



Report on the presence of Polychlorinated Dioxins and
Dibenzofurans in soil from ASSI-Köpmanholmen

*Sampling was performed in autumn 2000 - spring 2001
and analysis during spring - autumn 2001*

Rapport om förekomsten av dioxiner i jord från ASSI-
Köpmanholmen. Provtagning utförd hösten 2000 och analyser
under våren och hösten 2001.

Umea January 2002
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1. Methodology for Dioxins investigation

Methodology is presented in Table 1.

Tabel 1. Methodology

Description of investigation	Number
• Number of soil samples	22 4
• Number of analyzed samples	11 4
• Chemical analysis - Dioxins	15
• Evaluation	1

2. Sampling strategy

Soil samples for dioxin analysis were taken from 11 drilling holes (S1, S3-10, S12 and S14). Soil samples were taken from 0,2 and 1,0 meters depth and these samples were pooled together to create one sample per drilling. The pooling of soil samples were done after that each subsample were dried and sieved. Each pooled sample was created by equal weight of the dried and sieved subsamples.

This procedure were used since the previous history of soil covering of old surface layers is not fully known in the sampling area. The sampling sites are choosen depending on known activities in the area and efforts are made to cover some of the probable contaminated soil areas. At this stage it is impossible to conclude that this preliminary selection of areas is fully relevant. Another subset of soil samples were taken at a later stage by another consultant.

3. Analysis

Examples of chromatograms from mass spectrometer analysis from one of the more contaminated samples are shown below. All samples were analysed on a capillary column (DB-5ms 60m x 0.25mm x 0.25µm) connected to a Finnigan GC/MS-MS Ion trap.

4. Calculations

The toxic equivalentents are calculated using two slightly different methods. In the first case compounds under the detection limit (represented with a < sign and actual detection limit) is regarded as a zero value, and in the other case half of the detection limit is set as an actual value and included in the toxic equivalent value. The TEQ (toxic equivalent factors) used is presented in the tables below and can also be found in the reference "Martin Van den Berg et.al, Environmental Health Perspectives (1998), 106:775-792". In table 2 below and in the first four columns in table 6 also the estimated value of total amount of dioxins and dibensofurans divided on the congener groups tetra, penta, hexa, hepta and octa chlorinated substances are reported.

5. Positions of sampling places

2427	Berg.: Assi Kopmanholmen 1	S1
2428	Berg.: Assi Kopmanholmen 3	S3
2429	Berg.: Assi Kopmanholmen 4	S4
2430	Berg.: Assi Kopmanholmen 5	S5
2431	Berg.: Assi Kopmanholmen 6	S6
2432	Berg.: Assi Kopmanholmen 7	S7
2433	Berg.: Assi Kopmanholmen 8	S8
2434	Berg.: Assi Kopmanholmen 9	S9
2435	Berg.: Assi Kopmanholmen 10	S10
2436	Berg.: Assi Kopmanholmen 12	S12
2437	Berg.: Assi Kopmanholmen 14	S14

Note: sampling locations for the second set of samples are not available. It is 4 samples of soil. Two of these are brown sandy soil with stones, second two samples are grey without stones. Description of samples is identical S11 0.2-0.5 m deep and Y+1 or Y+2.

6. Results and discussions

The Table 2 shows the concentration of the most toxic polychlorinated dioxins and polychlorinated dibenzofurans as well as the total concentration of each congener group in the pooled (0,2 and 1,0 meter) soil samples. The results are shown in pg/g dry soil.

Table 2. Concentrations of the polychlorinated dioxins, polychlorinated dibenzofurans and the total concentration of each congener group in the pooled soil samples, pg/g of dry sample.

