Uptake of PCDDs, PCDFs and non-ortho PCBs in sheep from PCP contaminated sawmill soil

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Introduction

The terrestrial food-chain is susceptible to soil contamination. Soils contaminated with dioxins are often found in connection with wood-processing plants where chlorine and chlorine containing chemicals have been used. The congener and isomer patterns of the PCDDs and PCDFs in the vicinity of a specific plant depend on the technical processes and formulations used. The exposure of Finish sawmill workers to chlorophenol containing antistain agents showed unique profiles of PCDDs and PCDFs which could be related to the wood preservative Ky5, used for 5 decades until the end of the 1980s[1]. In the same way animals grazing on PCDD and PCDF contaminated soils obtain a pattern which reflects the dioxin composition of the soil and the consumption of such food provides a means of transferring this pattern to humans[2]. Deviant profiles from 'normal' and above background levels of TEQs in foods can occasionally be traced to these kinds of local hotspots by comparison of congener and isomer patterns. We compared the PCDD, PCDF and *non-ortho* PCB profile of muscle, fat and liver of sheep feeding at an old sawmill site with the profile of the top soil from the pastureland.

Materials and Methods

Samples

In 2003 and 2004 *soil* was collected (top soil at 0.0-0.02 m and deep soil at 0.2-1.0 m) at the sawmill site for analyses of chlorophenols, PCDDs and PCDFs. An extensive use of pentachlorophenol had taken place on the site from 1940s until 1970. Top soil was collected and pooled from a part used as pastureland. In November 2003 *sheep* that had grazed on the pastureland were slaughtered and sampled for muscle, fat and liver tissue to be analysed for dioxins. Samples were taken from sheep born in April 2003. Thus the exposure of dioxins is due to perinatal (transplacental and lactational) transfer as well as exposure by grazing on contaminated soil. All samples were transported in frozen condition to the laboratory for analyses of dioxin-like compounds and PCBs.

Chemical Analyses

The *soil* samples were analysed by GC-MS for chlorophenols, PCDDs and PCDFs. Levels were reported related to dry matter (105^{0}C) of the samples. Tissues from sheep were analysed for PCDDs, PCDFs, *non-ortho* PCBs and some marker/indicator PCBs. The tissue samples (fat, muscle and liver) were homogenised with Na_2SO_4 and fortified with ^{13}C-labelled internal PCDD, PCDF and *non-ortho* PCB standards. In addition, one laboratory blank sample and one reference (QA/QC) sample were analysed. The compounds were extracted from the tissue homogenates by supercritical fluid extraction (SFE) using CO_2 as extraction media. The dioxin (planar fraction) was obtained by using a PX-21 carbon column after first eluting off the non dioxin-like PCBs, and potential interferences were removed by silica column chromatography[3]. The lipid content of each sample was determined gravimetrically from a sub sample. Congener specific analyses and quantification of the analytes was performed by GC-HRMS, running in SIM mode, by EI ionization. The two most abundant ions of the chlorine cluster of the molecular ion for each compound was measured, as well as the ion for 12 ^{13}C labelled internal standards (IS) and 3 ^{13}C labelled recovery standards (RS).

Results and discussion

Levels in soil

In Table 1 levels in *ng/kg* dry matter (at 105^{0}C) of 2,3,7,8 substituted PCDDs and PCDFs and corresponding TEQs (WHO_{98}) in top soil from the pastureland and in the average of five deep soil samples at various locations on the disused sawmill site, are reported. The Swedish EPA has established recommended standards for use of contaminated soil/land[4]. According to these standards levels of dioxins should not exceed 10 ng TEQ/kg soil when the land is used as pastureland (sensitive land use). In this case the top soil contains ≤ 86 ng TEQ/kg (67 ng TEQ expressed as lower bound). It can also be seen that the 1234678-HpCDF is the congener of the highest concentration (except for OCDD) in both top soil and deeper soils, which indicates that chlorophenol of Ky5 type has

been used in the production[1]. Analyses of 15 chlorophenols in the top soil (Di-, Tri-, Tetra- and Pentachlorophenol) did not reveal traces of any chlorophenol above 0.01 mg/kg. In deeper soil layers however chlorophenols were still found at above the recommended standards by the Swedish EPA (PCP 0.1 mg/kg and total CP 2 mg/kg) for pastureland.

Table 1. Levels (*ng/kg* dry matter at 105^{0}C) of 2,3,7,8 substituted PCDDs and PCDFs in top soil (1 pool) and deep soil (0.2-1.0 m, n=5) in 2003 at a disused sawmill site operating from 1945 to 1970.

