THE FORMATION OF POLYCHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS FROM THE BLEACHING OF NEW ZEALAND PINUS RADIATA

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ABSTRACT

Analysis of oxygen delignified, bleached, New Zealand radiata pine kraft pulp for PCDDs and PCDFs has shown a reduction in the levels of these contaminants occurs with a decreasing chlorine multiple. However, the TCDD and TCDF isomer profiles observed are ones not normally associated with the chlorine bleaching of pulp. Instead these profiles are composed primarily of non 2,3,7,8- isomers, with, for the TCDFs, the 2,3,4,8- isomer dominating.

INTRODUCTION

The formation of PCDDs and PCDFs from the chlorine bleaching of pulp, and with the TCDF isomers in a characteristic 1,2,7,8-, 2,3,7,8-, 1,2,8,9- profile, is now well established (1-3). It is also recognised that by decreasing the chlorine multiple significant reductions in PCDD and PCDF formation can be effected (4,5). This paper reports on the bleaching of the soft wood Pinus Radiata at varying chlorine multiples and the observation of atypical TCDD and TCDF "chlorine bleach isomer profiles".

EXPERIMENTAL

Industrial kraft pulp from radiata pine at 27 kappa number (~4.0% lignin content) was oxygen delignified in the laboratory to 15.6 kappa number. Oxygen treated pulp was washed thoroughly to remove all dissolved material, dewatered and stored at 4°C. Prior to chlorination the moisture free pulp was adjusted to pH 2.0 by sulphuric acid addition. Aqueous solutions of chlorine and chlorine dioxide were added simultaneously to the pulp and the system reacted for 45 minutes at 35°C and 2.5% pulp concentration. The active chlorine content of the chlorine dioxide comprised 30% of the total applied. Bleaching was carried out at chlorine multiples of 0.16 (trial 1), 0.19 (trial 2), 0.22 (trial 3) and 0.25 (trial 4). A blank chlorination was also performed without active chemical application. Following the reaction, pulp was washed with deionised water then dewatered to 20% pulp concentration. Pulp samples for analysis were dried (33°C), spiked with $^{13}C_{12}$ surrogate standards subject to Soxhlet extraction and purified from acid modified silica, silica, alumina and carbon on Celite. Analysis was by high resolution gas chromatography-mass spectrometry on a VG 70 250S mass spectrometer with a VG 11-250J data system and a Hewlett-Packard 5890A gas chromatograph. Ionisation was by EI (28 eV) with a mass resolution of 10,000 (10% valley). Chromatography used a 30 m DB-5 and 60 m SP2331. Quality assurance criteria with respect to chromatographic retention times (±1 sec on $^{13}C_{12}$ standards and ±2 sec on external standards), chlorine cluster ratios (±10%) and $^{13}C_{12}$ recoveries have been applied.

RESULTS AND DISCUSSION

Levels of TCDDs and TCDFs quantified and the total toxic equivalents determined for the four bleached pulp samples (trials 1 to 4) and the blank pulp sample examined are reported in Table 1. Not unexpectedly, the blank pulp had the lowest PCDD and PCDF levels quantified. Further more, and consistent with other studies (4,5), a notable reduction was observed in the amounts of PCDDs and PCDFs formed from chlorine bleaching with a decreasing chlorine multiple.

Most surprisingly however, the 2,3,7,8-TCDF isomer was found only as a minor component of the TCDF profile. Instead the profile observed was one of primarily non 2,3,7,8-TCDF isomers, with the 2,3,4,8- isomer dominating. The formation of 1,2,7,8- and 2,3,7,8-TCDF has been associated with, *inter alia*, the chlorination of dibenzofuran (6). However, this mechanistic pathway cannot account for the formation of the 2,3,4,8-TCDF isomer, particularly when compared to the relative amounts of 2,3,7,8-TCDF formed. In addition, the TCDD profile was also dominated by non 2,3,7,8- isomers and particularly at lower chlorine multiples. The potential precursors and mechanistic routes to these isomers, which till now have not been associated with chlorine bleaching, will be discussed.

Table 1. PCDDs and PCDFs from the chlorine bleaching of Pinus Radiata, (ppt, dry weight basis).

Congener	Blank (a)	Trial 1 (0.16)#	Trial 2 (0.19)#	Trial 3 (0.22)#	Trial 4 (0.25)#
2,3,7,8-TCDF	<0.1	<0.2	0.099	0.89	2.2
1,2,7,8-TCDF	<0.07	<0.06	0.096	0.68	1.2
2,3,4,8-TCDF	ND	ND	1.2	2.4	10.0
Non 2,3,7,8-TCDF*	<0.07	1.6	1.3	1.5	11.0
2,3,7,8-TCDD	<0.08	<0.1	0.27	0.71	2.4
Non 2,3,7,8-TCDD	0.51	1.2	2.2	2.2	3.6
Total TE (NATO)	0.35	0.48	1.07	1.77	4.26

* For trials 2, 3 and 4 excludes 1,2,7,8- and 2,3,4,8-TCDF
For the blank and trial 1 excludes only 1,2,7,8-TCDF
a No active chemical application
Chlorine multiple in parenthesis
ND Not determined isomer specifically on SP 2331 capillary column

Under the most favourable bleaching conditions (trial 1) the principal contributors (71%) to the total TE of the sample was found to come from the penta- and hexa- congener groups. This compares to that of trial 4 where the tetra isomers account for 61% of the total TE and the PeCDDs/Fs and HxCDDs/Fs only 36%. Sources of these higher chlorinated congeners will also be discussed.

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