		2427	2428	2429	2430	2431	2432	2433	2434	2435	2436	2437	
		S1	S3	S4	S5	S6	S7	S8	S9	S10	S12	S14	
	I-TEF	[pg/g of dry sample]				[pg/g of dry sample]				[pg/g of dry sample]			
2378TCDD	1	< 2.1	< 2.1	6,0	< 2.3	< 2.3	< 2.2	< 1.8	< 2.0	< 2.3	< 2.3	< 1.9	
12378PeCDD	1	< 3.1	< 2.7	< 2.9	< 3.2	< 2.9	< 3.0	< 2.3	< 2.8	< 3.6	< 2.7	4,4	
123478HxCDD	0,1	< 3.3	< 3.4	< 3.3	< 3.8	< 3.4	< 3.9	< 3.1	< 3.3	3,8	< 3.1	5,5	
123678HxCDD	0,1	< 3.0	< 2.7	< 3.6	< 3.7	< 3.3	< 3.4	< 2.7	< 3.4	< 3.6	< 3.6	8,1	
123789HxCDD	0,1	< 2.7	< 2.4	< 3.3	< 3.4	< 3.0	< 3.1	3,8	< 3.1	< 3.2	< 3.3	5,2	
1234678HpCDD	0,01	< 3.4	18	4,2	< 3.8	10	7,0	5,2	7,1	63	22	110	
OCDD	0,0001	3,9	180	17	< 5.6	83	22	28	14	290	120	1000	
TCDDs		< 18	< 17	16	< 19	< 19	< 18	< 15	< 17	< 19	< 19	< 16	
PeCDDs		< 26	< 23	< 24	< 26	< 24	< 25	< 19	< 23	< 30	< 22	50	
HxCDDs		< 19	< 18	< 21	< 22	< 20	< 22	< 17	< 20	57	< 20	74	
HpCDDs		< 6.7	41	9,6	< 7.7	20	12	10	8,4	120	42	210	
Sum toxic isom		3,9	198,0	27,2	0,0	93,0	29,0	37,0	21,1	356,8	142,0	1133,2	
Sum of PCDDs		3,9	221	43	ND	103	34	38	22	467	162	1334	
2378TCDF	0,1	8,3	18	1000	< 2.0	170	3,9	< 0.9	0,53	10	56	280	
12378PeCDF	0,05	< 1.1	14	91	< 1.3	110	1,6	< 1.1	< 1.1	9,1	33	700	
23478PeCDF	0,5	< 0.8	6,8	64	< 1.0	45	< 1.5	2,2	< 0.6	4,4	17	160	
123478HxCDF	0,1	< 2.6	34	125	< 2.9	79	6,2	2,4	< 2.4	16	37	3100	
123678HxCDF	0,1	< 2.1	9,5	36	< 2.4	22	< 2.6	< 2.3	< 2.0	5,3	10	630	
234678HxCDF	0,1	< 2.3	< 2.5	5,9	< 3.1	2,6	< 5.0	< 2.4	< 2.0	2,7	2,5	190	
123789HxCDF	0,1	< 2.9	< 2.9	< 3.3	< 4.0	5,8	< 5.2	< 3.0	< 2.0	< 2.3	< 2.7	220	
1234678HpCDF	0,01	< 3.6	56	100	< 4.4	24	13	< 3.7	< 3.9	41	46	2000	
1234789HpCDF	0,01	< 3.5	13	26	< 4.2	11	< 4.2	< 4.2	< 5.1	7,8	9,3	650	
OCDF	0,0001	< 7.0	84	130	< 7.1	44	14	< 6.1	< 5.5	46	67	3100	
TCDFs		24	75	1900	< 13	450	19	16	15	52	150	770	
PeCDFs		< 9.2	54	320	< 11	290	11	21	< 9.2	41	120	1700	
HxCDFs		< 13	99	270	< 15	160	21	27	< 13	62	94	5600	
HpCDFs		< 11	100	170	< 13	51	20	< 12	< 13	72	83	3300	
Sum of PCDFs		24	412	2790	ND	995	85	64	15	273	514	14470	
Sum toxic isom		8,3	235,3	1577,9	0,0	513,4	38,7	4,6	0,5	142,3	277,8	11030,0	
Sum of PCDD/Fs		28	633	2833	ND	1098	119	102	37	740	676	15804	

Table 3. Concentrations of the polychlorinated dioxins, polychlorinated dibenzofurans and the total concentration of each congener group in the pooled soil samples, pg TEQ/g of dry sample (ND=1/2DL)

