LONG TERM MONITORING OF PCCD/F AND PCB EMISSIONS FROM INDUSTRIAL WASTES INCINERATION

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Introduction

The waste incineration is an essential process for chemical plants to drastically reduce the amount of side products that can not be converted or recycled. Generally, all wastes coming from processes involving chlorine are dangerous for the presence of highly toxic species, as PCDD/F, PCB and others chlorine containing compounds that are difficult to treat and, because of the low rate of degradation, can be persistent in the environment for long time.
These wastes most of the times are treated inside the facilities using incinerators dedicated to destroy organochlorine compounds.
At the present time not enough data are available to highlight the contribution of these incinerators to the global emission of PCDD/F, PCB or others toxic pollutants. Relevant data are already published regarding the content of PCDD/F in some wastes that can be burned in similar facilities[1] or in streams, generally waste waters, coming from these treatment plants. Data are also available regarding the content of PCDD/F and other organochlorine compounds in air near these facilities[2], but for these specific plants and their punctual emissions there is a lack of information as is mentioned in several national inventories[3,4]. These informations are very important to quantify the amount released in the air and to compare these data with others know sources of dioxin emission as MSW incinerators, that are the most relevant source of PCDD/Fs.

Material and Methods

In the last four years we monitored (as company policy and according with permission released by the authority for running these facilities) three incinerators for the treatment of liquid industrial wastes. Two of them (designed incinerator 1 and incinerator 2), that are similar on the design, are dedicated to the treatment of chlorinated wastes. The liquid chlorinated wastes are feed to the combustion chamber and atomized with steam and an ultrasound atomizer. Because of the large surface area, the droplets quickly vaporize leaving a highly combustible mixture of air, waste fumes and combustion air. Secondary air is added to the combustion chamber to complete the oxidation of the mixture. A good combustion is achieved, if necessary, with small addition amount of methane to keep the optimal the temperature range of the combustion chamber (1250±20°C with an excess of oxygen more than 6%). The fumes leaving the combustion chamber are cooled, the hydrochloric acid is recovered and the exhausted fumes washed with a solution of sodium hydroxide. The wastewater, after neutralization is sent to a treatment plant. These two plants can burn a total amount of 18720 tons chlorinated organic waste with a maximum content of chlorine of 20% , usually distillation residues, heavy ends and tars coming from the production of chlorinated aliphatic hydrocarbons.
The third incinerator (incinerator 3) is dedicated to burn side products as heavy ends, solvent residues, contaminated waters and chlorine containing compounds (maximum content of chlorine 2%). The liquid wastes are injected and vaporized into a primary chamber and incinerated below

the stoichiometric requirements. The resulting smoke and pyrolitic combustion products are then passed through a secondary combustion chamber where relatively high temperatures are maintained by the combustion of auxiliary fuel. The resulting fumes are cooled down with a water scrubber. The wastewaters are sent to other facilities for further treatments.
The emission sampling train consists of a heated probe containing a glass fiber filter, two stage cooling traps for the fumes, (the first at 2-4°C and the second at –30°C), an XAD-2 resin trap and a volumetric pump (TECORA ISOSTATIC PLUS system) able to keep, during the sampling, isokinetic conditions. The sampling, clean-up and quantification of PCDD/Fs were done using the method EN 1948(1-3). Cleanup and separation of PCDD/Fs from PCBs with silica, alumina and carbon disposable columns were performed with the automated system DIOXIN-PREP (Fluid Management System, USA).
The PCDD/Fs, PCBs were quantified by isotope dilution with ^{13}C labeled standards using HRGC/HRMS technique with HP 5890 and 6890 GC (60 or 30m DB5 J&W columns, 0.25mm i.d.) and a mass spectrometer FINNIGAN MAT 95S operating in EI mode at 10000 resolution (10% valley).

