Airborne chlorinated dioxins and furans in a pulp and paper mill

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Introduction

The formation of a range of chlorinated compounds during chlorine bleaching of kraft pulp is widely recognized[1]. The bleaching plant is the indisputable source of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in pulp and paper production. The levels of PCCDs/PCDFs in pulp and pulp mill effluents have been determined in numerous studies[2,3]. Yet, few studies have addressed the levels of PCDDs/PCDFs in the occupational environment in the pulp and paper industry[4]. In the present study concentrations of 2,3,7,8-substituted PCDDs/PCDFs in the workplace air were measured at a bleaching plant and paper and paperboard production lines of a paper mill.

Experimental

Pulp and paper mill characteristics and sampling locations. Softwood and hardwood pulp was bleached in a conventional five-stage bleaching sequence utilizing only chlorine dioxide at the first chlorination stage. The paper mill produced paperboard with three machines and paper with one machine. Samples were collected at the softwood bleaching plant, at two paperboard machines and at the paper machine. The first paperboard production line used a mixture of 50 % softwood and 50 % hardwood pulp. The second paperboard production line used a mixture of 13 % softwood pulp, 54 % hardwood pulp and 33 % broke. The paper production line used a mixture of 30 % softwood, 30 % hardwood and 40 % eucalyptus pulp.

Air sampling and sample treatment. Workplace air was sampled using a method developed by the Norwegian Institute of Air Research[5]. The sampler (Type II) was equipped with a glass fibre filter and two polyurethane foam (PUF) plugs. The glass fibre filters (Type A/E, 76 mm O.D., Gelman Sciences, Ann Arbor, MI, USA) were heated at 400 °C in a muffle furnace for 4 h before use. The flexible PUF with a density 25 kg/m^3 was cut into plugs measuring 10 cm in length and 6 cm in diameter (D.P. Sunde & Co.,

1903 Gan, Norway). The PUF plugs were precleaned by repeated squeezing in toluene at 90-100 °C, in acetone and in hexane:diethylether (1:1) and then Soxhlet-extracted with toluene for 24 hours. The plugs were dried at 100 °C and stored in tightly wrapped aluminum foil until used. Prior to sample collection, the glass fibre filter was spiked with ^{37}Cl-labelled 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) to determine the sampling efficiency and possible breakthrough to the second PUF plug. Air samples of approximately 100 m^3 were collected at a sampling rate of 0.07 m^3/min.

PCDDs and PCDFs were isolated by concurrent Soxhlet-extraction of the glass fibre filter and the first PUF plug with dichloromethane for 12 h. The second PUF plug was similarly extracted. Before extraction, analytical $^{13}C_{12}$-labelled 2,3,7,8-substituted recovery standards were added to the PUF plug. The samples were purified in a three-step column chromatography procedure using sulphuric acid impregnated silica gel, activated carbon (Carbopack) and acid alumina. The method is a modification of the procedure reported by Swanson[2]. The final extract was evaporated to dryness and reconstituted in 10 µl of nonane containing $^{13}C_6$-labelled 1,2,3,4-TCDD as an internal standard.

Gas chromatography-mass spectrometry. Gas chromatographic separation was carried out on SP 2331 (Supelco, 60 m x 0.20 mm I.D., 0.25 µm film thickness) and HP-5 (Hewlett-Packard, 50 m x 0.32 mm I.D., 0.32 µm film thickness) columns. Mass spectrometric analyses were done both in electron impact (VG Autospec, mass resolution 10 000:1) and negative ion chemical ionization mode (HP-5989A MS Engine quadrupole mass spectrometer). Quantitation was performed using the multiple ion monitoring technique.

Results and Discussion

The clean-up of the glass fibre filter and PUF plugs removed effectively any interfering compounds and produced no procedural background. The retention capacity of the PUF adsorbent for PCDDs/PCDFs has been shown to be adequate[6]. The migration of the 2,3,7,8-substituted PCDDs/PCDFs congeners from the glass fibre filter to the PUF adsorbent is dependent upon the chlorination level, with the less chlorinated, more volatile isomers generally desorbing more efficiently. Our results showed that the ^{37}Cl-labelled 2,3,7,8-TCDD used as a sampling spike did not migrate from the first PUF plug to the second.

No attempt was made to distinguish between gaseous and particulate phases and hence the results represent substances captured by the glass fibre filter and first PUF plug. We report findings either as concentrations, as not quantified (nq) or as not detected (nd), according to the criteria for reporting results incorporated in the quality assurance programme by Patterson *et al.*[7]. The limit of detection was in the sub pg/m^3 range for sample sizes of approximately 100 m^3.

