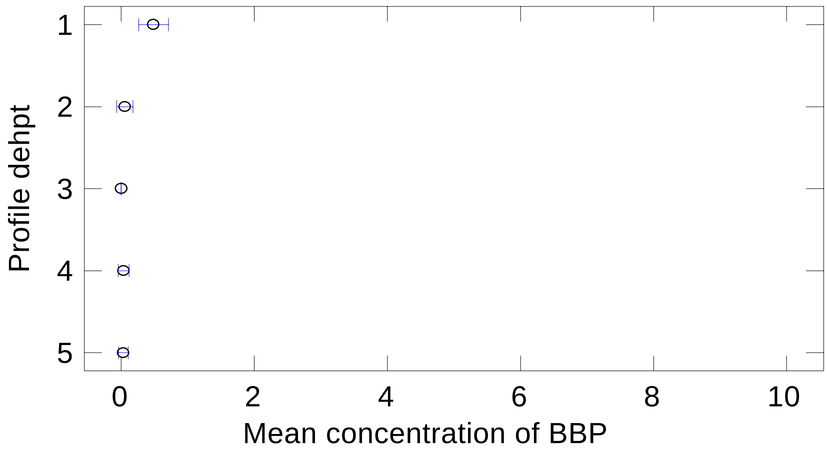


Figs. 2.3 - 2.4 Location 2 organically manured for 40 years. Profiles of DBP and DPP.

Fig. 2.5.1



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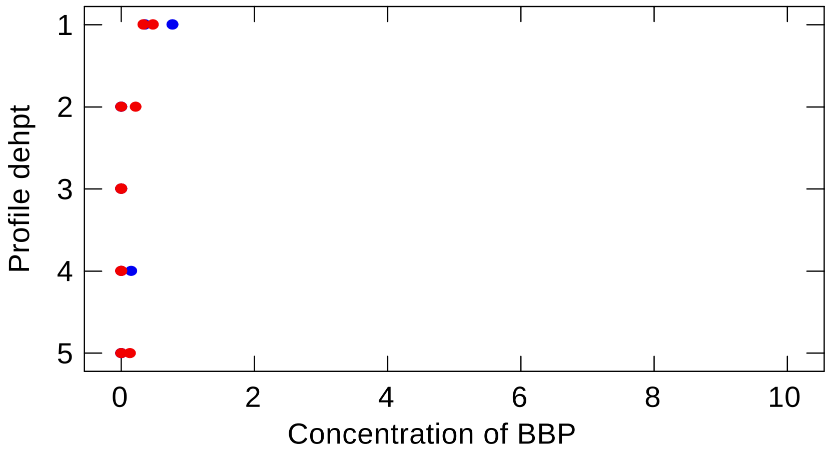

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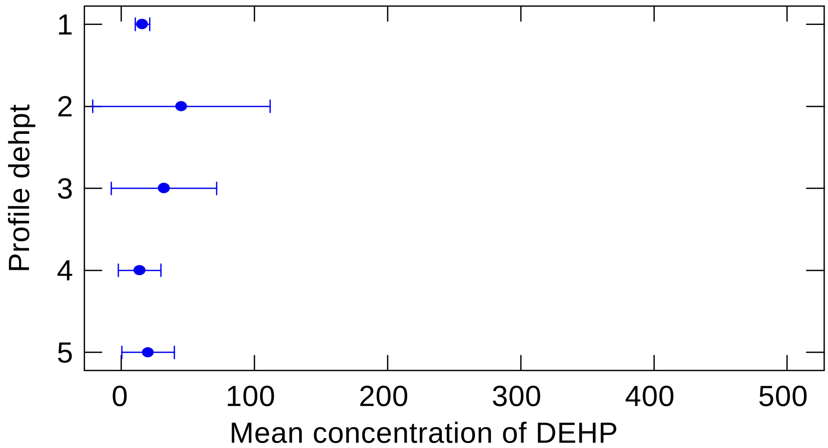

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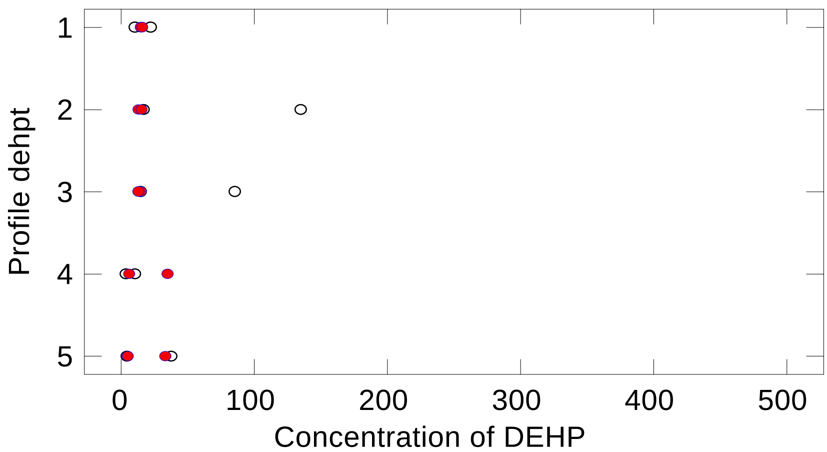
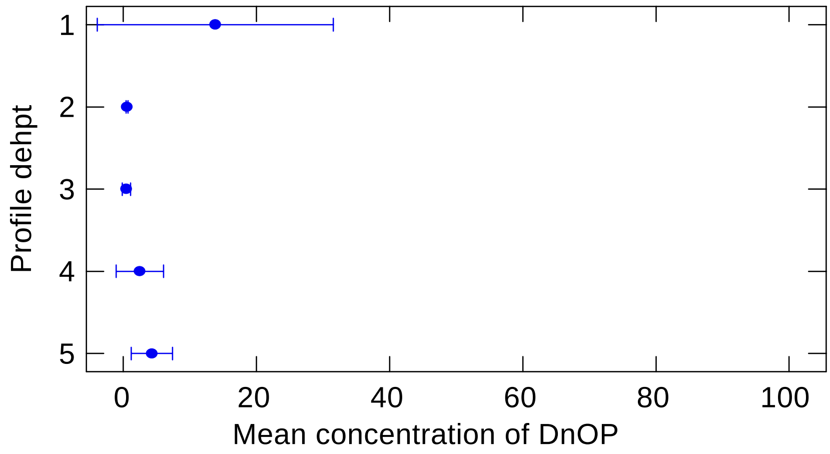


Figs. 2.5 - 2.6 Location 2 organically manured for 40 years. Profiles of BBP and DEHP.

Fig. 2.7.1



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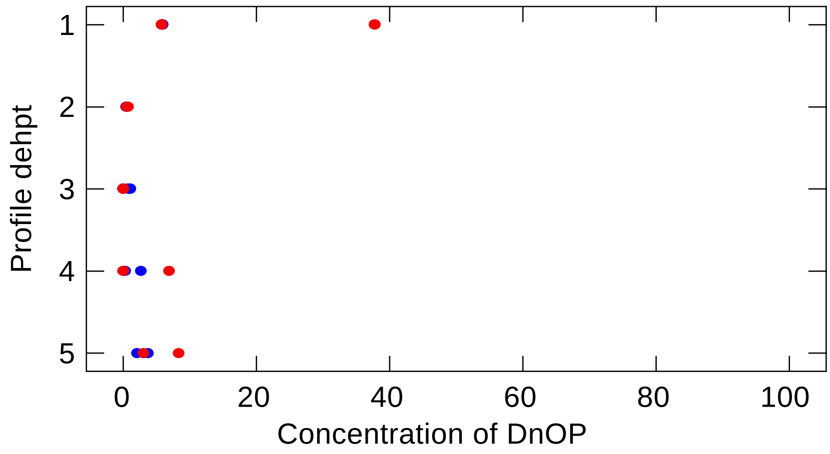

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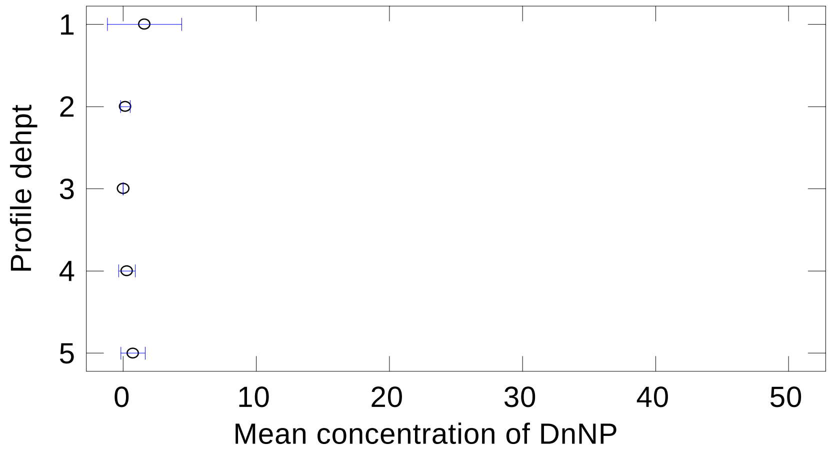

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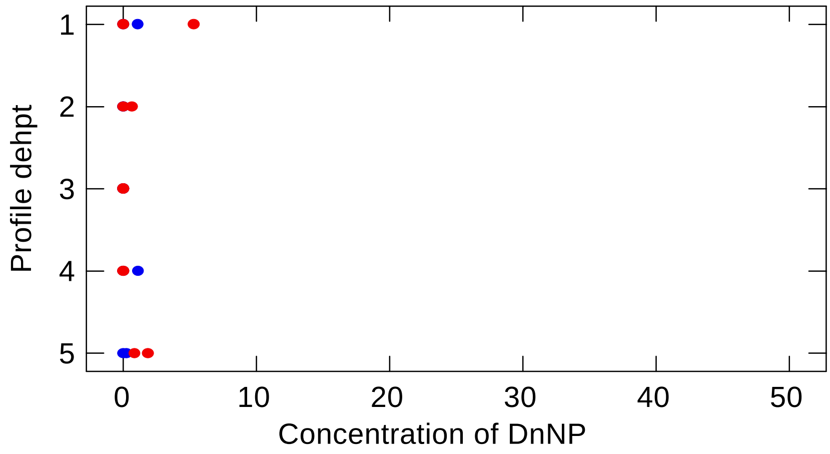
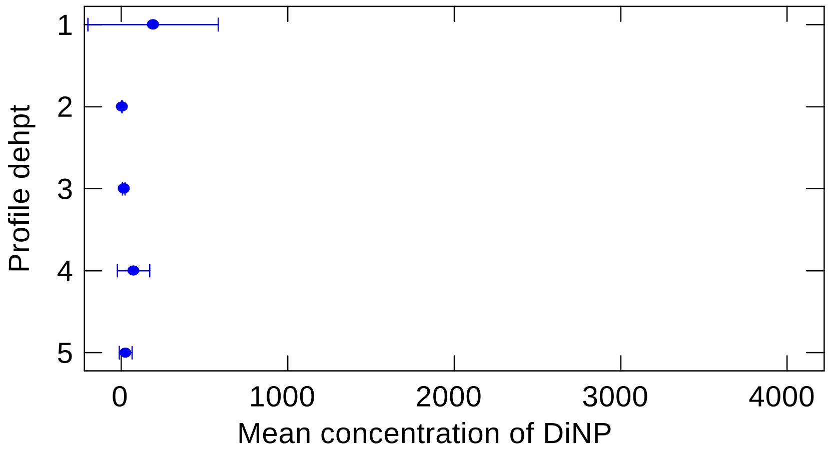


Figs. 2.7 - 2.8 Location 2 organically manured for 40 years. Profiles of DnOP and DnNP.

Fig. 2.9.1



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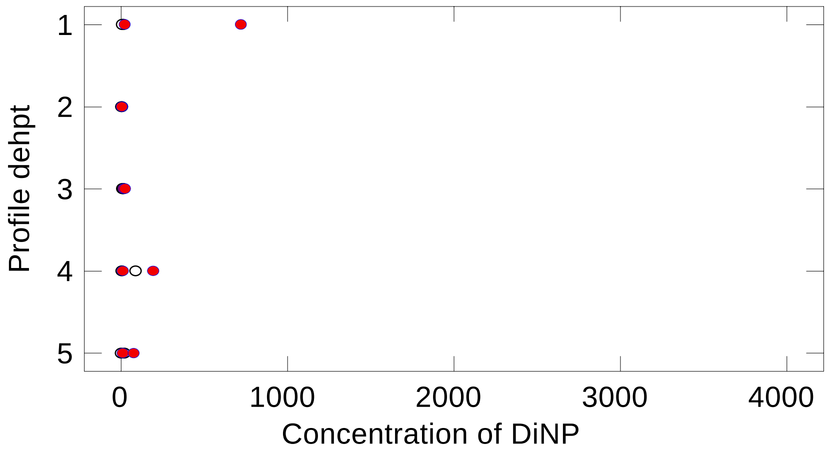
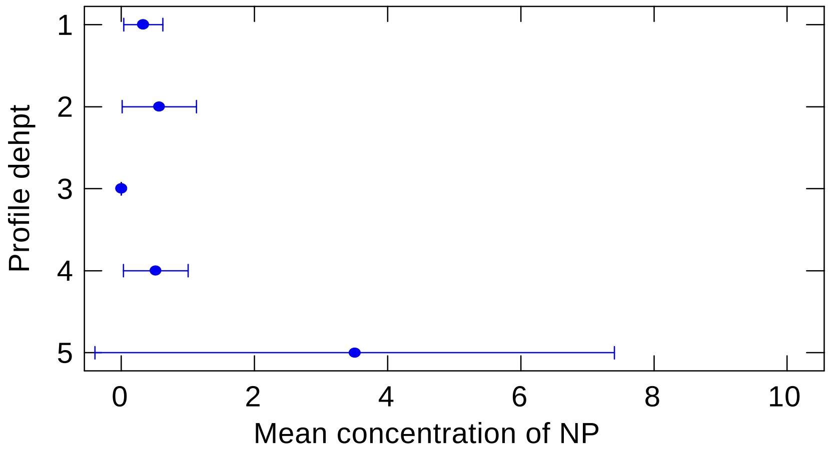


Fig. 2.9 Location 2 organically manured for 40 years. Profile of DiNP.

Fig. 3.1.1



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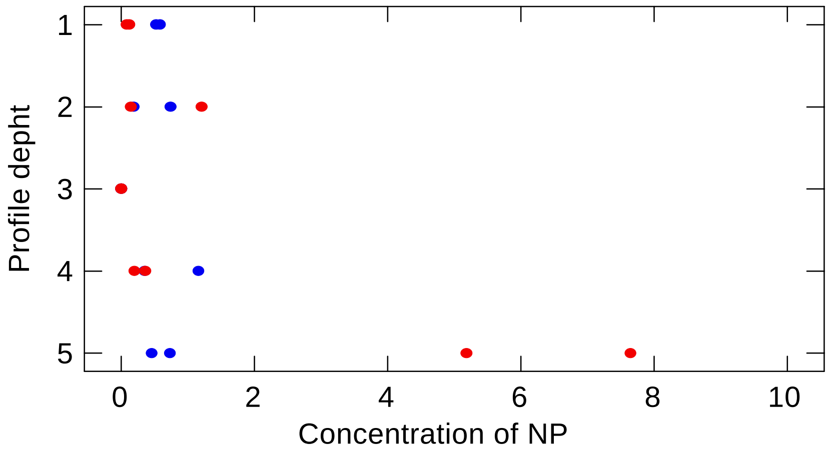


Fig. 3.2.1

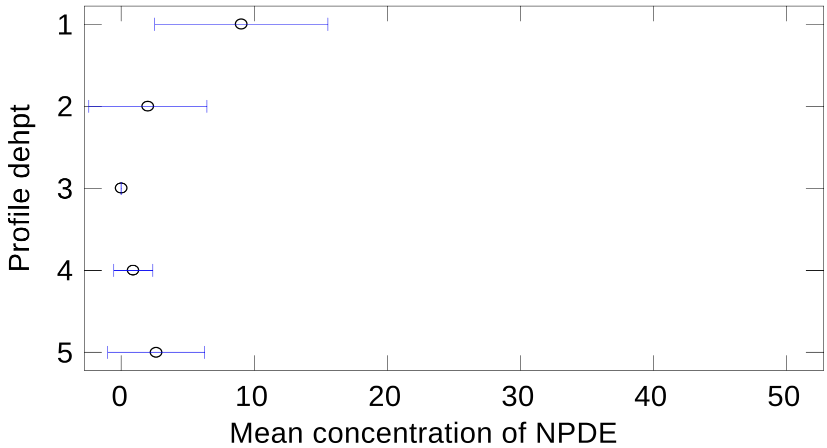
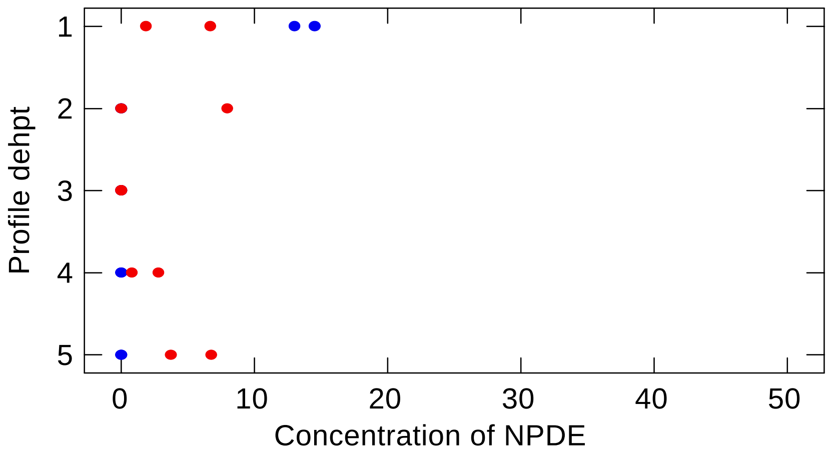


Fig. 3.2.2



Figs. 3.1 - 3.2 Location 3 organically manured for 5 years. Profiles of NP and NPDE.

