The Swedish Dioxin Survey: Summary of Results From PCDD/F and Coplanar PCB Analyses in Source-Related Samples

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INTRODUCTION

The major sources of PCDD/F are of anthropogenic origin. PCDD/F were first found to be formed in municipal waste incinerators (MSW) and later also in the bleaching of paper pulp using chlorine gas. One objective of the Swedish Dioxin Survey was to investigate other sources where the formation of PCDD/F could be suspected but where data was limited or not available. In a first step, a wide range of industries were chosen for study and samples were collected from one plant or site. Results from these samples have recently been published[1]. For those industries where high levels of PCDD/F were found, more plants were selected and new samples were collected for analysis. Sample types included smoke-stack gases, filter powder, sludges, effluent water, products and waste products. Some of the major findings in this second step of the survey are summarized here.

In the beginning of the survey, samples were only analyzed for the 17 2,3,7,8-chlorinated PCDD/F. At a later stage, it was possible to include the analysis of five coplanar PCBs in a number of samples. These were 3,3'4,4'-TeCB (CB 77), 3,3'4,4'5-PeCB (CB 126), 3,3',4,4'5,5'-HxCB (CB 169), 2,3,3',4,4'-PeCB (CB 105) and 2,3',4,4',5-PeCB (118).

MATERIALS AND METHODS

Samples were collected from a range of metallurgical processes including steel and iron mills, scrap-based steel mills, primary and secondary non-ferrous smelters and foundries, pulp mills using low-chlorine bleaching methods, chloralkali plants, cement and burnt lime production, several textile industries, dry cleaners and plastic producers among others. PCDD/F concentrations are given as TCDD-equivalents according to the Nordic model[2] and coplanar PCB concentratons are given as TCDD-equivalents according to the WHO-ECEH model[3].

RESULTS

Chloralkali industry

For the production of chlorine, several electrolytic processes can be used. The oldest and most common method involves the use of mercury as cathode and graphite electrodes as anode. This method has been used in Sweden until the late 1980s. Previous to 1972, this sludge was often released to receiving waters. A few samples of graphite electrode sludge were previously found to contain high levels of primarily PCDFs[4,5]. Newer methods use titanium electrodes and a diaphragm to separate the anode and cathode. This process does not use mercury. The sludge produced is deposited at local landfills or waste sites on the industry grounds.

The origin for the PCDF in the graphite sludge is still unclear, however, graphite electrodes can contain coal tar as the binding agent. Coal tar contains numerous PAHs including dibenzofuran which may have been chlorinated in the electrolytic process. For this reason, sludges produced using titanium electrodes were not expected to contain PCDD/F.

Figure 1 shows the levels of PCDD/F in a sample of graphite electrode sludge from a deposition site. This is compared with the levels found in sludge from the titanium electrode process. The levels of PCDFs are very high in both sludges, while the concentrations of PCDDs are very low or below detection levels. Both sludges show the typical PCDF pattern that has been found for chloralkali sludge within the survey. The high levels of PCDFs in sludge from the titanium process have yet to be explained. One possible explanation may be that PCDF are created by chlorination of PAHs present in the rubber linings of the electrolytic cell.

Fig. 1A. Sludge from chlorine gas production. Graphite electrodes(pg/g).

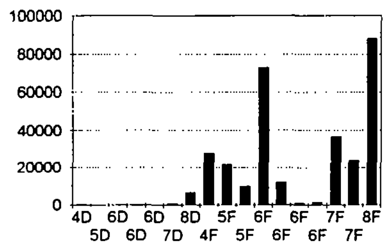
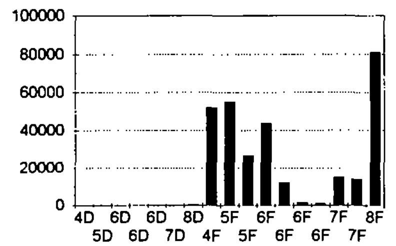


Fig. 1B. Sludge from chlorine gas production. Titanium electrodes(pg/g).



<u>Metallurgical processes</u>

Metallurgical processes include a wide range of activities, some which have been investigated for the presence of PCDD/F in smoke-stack gases and filter powder. There are however several processes, such as the use of scrap metal in steel production, where the formation of PCDD/F may be possible. In Sweden, regulations regarding the emission of PCDD/F is limited to smoke-stack gases and not to the large amount of other types of waste generated. For example the annual Swedish steel production of 4.5 million metric tons of steel produces 1.7 million metric tons of waste. The levels of PCDD/F as well as the handling and storage of this type of waste is therefore of importance. For example, PCDD/F concentrations ranged from 3000-12000 pg NTEQ/g and coplanar PCB concentrations from 200-1300 pg PCB-TEQ/g in filter powders from secondary non-ferrous smelters of different types.

Figures 2A-C shows PCDD/F levels in three examples of wastes from metallurgical processes. The representativeness of the PCDD/F levels produced in processes using scrap metal is difficult to evaluate. Scrap metal is a rather undefined raw material and can contain plastics, paints and oils such as chlorinated paraffins from tooling. The levels of coplanar PCBs were very high in some of these samples (Figure 2D).

