PCDD/F Emission of the French Iron and Steel Industry and Evaluation of the Impact in the Environment

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Introduction

PCDD/F emissions have been taken into account by the authorities in France in 1997-1998 with the publication of laws asking for an inventory of the main emitters. These laws have been complemented in 1999 by demands concerning sources emitting more than 1 g/year I-TEQ to reduce their emission and to evaluate the impact of the PCDD/F emission in the biosphere.

For the French Steel Industry, dioxin's study has started earlier, in 1995, in order to evaluate emissions of the major units of the Steel Industry . Since it has been revealed that some shops of the Steel Industry are PCDD/F sources, works have been oriented on the research of ways to reduce emission and the study of the impact of the sources in their neighborhood.

Several studies have been realized by the Steel Industry to evaluate the influence of raw materials inputs on PCDD/F emissions. At that time, no clear evidence has been proven even if chloride inputs and oily recycle materials are suspected to influence the emission levels. To evaluate more precisely the influence of such parameters, research is also being carried out on the ways of reducing PCDD/F emissions

Environmental impact studies have been carried out by USINOR in order to evaluate the influence of the emissions in the environment. Three sites representative of the French iron and steel industry have been selected and work has been carried out according to the following methodology :

- emission inventory, through measurement of PCDD/F concentrations in the exhaust fumes ;
- dispersion study of PCDD/F emission with a gaussian model (ISC model),
- measurement of PCDD/F concentrations in soils around the selected industrial facilities.

Material and methods

Measurements of PCDD/Fs concentrations in industrial exhaust fumes

Sampling and analysis of PCDDs and PCDFs present in the exhaust fumes of industrial facilities follow the European standard EN 1948-1,2,3. The European standard is divided into 3 parts :

- sampling (part 1),
- extraction and purification (part 2),
- analysis (part 3).

The principle of the measurements consists in sampling a representative part of the exhaust fumes (isokinetic conditions) from which the particulate matter is collected on a plan filter, while the gaseous fraction is adsorbed on a specific adsorbent (XAD2 resin) after condensation.

The samples are then brought to the laboratory for further extraction and analysis, the latter being carried out using isotope dilution high resolution gas chromatography/mass spectrometry (GC/HRMS). Before analysis, each sample is first spiked with a precise amount of a mixture of $^{13}C_{12}$-marked isomer standards to correct for analytical losses and ensure quality control, and finally, it is submitted to a multistep clean-up procedure.

Dispersal modeling study

The model used for this approach (ISC) is a gaussian model recommended by the Environmental Protection Agency (EPA). Such a model is appropriate for the modelisation of non reactive gaseous pollutants from an elevated source. The data required for such an approach are the characteristics of the emitter (size, emission rate, concentration of the pollutant in the fumes) and meteorological data as the dispersion of pollutants depend on the direction of the prevailing winds.

Measurements of PCDD/Fs concentrations in soils

Surface soil (0-5 cm) was collected from several sites (each sample is constituted of an average of 6 samples regularly distributed on a 100 m^2 square parcel). Selection of the 5 sampling points was made according to the results of the dispersal modeling study described above, 3 chosen in the vicinity of the plume impact, 2 chosen further for background levels.

The soil samples were partially dried and passed through a 2 mm mesh sieve in readiness for the experiment. The PCDD/Fs present in the samples were first extracted using a specific method according to the matrix type of the sample. The extracts were then purified and finally analyzed using the same method as that described above.

Results and Discussion

The evaluation of emissions from the major emitters of the steel industry is presented Table 1.

Table 1 : Emission of PCDD/F from the French Steel industry - 1998
(Ministère de l'Aménagement du Territoire et de l'Environnement)

Type of Unit	Number of Units	Number of measurements	PCDD/F conc. range ng/Nm3 I-TEQ	Average yearly emission g/y I-TEQ
Sinter plant	6	24	2.1 to 3,3	93
Electric Arc Furnace (EAF)	19	25	< 0,01 to 13	36
Coke plant	5	8	< 0.01 to 0.1	0
Total				129

As shown in Table 1, the major emitters identified refer to sinter plants. The emission of the Steel sector in France represents about 40% of the emission of UIOM evaluated by MATE at 300 g/y in 1998.

