

## PCDD/F CONTAMINATED SOILS IN NORTHERN SWEDEN AS AN OUTCOME OF WOOD PRESERVATION WITH CHLOROPHENOLS

Ylva Persson, Rolf Andersson, Lars Öberg and Mats Tysklind

Environmental Chemistry, Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden

### **Introduction**

Chlorophenols were widely used as a fungicide against blue stained wood in Sweden from the 1930's to the 1970's<sup>1</sup>. This treatment was most commonly done by dipping of freshly sawn timber in a solution containing chlorophenols. During the production of chlorophenol preservatives a number of byproducts are formed among which polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) have received most attention<sup>1-3</sup>.

Even though 25 years has passed since the Swedish stop of wood preservation with chlorophenols, these saw mill areas are sources of ground water contamination and the soil are highly contaminated with a number of chlorinated compounds<sup>4</sup>. This study is a screening of two sites where preservation with chlorophenols has taken place. The aim of the study is to compare the PCDD/F homolog profile and 2,3,7,8-congener patterns as a result of the use of chlorophenol products. The composition of PCDD/Fs has been shown to vary between different sources and the homolog profile of PCDD/Fs can be used to identify the source of contamination<sup>5</sup>.

During the period 1940 – 1978 the wood preservative Ky-5 was used at many saw mills throughout Sweden and Finland (in Finland Ky-5 was produced and used until 1984), and it was used at the two investigated sites. The main chlorophenols were 2,3,4,6-tetrachlorophenol, 2,4,6-trichlorophenol and pentachlorophenol. The composition varied between batches but the ratio between tetra-, tri- and pentachlorophenol was usually 8:1:1<sup>3</sup>. The preservative showed a distinct homolog profile of PCDD/Fs. PCDDs were present at concentrations of 1-5 ppm and PCDFs at 70-150 ppm<sup>1</sup>. Among the PCDFs there was a clear dominance of heptachlorinated dibenzofurans but also high levels of hexa- and octachlorinated dibenzofurans. The PCDDs consisted mostly of the hexa- and heptachlorinated congeners<sup>3</sup>. This pattern distinguishes Ky-5 from other preservatives where pentachlorophenol was the major component; preservatives of that kind have a PCDD/F homolog profile where OCDD is the most abundant congener<sup>5, 6</sup>.

### **Methods and Materials**

Soils from two different contaminated sites (A and B) were analysed. At these two former saw mills, wood preservation by dipping in chlorophenol preservatives took place. Today there are no industrial activities at the sites and the areas are subject to remediation. Soil samples were collected year 2001 and 2002. Each object is represented by five samples from the area of the dipping basin or the storage place. The chlorophenol contamination today is minor, at site A there are residual levels of chlorophenols in the soil and at site B there is a ground water contamination.

The chemical analyses were done according to Tysklind<sup>7</sup>. The soil samples were extracted with toluene during 16 hours using Soxhlet Dean-Stark equipment. Before the extraction internal standards (16 <sup>13</sup>C-labelled PCDD/F-congeners) was added. The clean-up was performed through a multilayered silica column, containing neutral silica, silica mixed with potassium hydroxide and

sulphuric acid, respectively, and a column containing aluminium oxide. The extracts were fractionated on a column with Carbon AX21/Celite. Possible losses during the clean up were estimated with two recovery standards ( $^{13}\text{C}$ -congeners), using the isotope dilution technique.

The analyses were performed with HRGC/HRMS (VG 70-S) and selective ion recording. Quantification of PCDDs and PCDFs was done by comparing native PCDD/Fs and  $^{13}\text{C}$ -standards in the sample with a quantification standard containing known amount of native and  $^{13}\text{C}$ -congeners (quantification standards, internal and recovery standard).

