



## Airborne chlorinated dioxins and furans in a pulp and paper mill

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### ABSTRACT

The concentrations of airborne 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins and dibenzofurans measured at a pulp and paper mill ranged from 0.04 to 1.9 pg/m<sup>3</sup>. The paper mill used softwood and hardwood pulp which was bleached with solely chlorine dioxide in the first chlorination stage. The chlorinated furans dominated in all samples, while very few dioxins were detected. No 2,3,7,8-tetrachlorodibenzo-*p*-dioxin was detected. The highest concentration was measured for 1,2,3,4,6,7,8-heptachlorodibenzofuran, which was present in all samples. The toxic equivalent concentrations varied between 0.002 and 0.2 pg/m<sup>3</sup> using the international toxic equivalency factors. The congener profile of a paper dust sample was similar to that of the corresponding air samples.

### INTRODUCTION

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

## EXPERIMENTAL

### Pulp and Paper mill characteristics and sampling sites

Softwood and hardwood pulp was bleached in a conventional five-stage bleaching sequence utilizing only chlorine dioxide at the first chlorination stage<sup>5</sup>. In a modification of the sequence a peroxide or oxygen treatment was applied after the first alkaline treatment combined with hypochlorite. This was followed by two sequential alkaline and chlorine dioxide treatments. The paper mill produced paperboard with three machines and paper with one 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 samples were collected at the first chlorination stage in the softwood bleaching plant and at the wire section, dryer section and the slitting machine, in the paper mill. Paper dust was also collected from the surface of the slitting machine.

### Air sampling and sample treatment.

Workplace air was sampled with a method developed by the Norwegian Institute of Air Research<sup>6</sup>. 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 precleaned filters were wrapped in aluminium foil and stored in a desiccator before use. The flexible PUF with a density of 25 kg/m<sup>3</sup> was cut into plugs 10 cm long 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 v/v) and then Soxhlet-extracted with toluene for 24 h. The plugs were dried at 100 °C and stored in wrapped aluminium foil until used. The filter was placed in an aluminium filter holder attached to a glass cylinder (Quickfit; Corning Process Systems Cat. Ref. PS/300, Staffordshire, Great Britain) housing the two polyurethane plugs.

Prior to sample collection, the glass fibre filter was spiked with <sup>37</sup>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<sup>3</sup> were collected at a sampling rate of 0.07 m<sup>3</sup>/min, i.e. the sampling time was approximately 24 h. The process both at the pulp and paper mill operated continuously in three 8-h work shifts.

PCDDs and PCDFs were isolated by concurrent Soxhlet-extraction of the glass fibre filter and the first PUF plug with dichloromethane for 12 h. Before extraction, analytical <sup>13</sup>C<sub>12</sub>-labelled 2,3,7,8-substituted recovery standards were added to the PUF plug. The second PUF plug was similarly extracted. The dichloromethane extract was exchanged into n-hexane with a TurboVap evaporator (Zymark Corporation, Hopkinton, MA, USA). The paper dust sample (5 g) was extracted as described for the air samples.

The n-hexane extract was 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 described by Swanson<sup>2</sup>. The chromatography columns (30 cm x 6 mm I.D.) were equipped with a 70 ml reservoir. Column 1 was packed with 1.5 g of 40 % (w/w) concentrated sulphuric acid (ultra pure) on solvent-washed (methanol, dichloromethane) silica gel (Machery & Nagel, Kieselgel 60, 70-230 mesh) and 0.5 g of solvent-washed, activated (140 °C) silica gel. Column 2 was packed with 0.8g of activated (140 °C) 18 % (w/w) Carbopack C (Supelco) on Celite 545 (Fluka). Column 3 was packed with 1 g of solvent-washed and activated (200 °C) acidic aluminium oxide (Bio-Rad, AG-4). All columns contained, at the bottom and the top of the adsorbent, a 4-5 mm layer of solvent-washed (hexane, dichloromethane) and activated (200 °C) sodium sulphate. Columns 1, 2 and 3 were conditioned before use with n-hexane, toluene - n-hexane:dichloromethane (1:1, v/v) - n-hexane and n-hexane, respectively.