Fig. 3.3.1

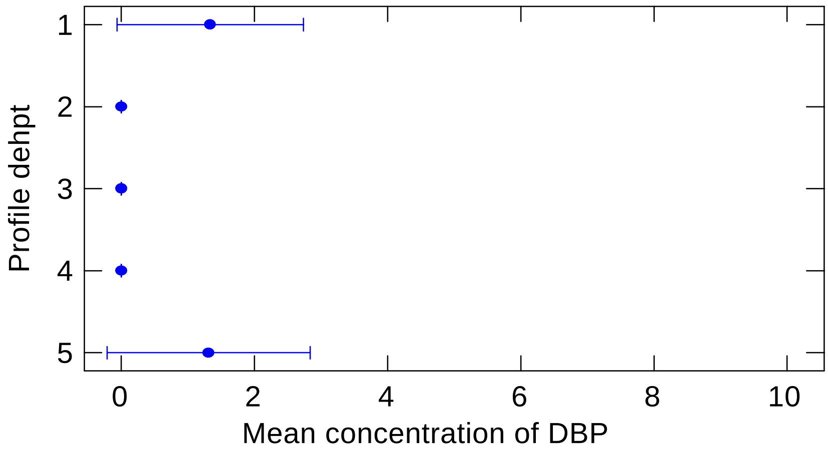


Fig. 3.3.2

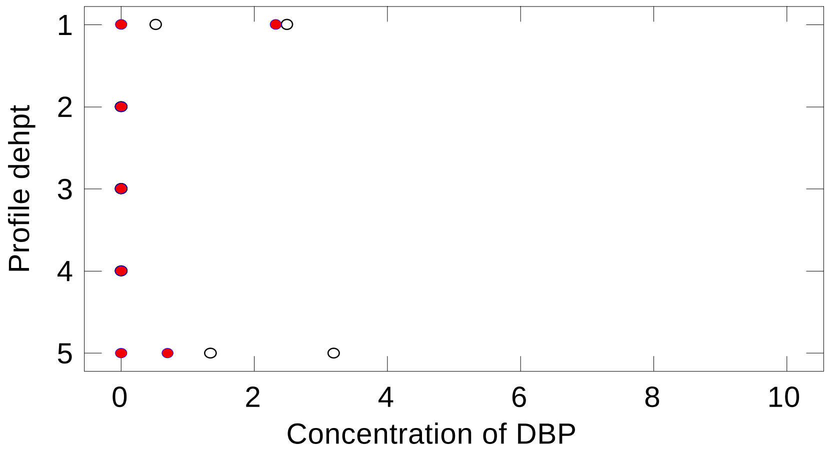
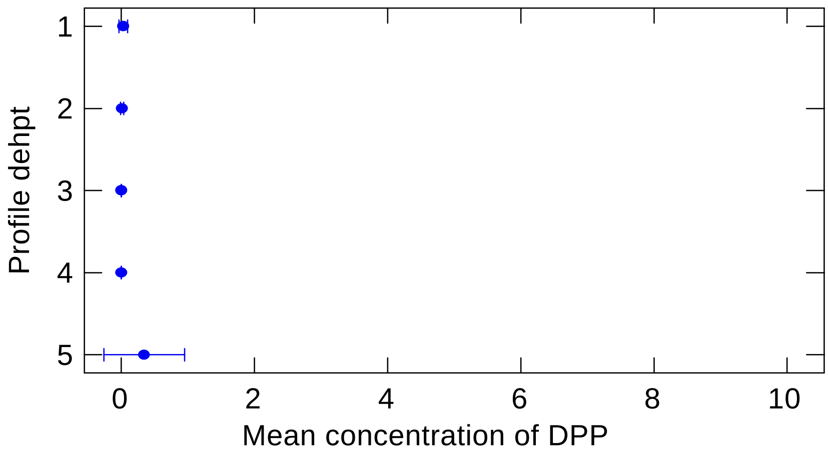


Fig. 3.4.1



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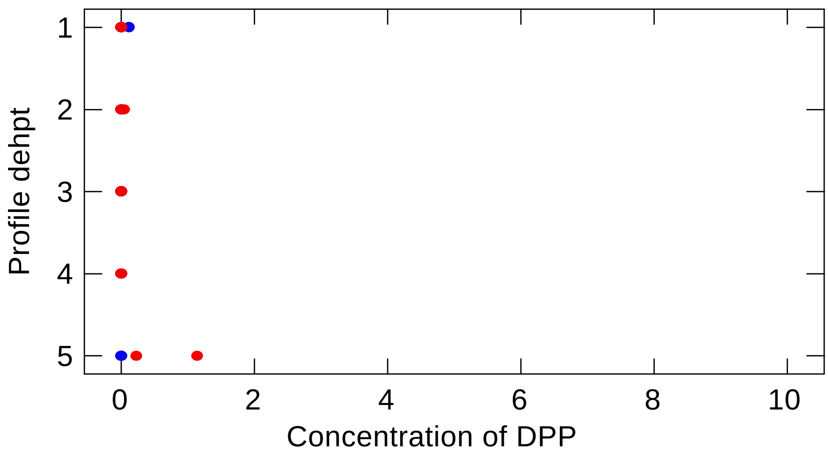
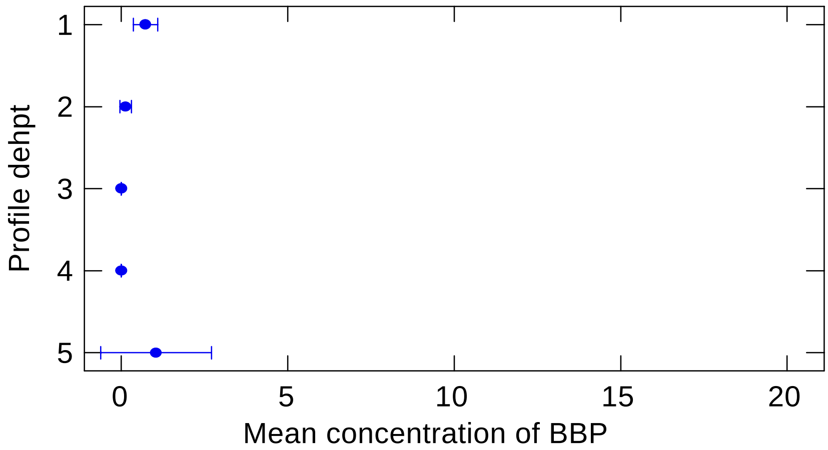


Figs. 3.3 - 3.4 Location 3 organically manured for 5 years. Profiles of DBP and DPP.

Fig. 3.5.1



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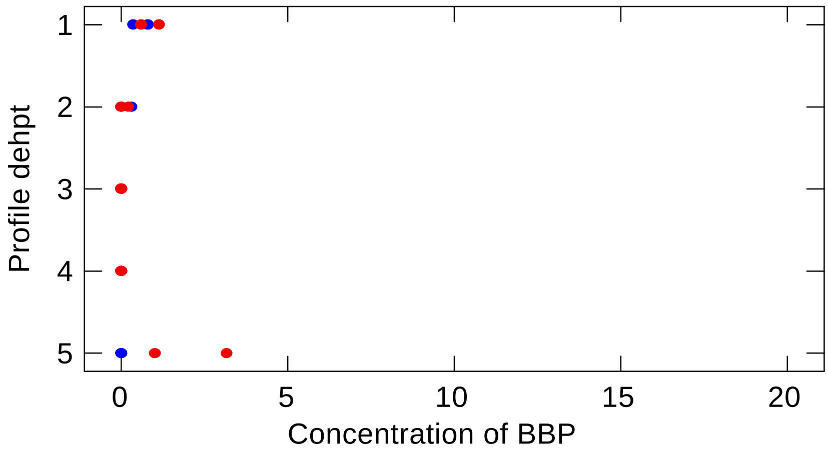
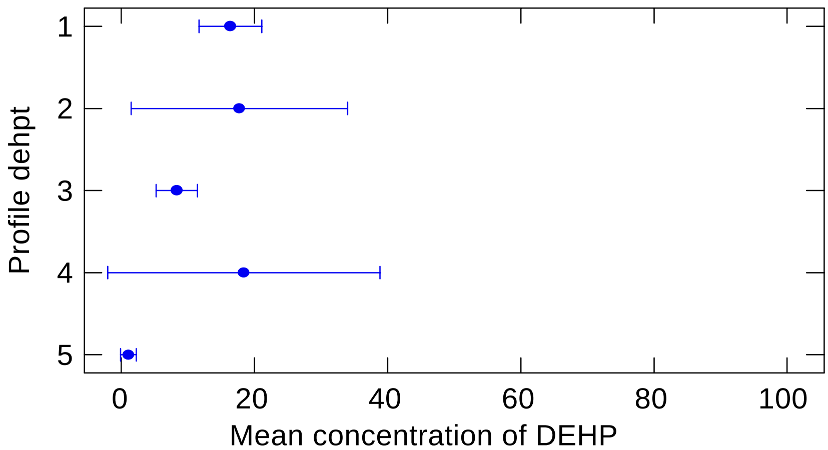


Fig. 3.6.1



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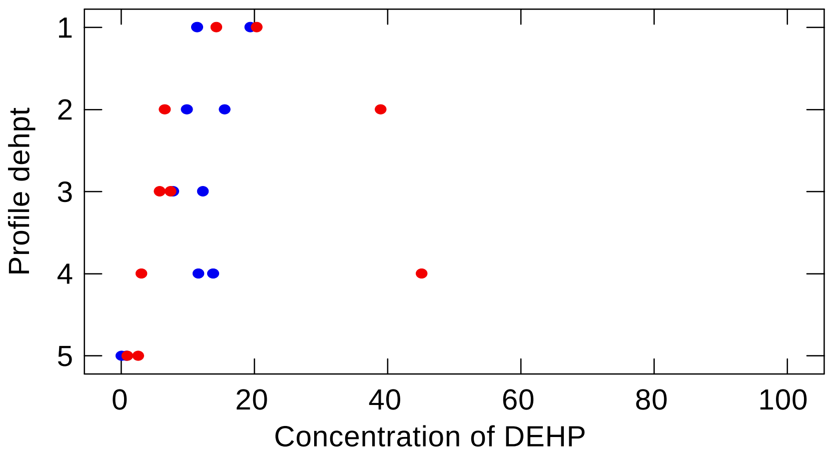
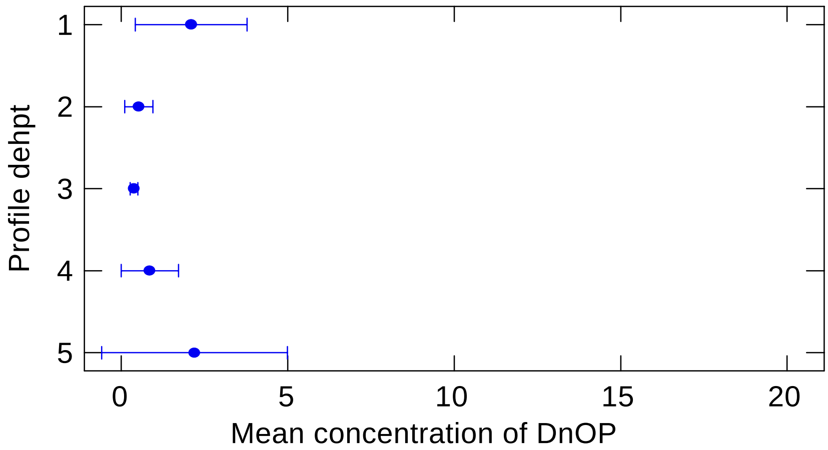


Figs. 3.5 - 3.6 Location 3 organically manured for 5 years. Profiles of BBP and DEHP.

Fig. 3.7.1



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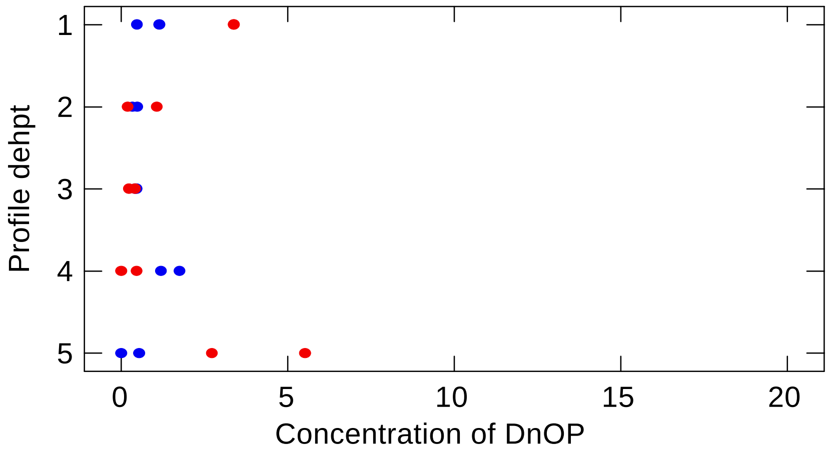
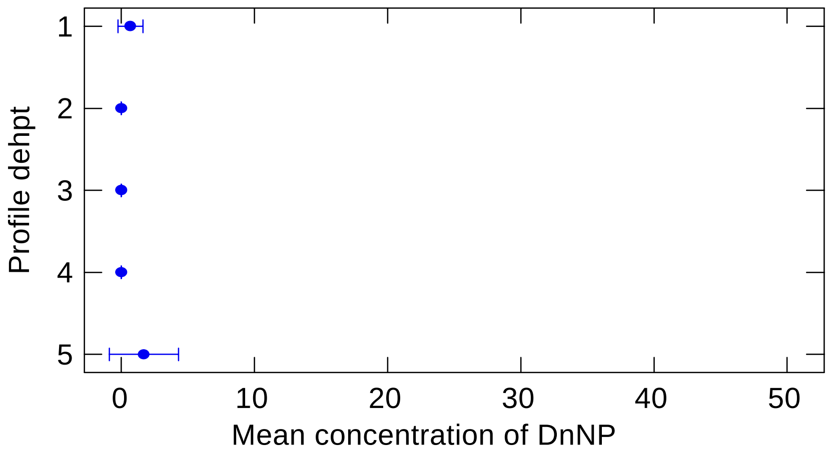


Fig. 3.8.1



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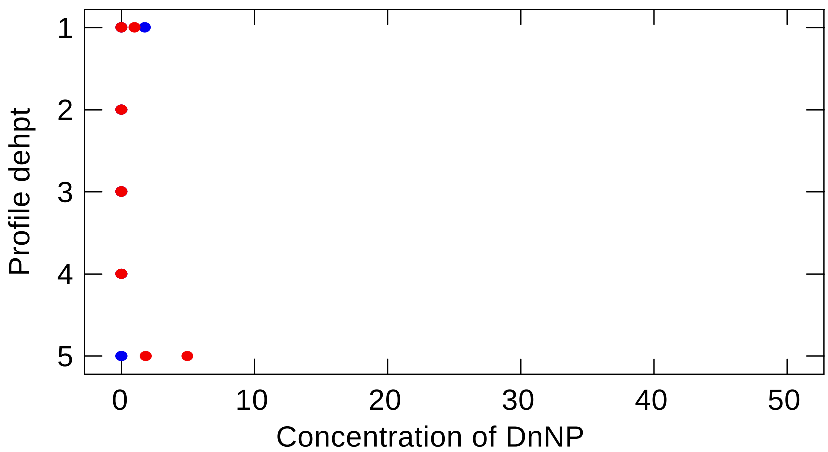


Figs. 3.7 - 3.8 Location 3 organically manured for 5 years. Profiles of DnOP and DnNP.

Fig. 3.9.1

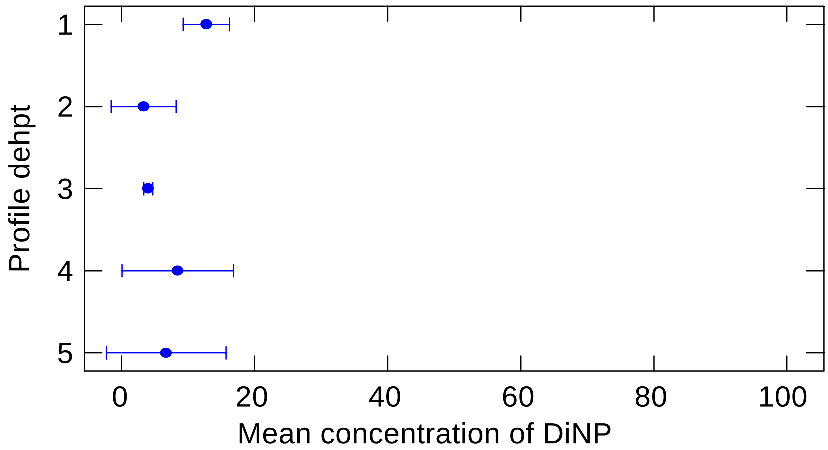


Fig. 3.9.2

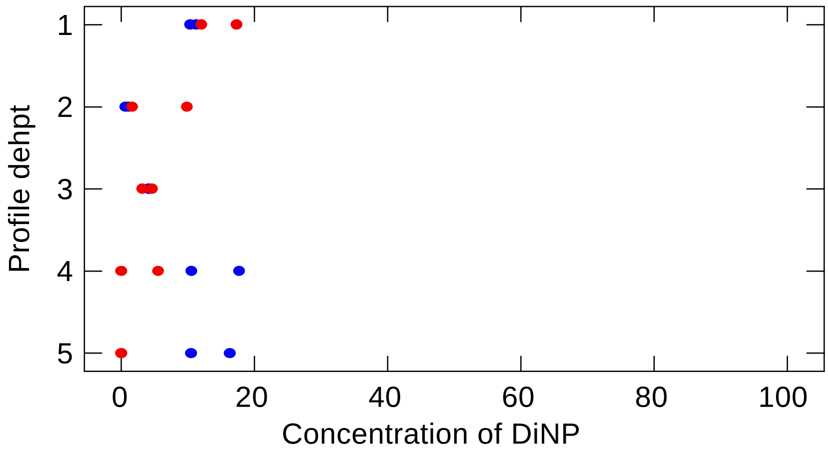


Fig. 3.9 Location 3 organically manured for 5 years. Profile of DiNP.

Fig. 4.1.1

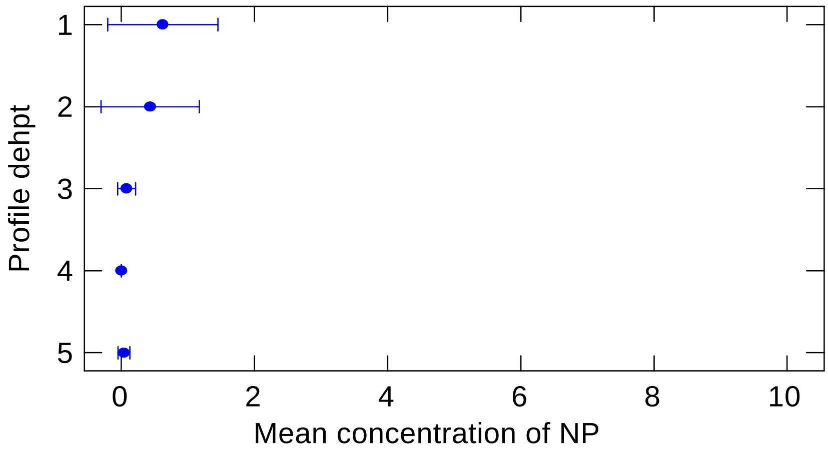


Fig. 4.1.2

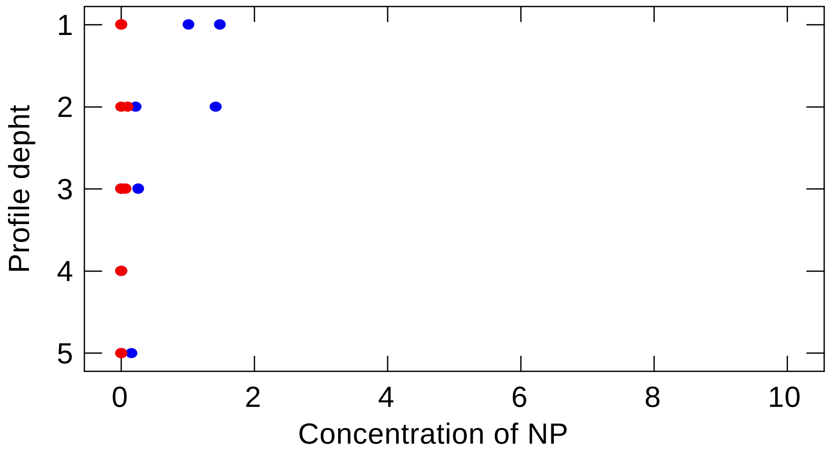


Fig. 4.2.1

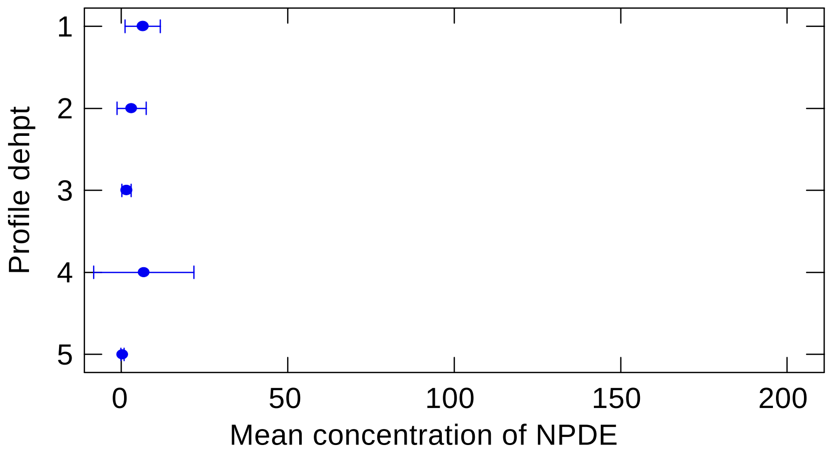
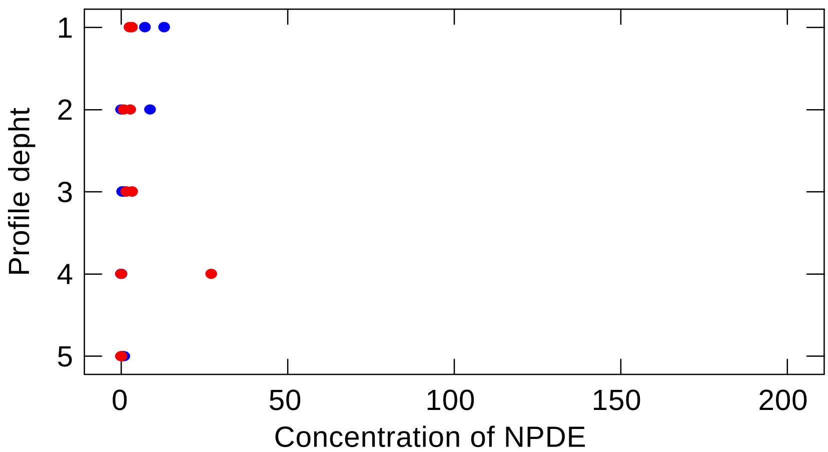


Fig. 4.2.2



Figs. 4.1 - 4.2 Location 4, artificially fertilised, cultivated. Profiles of NP and NPDE.