The mean recovery (after extraction and purification) of the $^{13}C_{12}$-labelled standards from the glass fibre filter and PUF plug was 91 % (SD 6 %, range 77-98 %, n=14). The concentrations of 2,3,7,8-PCCDs/PCDFs in air ranged from 0.04 to 1.9 pg/m^3 at the pulp

and paper mill (Table 1). Few chlorinated dioxins were detected, the chlorinated furans being the major component in all samples. No 2,3,7,8-TCDD was detected. 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) was detected at all sampling locations, except the dry end at the second paperboard machine. The highest concentration of a single isomer, 1.9 pg/m^3 for 1,2,3,4,6,7,8-heptachlorodibenzofuran (1,2,3,4,6,7,8-HpCDF), was found at the slitting machine of the first paperboard production line. This isomer was present in all samples. The lowest concentrations were detected at the dry end of the second paperboard machine. Analysis of paper dust collected at the slitting machine confirmed the congener profile detected. The PCDD/PCDF airborne toxic equivalent concentrations, using the toxic equivalency factors proposed by Safe[8], ranged from 0.02 to 0.30 pg/m^3. The highest value was obtained for a sample collected at the slitting machine of the first paperboard production line.

Conclusions

Although the airborne levels were mostly low, a potential for inhalation exposure to PCDDs and PCDFs did exist at the bleaching plant and paper mill.

References

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Table 1. Ranges of PCDD/PCDF concentrations (pg/m^3) in air samples collected during pulp and paper production

	SAMPLING LOCATION							
^{12}C-congener	A (n = 2)	B1 (n = 2)	B2 (n = 4)	C1 (n = 1)	C2 (n = 1)	D1 (n = 1)	D2 (n = 2)	D3 (n = 1)
2378-TCDD	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.1)	nq (0.1)	nd (0.1)	nd (0.1)	nd (0.1)
12378-PnCDD	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.1)	nd (0.2)	nd (0.1)
123478-HxCDD	nd (0.04)	nd (0.1)	nd (0.1)	nd (0.08)	nd (0.07)	nd (0.1	nd (0.1)	nd (0.07)
123678-HxCDD	nd (0.07)	nq (0.2)	0.06-0.08	0.12	nd (0.08)	nd (0.1)	nd (0.1)	nd (0.08)
123789-HxCDD	nd (0.06)	nd (0.2)	nd (0.2)	nd (0.15)	nd (0.13)	nd (0.2	nd (0.2)	nd (0.1)
1234678-HpCDD	nq (0.2)	0.37(nq 0.2)	0.16-0.37	nd (0.2)	nd (0.15)	0.1	0.22(nd 0.3)	nd (0.2)
2378-TCDF	0.49-0.64	0.4	0.17-0.41	0.26	nq (0.04)	0.28	0.38-0.41	0.2
12378-PnCDF	0.10-0.15	nq (0.05)	nq (0.04)	nd (0.02)	nd (0.2)	nq (0.1)	nq (0.07)	nq (0.03)
23478-PnCDF	0.16-0.21	0.14-0.17	0.04-0.13	nd (0.03)	nd (0.02)	nd (0.03)	0.08- 0.09	0.07
123478-HxCDF	0.10-0.14	0.14-0.16	0.10-0.01	0.08	nd (0.04)	nq (0.04)	nq (0.1)	0.04
123678-HxCDF	nd (0.01)	0.06(nq 0.04)	nq (0.05)	nd (0.04)	nd (0.03)	nd (0.04)	nq (0.1)	nq (0.04)
123789-HxCDF	nd (0.05)	nd (0.05)	nd (0.05)	nd (0.04)	nd (0.04)	nd (0.05)	nd (0.05)	nd (0.04)
234678-HxCDF	nq (0.01)	nd (0.01	nd (0.1)	nd (0.01)	nd (0.1)	nd (0.13)	nd (0.3)	nd (0.16)
1234678-HpCDF	0.17-0.19	0.68-1.1	0.33-1.9	1.3	0.23	0.47	0.85-0.95	0.62
1234789-HpCDF	nd (0.09)	nd (0.1)	nd (0.1)	nd (0.14)	nd (0.13)	nd (0.2)	nd (0.2)	nd (0.12)
OCDF	nd (0.2)	nd (0.1)	0.48-1.3	0.33	nd (0.17)	0.17	0.5	0.36

A = softwood bleaching plant; B1 = paperboard production line I; wire section; B2 = paperboard production line I, slitting machine; C1 = paperboard production line II, wire section; C2 = paperboard production line II, dry end; D1 = paper production line, wire section; D2 = paper production line, dry end; D3 = paper production line, slitting machine.
n = number of samples; nd = not detected, value in parentheses denotes limit of detection; nq = not quantified, value in parentheses denotes limit of quantification; TCDD/TCDF = tetrachlorodibenzo-*p*-dioxin/dibenzofuran; PnCDD/PNCDF = pentachlorodibenzo-*p*-dioxin/dibenzofuran; HxCDD/HxCDF = hexachlorodibenzo-*p*-dioxin/dibenzofuran; HpCDD/HpCDF = heptachlorodibenzo-*p*-dioxin/dibenzofuran; OCDD/OCDF = octachlorodibenzo-*p*-dioxin/dibenzofuran.