Lab nr		2427	2428	2429	2430	2431	2432	2433	2434	2435	2436	2437	
Sampling nr		S1	S3	S4	S5	S6	S7	S8	S9	S10	S12	S14	
	I-TEF	[pgTEQ/g of dry sample] ND=1/2DL				[pgTEQ/g of dry sample] ND=1/2DL				[pgTEQ/g of dry sample] ND=1/2DL			
2378TCDD	1	1,05	1,05	6,0	1,15	1,15	1,1	0,90	1,0	1,15	1,15	0,95	
12378PeCDD	1	1,55	1,35	1,45	1,6	1,45	1,5	1,15	1,4	1,8	1,35	4,4	
123478HxCDD	0,1	0,165	0,17	0,165	0,19	0,17	0,195	0,155	0,165	0,38	0,155	0,55	
123678HxCDD	0,1	0,15	0,135	0,18	0,185	0,165	0,17	0,135	0,17	0,18	0,18	0,81	
123789HxCDD	0,1	0,135	0,12	0,165	0,17	0,15	0,155	0,38	0,155	0,16	0,165	0,52	
1234678HpCDD	0,01	0,017	0,18	0,042	0,019	0,10	0,070	0,052	0,071	0,63	0,22	1,1	
OCDD	0,0001	0,00039	0,018	0,0017	0,00028	0,0083	0,0022	0,0028	0,0014	0,029	0,012	0,10	
TCDDs													
PeCDDs													
HxCDDs													
HpCDDs													
Sum of PCDDs		3,1	3,0	8,0	3,31	3,19	3,19	2,77	2,96	4,33	3,23	8,43	
2378TCDF	0,1	0,83	1,80	100	0,10	17	0,39	0,045	0,053	1,0	5,6	28	
12378PeCDF	0,05	0,0275	0,70	4,55	0,0325	5,5	0,080	0,0275	0,0275	0,455	1,65	35	
23478PeCDF	0,5	0,20	3,4	32	0,25	22,5	0,375	1,1	0,15	2,2	8,5	80	
123478HxCDF	0,1	0,13	3,4	12,5	0,145	7,9	0,62	0,24	0,12	1,6	3,7	310	
123678HxCDF	0,1	0,105	0,95	3,6	0,12	2,2	0,13	0,115	0,10	0,53	1,0	63	
234678HxCDF	0,1	0,115	0,125	0,59	0,155	0,26	0,25	0,12	0,10	0,27	0,25	19	
123789HxCDF	0,1	0,145	0,145	0,165	0,20	0,58	0,26	0,15	0,10	0,115	0,135	22	
1234678HpCDF	0,01	0,018	0,56	1,0	0,022	0,24	0,13	0,185	0,0195	0,41	0,46	20	
1234789HpCDF	0,01	0,0175	0,13	0,26	0,021	0,11	0,021	0,021	0,0255	0,078	0,093	6,5	
OCDF	0,0001	0,00035	0,0084	0,013	0,00036	0,0044	0,0014	0,000305	0,00028	0,0046	0,0067	0,31	
TCDFs													
PeCDFs													
HxCDFs													
HpCDFs													
Sum of PCDFs		1,6	11	155	1,05	56,3	2,26	2,00	0,70	6,66	21,4	584	
Sum of PCDD/Fs		4,7	14	163	4,4	59,5	5,4	4,8	3,7	11	25	592	

Table 4. Concentrations of the polychlorinated dioxins, polychlorinated dibenzofurans and the total concentration of each congener group in the pooled soil samples, pgTEQ/g of dry sample (ND=0)

Lab nr		2427	2428	2429	2430	2431	2432	2433	2434	2435	2436	2437	
Sampling nr		S1	S3	S4	S5	S6	S7	S8	S9	S10	S12	S14	
	I-TEF	[pgTEQ/g of dry sample] ND=0				[pgTEQ/g of dry sample] ND=0				[pgTEQ/g of dry sample] ND=0			
2378TCDD	1	ND	ND	6,0	ND	ND	ND	ND	ND	ND	ND	ND	
12378PeCDD	1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4,4	
123478HxCDD	0,1	ND	ND	ND	ND	ND	ND	ND	ND	0,38	ND	0,55	
123678HxCDD	0,1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0,81	
123789HxCDD	0,1	ND	ND	ND	ND	ND	ND	0,38	ND	ND	ND	0,52	
1234678HpCDD	0,01	ND	0,18	0,042	ND	0,10	0,070	0,052	0,071	0,63	0,22	1,1	
OCDD	0,0001	0,00039	0,018	0,0017	ND	0,0083	0,0022	0,0028	0,0014	0,029	0,012	0,10	
TCDDs													
PeCDDs													
HxCDDs													
HpCDDs													
Sum of PCDDs		0,00039	0,198	6,0	ND	0,11	0,072	0,43	0,072	1,04	0,232	7,5	
2378TCDF	0,1	0,83	1,80	100	ND	17	0,39	ND	0,053	1,0	5,6	28	
12378PeCDF	0,05	ND	0,70	4,55	ND	5,5	0,080	ND	ND	0,455	1,65	35	
23478PeCDF	0,5	ND	3,4	32	ND	22,5	ND	1,1	ND	2,2	8,5	80	
123478HxCDF	0,1	ND	3,4	12,5	ND	7,9	0,62	0,24	ND	1,6	3,7	310	
123678HxCDF	0,1	ND	0,95	3,6	ND	2,2	ND	ND	ND	0,53	1,0	63	
234678HxCDF	0,1	ND	ND	0,59	ND	0,26	ND	ND	ND	0,27	0,25	19	
123789HxCDF	0,1	ND	ND	ND	ND	0,58	ND	ND	ND	ND	ND	22	
1234678HpCDF	0,01	ND	0,56	1,0	ND	0,24	0,13	ND	ND	0,41	0,46	20	
1234789HpCDF	0,01	ND	0,13	0,26	ND	0,11	ND	ND	ND	0,078	0,093	6,5	
OCDF	0,0001	ND	0,0084	0,013	ND	0,0044	0,0014	ND	ND	0,0046	0,0067	0,31	
TCDFs													
PeCDFs													
HxCDFs													
HpCDFs													
Sum of PCDFs		0,830	10,9	155	ND	56,3	1,22	1,34	0,053	6,55	21,3	584	
Sum of PCDD/Fs		0,83	11	161	ND	56,4	1,3	1,8	0,13	7,6	21	591	