Fig. 4.3.1

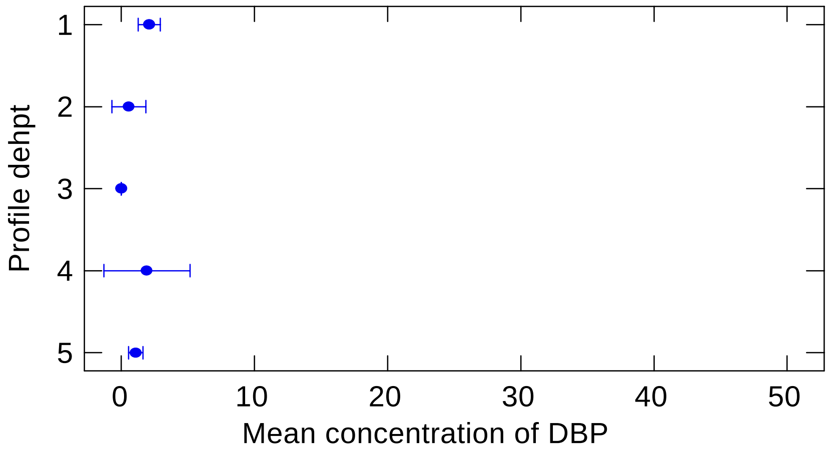


Fig. 4.3.2

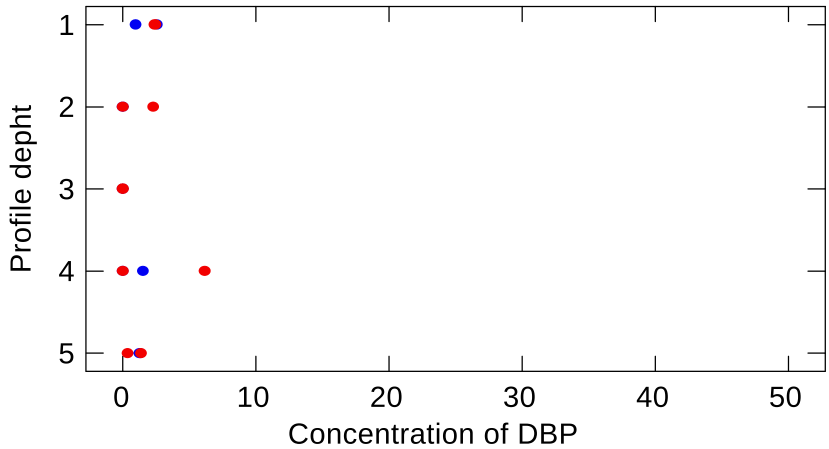


Fig. 4.4.1

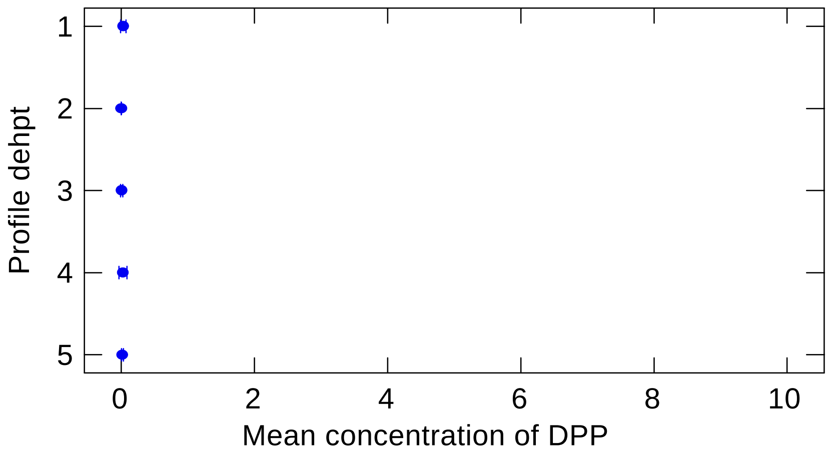
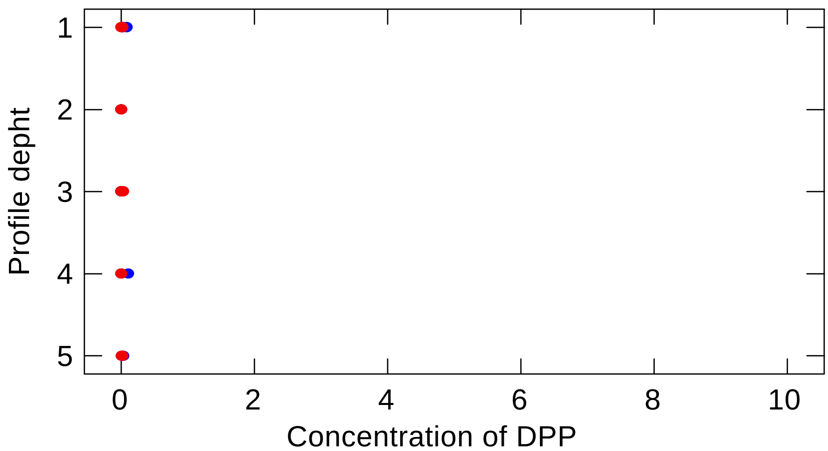


Fig. 4.4.2



Figs. 4.3 - 4.4 Location 4, artificially fertilised, cultivated. Profiles of DBP and DPP.

Fig. 4.5.1

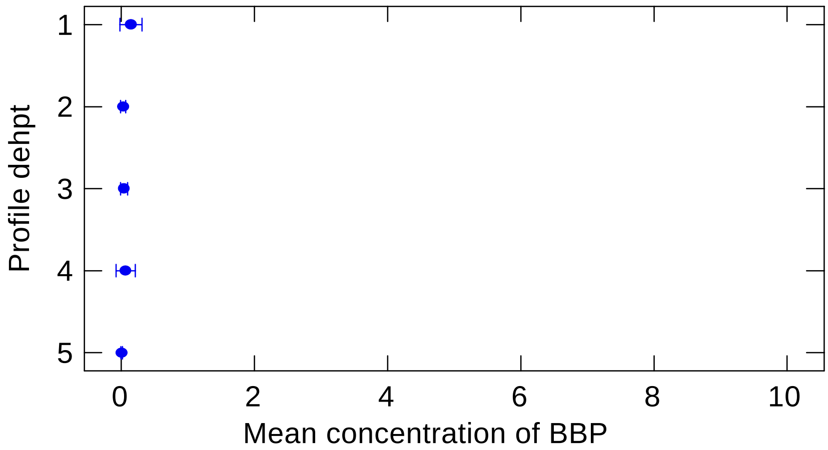


Fig. 4.5.2

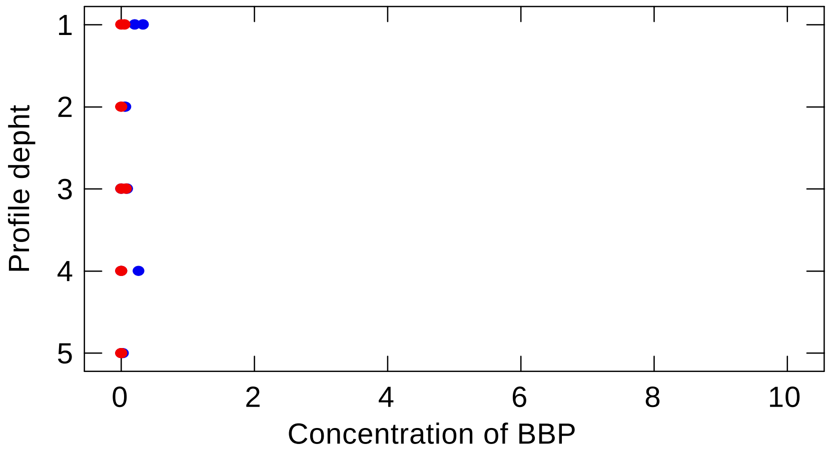


Fig. 4.6.1

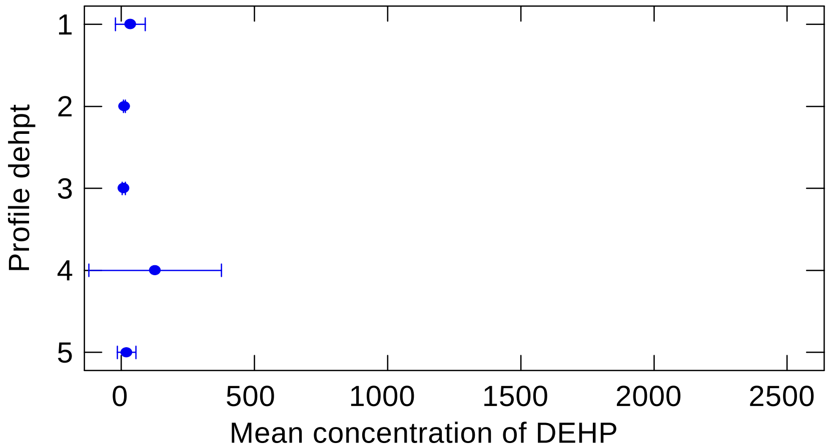
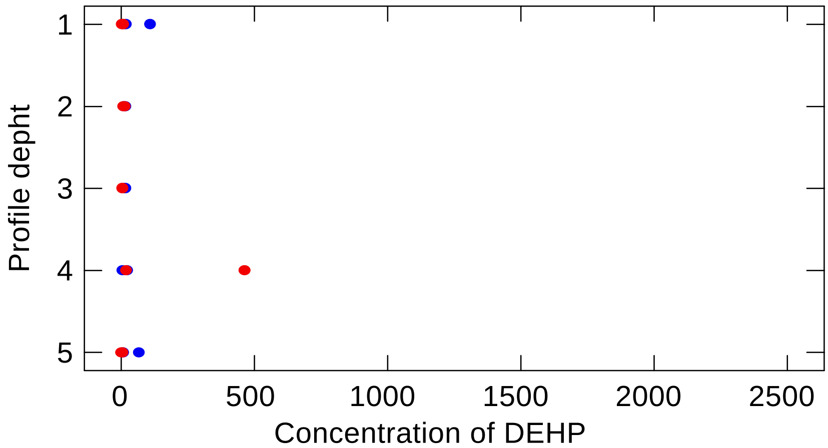


Fig. 4.6.2



Figs. 4.5 - 4.6 Location 4, artificially fertilised, cultivated. Profiles of BBP and DEHP.

Fig. 4.7.1

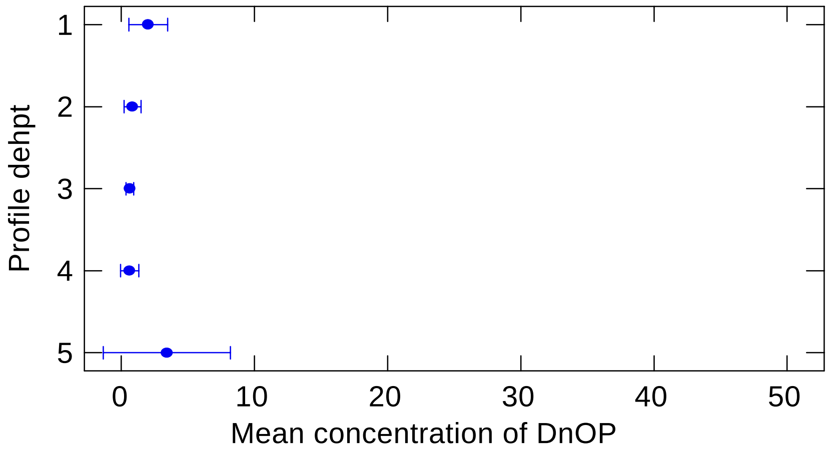


Fig. 4.7.2

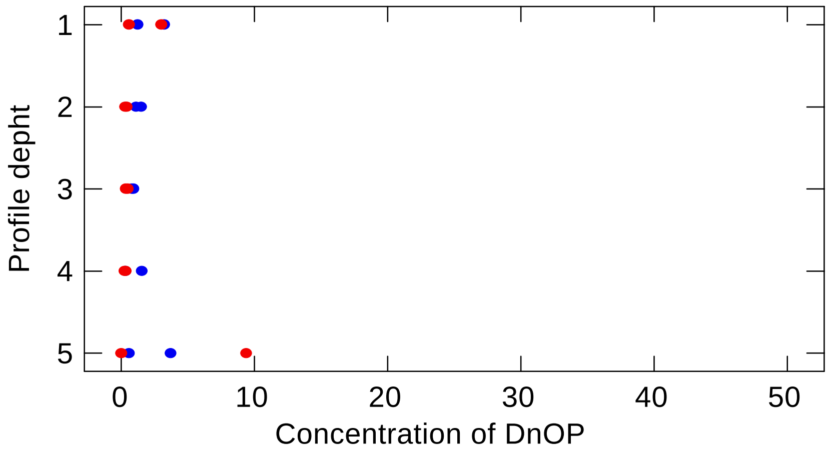
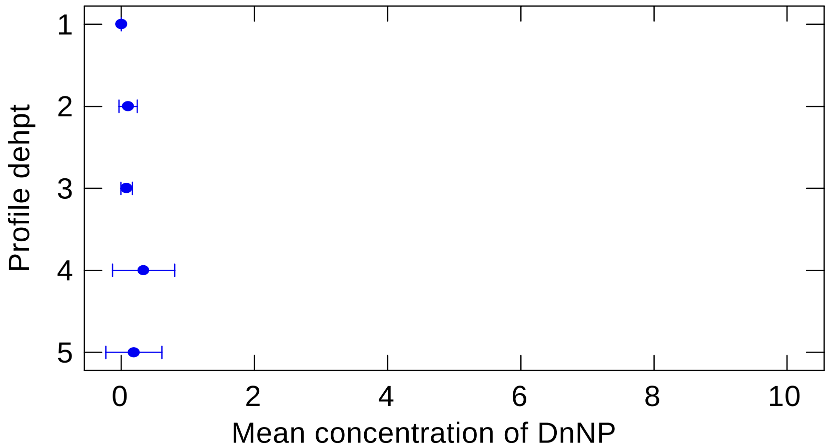


Fig. 4.8.1



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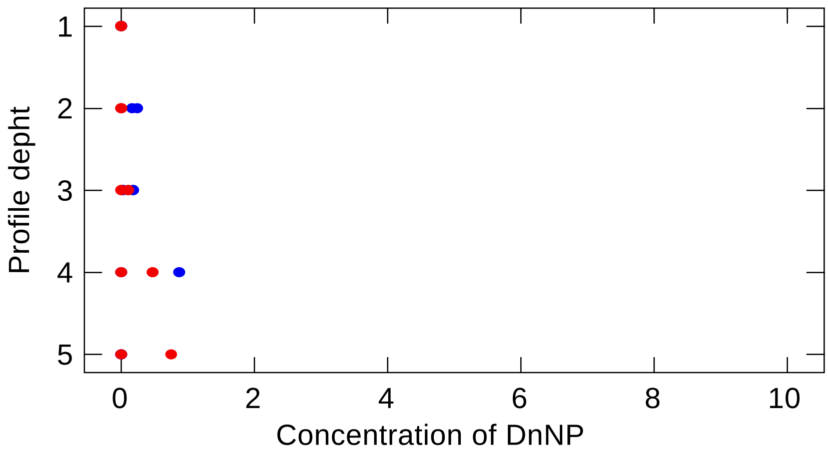


Figs. 4.7 - 4.8 Location 4, artificially fertilised, cultivated. Profiles of DnOP and DnNP.

Fig. 4.9.1

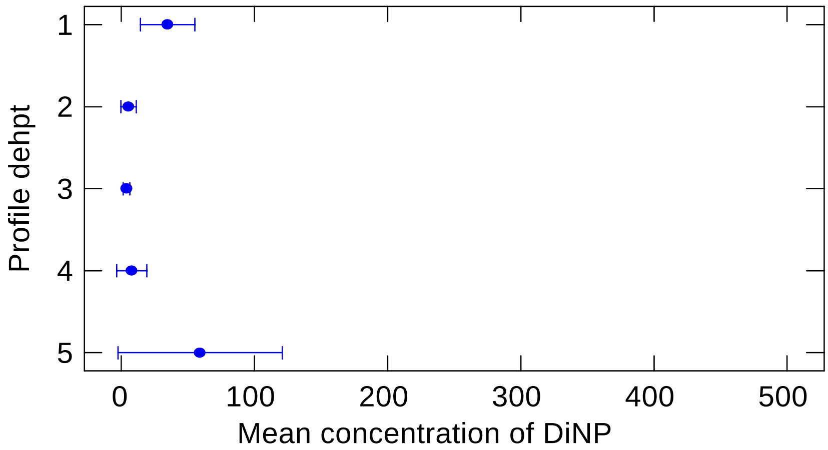


Fig. 4.9.2

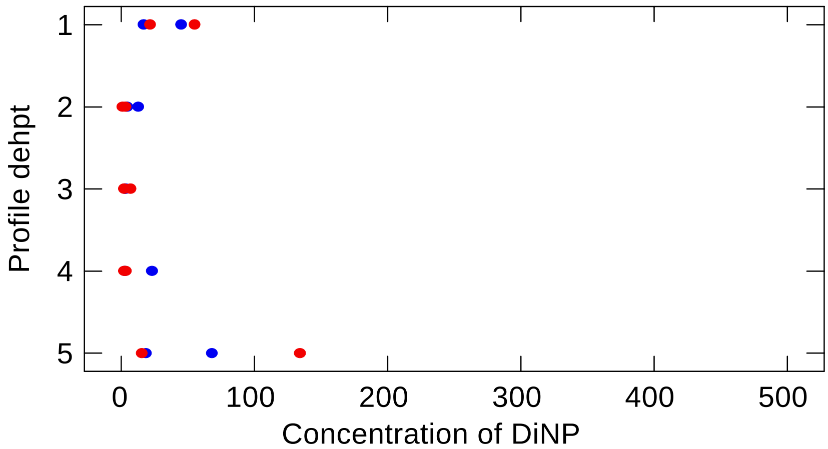


Fig. 4.9 Location 4, artificially fertilised, cultivated. Profile of DiNP.