The concentrated sample (1 ml) was applied to the first column followed by three 1 ml n-hexane washes and eluted with 20 ml of n-hexane. The whole n-hexane portion was eluted through the carbon column followed by 4 ml of a mixture of n-hexane and dichloromethane (1:1, v/v). This eluate was discarded. The PCDDs and PCDFs were eluted from the carbon column with 70 ml of toluene. The toluene eluate was exchanged into n-hexane and the concentrate (1 ml) applied to the third, alumina, column followed by two 1 ml n-hexane washings and 7 ml of n-hexane. The PCDDs and PCDFs were eluted with 12 ml of a mixture of n-hexane and dichloromethane (1:1, v/v). The final extract was evaporated to dryness and reconstituted in 10 µl of nonane containing <sup>13</sup>C<sub>6</sub>-labelled 1,2,3,4-TCDD as an internal standard.

### Gas chromatography-mass spectrometry

Gas chromatographic separation was carried out on a) SP 2331 (Supelco, 60 m x 0.20 mm I.D., 0.25 µm film thickness) and b) HP-5 (Hewlett-Packard, 50 m x 0.32 mm I.D., 0.17 µm film thickness) columns. The column temperature programs were a) 2 min at 100 °C, increased from 100 °C to 220 at 20 °C/min, 2 min at 220 °C, increased from 220 °C to 250 at 15 °C/min, 1 min at 250 °C, increased from 250 °C to 270 °C at 1 °C/min and held at 270 °C for 30 min; and b) 2 min at 160 °C, increased from 160 °C to 300 °C at 3 °C/min and held for 2 min at 300 °C. Splitless injection on a Grob-type split-splitless injector operating at 260 °C and a splitless period of 0.5 min was used.

Mass spectrometric analyses were done both in electron impact (VG Autospec Q, mass resolution 10 000:1) and negative ion chemical ionization (NCI) (HP-5989A MS Engine quadrupole mass spectrometer) modes. The Autospec Q mass spectrometer was operated with an ionization energy of 30 eV, a source temperature of 250 °C and transfer line temperature of 270 °C. The quadrupole mass spectrometer was run with methane as reactant gas and the temperature of the transfer line, ion source and quadrupole was 300 °C, 150 °C and 100 °C, respectively.

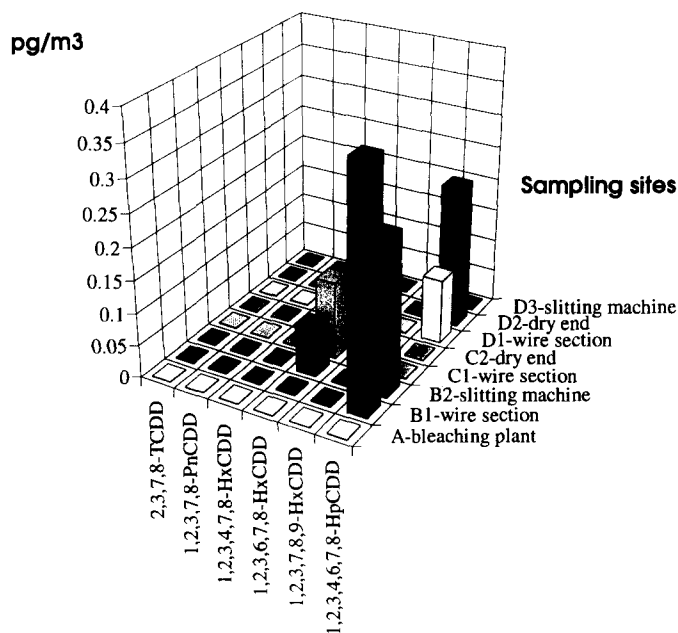
Quantitation was performed using the isotope dilution technique<sup>7</sup> in the multiple ion mode. NCI mass spectra were recorded for confirmation of the isotope cluster of the quantified hexa-, hepta- and octachlorinated congeners. The recorded mass range for the mass spectra covered  $M^{\cdot-} - 4$  and  $+ 10$  a.m.u.