Recovery values of the whole analytical procedure are presented in Table 5.

Table 5. Recovery values

¹³ C ₁₂ labeled standards	Recovery			
	3347	3348	3349	3350
2378TCDD	88%	76%	83%	78%
12378PeCDD	93%	75%	87%	79%
123478HxCDD	55%	72%	68%	83%
123678HxCDD	86%	58%	73%	54%
1234678HpCDD	71%	69%	79%	64%
OCDD	85%	66%	89%	71%
2378TCDF	77%	70%	78%	72%
12378PeCDF	75%	66%	75%	68%
23478PeCDF	80%	68%	77%	71%
123478HxCDF	99%	79%	90%	86%
123678HxCDF	68%	61%	82%	67%
234678HxCDF	91%	66%	91%	93%
123789HxCDF	79%	71%	85%	72%
1234678HpCDF	74%	64%	78%	69%
1234789HpCDF	96%	83%	102%	88%

Table 6. Concentrations of the polychlorinated dioxins, polychlorinated dibenzofurans and the total concentration of each congener group in the pooled soil samples.

		3347	3348	3349	3350	3347	3348	3349	3350	3347	3348	3349	3350
		SN1	SN2	SN3	SN4	SN1	SN2	SN3	SN4	SN1	SN2	SN3	SN4
	I-TEF	[pg/g of dry sample]				[pgTEQ/g of dry sample] ND=0				[pgTEQ/g of dry sample] ND=1/2DL			
2378TCDD	1	< 1.4	< 2.0	< 1.3	< 2.2	ND	ND	ND	ND	0,70	1,0	0,65	1,1
12378PeCDD	1	< 1.3	< 2.0	< 1.3	< 2.1	ND	ND	ND	ND	0,65	1,0	0,65	1,05
123478HxCDD	0,1	< 2.6	< 2.8	< 2.1	< 2.6	ND	ND	ND	ND	0,130	0,14	0,11	0,13
123678HxCDD	0,1	< 1.3	< 2.6	< 1.6	< 3.0	ND	ND	ND	ND	0,065	0,13	0,075	0,15
123789HxCDD	0,1	< 1.7	< 3.4	< 1.9	< 3.9	ND	ND	ND	ND	0,085	0,17	0,095	0,195
1234678HpCD	0,01	10	10	13	21	0,10	0,10	0,13	0,21	0,10	0,10	0,13	0,21
OCDD	0	54	130	87	160	0,0054	0,013	0,0087	0,016	0,0054	0,013	0,0087	0,016
TCDDs		< 4.2	< 6.0	< 4.0	14								
PeCDDs		< 4.0	< 6.0	< 3.8	< 6.4								
HxCDDs		11	< 9.0	13	< 9.1								
HpCDDs		15	13	21	39								
Sum of toxic izom		64,0	140,0	100,0	181,0								
Sum of PCDDs		80,0	143	121	213,0	0,105	0,113	0,139	0,226	1,74	2,55	1,71	2,85
2378TCDF	0,1	17	3,8	20	18	1,7	0,38	2,0	1,8	1,7	0,38	2,0	1,8
12378PeCDF	0,05	9,6	3,8	12	11	0,48	0,19	0,60	0,55	0,48	0,19	0,60	0,55
23478PeCDF	0,5	4,7	2,8	8,2	13	2,35	1,4	4,1	6,5	2,35	1,4	4,1	6,5
123478HxCDF	0,1	5,1	2,3	27	16	0,51	0,23	2,7	1,6	0,51	0,23	2,7	1,6
123678HxCDF	0,1	1,6	< 1.6	1,3	7,7	0,16	ND	0,13	0,77	0,16	0,080	0,13	0,77
234678HxCDF	0,1	< 1.1	< 2.0	< 1.1	< 1.6	ND	ND	ND	ND	0,055	0,10	0,055	0,080
123789HxCDF	0,1	< 12	< 14	< 14	< 14	ND	ND	ND	ND	0,60	0,70	0,70	0,70
1234678HpCD	0,01	13	32	20	44	0,130	0,32	0,20	0,44	0,130	0,32	0,20	0,44
1234789HpCD	0,01	4,0	1,7	5,8	5,1	0,040	0,017	0,058	0,051	0,040	0,017	0,058	0,051
OCDF	0	26	51	42	67	0,0026	0,0051	0,0042	0,0067	0,0026	0,0051	0,0042	0,0067
TCDFs		35	17	13	66								
PeCDFs		27	17	37	56								
HxCDFs		29	24	44	68								
HpCDFs		27	55	40	77								
Sum of PCDFs		144	164	176	334	5,37	2,54	9,79	11,7	6,03	3,42	10,5	12,5
Sum toxic izom		81	97	136	182								
Sum of PCDD/Fs		224	307	297	547	5,5	2,7	10	12	7,8	6,0	12	15

