

Fingerprints of Dioxin from Thermal Industrial Processes

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Introduction

Dioxin emissions from most combustion processes are detected as a mixture of 75 PCDD and 135 PCDF isomers. The composition of such a PCDD and PCDF mixture is often referred to as "fingerprint" or "signature". Fingerprinting of dioxins has found interesting applications in source identification, atmospheric transport and transformation studies as well as formation mechanism elucidation. Kjeller et al. (1,2) have used principal component analysis to study the fingerprints of dioxin in environmental samples, and deduced the typical fingerprint for combustion sources, PCP use, etc. Gregor Rigo et al. (3) have used a combination of chemometric methods including multiple regression analysis, principal component analysis, hierarchical cluster analysis and engineering modeling to examine the relationship between chlorine levels in waste stream and dioxin emissions from combustors; fingerprinting has been an important component of the statistical approach adopted by Gregor Rigo et al. Other recent papers dealing with the fingerprints of dioxin are such as Cleverly et al. (4), Schramm et al. (5), Jones (6), Hagenmaier et al. (7).

Material and Methods

As a preliminary work of the E.U. project "Minimization of Dioxins in Thermal Industrial Processes: Mechanisms, Monitoring and Abatement (MINIDIP)", a data base has been developed which contains dioxin measurement data collected from various industrial sectors such as iron and steel manufacturing, non-ferrous metals production and recycling, cement kilns, hazardous and municipal waste incineration, etc. This data base presently contains the data of about 40 plants; total number of dioxin samples is about 300. The spreadsheet EXCEL has been used for data input, manipulation and graphical presentation. Local comparison of the fingerprints may be made by visual inspection of the graphs, whereas global comparison may be made by utilizing chemometric methods.

Results and Discussion

Several examples of the PCDD and PCDF homologue distribution in the gaseous emissions from ferrous and non-ferrous metals production are shown in Fig. 1 where the PCDD and PCDF homologues of each sample are normalized to the total weight of PCDDs and PCDFs of the sample. For the PCDF homologues a maximum is seen locating most often at P₅CDF and sometimes at T₄CDF; this type of distribution is similar to typical municipal incinerator emissions given by e.g. Brzuzy and Hites (8).

On the other hand, for the PCDD homologues a maximum is seen locating at T₄CDD; this type of distribution is very different from that of municipal waste incinerators where usually a maximum is located at O₈CDD, see e.g. (8). The total amount of PCDD is smaller than that of PCDF in most processes shown in Fig. 2; however in the two data sets for steel and iron furnaces, the total amount of PCDD is about equal to or larger than PCDF, which is probably not a common observation. Elsewhere, for steel recycling plants the total amount of PCDD is much smaller than that of PCDF reported by Jager (9).

Two examples of the 2,3,7,8 chlorine-substituted congener profile are given in Fig. 2 where each 2,3,7,8-congener is normalized to the total weight of all 2,3,7,8-congeners. The congener profile of the copper smelter is typical for thermal processes and is similar to that of waste incinerators presented by Cleverly et al. (4). However, the congener profile of the aluminum plant is dramatically different from that of the copper smelter or waste incinerators; the dominance of the 2,3,7,8-T₄CDF congener is rarely observed elsewhere; only in a congener profile for secondary lead smelter given in (4) can such a dominance by 2,3,7,8-T₄CDF be seen. For most thermal or combustion-based metallurgical processes a 2,3,7,8-congener profile resembling that of the copper smelter in Fig. 2 is more common. In sum, there are similarities between the dioxin fingerprints from industrial metallurgical processes and waste incinerators, but there are also important differences. These may be related to the different process conditions and PCDD and PCDF formation mechanisms; the details are not fully understood at present and require continued investigation.