Fig. 2A. Smokestack filter powder. Copper industry(pg/g).

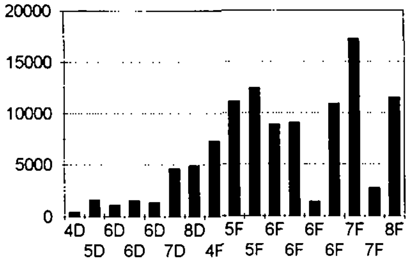


Fig. 2B. Venturi fume dust sample. Aluminum industry (pg/g).

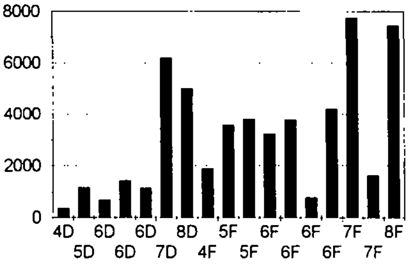


Fig. 2C. Sludge from scrap metal burning(pg/g).

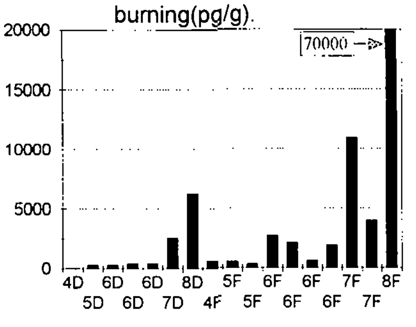
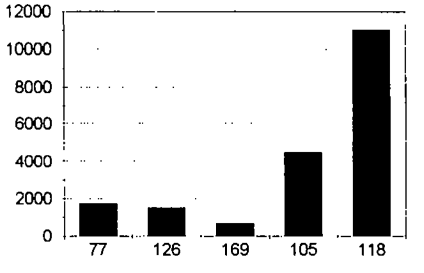


Fig. 2D. Sludge from scrap metal burning. Coplanar PCBs(pg/g).



Miscellaneous industrial sources

A number of other activities were also investigated, ranging from large scale industrial production to small industries. Examples of these are cement production, ceramics production, textile industries and distillation residues from dry cleaning. Figure 3 shows PCDD/F results from these four such processes. A certain amount of the cement filter powder ends up in the final cement product and some is released directly into the environment by the ventilation system at the plant.

Fig.3A. Still bottom sludge from dry cleaning(pg/g).

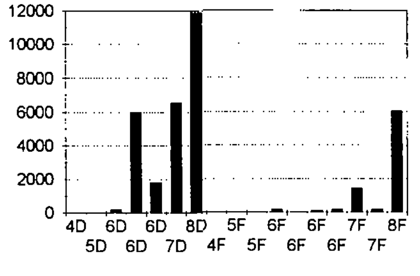


Fig. 3B. Filter powder cement industry(pg/g).

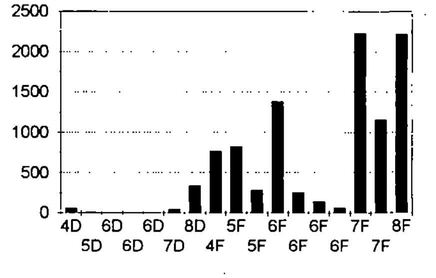


Fig. 3C. Powder glazing by NaCl volatilisation. Ceramic industry(pg/g)

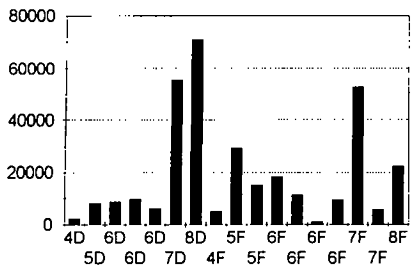
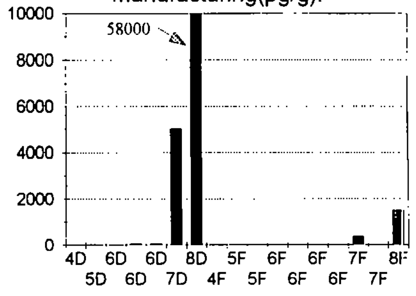


Fig. 3D. Sludge from textile manufacturing(pg/g).



CONCLUSIONS

The main focus on PCDD/F sources has mainly been on large industrial processes. However, the high levels of PCDD/F in the distillation residues from dry cleaning, for example, show the necessity of including small scale processes in the search for sources, since the use of such processes might be widespread. One of the major PCDD/F sources in Sweden is the metallurgical industry. The chloralkali industry is still producing PCDF-contaminated sludges in spite of changing to titanium electrodes. PCDD/F and coplanar PCB may end up in products such as cement and plastic which will be released to the environment over long time. The proper deposition of PCDD/F-contaminated wastes is thus very important.

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