Results and discussion
Table 1 shows the results of the relevant work done on the monitoring the emission of incinerators located inside the industrial area of Porto Marghera, dedicated exclusively to the treatment of industrial wastes. Incinerator 1 and 2, specially dedicated to the treatment of waste containing organochlorine compounds run all the time at lest 20 times below the limit of 0.1ng/Nmc TEQ. The maximum value was 5.17 and 1.64pg/Nmc total TEQ, respectively for incinerator 1 and 2. The TEQ average values of 0.74 and 0.27 and the TEQ median values of 0.03 and 0.02pg/Nmc indicate very low level of emission. The estimated contribution of these two incinerators operating 70% of the time during the year, considering the maximum value of TEQ, can account for an emission of respectively 0.26mg/y and 0.04mg/y of PCDD/Fs TEQ for incinerator 1 and 2. As reported in the inventory of dioxin sources in US for 162 similar plants a total emission, ranging from 2.2 to 12.8g TEQ/y, with value of 13.5 to 79.0mg TEQ/y estimated for each facility. Other values were recently reported on an updated UK emission inventory[3] for chemical waste combustion. Emissions of 2 to 870mg TEQ/y were found (10 sites analyzed).
If we refer the TEQ emitted per kg of waste, as shown in the table 1, we calculated a value of 0.28 and 0.089mg/y for the two incinerators burning the maximum amount of waste permitted .
The third incinerator seems slightly different from the first two. The average emission is 15.3 pg/Nmc with a calculated emission of 3.75mg TEQ/y. The amount of TEQ per kg of waste was calculated and is listed in table 1. This value is close to the value of 3800pg/kg used as TEQ emission factor for hazardous waste incinerators[3].
Differences can be found in the distribution of congeners as is shown in Figg. 1-2 . Incinerator 1 and 2 shows the same distribution of congeners (we repot here only the distribution of congeners for incinerator 2) and have the level of TCDF higher than the third but are lower in content of HpCDF. Generally the pattern of congeners reported in the literature is closer to that of incinerator 3[4], but minor variations can be explained with the different type of wastes probably with different content of chlorinated benzenes. The other congeners seem not be influenced by the type of incinerator.
Table 2 shows the data of PCBs analyses on the same samples. No major differences can be found among the incinerators. These species are not produced inside the plant and can be regarded as

endemic species and not related to the incineration of specific wastes. This is probably the reason why we did not find variations on the concentration during the four years monitoring.

References

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Table 1. Summary of the results of PCDD/F analysis on industrial chemical waste incinerators

	Incinerator 1	Incinerator 2	Incinerator 3
N. Analysis	24	23	33
TEQ (*) (pg/Nmc)			
Min	N.D.	N.D.	N.D.
Max	5.17	1.64	589
Average	0.74	0.27	15.3
Median	0.03	0.02	2.13
TEQ(*) (pg/kg waste)			
Min	N.D.	N.D.	N.D.
Max	30.81	9.77	3342
Average	4.41	1.61	267
Median	0.18	0.12	8.21

(*) Values below the detection limits were set to zero

Table 2. Summary of the results of PCB analysis on industrial chemical waste incinerators.

	Incinerator 1	Incinerator 2	Incinerator 3
N. Analysis	21	23	33
Conc. (ng/Nmc)			
Min	N.D.	0.5	0.6
Max	57.7	85.0	26.7
Average	6.04	6.37	4.43
Median	3.27	2.28	2.10

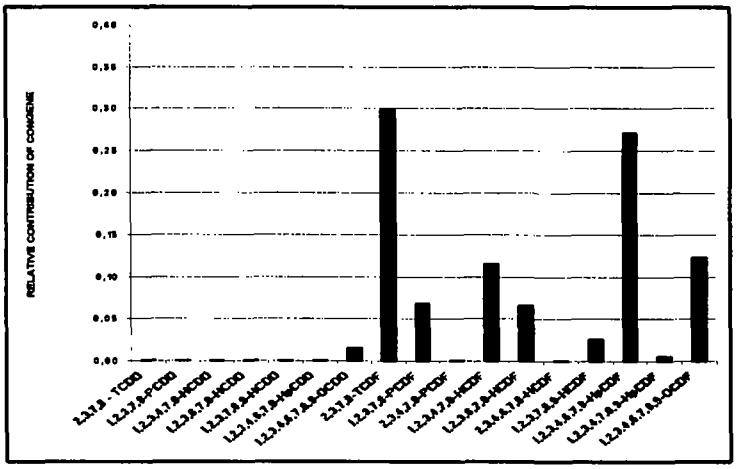

Fig. 1. PCDD and PCDF congeners profile of emission from incinerator 2

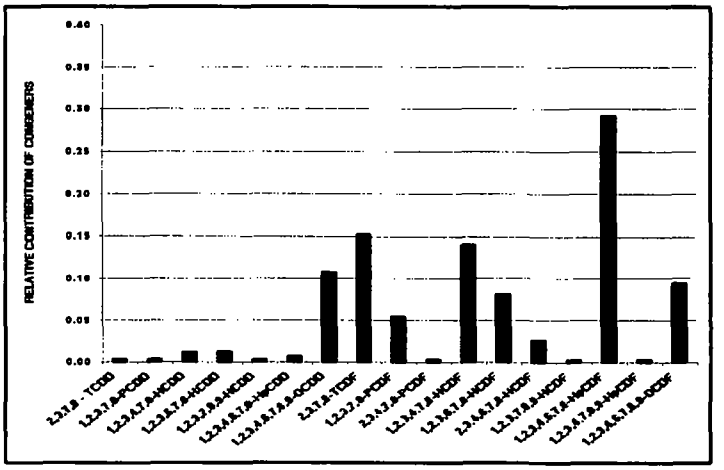

Fig. 2. PCDD and PCDF congeners profile of emission from incinerator 3