Isomer Top soil Top soil Deep soil Deep soil ng/kg ng TEQ/kg ng/kg ng TEQ/kg
2378-TCDF ≤ 3 ≤ 0.3 ≤ 5 ≤ 2.7
12378-PeCDF 18 0.9 ≤ 23 ≤ 1.2
23478-PeCDF 6 3 32 16
123478-HxCDF ≤ 20 ≤ 2 153 15
123678-HxCDF 11 1.1 115 12
234678-HxCDF 14 1.4 14 1.4
123789-HxCDF ≤ 2 ≤ 0.2 ≤ 253 ≤ 25
1234678-HpCDF 460 4.6 9256 93
1234789-HpCDF ≤ 10 ≤ 0.1 204 2
OCDF 160 0.016 7700 1
2378-TCDD ≤ 20 ≤ 20 ≤ 4 ≤ 4
12378-PeCDD ≤ 40 ≤ 40 49 49
123478-HxCDD ≤ 30 ≤ 3 ≤ 60 ≤ 6
123678-HxCDD 67 6.7 561 56
123789-HxCDD ≤ 40 ≤ 4 135 14
1234678-HpCDD 270 2.7 4828 48
OCDD 1400 0.14 16540 2
Σ PCDF/PCDD ≤ 2 571 **≤ 86**[a] ≤ 39 932 ≤ **346**

[a] Upper bound PCDD/F $_{WHO}$-TEQ 86 ng/kg and Lower bound PCDD/F $_{WHO}$-TEQ 67 ng/kg

Levels in sheep

In Table 2 levels of PCDDs, PCDFs, non-ortho PCBs (*pg/g* lipid weight) and PCB #153, #138, #180 and #170/190 (*ng/g* lipid weight) in fat, muscle/mutton and liver of sheep grazing on the contaminated top soil are presented. Lower bound and upper bound toxic dioxin equivalent are calculated for the congener groups and for total PCDDs and PCDFs to be compared with the current EU food and feed regulations for dioxin-like toxicity[5]. When included the *non-ortho* PCBs contribute by 40-50% of the total TEQs. They have also been found in Ky5 type chlorophenol formulas. The levels of a few marker/indicator PCBs were determined, and not found to be elevated.

Table 2. Levels of PCDD, PCDF, *non-ortho* PCB (*pg/g* lipid weight) and PCB #153, #138, #180 and #170/190 (*ng/g* lipid weight) in fat, muscle/mutton and liver of sheep grazing on contaminated soil at a disused sawmill site.

Isomer Fat Liver Muscle
2378-TCDF < 0.06 < 0.40 < 0.10
12378-PeCDF 0.40 < 0.28 < 0.30
23478-PeCDF 0.99 18 1
123478-HxCDF 2.8 47 2.1
123678-HxCDF 1.3 40 1.1
234678-HxCDF 1.2 71 1.1
123789-HxCDF < 0.18 < 0.78 < 0.14
1234678-HpCDF 18 1800 18
1234789-HpCDF 0.28 22 0.35
OCDF 0.55 136 0.67
Lower bound PCDF $_{WHO}$-TEQ 1.3 43 1.1
Upper bound PCDF $_{WHO}$-TEQ 1.3 43 1.2
2378-TCDD 0.13 < 0.29 < 0.19
12378-PeCDD 1.4 2.2 1.2
123478-HxCDD < 0.45 1.5 < 0.40
123678-HxCDD 6.5 11 5.0
123789-HxCDD 1.2 2.2 0.98
1234678-HpCDD 3.6 63 3.6
OCDD 2.5 78 3.3
Lower bound PCDD $_{WHO}$-TEQ 2.4 4.4 1.9
Upper bound PCDD $_{WHO}$-TEQ 2.4 4.6 2.0

Lower bound PCDF/D $_{WHO}$-TEQ	**3.7 47 3.0**
Upper bound PCDF/D $_{WHO}$-TEQ	**3.7 49 3.2**
PCB #77	2.2 13 32
PCB #126	40 126 38
PCB #169	8.1 4.3 10
Lower bound non-o PCB $_{WHO}$-TEQ	*4.1 13 3.9*
Upper bound non-o PCB $_{WHO}$-TEQ	*4.1 13* 3.9
Lower bound sum $_{WHO}$-TEQ	**7.8 60 6.9**
Upper bound sum $_{WHO}$ –TEQ	**7.8 61 7.1**
Non dioxin-like PCBs	
PCB #153	13 15 12
PCB #138	6.9 10 6.5
PCB #180	9.9 8 8.9
PCB #170/180	5.4 5 4.6

The legacy of the extensive use of chlorophenols in Nordic wood processing countries is today still seen in the uptake and introduction of dioxins into the marine as well as the terrestrial food chain. It can be concluded that uptake by sheep grazing on pastureland contaminated with dioxins at a level of Σ PCDF/PCDD corresponding to 67-86 ng $_{WHO98}$TEQ /kg in top soil will result in levels in the meat (mutton) and fat close or above the maximum limit levels, 3 pg TEQ/g fat, set by EU. In the liver levels will far exceed the maximum levels 6 pg TEQ/g fat. The action levels are 2/3 of maximum levels and should be used as early warning and trigger action on source identification and measures for elimination. It is therefore advisable not to use pasturelands contaminated above the Swedish recommended level of 10 ng TEQ/kg soil for sheep farming. However, from the consumers' point of view, a portion of 150 g mutton, at the maximum limit of 3 pg/g fat, compared to consumption of 150 g Baltic salmon or herring, at the maximum limit of 4 pg/g fish, correspond to total TEQ intakes of 45 pg versus 600 pg.

References

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