Fig. 5.1.1

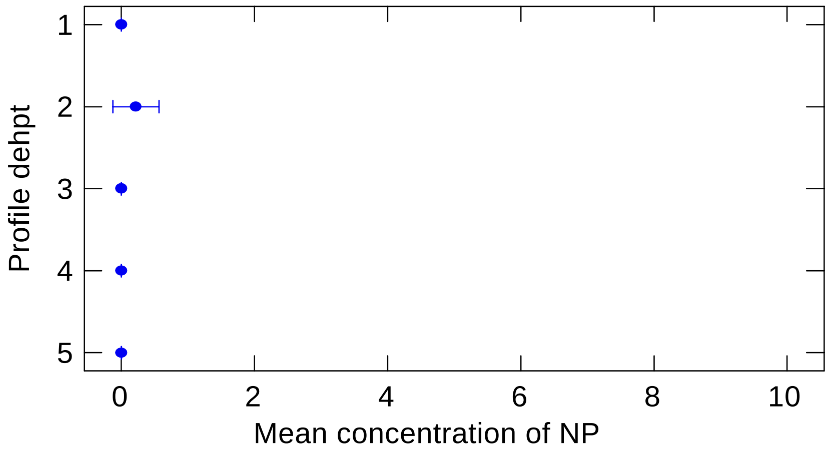
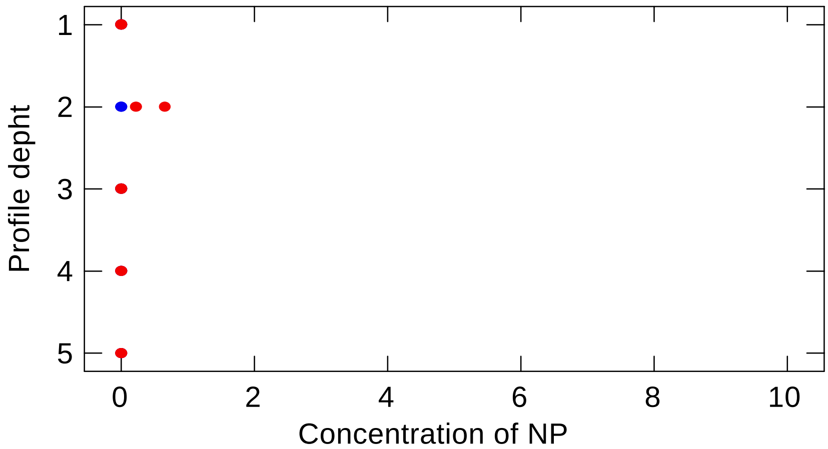


Fig. 5.1.2



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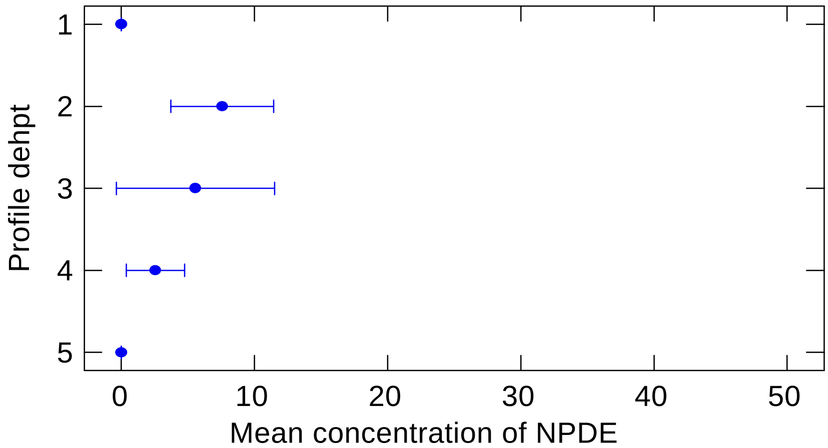

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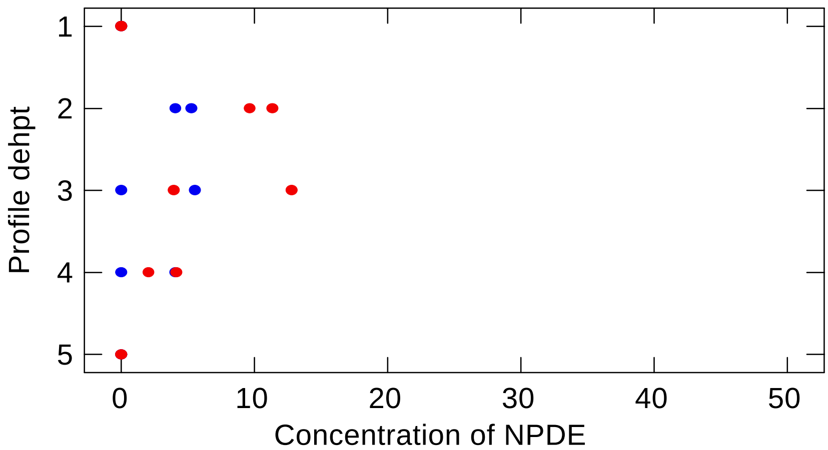


Figs. 5.1 - 5.2 Location 5 low level sludge amended, cultivated. Profiles of NP and NPDE.

Fig. 5.3.1

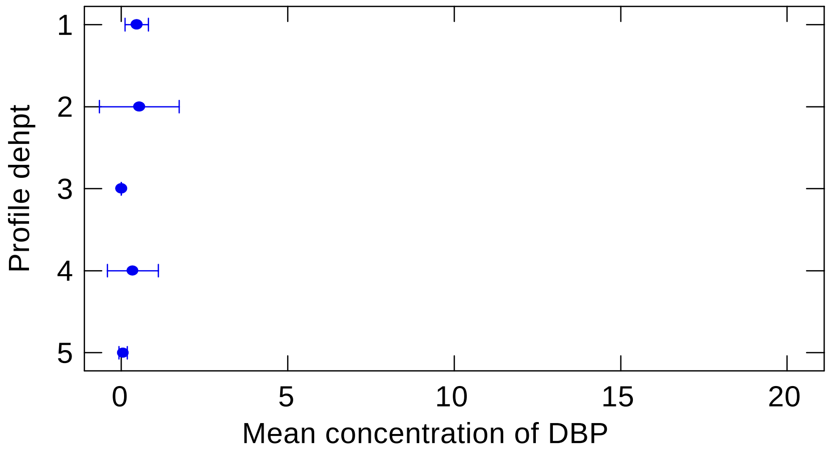


Fig. 5.3.2

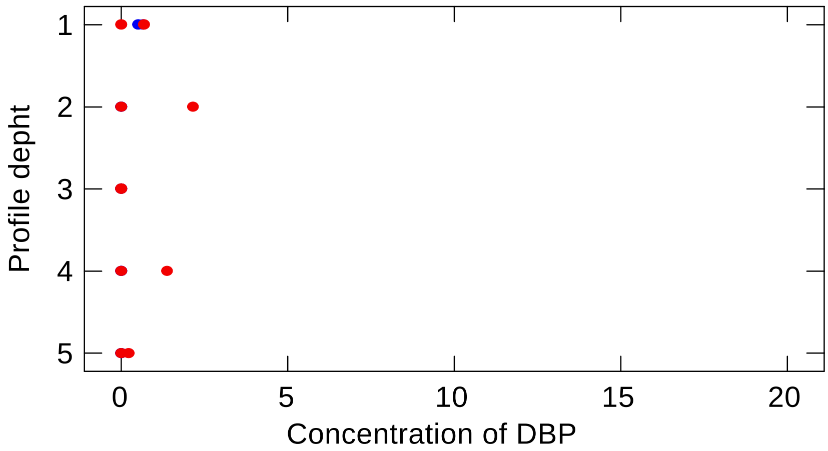


Fig. 5.4.1

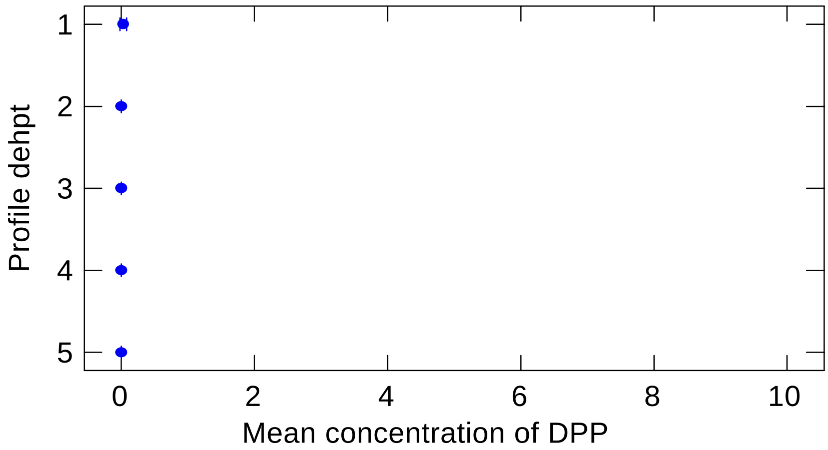
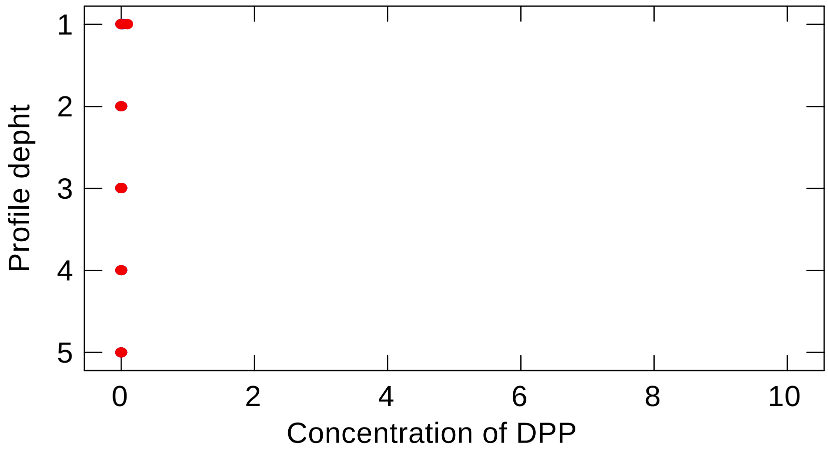


Fig. 5.4.2



Figs. 5.3 - 5.4 Location 5 low level sludge amended, cultivated. Profiles of DBP and DPP.

Fig. 5.5.1

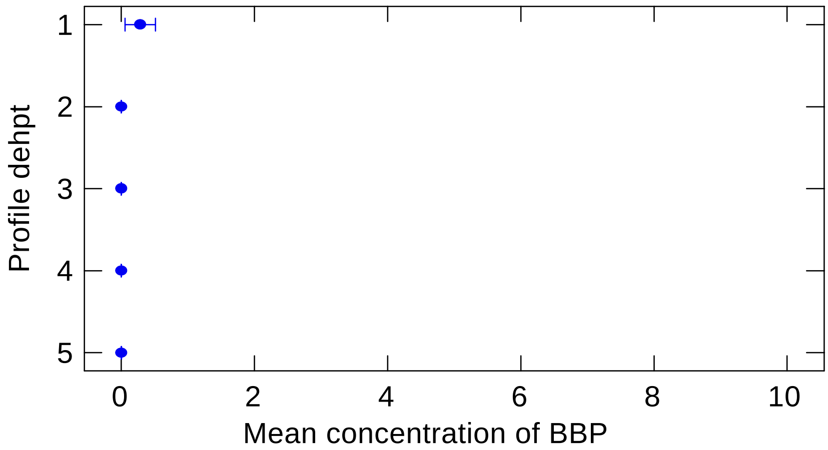


Fig. 5.5.2

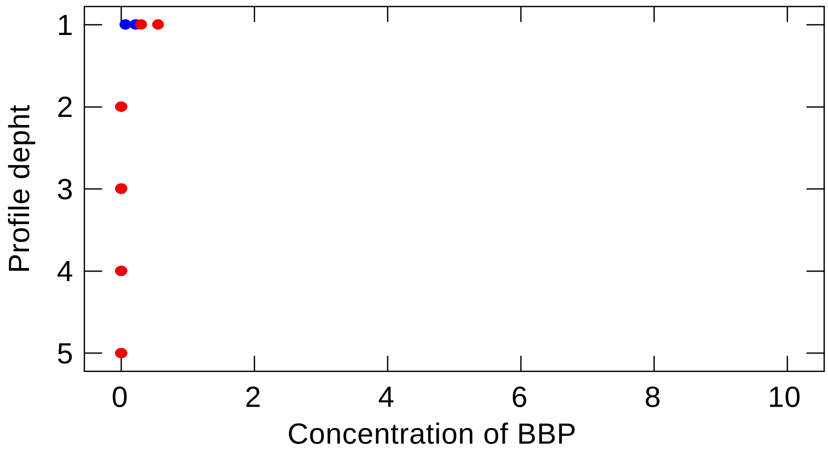


Fig. 5.6.1

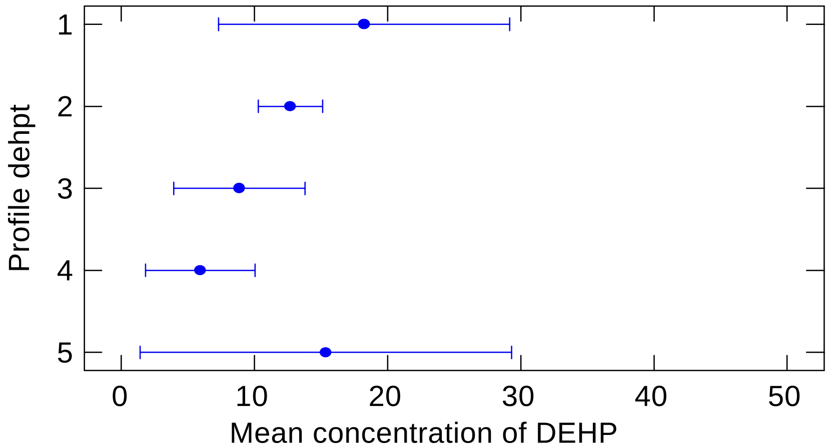
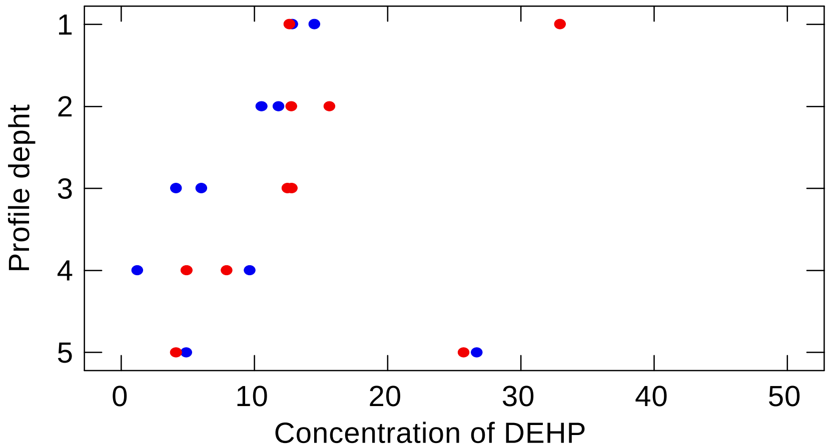


Fig. 5.6.2



Figs. 5.5 - 5.6 Location 5 low level sludge amended, cultivated. Profiles of BBP and DEHP.

Fig. 5.7.1

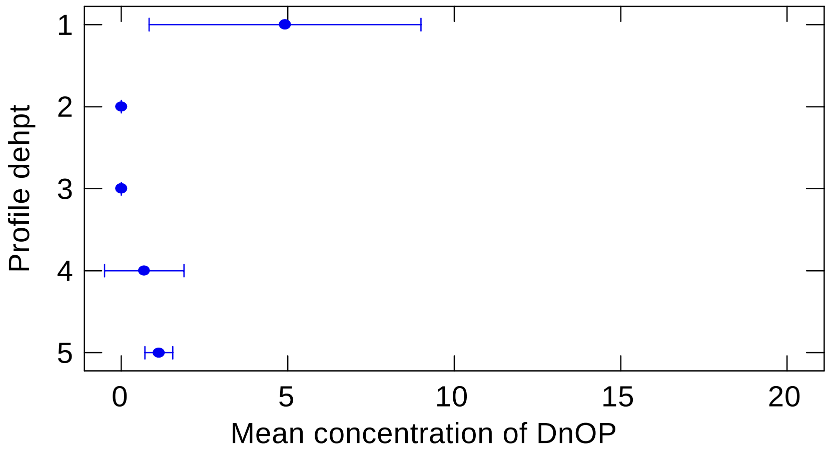
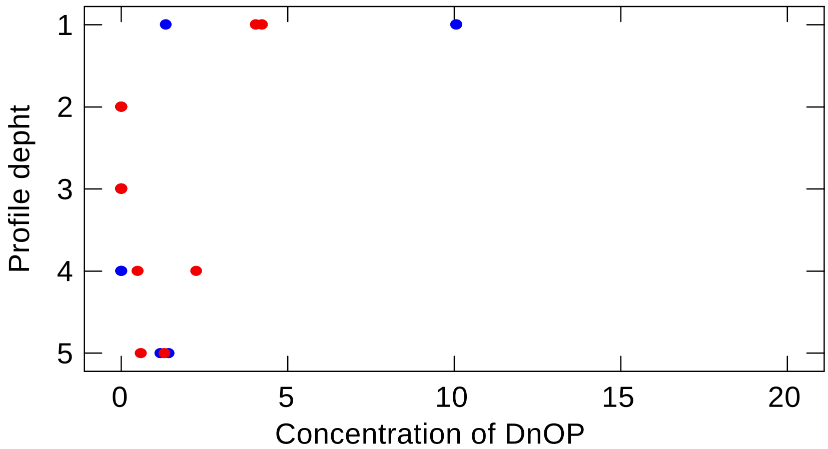


Fig. 5.7.2



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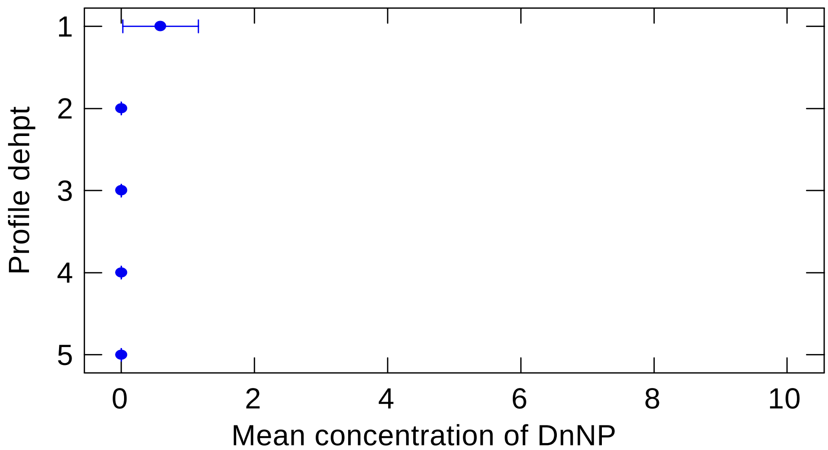
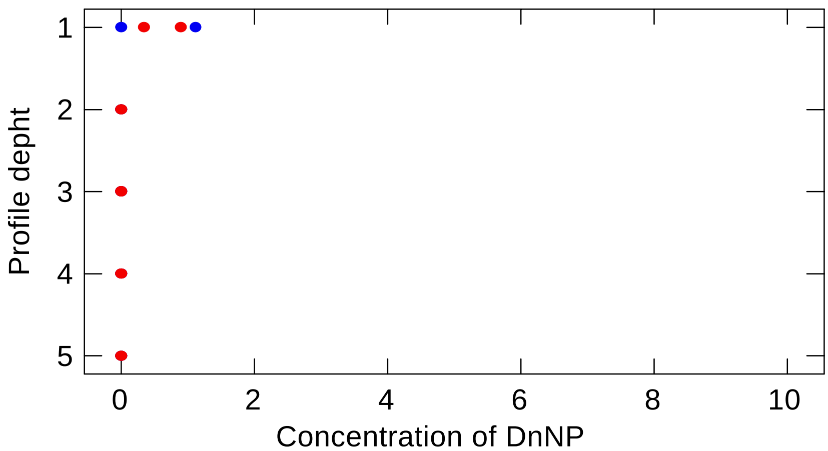


Fig. 5.8.2



Figs. 5.7 - 5.8 Location 5, low level sludge amended, cultivated. Profiles of DnOP and DnNP.