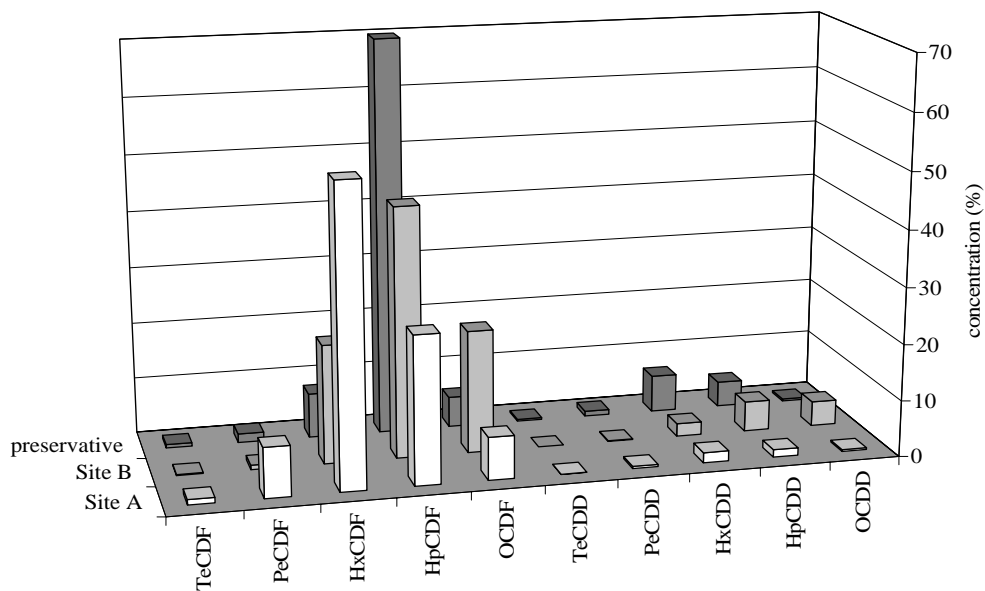
### Results and discussion

Table 1 shows the concentration of PCDD/F of five samples analysed at each site. At site A all samples are from shallow depth and it is not possible to see any trend in the vertical profile. At site B the concentrations are lowest at the deepest sample depth (B 5) which can be a result of declining concentration. The toxic equivalents demonstrate that among sites contaminated with PCDD/Fs from wood preservative Ky-5, it is the less toxic 2,3,7,8-substituted congeners that dominate. Though, the levels are high regardless of which concentration is in focus.

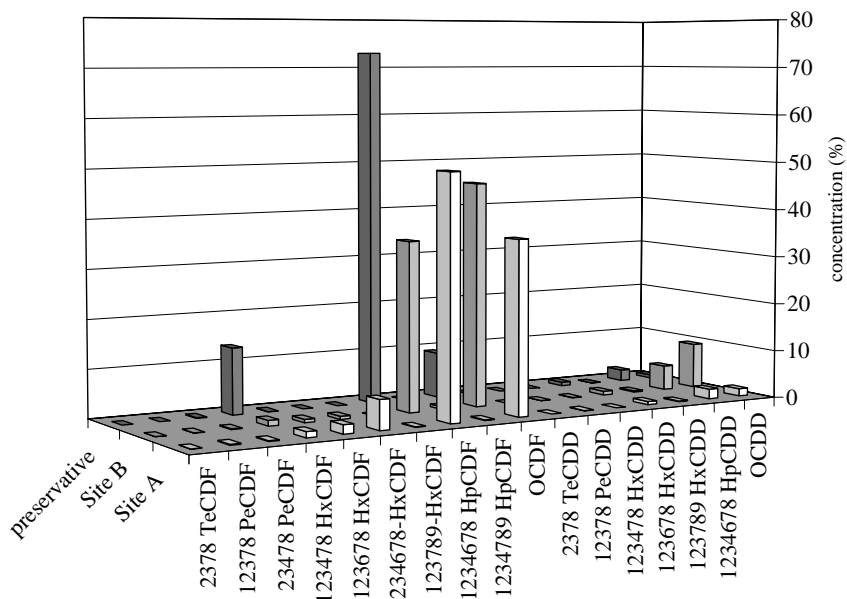
**Table 1. Total concentration of PCDD/Fs, concentration of 2,3,7,8-PCDD/Fs and WHO-TEQs of 2,3,7,8-PCDD/Fs of each analysed sample from the two sites.**

