

## Formation of Chloroaromatics at a Metal Reclamation Plant and Efficiency of Stack Filter in their Removal from Emission

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### 1. Introduction

In 1990, sampling and emission analyses of polychlorophenols (PCP's), polychlorobiphenyls (PCB's), polychlorodibenzo-p-dioxins (PCDD's) and polychlorodibenzofurans (PCDF's) were done from seven different processes at a large metal reclamation plant in Heinola, South Finland<sup>1)</sup>. The results showed that emissions of PCP's, PCDD's and PCDF's from some processes, especially from aluminium smelter, turning dryer and car shredder, were of concern. After these studies, technical improvement of processes and gas cleaning were undertaken to decrease and control emissions of these and other chloroaromatic substances.

In order to study whether the emissions had been decreased, new samples were taken from aluminium smelting and car shredding in 1993. PCP's, PCB's, PCDD's and PCDF's, polychlorobenzenes (PCBz's), polychloronaphthalenes (PCN's), polychlorodiphenyl ethers (PCDE's), polychlorodibenzothiophenes (PCDT's) and polychlorothianthrenes (PCTA's)<sup>2)</sup> were analyzed. Simultaneously, also environmental samples in the vicinity of the factory were studied (will be reported separately).

### 2. The Metal Reclamation Processes Analyzed

In aluminium smelting (ALS) there are two different lines: rotary-furnace-line and induction-furnace-line. In the rotary-furnace-line, sodium/potassium-chloride salt is used as flux. Raw materials in the rotary-furnace-line are floated aluminium, dried turnings, aluminium sheets and aluminium dross. After injection of dry calcium hydroxide the gases from smelting go to a cooler and to a baghouse filter. Gases are blown out through a 42 m high stack. The process phases controlled were dust temperatures before and after the baghouse filter as well as the composition of the input (scrap aluminium) into the smelting furnaces.

In car shredder (CSH) old cars are crushed with a big hammer mill. Resulting "crush" is taken to a screening system (wind screen, magnet), where the light and heavy fraction and magnetic and non-magnetic metals are separated. The dust, light particulates and gases from the crushing process are led through a cyclon and scrubber and the cleaned gases are released through a 10 m high ventilation pipe.

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## 3. Sampling and Emission Analysis

Sampling of the stack emissions was made by SNV method<sup>3</sup>. Stack samples were collected four times in 1993 from emissions of aluminium smelter (ALS; before and after baghouse filter) and from emissions of car shredder (CSH; before and after scrubber). The samples were taken by a consulting company (P. Ristola Oy) and analyzed (particles and vapors together) by the Universities of Kuopio and Jyväskylä. Analysis methods have been described previously<sup>2,4-6</sup>.

## 4. Results and Discussion

Fifteen different congeners of chlorophenols (PCP's; P = 2-5) were detected in stack of ALS. Major components were 2,4-dichlorophenol (35-75 % of total), 2,4,6-trichlorophenol (20-46 %), 2,3,4,6-tetrachlorophenol (2.3-11.5%) and pentachlorophenol (0.8-4.9%). Average (N=4) total chlorophenol emission before filter was SPCP =  $64 \pm 26 \mu\text{g}/\text{m}^3$  and after filter  $37 \pm 34 \mu\text{g}/\text{m}^3$  (filtering recovery 43%). In CSH samples PCP's were mainly below the limit of determination ( $0.1 \mu\text{g}/\text{m}^3$  for dichlorophenols and  $0.04 \mu\text{g}/\text{m}^3$  for the others). From the few detected congeners, most often 2,3,4,6-tetrachlorophenol was measured ( $0.01$ - $0.15 \mu\text{g}/\text{m}^3$ ), but it occurred at the similar levels in blank samples, as well.

Eleven chlorobenzene congeners (3-6CBz) were measured in ALS. Average total emission before filter was SPCBz =  $105 \pm 65 \mu\text{g}/\text{m}^3$  and after filter  $52 \pm 24 \mu\text{g}/\text{m}^3$  (filtering recovery 51 %). In CSH, chlorobenzene emissions were two orders of magnitude lower than in ALS.

