POLYCHLORINATED DIBENZO-P-DIOXIN AND DIBENZOFURAN LEVELS AND PATTERNS IN SAMPLES FROM DIFFERENT SWEDISH INDUSTRIES ANALYZED WITHIN THE SWEDISH DIOXIN SURVEY

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INTRODUCTION

One goal of the Swedish Dioxin Survey is to identify sources of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) to the environment. To study and identify possible sources, samples were collected from foundries, iron works processes (iron plant and coke oven plants), textile industry, rubber industry, pharmaceutical industries, the distillation of mercury-containing wastes, a ceramic process (glazing by volatilization of sodium chloride) and other processes.

MATERIALS AND METHODS

Sludge, scrapings and filter powder from smoke stacks, effluent water and smoke stack gas samples were collected during 1990-91. Smoke stack gases were collected by consultants in the presence of representatives of the local county administrations according to Swedish EPA guidelines[1]. All other samples were collected by representatives from the local county administrations. Process-related data were recorded at the time for sampling. A limited description of the samples collected is given in Table 1.

The coded samples were extracted, worked-up and analyzed at the Institute of Environmental Chemistry, University of Umeå, using high resolution GC/MS[2,3]. TCDD-equivalents are calculated according to the Nordic model (NTEQ)[4].

RESULTS AND DISCUSSION

A summary of the analytical results is given in Table 1. Examples of congener patterns for samples from four different industrial processes are given in Figure 1.

Metallurgical processes are now considered to be a major source of PCDD/F emissions now that emissions from waste incinerators and bleached pulp mills have

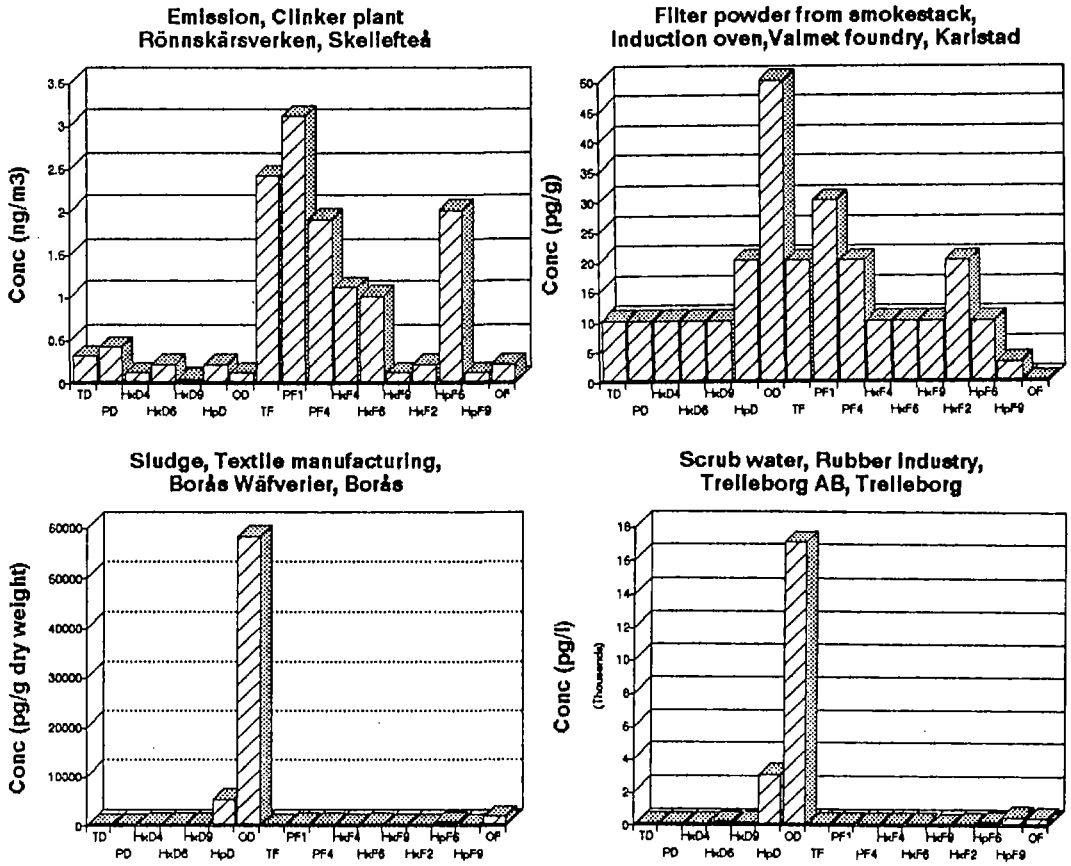
Table 1. Levels of Nordic TCDD-equivalents in samples from different Swedish industries