Fig. 5.9.1

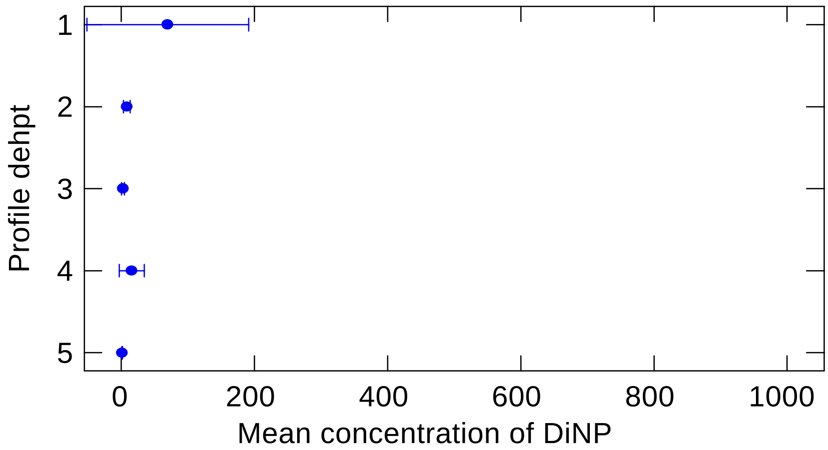


Fig. 5.9.2

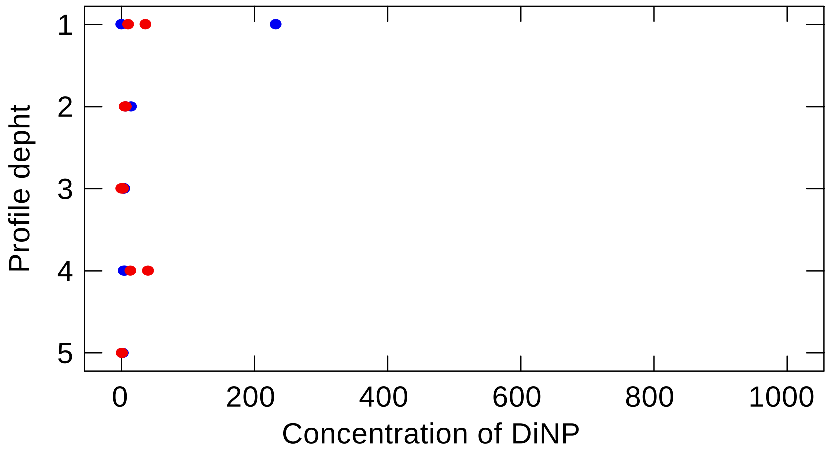
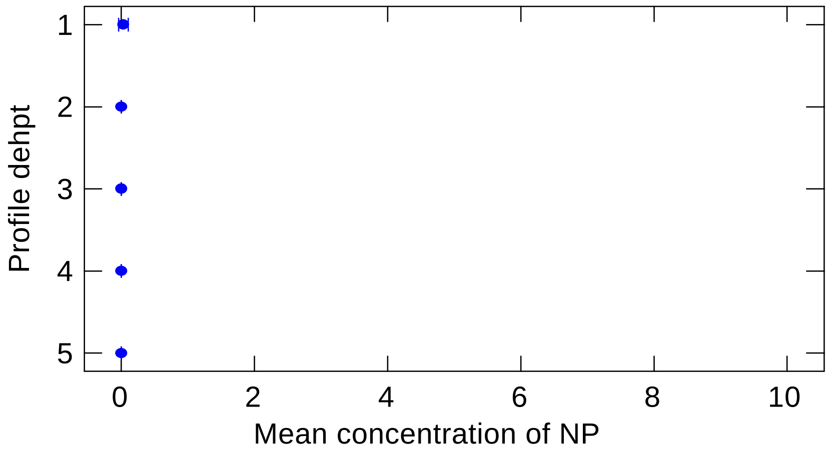


Fig. 5.9 Location 5 low level sludge amended, cultivated. Profile of DiNP.

Fig. 6.1.1



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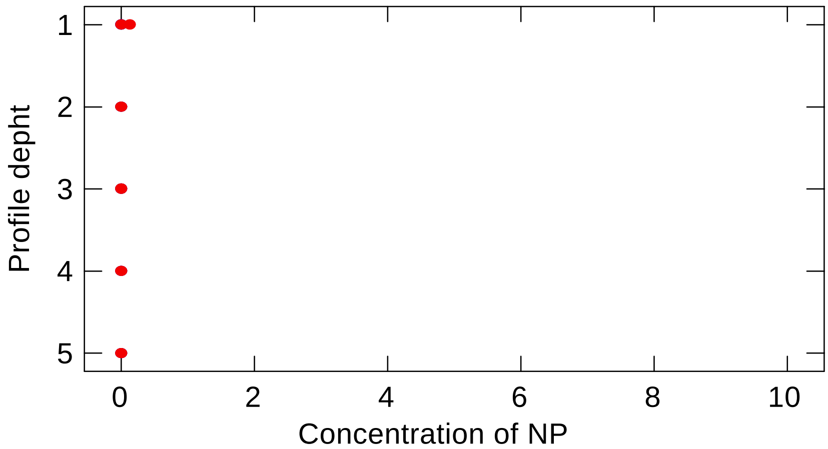

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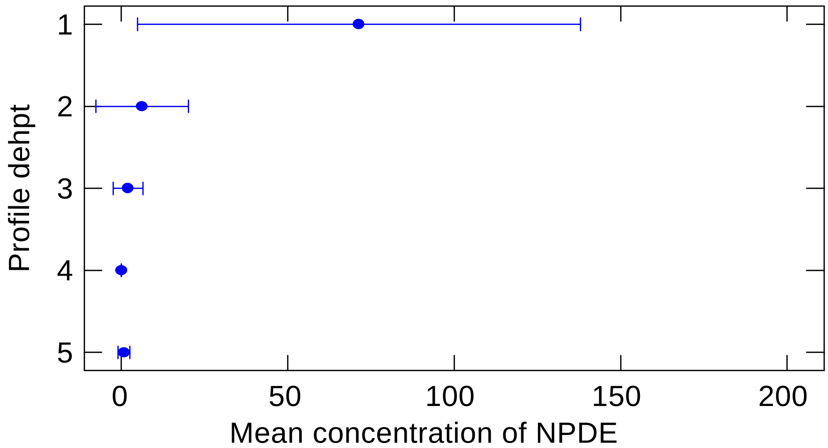

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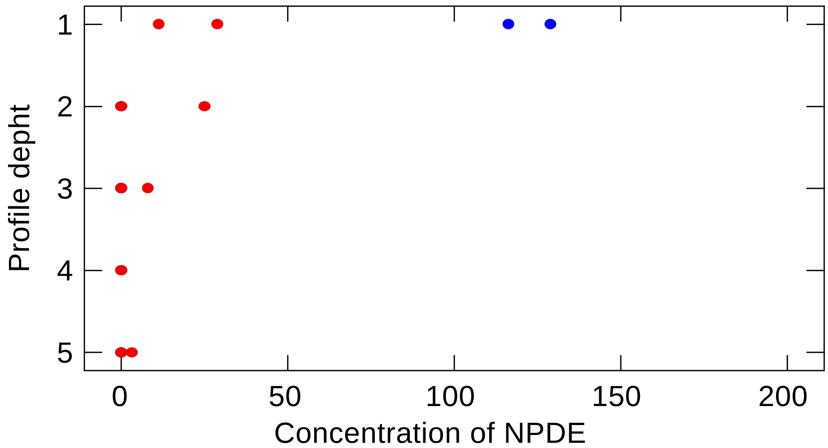
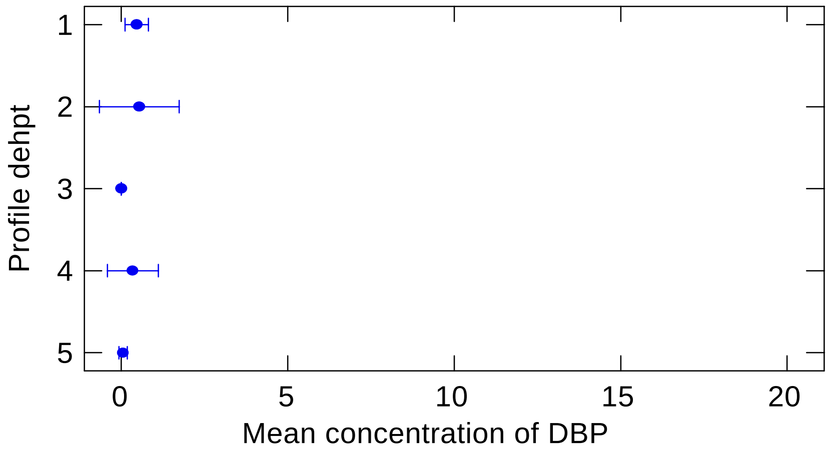


Figs. 6.1 - 6.2 Location 6, medium level sludge amended, cultivated. Profiles of NP and NPDE.

Fig. 6.3.1



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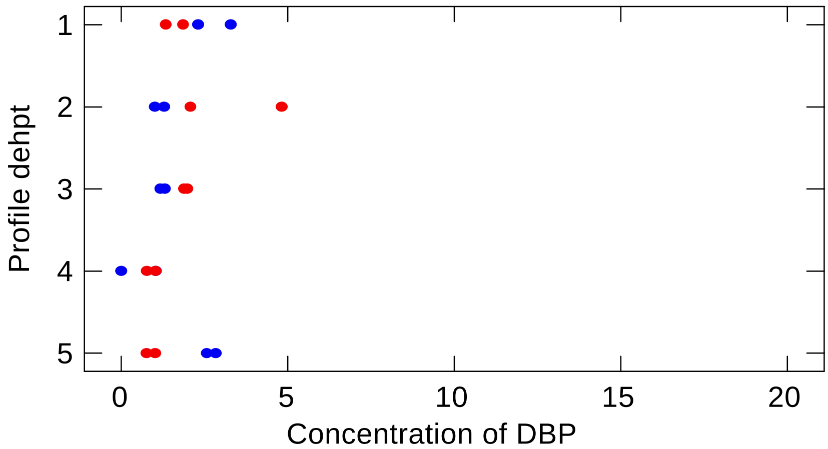
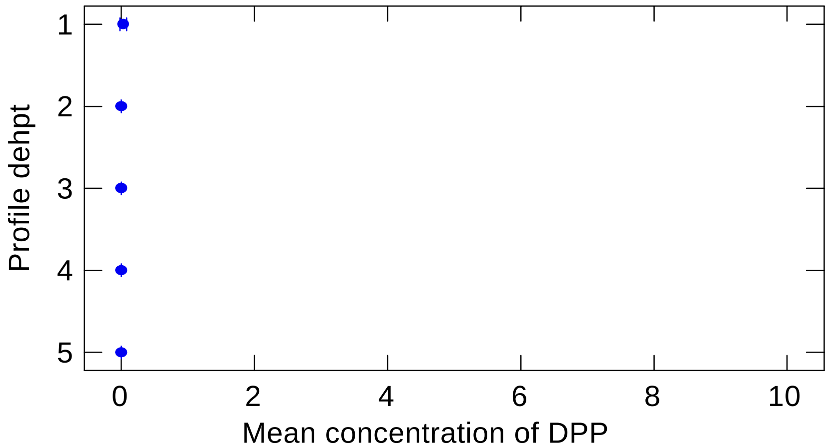


Fig. 6.4.1



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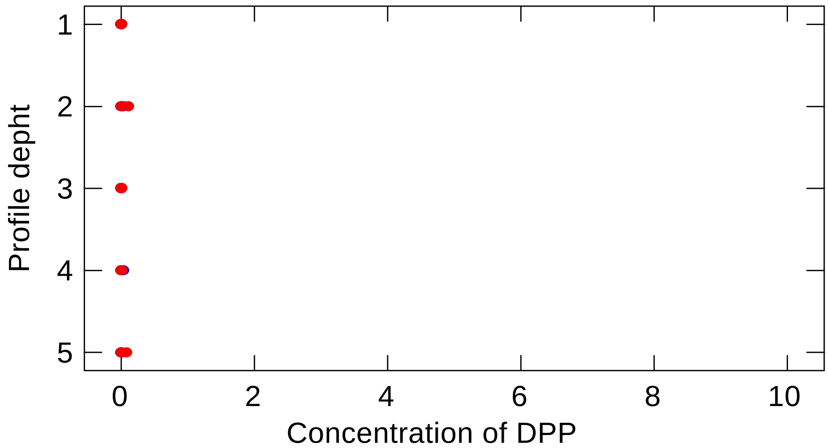


Figs. 6.3 - 6.4 Location 6, medium level sludge amended, cultivated. Profiles of DBP and DPP.

Fig. 6.5.1

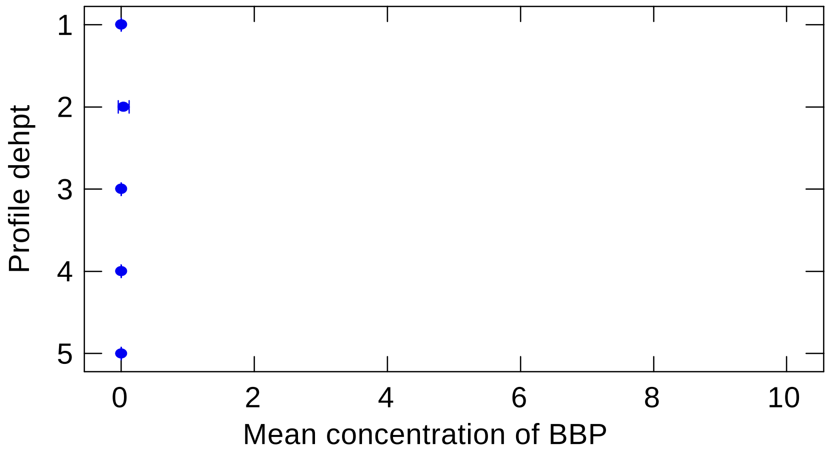


Fig. 6.5.2

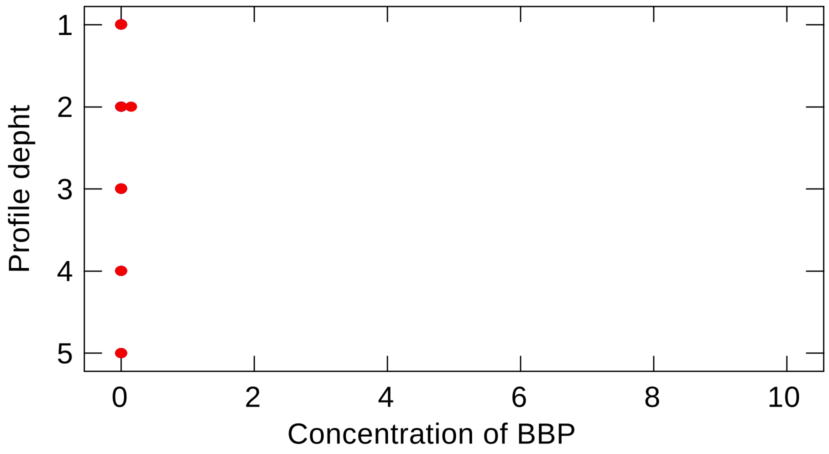


Fig. 6.6.1

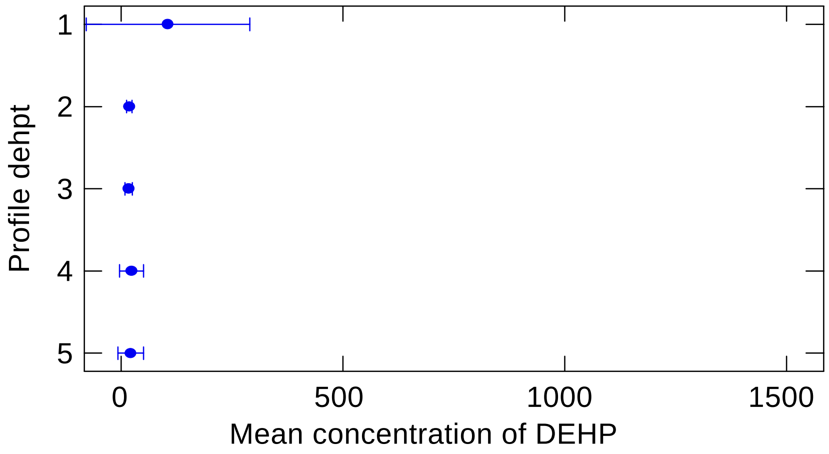
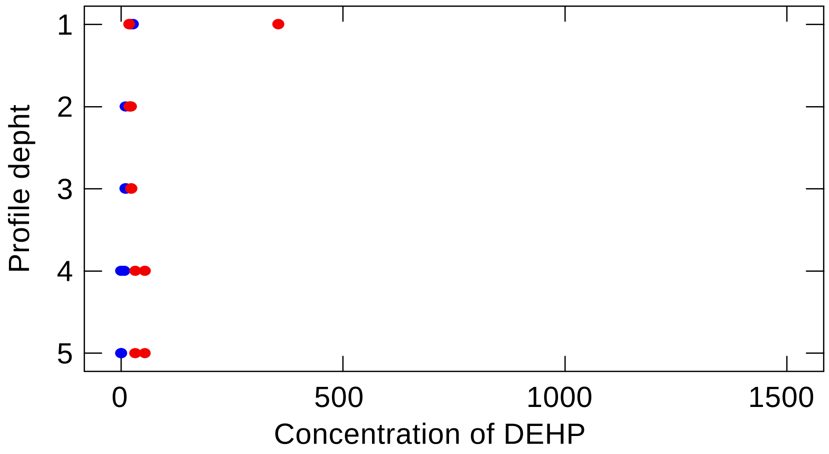


Fig. 6.6.2



Figs. 6.5 - 6.6 Location 6, medium level sludge amended, cultivated. Profiles of BBP and DEHP.

Fig. 6.7.1

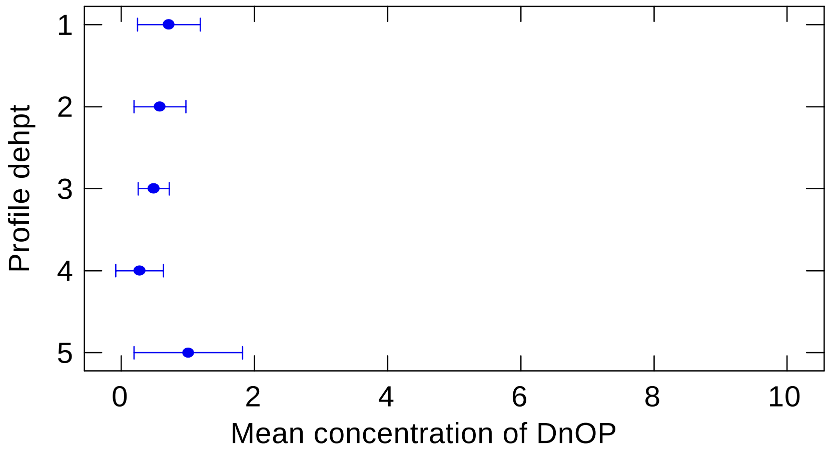


Fig. 6.7.2

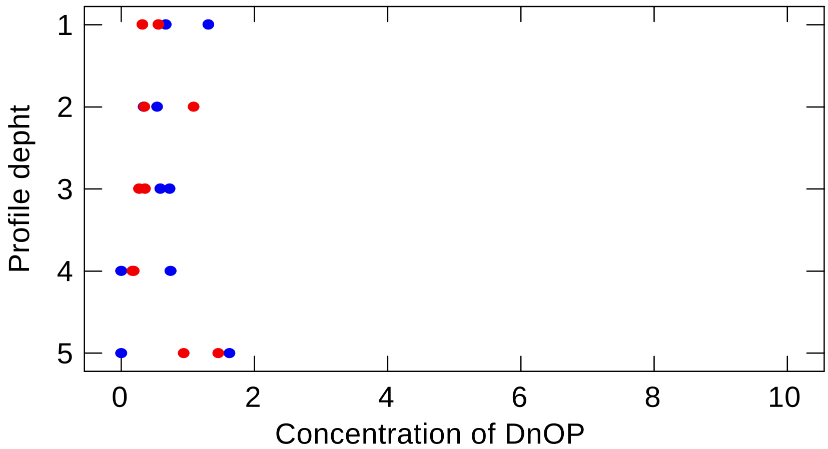


Fig. 6.8.1

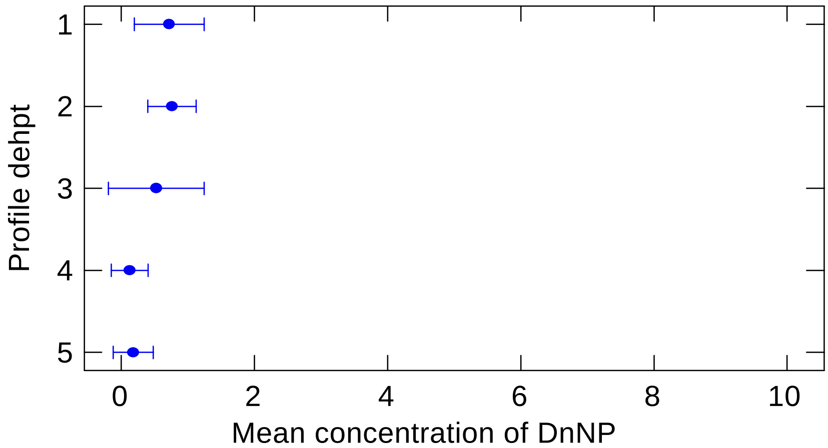
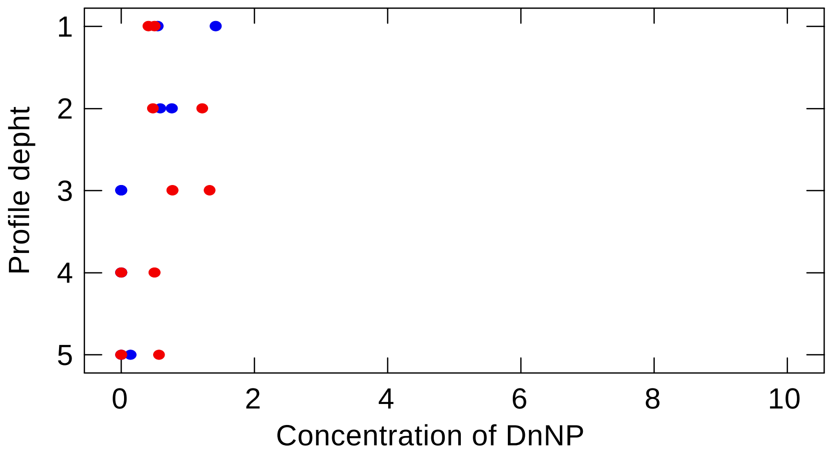


Fig. 6.8.2



Figs. 6.7 - 6.8 Location 6, medium level sludge amended, cultivated. Profiles of DnOP and DnNP.