Figure 1. Concentration of I-TEQ values for PCDD, PCDF and sum PCDD/F in pg/g dry soil.

Concentration of I-TEQ values for PCDD, PCDF and sum PCDD/F in pg/g dry soil.

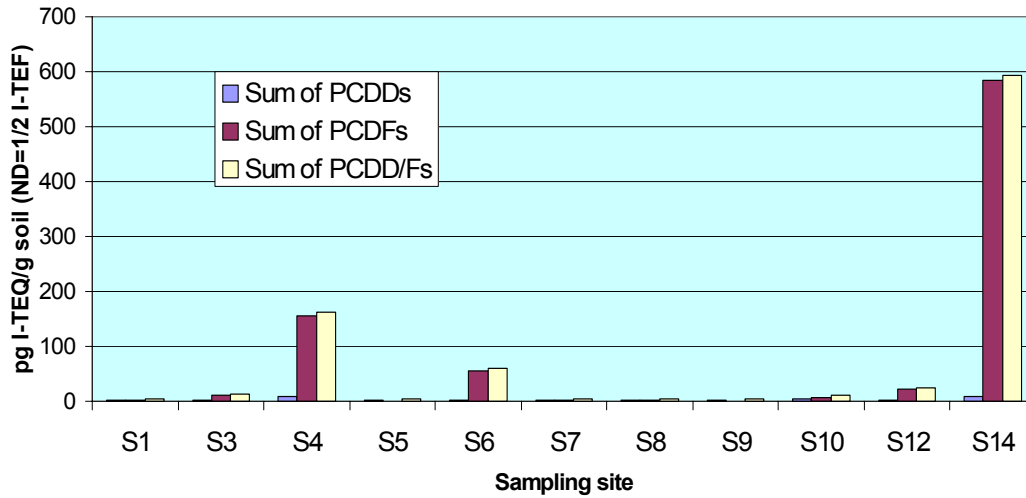


Figure 2. Concentration of I-TEF values for PCDD, PCDF and sum PCDD/F in pg/g dry soil.