Industry	*Sludge pg/g dry weight*	*Effluent pg/liter*	*Powder pg/g dry weight*	*Smoke stack gas ng/M³*	*Annual Emission g NTEQ*
Clinker plant, Rönnskärsverken (metallurgical plant), Skellefteå, 2 samples				*1.10*	*0.06*
Slag fuming plant, Rönnskärsverken, 2 samples				*0.025*	*0.03*
Converter plant, Rönnskärsverken				*0.001*	
Sinter plant, SSAB Oxelösund, 2 samples				*0.75*	*2.2*
Coke plant, SSAB Oxelösund	*12*				-
Coke plant, SSAB Luleå	*0.33*				-
Foundry, cupola oven, cleaning of scrub water, Volvo Komponenter AB, Skövde	*440*				-
Aluminium foundry, filter powder, Ljunghäll AB, Södra Vi			*480*		-
Foundry, induction oven, filter powder, Valmet Foundry AB, Karlstad			*23000*		-
Foundry, induction oven (4 000 ton/year), Ovako Gjuteri AB, Arvika, 3 samples			*10*	*0.023*	*0.005*
1° Aluminium production, filter powder, GA-Metall AB, Sundsvall			*0.00*		-
Ceramic glazing, powder from smoke stack, Höganäs AB			*17000*		*0.01*
Mercury distillation, charcoal filter, Skoghall Kemi AB			*9700*		-
Textile manufacturing, Borås Wäfverier AB, Borås	*130*				-
Dry cleaning sorbtex mats with perchloroethylene, 4 Ess, Trollhättan	*140 (still bottom)*	*27*			$<1\times10^{-7}$
Dry cleaning clothing with perchloroethylene, 4 Ess, Trollhättan	*170 (still bottom)*	*18*			$<1\times10^{-7}$
Rubber industry, scrub water, Trelleborg AB, Trelleborg		*110*			1.1×10^{-5}
Pharmaceutical industry, ASTRA AB, Södertälje	*2.5*				-
Pharmaceutical industry, Pharmacia AB, Uppsala	*2.8*				-
Lime burning, Storungs				*0.005*	*0.002*
Carbon black, Nordisk Carbon Black, Malmö			*0.0*		-

been reduced. In this study, two such point sources were found to emit PCDD/F. These are the sinter plant connected to the SSAB iron plant in Oxelösund, and several plants at Rönnskärsverken, a large metallurgical plant in Skellefteå. Both industries are located along the Baltic Sea coast.

PCDD/F have previously been analyzed at Rönnskärsverken and were thought to

Figure 1. PCDD/F pattern in different samples collected within the Dioxin survey



Abbreviations; TD = 2,3,7,8-TCDD, PD = 1,2,3,7,8-PCDD, HxD4 = 1,2,3,4,7,8-HxCDD, HxD6 = 1,2,3,6,7,8-HxCDD, HxD9 = 1,2,3,7,8,9-HxCDD, HpD = 1,2,3,4,6,7,8-HpCDD, OD = OCDD, TF = 1,2,7,8-TCDF, PF1 = 1,2,3,7,8-PeCDF, PF4 = 2,3,4,7,8-PeCDF, HxF4 = 1,2,3,4,7,8-HxCDF, HxF6 = 1,2,3,6,7,8-HxCDF, HxF9 = 1,2,3,7,8,9-HxCDF, HxF2 = 2,3,4,6,7,8-HxCDF, HpF6 = 1,2,3,4,6,7,8-HpCDF, HpF9 = 1,2,3,4,7,8,9-HpCDF, OF = OCDF

mainly be a problem in emissions from scrap metal melting. In this study, smoke stackgas emissions from the clinker plant and the slag fuming plant were also found to emit PCDD/F. The congener pattern from the clinker plant is dominated by PCDFs, especially lower chlorinated congeners. PCDD/F levels in two samples taken on two different occasions from the clinker plant vary by a factor 10. Fig. 1 shows the congener pattern for the sample with the highest PCDD/F level from the clinker plant.

Both steel and aluminium foundries are sources of PCDD/F. Except for slightly higher OCDD levels and lower OCDF levels all other 2,3,7,8-chlorinated congeners are present at similar levels (Fig. 1).

It is well known that 2,3,4,7,8-PeCDF is one of the dominant PCDD/F found in biota from the Baltic Sea, especially when compared to levels in aquatic biota in the US

and Canada[5]. 2,3,4,7,8-PeCDF is one of the dominant congeners in emissions from the clinker plant and is also emitted by foundries. Metallurgical processes may thus be part of the explanation for the high levels of this congener in the Baltic Sea.

The ceramic industry in Höganäs glazes ceramics by volatilization of sodium chloride in a coal-fired oven. The congener pattern is similar to that of other incineration processes. Each procedure produces large amounts of PCDD/F but the yearly emissions are moderately low since the procedure is only performed every second month.

Skoghall Kemi has produced chlorine gas since 1917 in a chloralkali process resulting in a mercury- and PCDD/F-contaminated sludge. The sludge is now distilled to remove the mercury which releases the PCDD/F. The gas passes through a charcoal filter which was found to contain high PCDD/F levels. Investigation of PCDD/F levels in smoke stack gases after the filter is now being performed by the company.

Sludge samples from textile manufacturing contain high levels of hepta- and octachlorinated PCDD (Fig. 1). This may indicate the presence of pentachlorophenol in the raw cotton. Another possible source of these congeners may be dyes used in coloring fabric. Remmers et al.[6] found very high levels of hepta- and octachlorinated PCDD/F in the dye carbazole violet for example.

Elevated hepta- and octachlorinated PCDD levels were also found in still bottoms and effluent water from the dry cleaning of oil absorbent mats (sorbtex) as well as clothing at one small dry cleaners. Still bottoms from dry cleaning with perchloroethylene have previously been shown to contain PCDD/F[7], especially hepta- and octachlorinated PCDD.

Elevated PCDD/F levels were found in the scrub water from the vulcanization process in a rubber industry and the pattern was dominated by hepta- and octachlorinated PCDD (Fig. 1). Samples from pharmaceutical and lime burning industries and from carbon black contained very little or no PCDD/F.

Our results indicate that some industrial processes that have not been investigated before might be important sources for the emission of PCDD/F to the environment. These include a number of metallurgical processes. Many of the industries studied are small but their combined emissions still result in large amounts of PCDD/F being released into the environment. Some caution is advised though as in most cases, samples have been collected on one occasion and the results must now be followed up.

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