Fig. 6.9.1

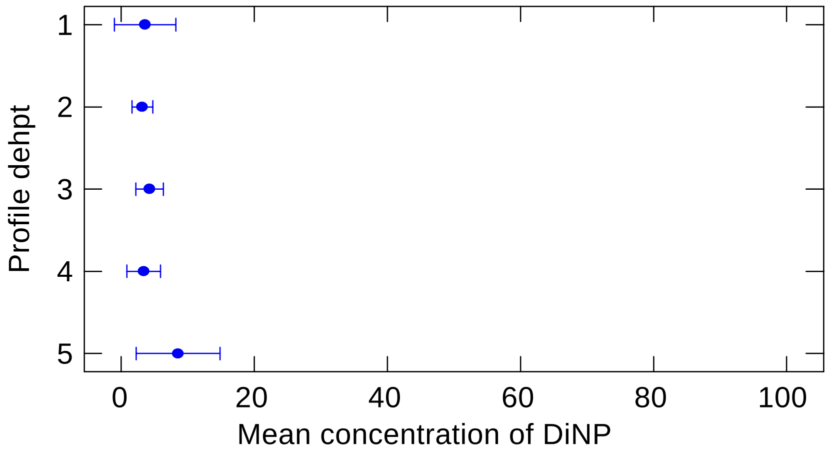


Fig. 6.9.2

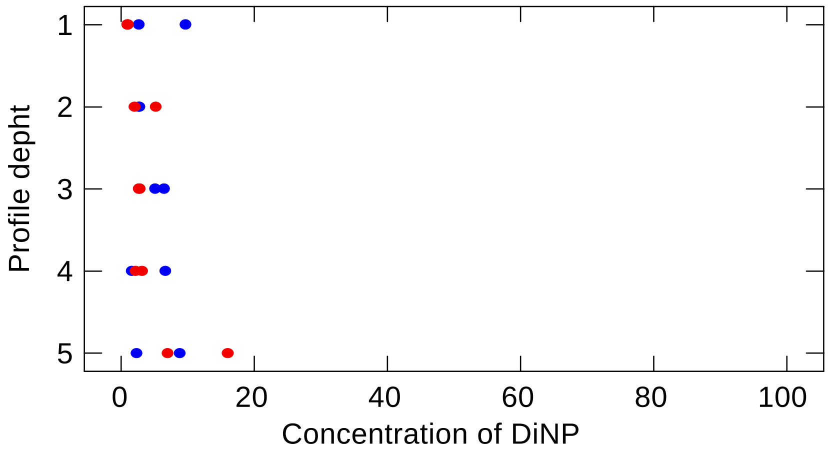


Fig. 6.9 Location 6, medium level sludge amended, cultivated. Profile of DiNP.

Fig. 7.1.1

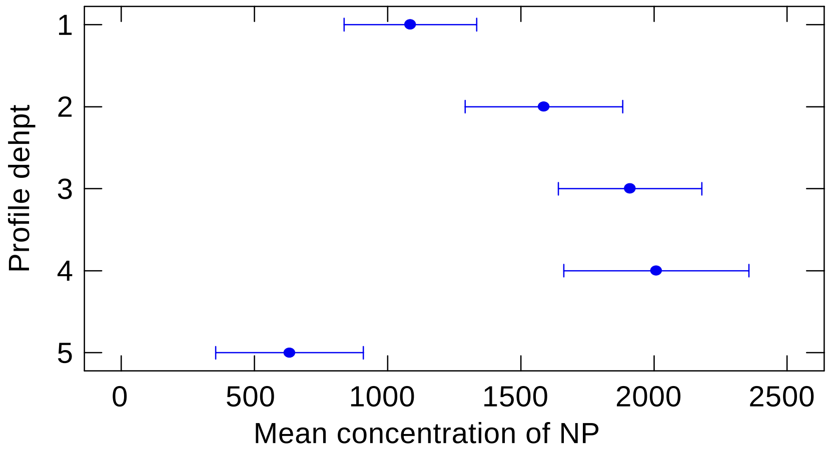


Fig. 7.1.2

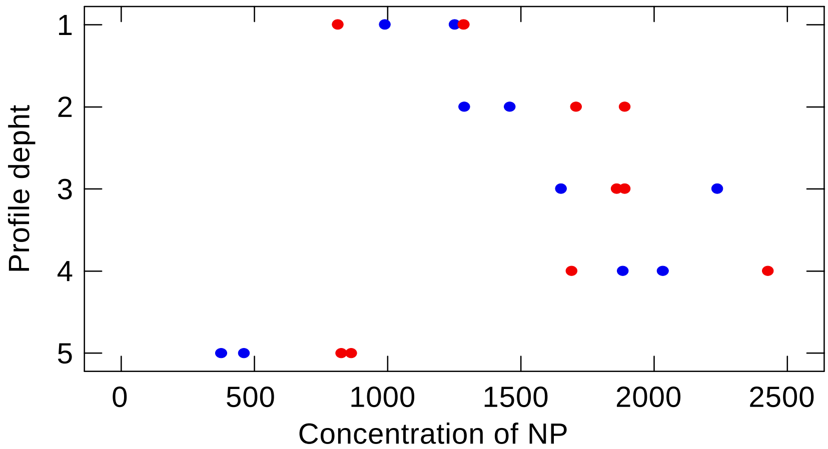


Fig. 7.2.1

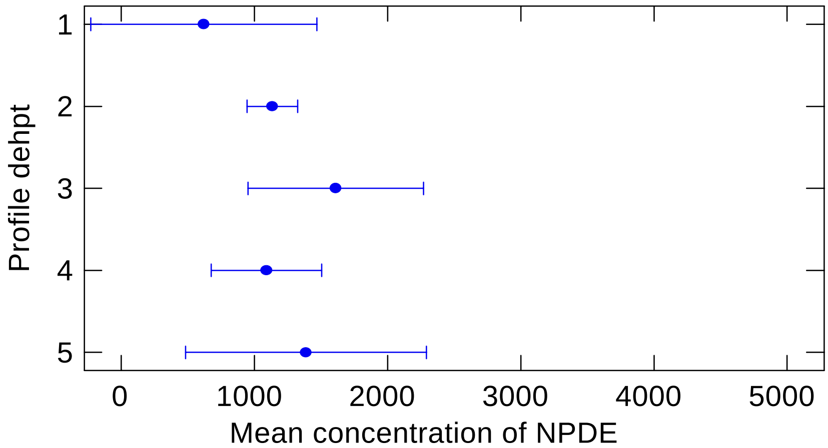
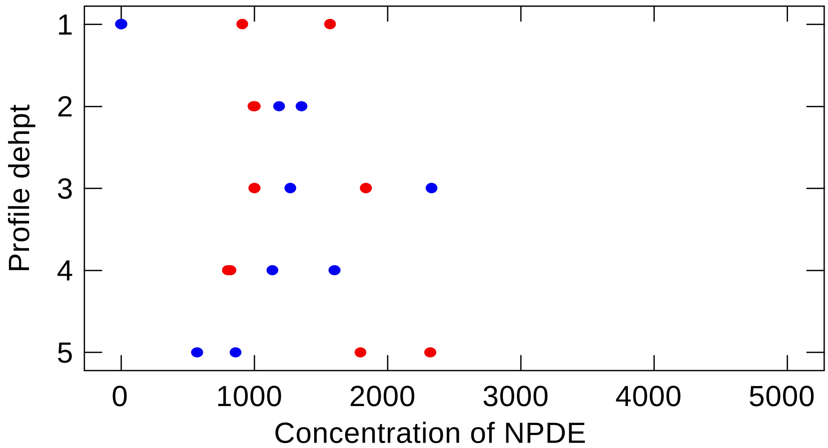


Fig. 7.2.2



Figs. 7.1 - 7.2 Location 7, formerly heavily sludge amended. Profiles of NP and NPDE.

Fig. 7.3.1

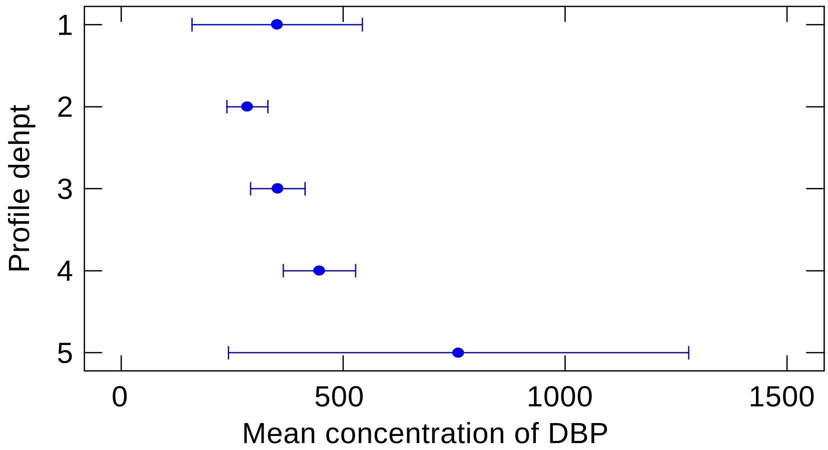


Fig. 7.3.2

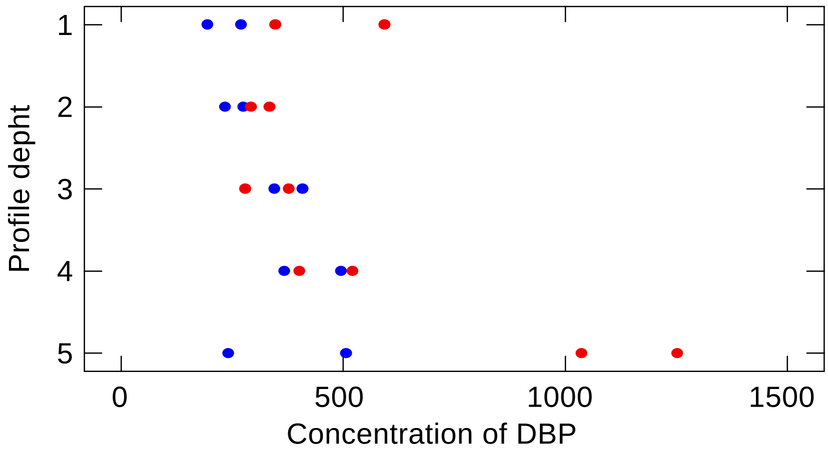
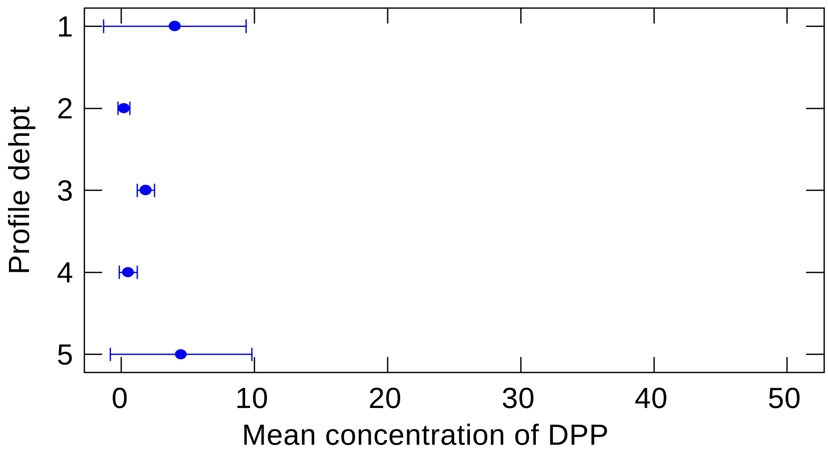


Fig. 7.4.1



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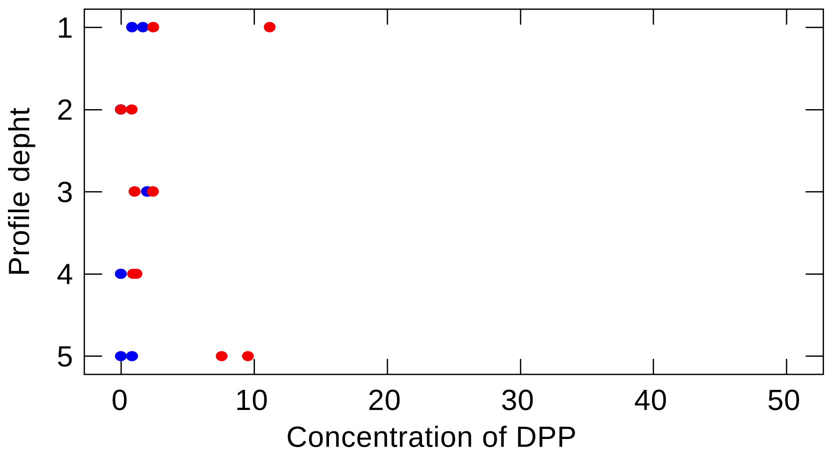


Figs. 7.3 - 7.4 Location 7, formerly heavily sludge amended. Profiles of DBP and DPP.

Fig. 7.5.1

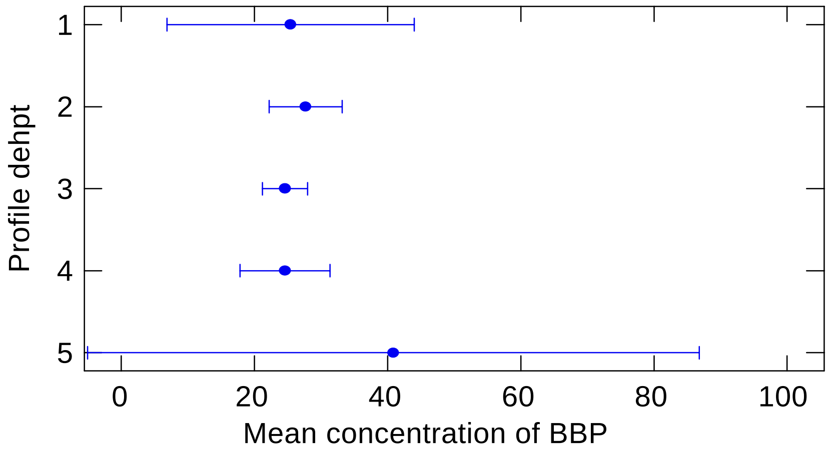


Fig. 7.5.2

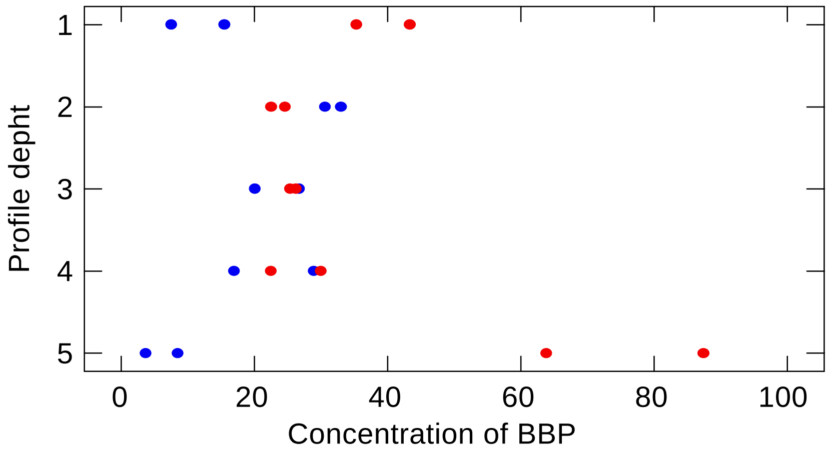
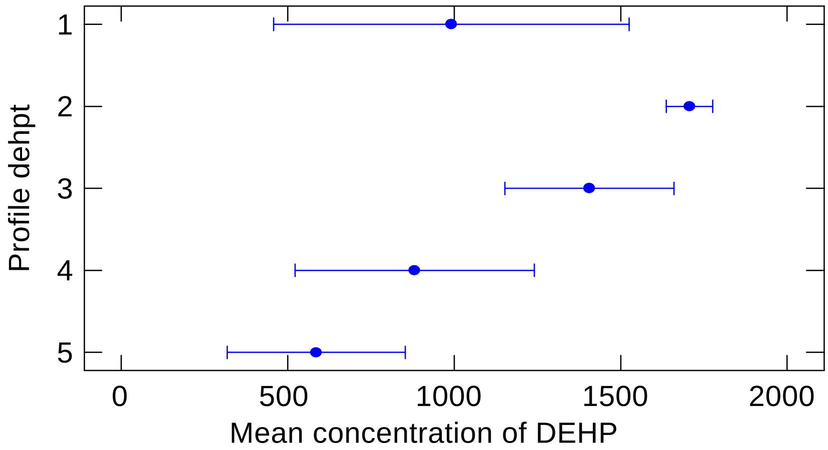


Fig. 7.6.1



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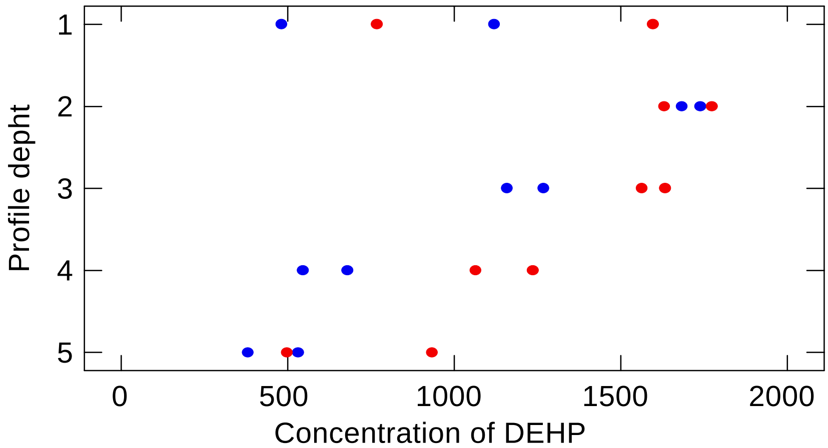


Figs. 7.5 - 7.6 Location 7, formerly heavily sludge amended. Profiles of BBP and DEHP.