## RESULTS AND DISCUSSION

The cleaning 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<sup>8</sup>. 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 <sup>37</sup>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 the 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 of Patterson *et al.*<sup>9</sup>. The detection limit was in the sub pg/m<sup>3</sup> range for sample sizes of approximately 100 m<sup>3</sup>. The mean recovery (after extraction and purification) of the <sup>13</sup>C<sub>12</sub>-labelled standards from the glass fibre filter and PUF plug was 91 % (SD 6 %, range 77-98 %, n=14).

The air sample results are presented in Table 1 along with the detection limits. The concentrations of 2,3,7,8-PCDDs/PCDFs in air ranged from 0.04 to 1.9 pg/m<sup>3</sup> at the pulp and paper mill. Few chlorinated dioxins were detected, in fact only two congeners were quantified, i.e. the 1,2,3,6,7,8-hexa- and the 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin. It is noteworthy that no 2,3,7,8-TCDD was detected. Moreover, no chlorinated dioxins were detected at the bleaching plant. The congener profile of the dioxins is shown in Figure 1.



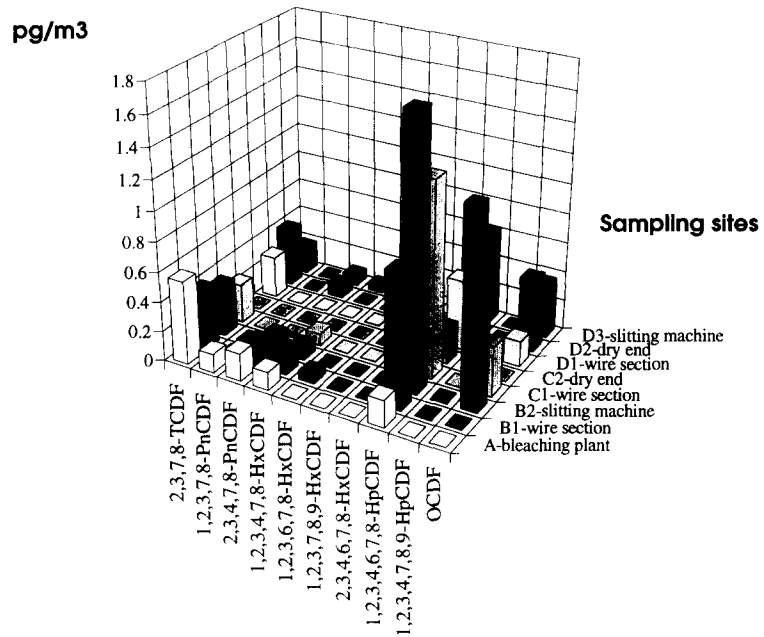
**Figure 1.** Congener profile of the chlorinated-*p*-dioxins at the different sampling sites. The sampling sites are explained in Table 1.

Table 1. Ranges of PCDD/PCDF concentrations (pg/m<sup>3</sup>) in air samples collected during pulp and paper production and in paper dust (pg/g) collected at the slitting machine in the paper mill.