Site	Soil sample	Depth (m)	Total concentration PCDD/Fs (pg/g dw)	Concentration 2,3,7,8-PCDD/Fs (pg/g dw)	WHO-TEQ (pg/g dw)
A	1	0.2-0.3	15 000	9 000	82
	2	0.3-0.4	5 100	2 400	18
	3	0.3-0.4	11 000	6 600	42
	4a	0.2-0.3	220 000	37 000	730
	4b	0.3-0.4	67 000	12 000	290
B	1	0.0-0.5	260 000	120 000	1 100
	2	0.3-1.0	490 000	240 000	2 000
	3	0.5-1.0	1 010 000	490 000	3 900
	4	1.0-1.8	390 000	160 000	2 200
	5	1.7-2.0	5 400	1 900	30

Figure 1 shows correlation of the average homolog profile between the two sites and the preservative Ky-5 that has been used. Data concerning the preservative is according to Vartiainen<sup>8</sup>. Site B shows a good correlation with the preservative, with a large proportion of heptachlorinated as well as hexa- and octachlorinated dibenzofurans. At site A the profile differs somewhat from the preservative; most likely due to a heterogeneous contamination.



**Figure 1. Comparison of homolog distribution of PCDD/Fs at site A and B, and the preservative Ky-5<sup>8</sup>.**



**Figure 2. Distribution of 2,3,7,8-substituted congeners compared with the preservative Ky-5<sup>8</sup>.**

The congener pattern of 2,3,7,8-substituted PCDD/Fs is illustrated in Figure 2. These contribute at site A with approximately 20% of the total amount and at site B with 50% (see Table 1). Both sites correspond proportionally to the preservative with 1,2,3,4,6,7,8-HpCDF most prominent. The amount of 1,2,3,4,7,8-HxCDF and OCDF differs somewhat, the contaminated soils have a higher percent of OCDF and lower percent of 1,2,3,4,7,8-HxCDF than the preservative.

### **Conclusions**

The extensive use of chlorophenols for wood treatment, which took place in Sweden until the 1970's, makes these sites a potentially widespread and significant problem. At the two investigated saw-mill sites in Northern Sweden, the concentration of PCDD/Fs was high. Although the less toxic congeners were most abundant, the total WHO-TEQ values were at site B found to be as high as 1000-4000 pg TEQ/g dw soil. It was possible to verify which preservative was used by studying the homolog profile of the PCDD/Fs. The distinct PCDD/F pattern of Ky-5 was shown in the soil samples analyzed.

### **Acknowledgement**

Data in this study were included with kind permission from Tyréns and Skellefteå municipality. Financial support was received from EUs structural funds, Objective 1. This project is performed within North Sweden Soil Remediation Center (MCN).

### **References**

1. Levin, J. O., Rappe, C., Nilsson, C. A., (1976) *Scandinavian Journal of Work Environment and Health* 2, 71
2. Rappe, C., Buser, H R; (1978) *Chemosphere* 12, 981
3. Assmuth, T., Vartiainen, T; (1994) *Chemosphere*, 28, 971
4. Assmuth, T., Vartiainen, T. (1995) *Chemosphere*, 31 2853
5. Koch, M., Knoth, W., Rotard, W., (2001) *Chemosphere*, 43, 737
6. Hagenmaier, H., Brunner, H., (1987) *Chemosphere*, 16, 1759
7. Tysklind, M., Andersson, R., Rappe, C., Stout, D., (2002) *Organohalogen Compounds*, 57, 345
8. Vartiainen, T., Lampi, P., Tolonen, K., Tuomisto, J.,(1995) *Chemosphere*, 30, 1439