PCB's were measured in first two analysis periods (Spring 1993) as congener profiles (groups of congeners with the same chlorine number: 3-7CB's). In the next two periods (Autumn 1993), isomer-specific analyses of ten major congeners (IUPAC numbers 8, 18, 28, 52, 101, 105, 118, 138, 153 and 180) and the two coplanar PCBs (IUPAC numbers 77 and 126) were performed. Isomer profile of the PCB emission in ALS (Fig. 1) was similar to the commercial PCB's (Arochlor, Phenoclor, Kanechlor and Clophen) with ca. 40 % Cl-level<sup>7</sup>. Total PCB emission from ALS was approximately SPCB =  $10 \mu\text{g}/\text{m}^3$  before and  $2.7 \mu\text{g}/\text{m}^3$  after filter (filtering recovery 73 %). Toxic PCB congeners occurred in following concentrations in ALS (TEF's according to Safe<sup>8</sup>):

Congener	Before filter $\text{ng}/\text{m}^3$		After filter $\text{ng}/\text{m}^3$		Filter recovery	
	Conc	TEQ	Conc.	TEQ	Conc.	TEQ
PCB 77	159	.159	13.8	.0138	91 %	
PCB 105	nd	nd	6.7	.0067	nd	
PCB 118	901	.0090	303	.0030	66 %	
PCB 126	24.9	2.49	nd	nd	100 %	
Sum of TEQ's		2.66		.0253		99 %

In CSH, emissions were SPCB =  $0.94 \mu\text{g}/\text{m}^3$  before and  $0.26 \mu\text{g}/\text{m}^3$  after scrubber (scrubber recovery 72 %). Lower chlorinated PCBs (8, 18, 28 and 52) were relatively more abundant than in ALS. The only toxic congener detected in CHS was PCB 118 at level  $22.5 \text{ ng}/\text{m}^3$  before and  $20.0 \text{ ng}/\text{m}^3$  after scrubber.

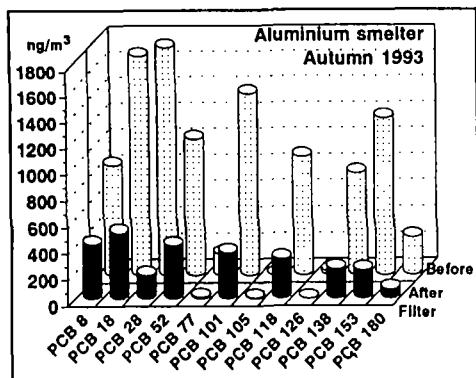


Fig. 1. Average emissions of individual PCB's in ALS

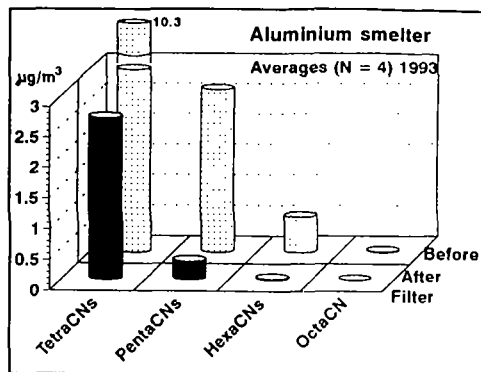


Fig. 2. Average emissions of polychloro-naphthalene congener groups in ALS

PCN emissions in ALS are shown as congener groups in Fig. 2. Total 4-8CN emissions were SPCN = 13.6 µg/m³ before and 2.98 µg/m³ after filter (filtering recovery 78 %). Taking TEF-value 0.001 for Hexa- and Octa-CN's<sup>9</sup>, TEQ's were 0.60 µg/m³ before and 0.026 µg/m³ after filter (TEQ recovery 96 %).