Fig. 7.7.1

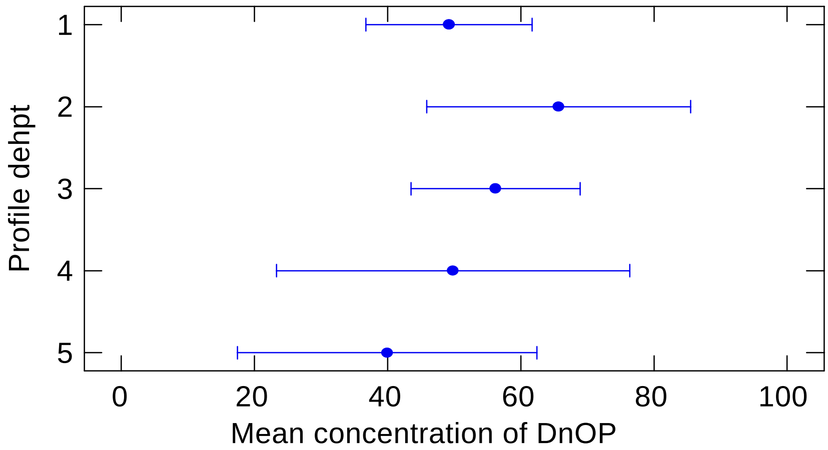


Fig. 7.7.2

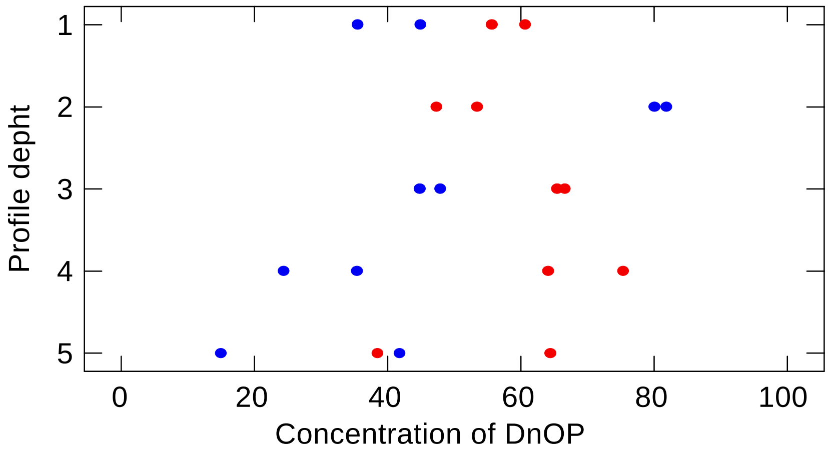


Fig. 7.8.1

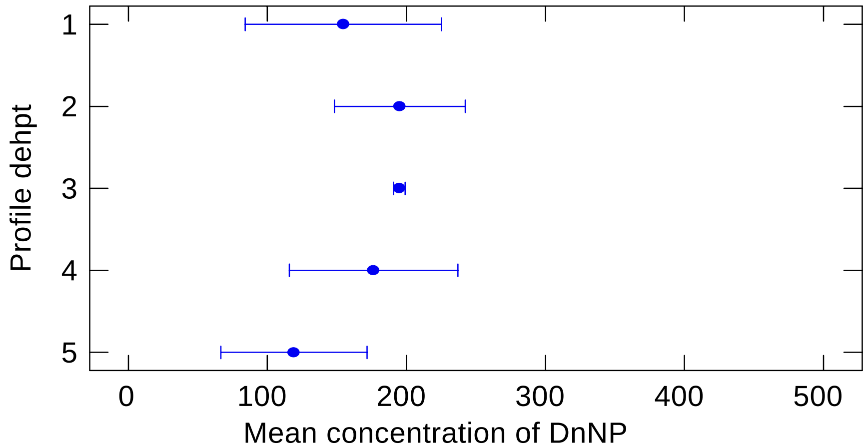
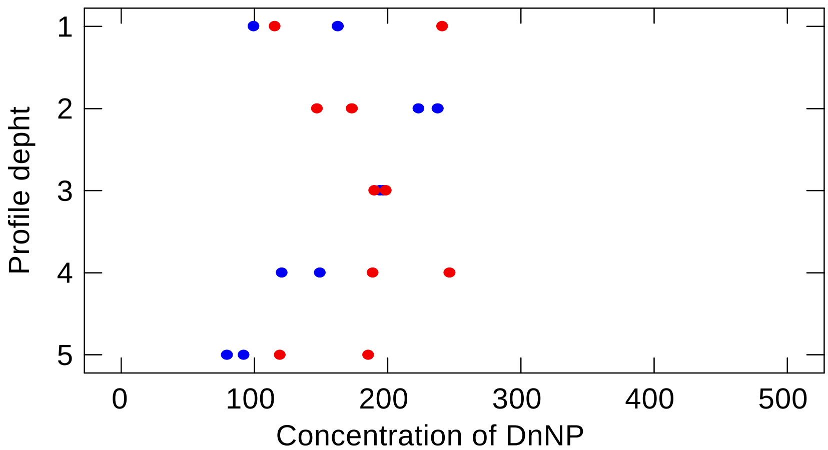


Fig. 7.8.2



Figs. 7.7 - 7.8 Location 7, formerly heavily sludge amended. Profiles of DnOP and DnNP.

Fig. 7.9.1

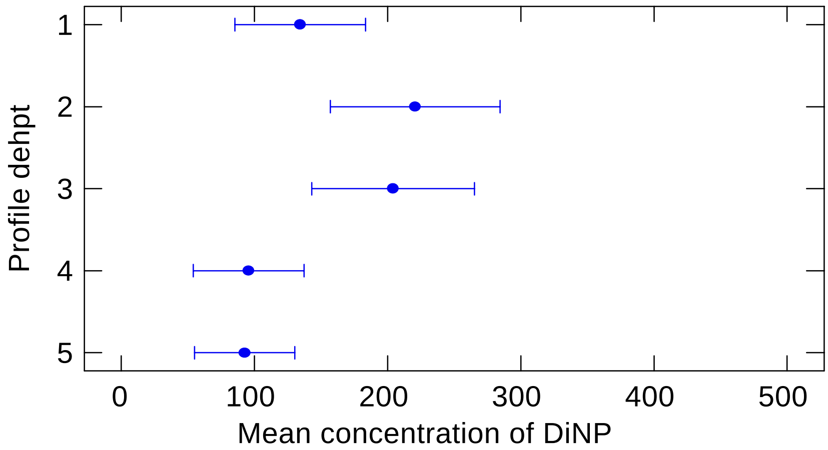


Fig. 7.9.2

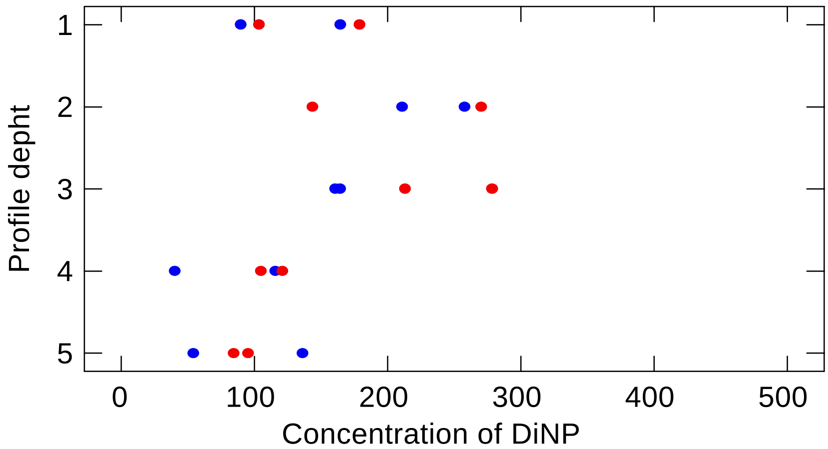


Fig. 7.9 Location 7, formerly heavily sludge amended. Profile of DiNP.

Fig. 8.1.1

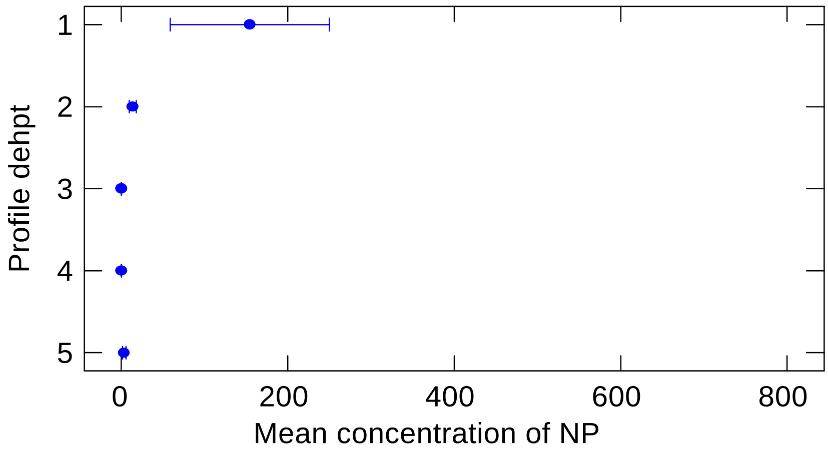


Fig. 8.1.2

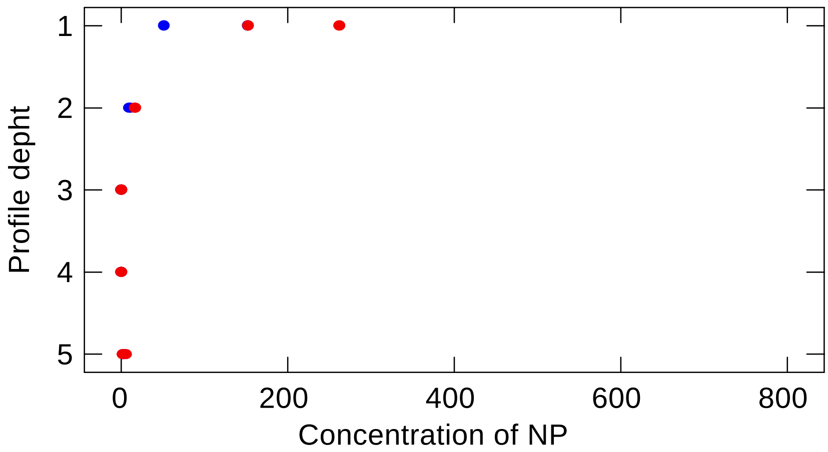


Fig. 8.2.1

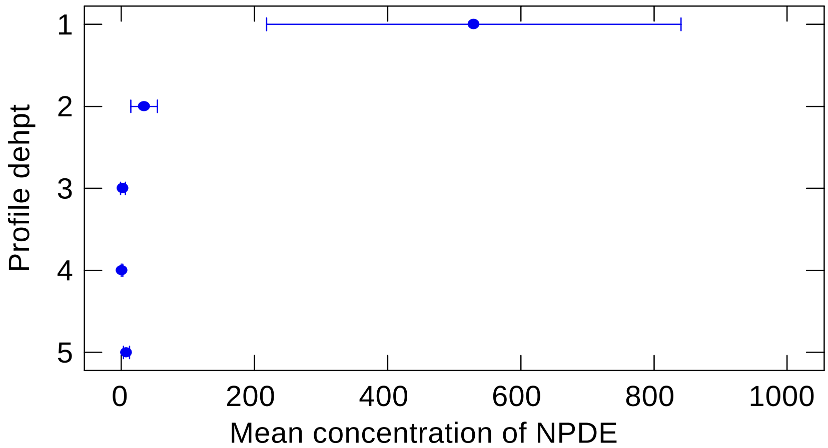
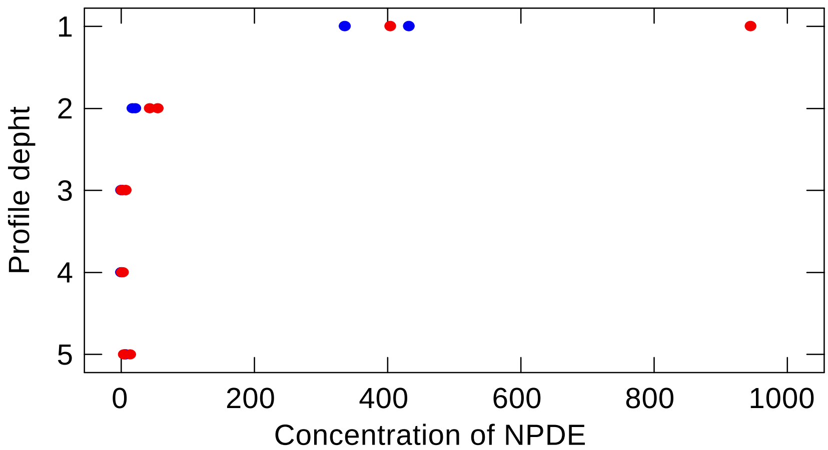


Fig. 8.2.2



Figs. 8.1 - 8.2 Location 8, meadow in sludge storage run-off zone. Profiles of NP and NPDE.

Fig. 8.3.1

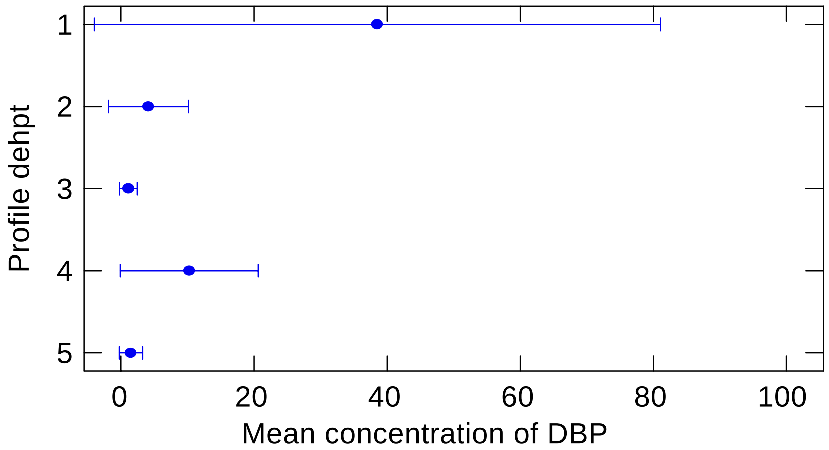


Fig. 8.3.2

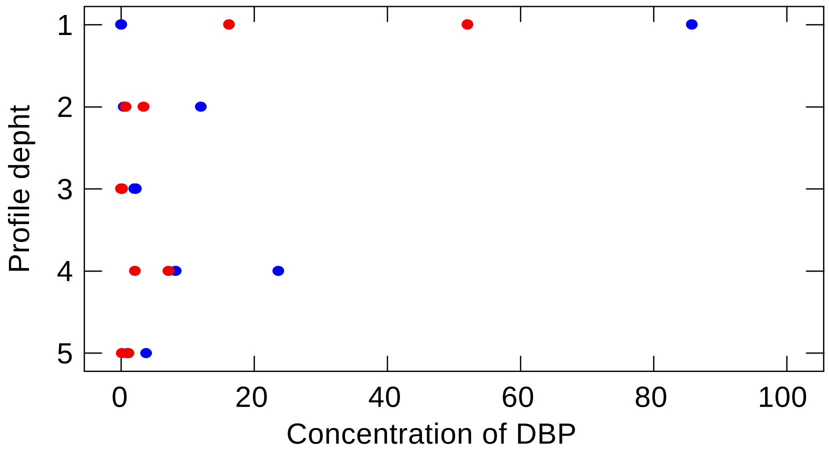


Fig. 8.4.1

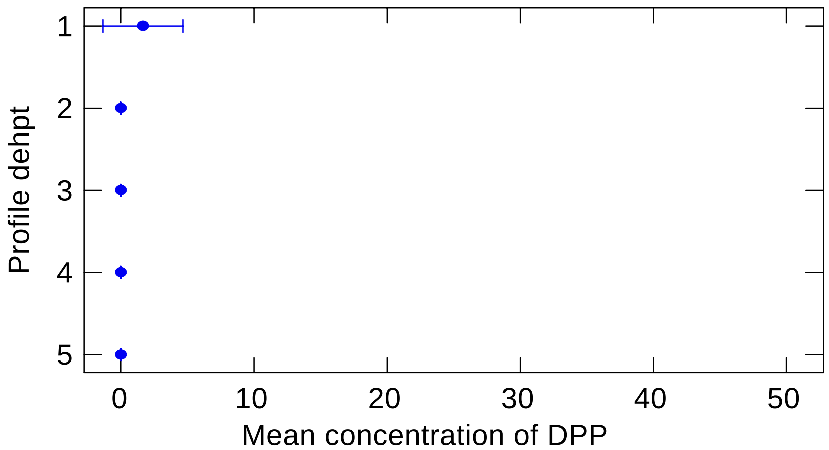
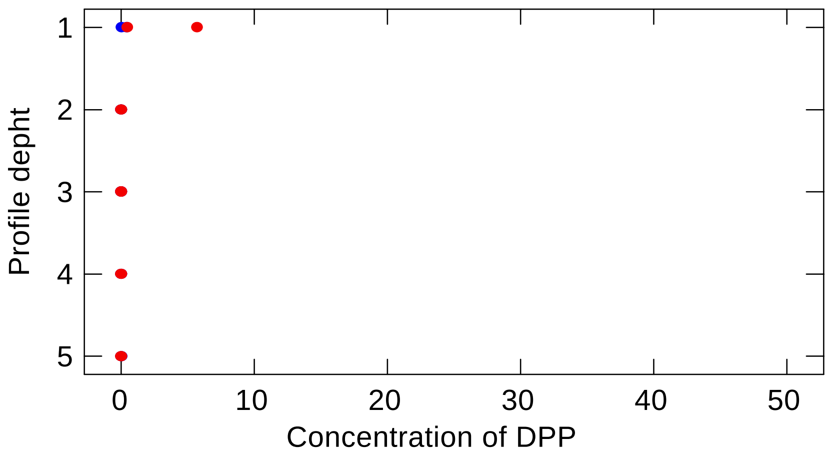


Fig. 8.4.2



Figs. 8.3 - 8.4 Location 8, meadow in sludge storage run-off zone. Profiles of BBP and DPP.

Fig. 8.5.1

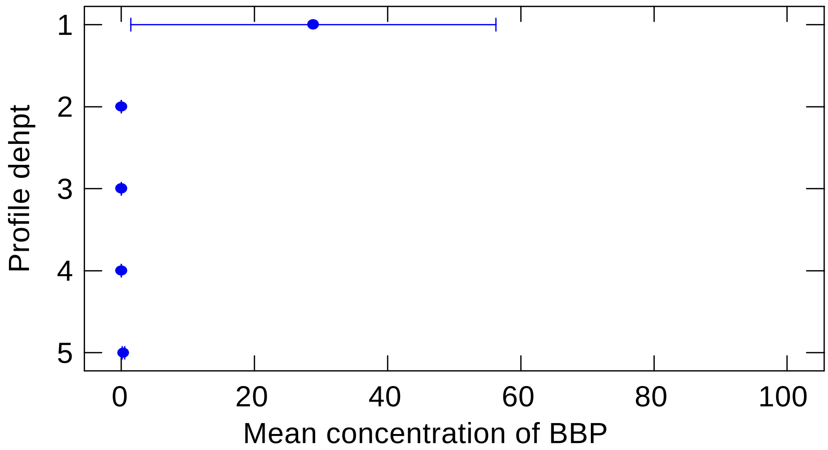


Fig. 8.5.2

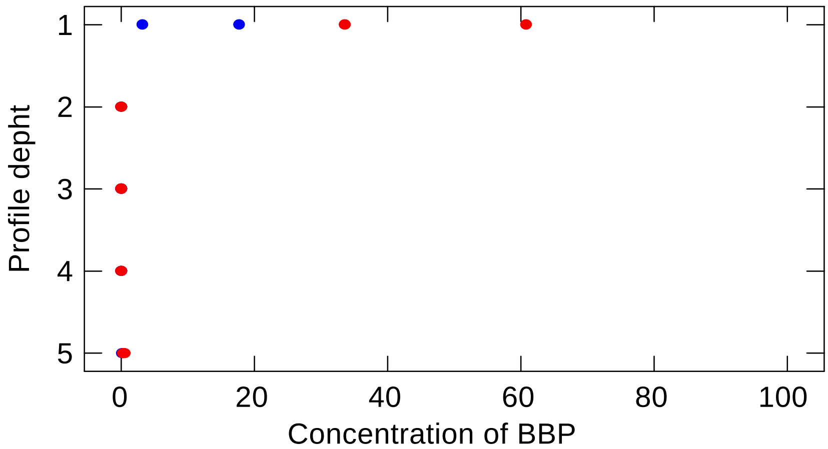


Fig. 8.6.1

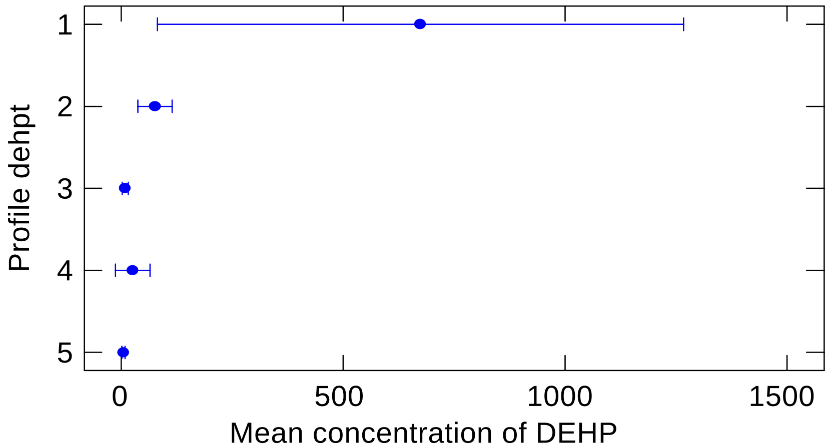
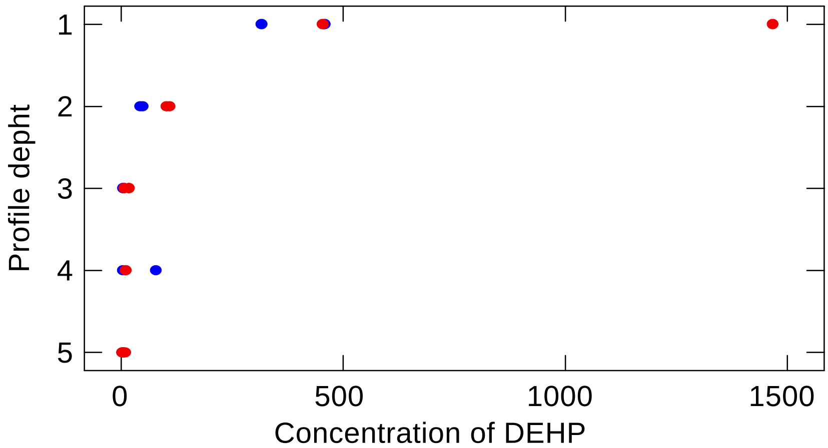


Fig. 8.6.2



Figs. 8.5 - 8.6 Location 8, meadow in sludge storage run-off zone. Profiles of BBP and DEHP.