References

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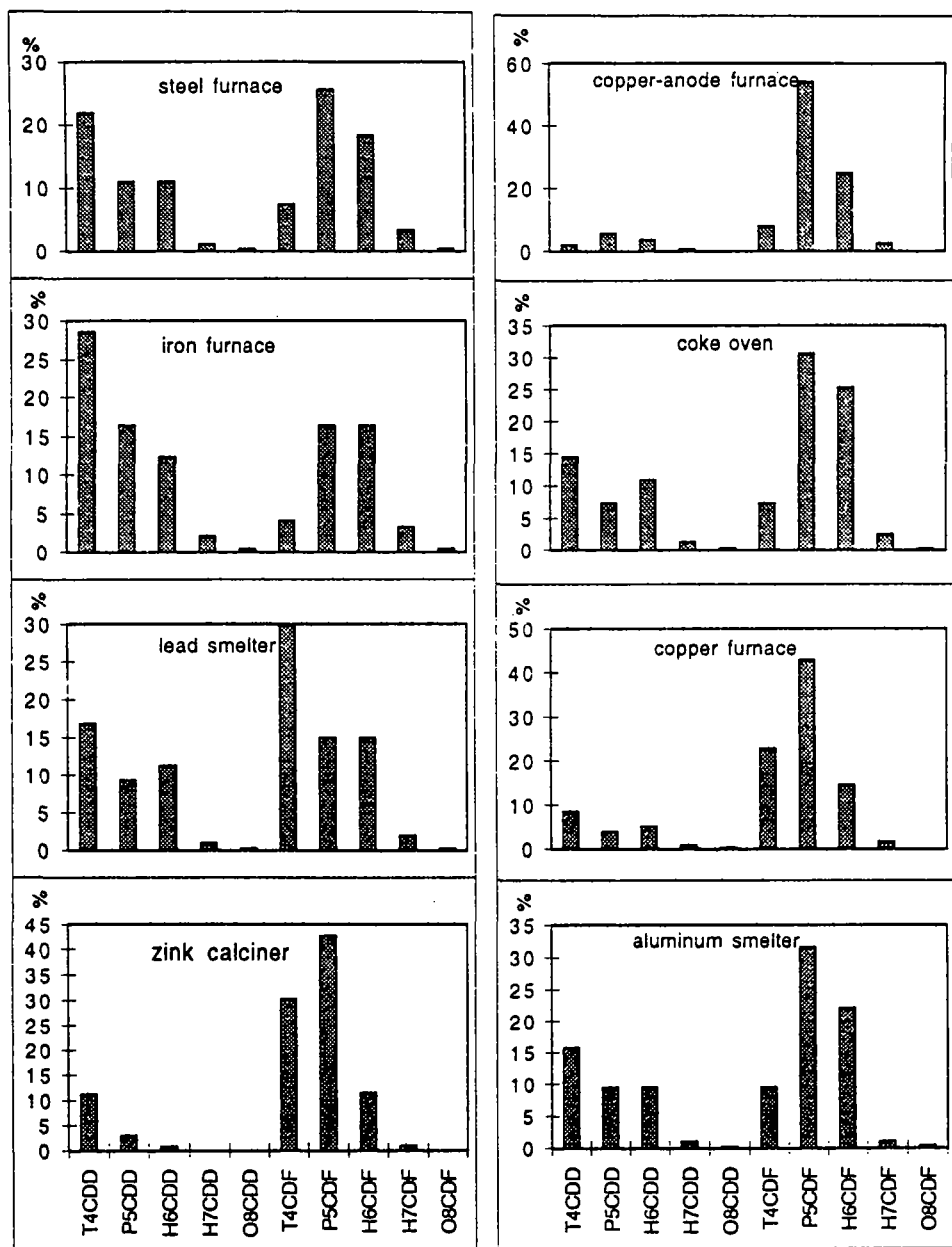


Fig. 1 PCDDs and PCDFs from metallurgical processes

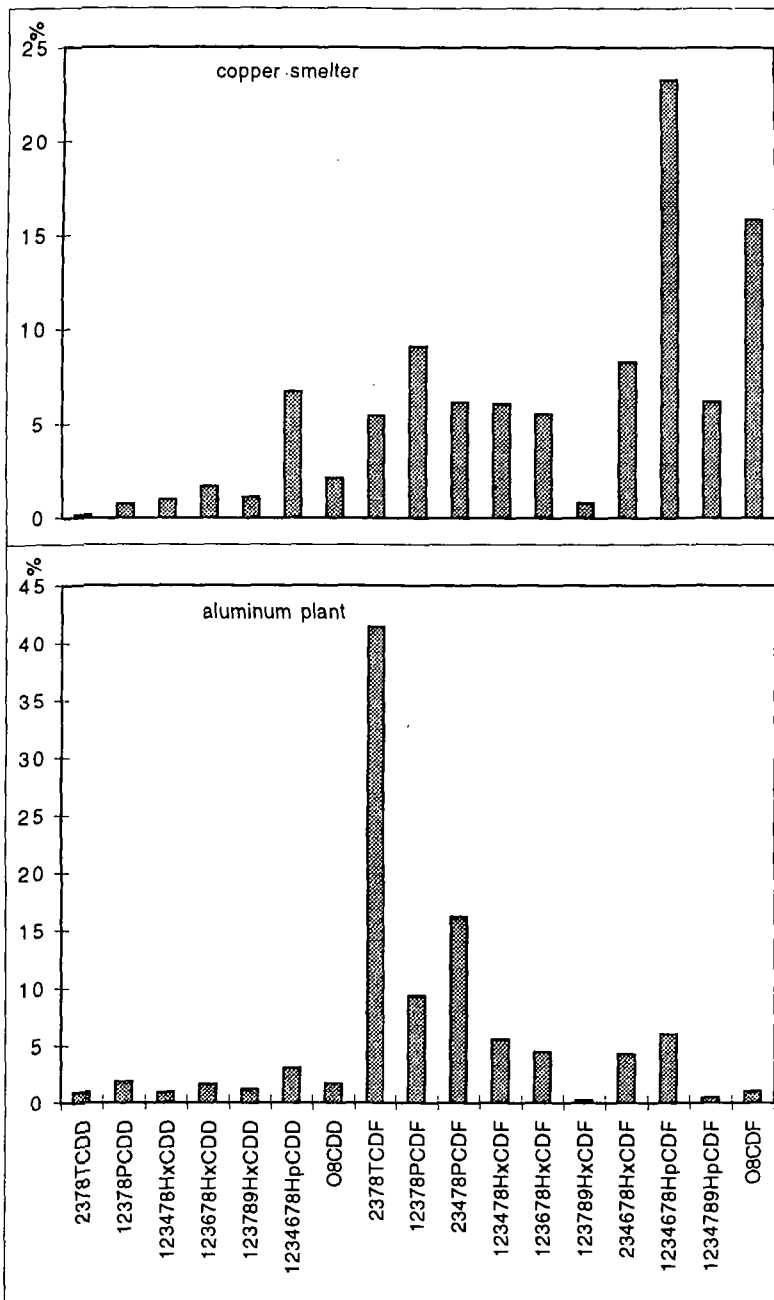


Fig. 2 The 2,3,7,8 chlorine-substituted congeners