Seventeen toxic PCDD's and PCDF's were measured as individual compounds. The resulting isomer profiles in ALS emissions are presented in Fig. 3. Congener profiles of all PCDD's and PCDF's are shown in Fig. 4.

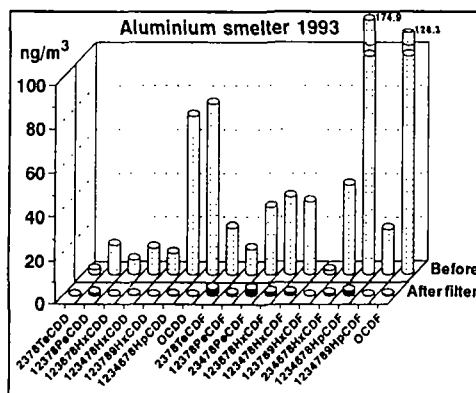


Fig. 3. Averages (N = 4) of toxic PCDD's and PCDF's in stack of ALS.

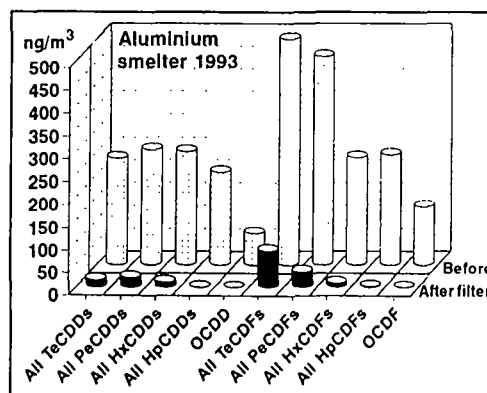


Fig. 4. Sums of all 4-8CDD's and 4-8CDF's in stack of ALS.

In ALS, nontoxic 4-5CDD/F's were most abundant (Figs 3 and 4). Total emissions of PCDD/F's were 2.6 µg/m³ before and 0.21 µg/m³ after filter (recovery 92 % for all, 99 % for hepta- and octa-congeners). Nordic TEQs were 43.7 ng/m³ before and 2.97 ng/m³ after filter (recovery 93 %).

In CSH, 1234678HpCDF, OCDF and OCDD were main isomers in emission (all 4-8CDD/F's only 6.07 ng/m³; as Nordic TEQ = 0.034 ng/m³) before scrubber, and they were effectively (98 %) removed in scrubbing.

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PCDEs (50 congeners) were all below the limit of determination ( $< 2 \text{ ng/sample}$ ;  $< 4 \text{ ng/Nm}^3$ ) in six samples from ALS and CSH studied in autumn and in the blank samples. Tri-, tetra- and penta-CDT's were measured in stack of ALS. Their total levels were SPCDT =  $498 \text{ ng/m}^3$  before and  $49 \text{ ng/m}^3$  after filter (recovery 90 %). PCDT's in CSH and PCTA's in both ALS and CSH were non-detectable ( $< 0.2 \text{ ng/m}^3$ ). To summarize, recoveries in ALS filter and in CSH scrubber were the following:

Compound group	PCP	PCBz	PCB	pPCB	PCN	PCDD/F	TEQ(Nor)	PCDT
Rec. in ALS Filter (%)	43	51	73	95	78	92	92	90
Rec. in CHS Scrubber	27	50	72	nd	nd	98	nd	nd

## 5. Conclusions

The present results indicate that, in addition to PCP's, PCB's and PCDD/F's<sup>1)</sup>, chlorobenzene and chloronaphthalene emissions from thermic metallurgical processes might be of serious environmental concern. In ALS, origin of PCB emissions may be from electrical equipments in cars, as seen in their isomer profiles. Congener profiles of PCDD/F's are consistent with the DE NOVO pathway of their formation, where nontoxic 4-5C-congeners dominate. Compared to emissions before technical improvement, best reduction of emissions was achieved by collecting the dust and by cleaning stack gases. As a rule, higher filtering and scrubbing recoveries were obtained for the less volatile and higher chlorinated compounds.

## 6. References

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