Fig. 8.7.1

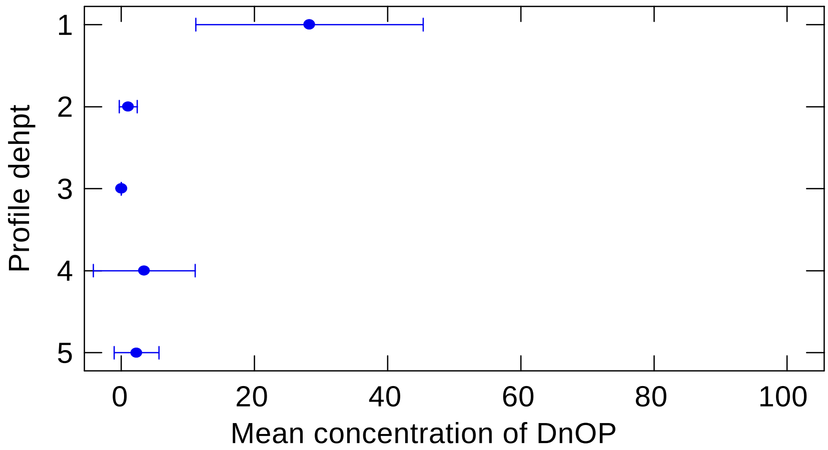


Fig. 8.7.2

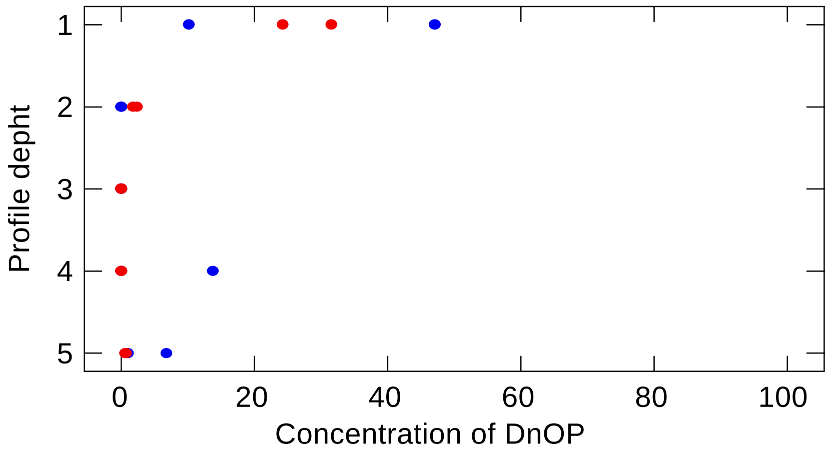
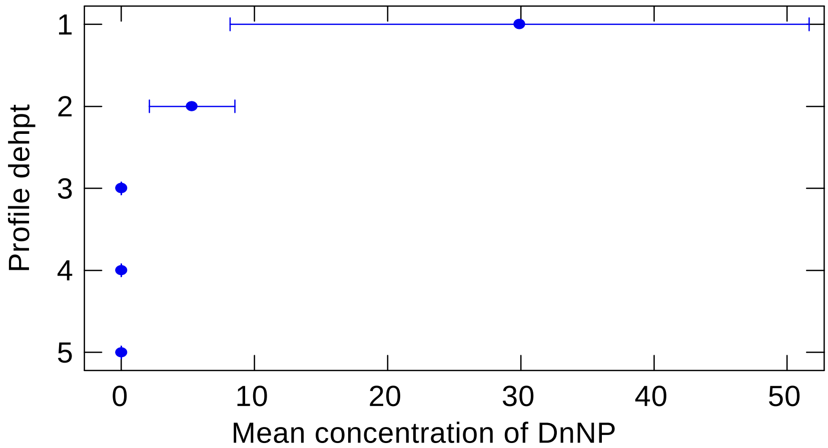


Fig. 8.8.1



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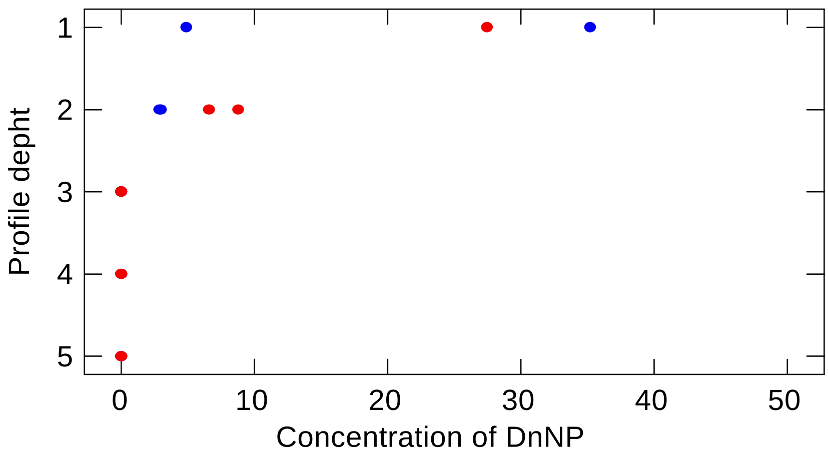

Figs. 8.7 - 8.8 Location 8, meadow in sludge storage run-off zone. Profiles of DnOP and DnNP.

Fig. 8.9.1

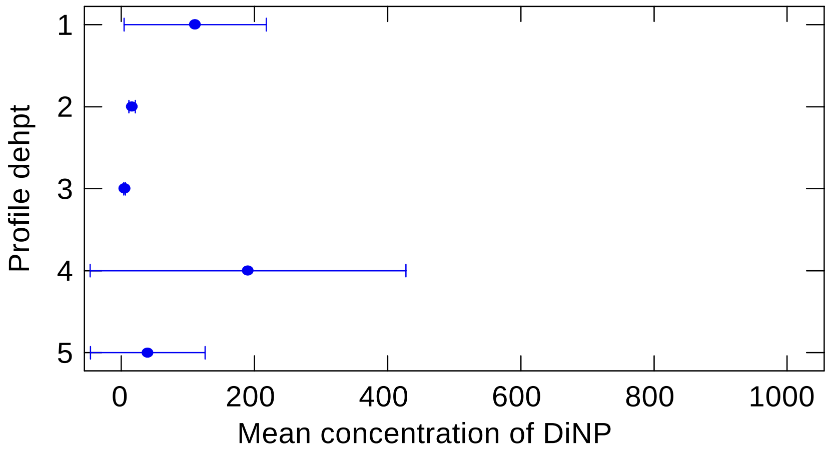

Fig. 8.9.2

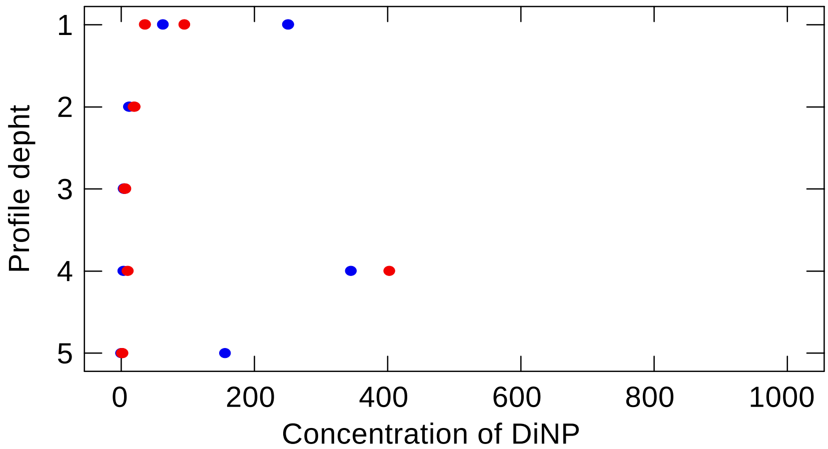

Fig. 8.9 Location 8, meadow in sludge storage run-off zone. Profiles of DiNP.

Appendix D. Statistics

As previously noted, two sample cores were taken at different positions at each site. Each core were subsequently subdivided into 5 primary samples. The primary samples were analysed in double determinations, leading to two so-called sister profiles with ten results in each, four results for each depth and substance (Fig. 1).

Profile A		Profile B	
a_{11}	a_{21}	b_{11}	b_{21}
a_{21}	a_{22}	b_{21}	b_{22}
a_{31}	a_{32}	b_{31}	b_{32}
a_{41}	a_{42}	b_{41}	b_{42}
a_{51}	a_{52}	b_{51}	b_{52}

Fig. 1 Analytical results for sister profiles.

The statistics are carried out for all profiles, depths and substances. The following is an overview of the statistical results.

t-test for sister profiles

An important question is whether the results for each depth for sister profiles are different. This was tested by performing a t-test for each depth between the two averages of the pairs of results for profile a and b, making a total of five tests for each site. It was found that only few of the t-tests showed significant difference between the sister profile results. It must thus be concluded that the concentrations in each depth are comparable for sister profiles.

Within depth variance

Pooling the 5 within-depth variances for the double determinations in each profile leads to the *pooled within depth variance*, which is a measure for the combined sampling and analytical variation. A further important question is thus whether the pooled within-depth variances for sister profile pairs are significantly different. This was tested by F-tests making one test for each location and substance. It was found that about the half of the within depth variance pairs differed significantly. This was somewhat surprising, since the pooled within depth variance is a measure for the sampling and analytical variation, which was expected to be comparable for sister profiles. Furthermore, the t-tests mentioned above showed no significant differences for the corresponding averages of sister profiles, hence it is reasonable to expect that the variances also should be comparable. A closer examination of the within-depth variances revealed that some variances differed much from the others, especially in the top layer, but also sporadically in the deeper layers, and that a pronounced tendency was that the high concentrations showed large within depth variances. Since there is no reason to believe that the analytical variation is different for sister profiles, the difference in variances may be due to sampling variation. An explanation for this might be that the samples were not homogenised before the sub-samples were taken from the primary samples, and that the deviating variances maybe reflect the sporadic occurrence of xenobiotic “spots” or “holes” in the soil matrix. This line of thought is further investigated in the following by means of Bartletts test.

Between depth variance

The variance between the 5 averages of the double determinations in each profile, *the between depth variance*, is a measure for the variation as a function of the depth for each profile. In the same way as the within-depth variance, it can be tested whether the two between depth variance of corresponding sister profile differ significantly by F-tests. It was found that in about the half of the tests the variances differed significantly, showing that the depth variation for sister profiles in these cases were different. In contrast to what is the case for the within-depth variance this is hardly surprising, since the sister profiles are taken a certain distance apart at the location, where different layer conditions in the soil may exist.

F-test between/within depth

An important issue is whether a depth variation is discernible in a profile, i.e. a significant variation between different depths can be seen, which is not overshadowed by the within-depth variation. It can be tested whether the between-depth variance is significantly larger than the within-depth variance in the same profile, by means of F-tests. It was found that about half of the test showed significant difference, i.e. that about the half of the profiles showed a larger variation between depth than within depth.

Quadruple determinations

The above mentioned test taken together are hardly conclusive, since in all cases about half of the tests showed significant differences. A reason for this is that some variances are much larger than others, in many cases due to a single analytical result, leading to very high pooled variances. Also, in many cases multiple non-detects in the data leads to zero variance. Still another reason is the low number of degree of freedom (1 for duplicates) of the variances. These difficulties can be handled concerted by disregarding the individuality of sister profiles, treating the data as quadruple determinations for each depth. This approach leads to 5 within-depth variances with 3 degrees of freedom for each location. In this way the same between/within variance F-tests as mentioned can be carried out. Table 1 gives an overview of this statistics. To facilitate comparison with the concentrations, the within depth and between depth variations are given as the standard variations (i.e. the square-roots of the variances), and significant differences between/within variances found by the F-test are marked with bold types in the “between depth” section of Table 2.

Bartletts test

Since the variances for each depth, treating the data as quadruple determinations, displayed pronounced differences within the same location, it was suspected that the variances did not belong to the same normal distributions, a phenomenon referred to as variance in-homogeneity. This was tested by means of Bartletts test. Significant deviations by this test (i.e. the variance in-homogeneities) are marked with boldface in the “within depth” section of Table 1.

Table 1 Pooled between depth and within depth standard deviations

Site	Loc	NP	NPDE	DBP	DPP	BBP	DEHP	DnOP	DnNP	DiNP
Statistics					***Between depth standard variation***					
Preserved	1	**0.9**	5.8	6.7	0.02	0.3	35	2.5	0.2	55
Manured 40y	2	**1.3**	4.7	2.2	0.06	**0.4**	26	11	1.3	150
Manured 5y	3	2.9	7.1	1.4	0.3	1.0	15	1.7	1.5	7.6
Art fertiliser	4	0.6	5.8	1.8	0.03	0.1	99	2.4	0.3	**48**
Low sludge	5	0.2	6.8	0.5	0.03	**0.3**	9.9	**4.1**	0.5	57
Norm sludge	6	0.03	**62**	1.3	0.03	0.03	75	0.5	0.6	4.5
High sludge	7	**1160**	740	380	3.9	14	**890**	19	64	**120**
Runoff	8	**135**	**460**	**32**	1.5	26	**580**	**24**	**26**	93
Statistics					***Within depht standard variations***					
Preserved	1	**0.5**	4.7	**7.1**	0.03	0.1	**35**	**1.6**	0.2	**33**
Manured 40y	2	**0.5**	3.3	**2.5**	0.04	0.1	**33**	**7.4**	**1.2**	**160**
Manured 5y	3	**1.6**	3.5	0.8	**0.2**	**0.7**	**11**	**1.4**	1.1	**5.5**
Art fertiliser	4	**0.5**	**6.7**	1.5	0.03	**0.1**	**104**	**2.0**	0.3	**27**
Low sludge	5	**0.1**	3.0	**0.6**	0.02	0.1	7.6	**1.7**	0.2	**50**
Norm sludge	6	0.03	**27**	1.0	0.03	**0.0**	**76**	0.4	0.4	3.5
High sludge	7	260	590	**230**	**3.1**	**20**	300	18	**47**	47
Runoff	8	**39**	**130**	**18**	**1.2**	**11**	**240**	**7.7**	8.8	**110**

Significant differences for between/within variances F-test marked with **bold** in the between depth section
Significant differences for Bartletts test for within variances marked with **bold** in the within depth section

As can be seen from Table 1, the between depth standard deviations are generally larger than the within depth standard deviations, and it is evident that large differences between standard deviations for different locations exist. Furthermore, comparing the standard deviations with the average concentrations given in Table 2 it is seen that the highest variations are generally found for the highest concentrations.

As seen from the bold markings in the between-section of Table 1, significant differences for between/within depth variances are found for NP and DEHP for the Location 7 and 8, where the highest concentrations are found. Location 8 displays the highest number of significant differences, which seems reasonable since this location displays a very pronounced profile as seen from Fig. 11 in the report, and from Figs. 8.1.1 to 8.9.2 in Appendix C.

As can be seen from the bold markings in the within-section, many cases of variance in-homogeneity were found by Bartletts test. In these cases it is strictly speaking not meaningful to pool the within depth variances, and consequently to perform the F-tests for between/within variance. If the test is nevertheless carried out irrespectively such as done above, the level of significance is rendered undetermined, leading to a less sensitive test.

Outliers

In several cases, the variance in-homogeneity is caused by a single result, which does not belong to the same normal distribution as the other results in the variance. This may be due to a spurious result, or *outlier*. In addition to Bartletts test, an outlier is characterised by a significant deviation from the average of the other results of the quadruple determination. The outliers are marked with an * in the results tables of Appendix

B. The averages of the report results tables and figures are calculated by the exclusion of outliers.

Sites versus reference

An important question is whether the general levels found at the different locations are elevated compared to the reference Location 1, the preserved unfertilised area. This can be tested by means of t-tests comparing the grand mean for each site with the reference grand mean, using the pooled total variance for the respective site and the reference. In Table 2 the grand mean and the total standard deviation for all sites are shown. Significant differences (p=0.05) between sites and reference are marked in bold in the grand mean section of the table

As can be seen from Table 2, for location 7, the high sludge amended area, all substance concentrations are significantly higher than the preserved reference area. None of other sites (with a single exception) differ significantly from the reference, and consequently do not differ from each other. The above t-tests uses the *total variance* for each site, but a somewhat more sensitive can be performed using the *pooled within-depth variance* for each site instead. This test leads to some additional significant differences, marked in ***bold italics*** in Table 2. As can be seen, these are all in the row for location 8, the runoff zone.

Table 2 Grand means and total standard variations

Site	Loc	NP	NPDE	DBP	DPP	BBP	DEHP	DnOP	DnNP	DiNP
					Grand means					
Preserved	1	0.47	2.9	2.1	0.01	0.09	16	1.2	0.04	20
Manured 40y	2	0.47	2.6	1.6	0.01	0.12	25	4.3	0.56	62
Manured 5y	3	0.98	2.9	0.5	0.08	0.38	12	1.2	0.48	7.1
Art. fertil.	4	0.24	3.6	1.1	0.02	0.06	40	1.5	0.14	22
Low sludge	5	0.04	3.1	0.3	0.01	0.06	12	1.3	0.12	19
Med sludge	6	0.01	16.09	1.7	0.01	0.01	38	0.61	**0.46**	4.6
High sludge	7	**1445**	**1168**	**439**	**2.2**	**29**	**1114**	**52**	**168**	**149**
Runoff	8	***34***	***115***	11	0.33	5.8	158	***7.0***	***7.0***	53
					Total Standard Deviations					
Preserved	1	0.58	4.9	7.0	0.03	0.17	35	1.8	0.18	39
Manured 40y	2	0.74	3.6	2.5	0.04	0.21	32	8.3	1.2	161
Manured 5y	3	1.9	4.5	1.0	0.26	0.75	12	1.5	1.20	6.0
Art. fertil.	4	0.47	6.5	1.5	0.03	0.10	103	2.1	0.26	32
Low sludge	5	0.15	4.1	0.57	0.02	0.14	8.2	2.4	0.32	51
Med sludge	6	0.03	37	1.1	0.03	0.03	76	0.47	0.46	3.7
High sludge	7	580	629	266	3.3	19	486	18	51	69
Runoff	8	71	240	21	1.3	15	341	13	14	121

Grand means significant larger than the reference (preserved area location 1) by t-test (p=0.05) marked with **bold** or ***bold italics*** (see text)

In conclusion, by a normal t-test only the highly sludge amended location 8 differs significantly from the preserved reference area. By a more sensitive t-test, also some significant differences in the runoff-zone can be seen.

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Addresses:

URL: http://www.dmu.dk

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

Management
Personnel and Economy Section
Research and Development Secretariat
Department of Policy Analysis
Department of Atmospheric Environment
Department of Environmental Chemistry
Department of Marine Ecology and Microbiology

National Environmental Research Institute
Vejlsøvej 25
PO Box 413
DK-8600 Silkeborg
Denmark
Tel: +45 89 20 14 00
Fax: +45 89 20 14 14

Department of Terrestrial Ecology
Department of Lake and Estuarine Ecology
Department of Streams and Riparian areas

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

Department of Landscape Ecology
Department of Coastal Zone Ecology

National Environmental Research Institute
Tagensvej 135, 4
DK-2200 København N
Denmark
Tel: +45 35 82 14 15
Fax: +45 35 82 14 20

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