Concentration of I-TEF values for PCDD, PCDF and sum PCDD/F in pg/g dry soil

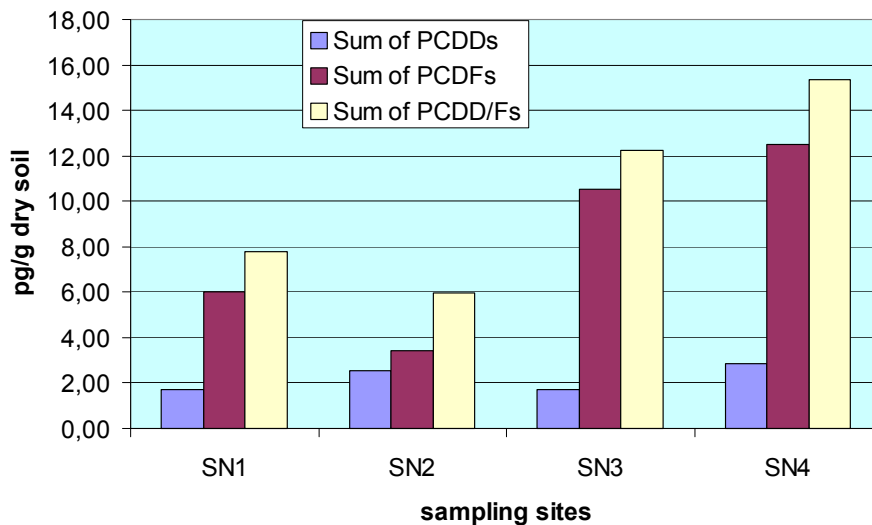


Figure 3. Normalized data of PCDF concentration in soil

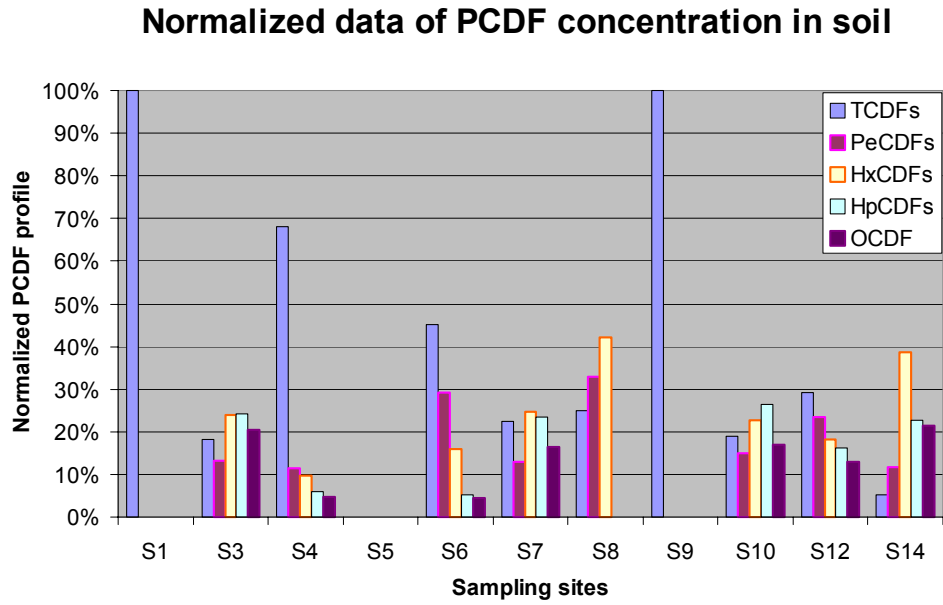