| <sup>12</sup> C-congener | SAMPLING SITES |               |               |               |               |               |               |               | Paper dust<br>pg/g |
|--------------------------|----------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|--------------------|
|                          | A<br>(n = 2)   | B1<br>(n = 2) | B2<br>(n = 4) | C1<br>(n = 1) | C2<br>(n = 1) | D1<br>(n = 1) | D2<br>(n = 2) | D3<br>(n = 1) |                    |
| 2378-TCDD                | nd (0.1)       | nd (0.1)      | nd (0.1)      | nd (0.1)      | nd (0.1)      | nd (0.1)      | nd (0.1)      | nd (0.1)      | 0.1                |
| 12378-PnCDD              | nd (0.1)       | nd (0.1)      | nd (0.1)      | nd (0.1)      | nd (0.1)      | nd (0.1)      | nd (0.1)      | nd (0.1)      | nq (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)     | nd (0.1)           |
| 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)     | 190                |
| 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)      | 60                 |
| 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)      | 350                |
| OCDD                     | nd (0.2)       | nd (0.2)      | nd (0.2)      | nd (0.4)      | nd (0.3)      | nd (0.4)      | nd (0.4)      | nd (0.3)      | 900                |
| 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           | 55                 |
| 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)     | 13                 |
| 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          | 30                 |
| 123478-HxCDF             | 0.10-0.14      | 0.14-0.16     | 0.01-0.1      | 0.08          | nd (0.04)     | nq (0.04)     | nq (0.1)      | 0.04          | 55                 |
| 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)     | 22                 |
| 123789-HxCDF             | nd (0.3)       | nd (0.1)      | nd (0.1)      | nd (0.01)     | nd (0.1)      | nd (0.13)     | nd (0.3)      | nd (0.16)     | 6.4                |
| 234678-HxCDF             | nq (0.05)      | nd (0.05)     | nd (0.05)     | nd (0.04)     | nd (0.04)     | nd (0.05)     | nd (0.05)     | nd (0.04)     | 28                 |
| 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          | 4200               |
| 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)     | 32                 |
| OCDF                     | nd (0.2)       | nd (0.1)      | 0.48-1.3      | 0.33          | nd (0.17)     | 0.17          | 0.5           | 0.36          | 3200               |

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, values in parentheses denote limit of detection; nq = not quantified, values in parentheses denote 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.

Chlorinated furans were the major component in all samples. 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) was detected at all sampling sites, except at the dry end of the second paperboard machine. The highest concentration of a single isomer, 1.9 pg/m<sup>3</sup> 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. The congener pattern of the chlorinated furans is presented in Figure 2.



**Figure 2.** Congener profile of the chlorinated furans at the different sampling sites. The sampling sites are explained in Table 1.

Other than 2,3,7,8-substituted congeners were also detected. These congeners were tentatively identified by comparison with reference chromatograms<sup>10</sup> and recording of the typical ion cluster for the respective regions. The congeners were the 1,3,4,6,7,8 + 1,2,4,6,7,8-, 1,2,4,6,8,9-hexa- and the 1,2,3,4,6,7,9-heptachloro furans. In addition, traces of the 1,2,7,8- and 2,3,6,7-TCDFs were observed. The concentrations, however, were too low to allow confirmation of their identity by isotope cluster monitoring.

Analysis of the paper dust collected at the slitting machine of the first paperboard production line confirmed the congener profile detected in the air sample of the paper mill. Four of the 2,3,7,8-substituted dioxins and all 10 2,3,7,8-substituted furans were, in fact, quantified in the dust sample. The concentrations ranged from the low pg/g to ng/g level (Table 1).

The PCDD/PCDF toxic equivalent concentrations, using the international toxic equivalence factors<sup>11</sup> ranged from 0.002 to 0.2 pg/m<sup>3</sup>. The highest value was obtained for a sample collected at the softwood bleaching plant followed by a sample from the slitting machine of the first paperboard production line. Our results are in the same order of magnitude as those reported by Crandall *et al.*<sup>4</sup>, 0.01 to 0.06 pg/m<sup>3</sup>, although these latter samples were analyzed only for the TCDD and TCDF congeners.

### CONCLUSIONS

The concentrations of airborne chlorinated dioxins and furans were mostly low. Nevertheless, potential inhalation exposure to PCDDs and PCDFs did exist at the bleaching plant and the paper mill.

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