In order to evaluate more precisely the impact of the sources in the environment, a study of the impact of selected sources has been realized by USINOR. The characteristic features of the selected sources are presented in Table 3.

Table 3 - Emission sources characteristics

Unit	Source	Gas flow Nm^3/h	PCDD/F conc. ng/Nm^3 I-TEQ	PCDD/F Emission µg/h
Sinter plants	SP n°2	820 000	3.0	6510
	SP n°3 stack 1	880 000		
	SP n°3 stack 2	470 000		
EAF n°1	EAF stack	350 000	0.7	245
EAF n°2	EAF baghouse	330 000	0.5	165

From the data given in Table 3, a dispersal modeling study was performed in order to predict the distance where the plume impact is maximum. The results of this approach are given in Table 4.

Table 4 - Maximum air concentration of PCDD/F (modelisation)

Sites	Conc. maxi fg/m^3 I-TEQ	Position of the maximum
Sinter plants	69	1500 m from the source
EAF n°1	25	1300 m from the source
EAF n°2	21	700 m from the source

It is pointed out that the concentrations calculated here are similar to those measured in ambient air in other European countries :
- concentrations in the range 21-217 fg/m3 I-TEQ (with a mean value of 83 fg/m3 I-TEQ) were measured in Bade-Wurtenberg[1], near industrial facilities ;
- concentrations in the range 50-550 fg/m3 I-TEQ were measured in Spain, the upper limit corresponding to sampling points close to incinerators.[2]

The maximum impact of the plume for EAF 2 is closer to the source than for the others. This may be due to the source configuration, as EAF 2 corresponds to diffuse emissions whereas the two other emitters have a chimney.

The environmental impact was characterized by measuring concentrations in soils. Sampling points were chosen in areas under the plume influence, in areas out of the plume influence but close to the emitter, and in background areas. The results are listed in Table 5.

Table 5 - PCDD/F concentrations in soil samples - pg/g I-TEQ

Soil sample	Sinter plants	EAF n°1	EAF n°2
upstream plume	2.42	0.95	0.01
center plume	5.29	1.24	0.07
downstream plume	0.33	0.05	0.07
near emitter - outside plume	0.12	0.61	0.05
background zone	0.35	0.07	0.04

It should be noted that the concentrations of PCDD/Fs measured in soils remain low in the vicinity of the selected sources.

However, it appears that the soil contamination in the area of the sinter plant is greater than for EAF1and 2. In addition, in this area the background level is 10 times higher than that of EAF2. This may indicate that other sources must contribute or must have contributed to the soil contamination. It is stressed that the concentrations near EAF2 are particularly low and similar whatever the sampling point. The background levels are similar in the environment of EAF1and 2.

It is also pointed out that the maximum concentration levels in soils are found in the area defined by the modeling study, which gives confidence in the results of the modelisation.

Isomers such as Cl_4PCDF and Cl_5PCDF are typical of industrial emissions, and particularly the 2,3,7,8PCDF isomer. Such compounds were not present in significant amounts around EAF 1 and 2, but were found around the sinter plant. This shows the contribution of this emitter to the soil contamination. Nevertheless, the pattern found around the sinter plant is not as strongly marked as that of other industrial sites, such as near Linz (upper Austria).[3] This indicates again that other emitters may have contributed to the soil contamination near the selected sinter plant.

Conclusions

The PCDD/F concentrations measured in the present study are consistent with the modeling study of the plume dispersion. In addition, it is stressed that all values are lower than the upper limit recommended in Germany for agriculture use of soils (40 pg/g I-TEQ). Furthermore, the measured concentrations are of the same order of magnitude as those found in other European countries, in urban and industrial areas.[4,5] They are even lower than concentrations measured in Great-Britain in 1986, in the vicinity of industrial facilities, where the mean value was 35 pg/g I-TEQ (the values being in the range 1-209 pg/g I-TEQ).[6]

Within the end of 2000, the present study will be complemented by studies focused on the following points :
- characterization of the emission impact in the environment using biomonitoring (with moss, kale and grass as bioindicator) ;
- research of ways and means in order to reduce PCDD/F emissions of sinter plants ; this will first go on by characterizing the influence of raw materials.

References

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