Figure 4. Normalized data of PCDD concentration in soil

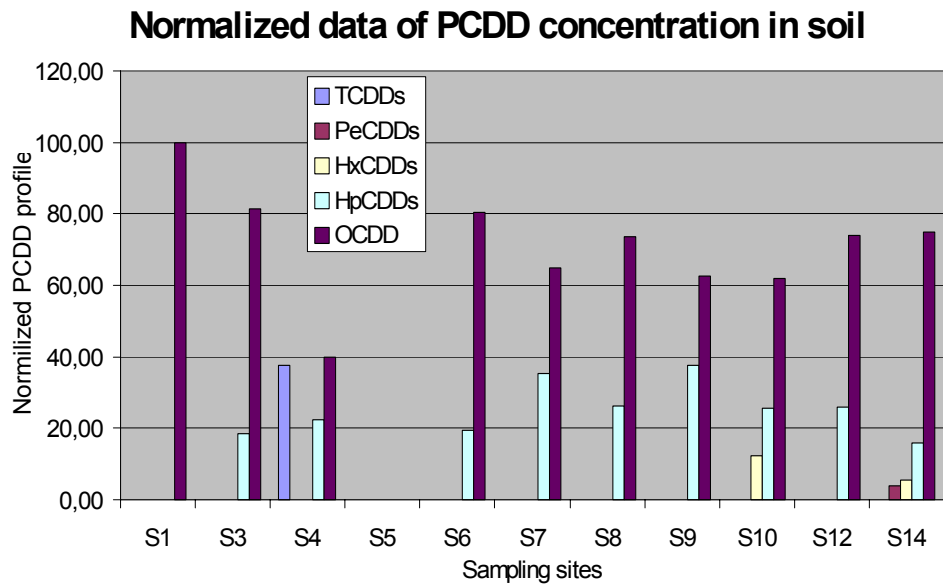


Figure 5. Normalized data of PCDD concentration in soil

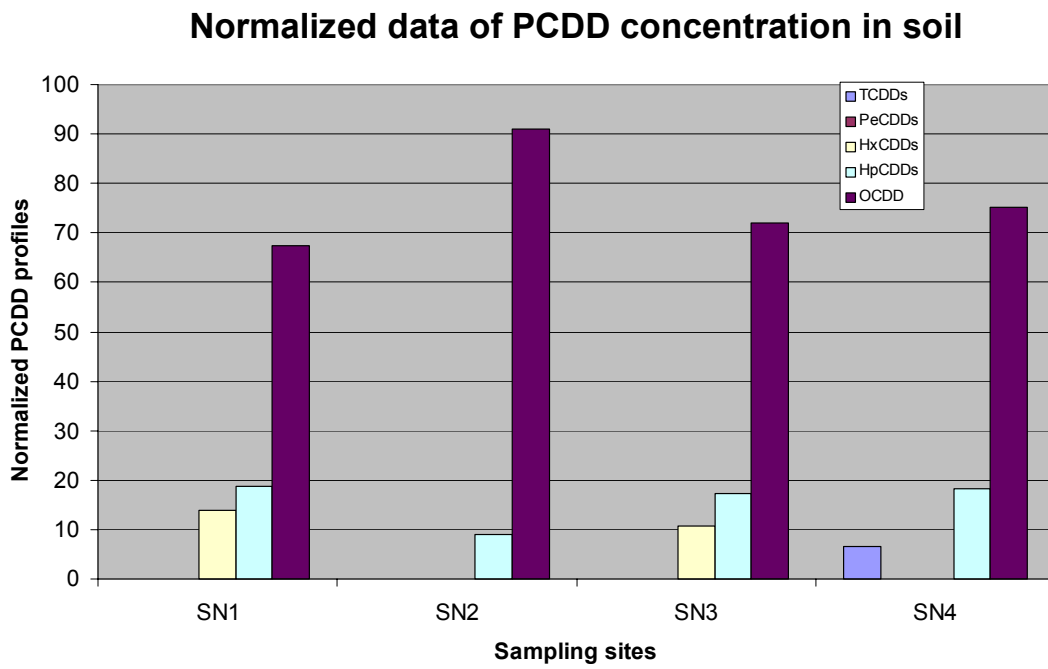
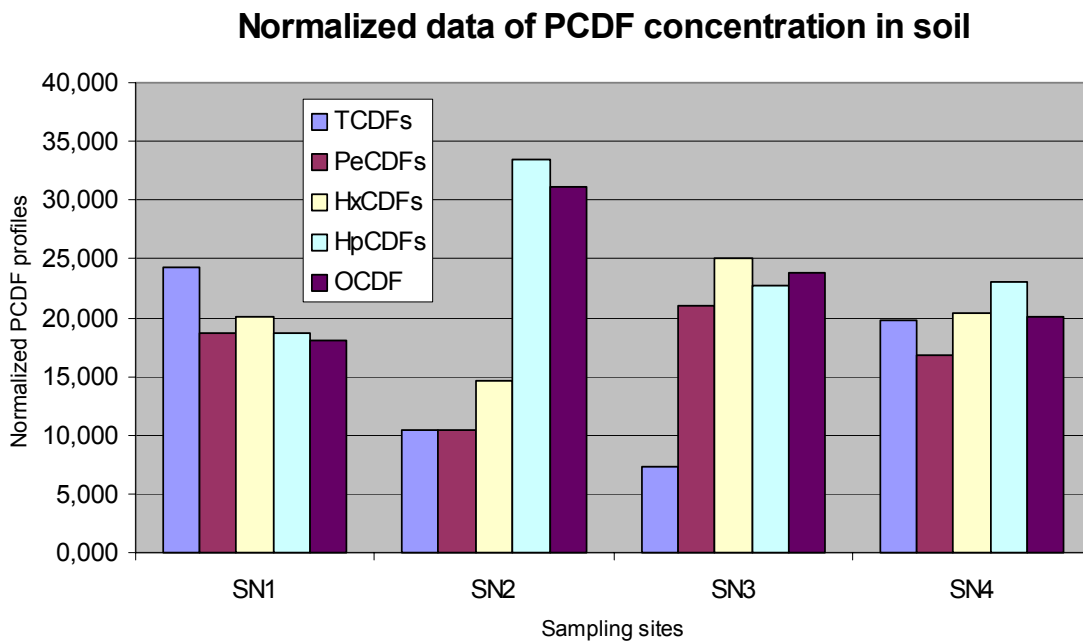


Figure 6. Normalized data of PCDF concentration in soil



Polychlorinated dibenzo-para-dioxins (PCDDs) and dibenzofurans (PCDFs) have received attention over the past two decades as environmental contaminants. PCDD/Fs are recognized as ubiquitous in virtually all compartments of the biosphere. Well established anthropogenic sources include emissions from metallurgical industries, municipal incinerators, pulp and paper mills, and production of numerous commercial chlorinated substances as well as production of chlorine gas itself.

Results obtained for the 18 soil samples are presented in Tables 1,2,3 as the individual and sum of the analytical results for the congeners, expressed in pg/g or pg I-TEQ/g of dry soil. This data is also shown graphically in Figures 1-6. Variations in the PCDD/Fs concentration (pg/g) of individual congeners are found between samples from the different collection areas. One obvious difference in the concentrations of the individual congeners, as well as the total amount of the most toxic congeners, is seen in comparing S14 and S3 with the rest of the samples (Table 1). There further appears in Table 1 a substantial higher concentration (pg/g) of PCDFs sum at sites S4, S6 and S12 than in other sites. The most polluted soil samples (S3, S4, S6, S12 and S14) by PCDF contains all six PCDF congeners as presented in Figure 2.

PCDD/F toxicity will be discussed on the basis of the results for congeners 2,3,7,8-tetraCDD, 1,2,3,7,8-pentaCDD, 1,2,3,6,7,8-hexaCDD, 1,2,3,7,8,9-hexaCDD, 1,2,3,4,6,7,8-heptaCDD, OCDD, 2,3,7,8-tetraCDF, 1,2,3,7,8-penta CDF, 2,3,4,7,8-pentaCDF, 1,2,3,4,7,8-hexaCDF, 123678HxCDF, 234678HxCDF, 123789HxCDF, 1234678HpCDF, 1234789HpCDF, OCDF (Tables 2,3 and 5). They accumulate most efficiently in living organisms and also have the greatest toxicity. The sum of PCDD/Fs (pg I-TEQ/g) in Figure 1 shows considerable differences in the toxicity of samples 1-14. Clearly, the toxicity of sample S14 is the overall highest (592 pg I-TEQ/g of dry soil). It is due mainly to the presents of PCDF (584 pg I-TEQ/g) in the sample. A comparison of normalized PCDF profiles with toxicity data reveals correlation between concentration of amount of two congeners OCDF and HpCDF with toxicity of sample. The data shows that toxicity increase with the increasing of OCDF and HpCDF concentrations.

Laboratory blanks were run for the elimination of background contamination. The quality of the methodology was shown by good recoveries of the spike.

7. Conclusions

Increased concentrations could be detected at some sampling points. Since the samples were pooled from two levels in the ground, the "true" level can be twice higher if all pollution is concentrated to one sampling level. In the case of Köpmanholmen this judgement is difficult to do, since a lot of soil moving has occurred in the past. Dioxins are usually concentrated in the topsoil, but in this case it is not known were the topsoil (from the past) is located.

From the chemical analysis it can also be concluded that at least two sources of dioxins has relevance in the area. Two distinct patterns can be seen in the samples, which indicate two different sources, where one source is the chlorine production step.

A very limited number of samples are taken in the area and the area to cover is relatively large. It is impossible to say that all, or even any, high-polluted places have been found during this study. Effort is made to choose the positions of sampling site by the knowledge of activities in the area. This is maybe not enough to be convinced that all hot

spots (or any) have been identified. Areas with higher concentrations might still remain to be found.

8. Suggestion for further studies

In order to get complete data on the state of the area that was under investigation further studies should be conducted. In the points that contains notable amount of Dioxins we suggest to study the concentration of PCDD/F on different depth to establish gradient in depth scale. Second step would involve investigations in the horizontal direction to look for the spots with highest concentration of Dioxins over polluted places. Furthermore more in hot spots we should verify presents of Dioxins in groundwater using SPMD.