Survey program on PCDD/F emissions from combustion waste management in Colombia

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Introduction

In May 2001, 122 countries signed the Stockholm Convention with the aim to protect the environment and human health from adverse effects caused by anthropogenic POPs. It entered into force on 17 May 2004 with 50 Parties that had ratified the Convention. At the moment, the treaty remains to be ratified by Colombian authorities since a minimum knowledge on POPs is not completely accomplished. Nevertheless, different strategies and surveillance programs have been undertaken and a number of measures have been enforced in order to ratify and comply with obligations included in the Stockholm Convention.

In this sense, stack gas emissions from thermal waste disposal constitutes important objectives since it is recognized to be an important source of POPs such as the well-known PCDDs/Fs. In 2002, Colombian authorities set a limit value of 0.1 ng I-TEQ/Nm^3 for PCDDs/Fs stack gas emissions from thermal waste management to be reached in 2012. At the present, these limits were re-visited through the Resolution 0886[2]. In this new regulation limits for PCDD/PCDF emissions were updated and catalogued depending on the type of facility and operating conditions. Table 1 summarizes the limits versus operating conditions established in Resolution 0886.

Table1. Limit values for PCDDs/PCDFs from stack gas emissions[2]

Operating conditions (kg/h)	Limit value (ng I-TEQ/Nm^3)				
	Before august 2005	After July 31 2005 until July 31 2006	After July 31 2006 until July 31 2009	After July 31 2009 until July 31 2012	August 2012
<100	20	5	2	1	0.2
100-500	10	2	1	0.5	0.1

About 368 operating plants in Colombia burn around 10.858 tons of refused industrial materials, 51.110 tons of urban solid waste (USW) and 30.386 tons of medical waste per year[3]; capacities are below 200 kg/h in all facilities. In most cases, configuration plants consist of a furnace connected directly to a stack without any air cleaning system installed. Furthermore, most incinerators are batch operated and have a low capacity resulting in an increase of POPs emissions. In this contribution, we report additional results on the framework of a survey program aiming to achieve experimental data from the incineration sector in Colombia. In particular, we report data from eight plants operating all over the country, which incinerated industrial refuse materials and pathological residues.

Materials and Methods

Sampling was undertaken in 2004. Table 2 summarizes sampling conditions. Stack gas samples were collected using the filter/condenser method as described in EN-1948:1996-1. Extraction, clean-up and instrumental analyses were conducted at the Environmental Catalysis Research Group in Colombia by a conventional liquid-solid adsorption chromatography in open glass columns using silica, florisil and alumina as adsorbents. Final extracts were analyzed by high resolution gas chromatography coupled to an ion-trap low resolution mass spectrometer (HRGC-QITMS/MS) in a CP-3800 GC coupled to a Saturn 2000 ion-trap spectrometer. In addition, some samples were also analyzed by high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC-HRMS) in Barcelona.

Table 2. Incinerator Operating Conditions.

Sample code	Waste	Capacity (kg/h)	Control systems	Comb T (ºC)	Post-comb T (ºC)	Stack gas T (ºC)	Fuel
E008-04	Snack	80	1	850	1100	167	Gas
E011-04	Organic and hydrocarbons	40	-	700	1100	460	LPG
E012-04	Medical and pathological	140	-	750	1050	525	Gas
E014-04	Industrial and medical	180	2	850	1100	135	Gas
E015-04	Medical and pathological	140	None	850	1200	500	LPG

E017-04	Medical and pathological	100	None	1045	1195	320	LPG
E023-04	Pharmacy products	150	3	850	1150	40	LPG
E032-04	Medical, industrial and chemicals	190	4	900	1190	81	LPG

1. Scrubber, Bag filter and Cyclone; 2 Scrubber and ESP; 3. Heat exchanger, Cyclones, Bag filter and Activated carbon; 4. Bag filter and Cyclone

Results and Discussion

Table 3 summarizes the concentration of PCDDs/Fs expressed in ng I-TEQ/Nm^3. Overall findings resulted in relatively high concentrations with values ranging from 2 to 344 ng I-TEQ/Nm^3, nevertheless, these results are consistent to those reported in dioxin 2004 with values between 0.8-30 ng I-TEQ/Nm^3 in samples collected at three incineration plants of Medellín[1] (Colombia). This fact can be explained because plants are operating with limited air pollution control measures Although, the relatively high concentration found in almost all cases studied, plants E008, E011, E012 and E023 met limit values established in the Resolution 0886[2].

Table 3. Levels of PCDDs/PCDFs in emissions from waste incinerators (ng I-TEQ/Nm^3).

Sample code	HRGC/LRMS (ng I-TEQ/Nm^3)	Limit value (ng I-TEQ/Nm^3)
E008-04	11.41*	20
E011-04	16.79*	20
E012-04	6.94*	10
E014-04	39.20**	10
E015-04	12.32	10
E017-04	343.78	10
E023-04	2.27*	10
E032-04	23.41	10

*The levels are lower than those established in the 0886 resolution until July 31 2005.
**Value obtained by HRGC/HRMS.

International well-accepted procedures include HRGC-HRMS as instrumental technique for dioxin analysis[4]. Other methods also include the use of HRGC-LRMS; for instance, method 8280A[5] permits the use this instrumental technique in the quantitative measurement of PCDD/Fs in water, soil, fly ash, and chemical waste samples, including fuel oil and sludge matrices. In addition, a number of studies showed good correlation between results achieved by gas chromatography ion-trap tandem mass spectrometry (HRGC/ITD-MS/MS)[6]. In this sense, selected samples were analyzed by both HRGC/HRMS and HRGC/ITD-MS/MS within the quality control and quality assurance measures (QA/QC). The results are given en Table 4. Despite, slightly lower results obtained by HRGC/ITD-MS/MS, no remarkable differences were obtained in terms of TEQ values by using both techniques, high and low resolution mass spectrometry. Moreover, comparable dioxin fingerprint was observed in all cases studied. In consequence, these findings demonstrated the suitability of this technique to be used as a preliminary tool to evaluate progress on dioxin abatement measures in waste incinerator sector after the implementation of air pollution control systems. In addition, reliable data can be also achieved with the aim to elaborate a preliminary dioxin inventory in Colombia. Furthermore, Colombian resolution 0886[2] permits the use of HRGC-LRMS until mid-2006.

Table 4. Comparison results of PCDD/PCDF analysed by HRGC/HRMS and HRGC/QITMS/MS.

Sample code	HRGC/HRMS (ng I-TEQ/Nm^3)	HRGC/LRMS (ng I-TEQ/Nm^3)
E008-04	14.44	11.41
E011-04	14.17	16.79
E012-04	6.97	6.94
E015-04	15.65	12.32

In conclusion, the study contributes to a better knowledge of PCDD/F emissions in Colombia which help to complete the inventory required by the Stockholm Convention. The results achieved in this survey evidenced emissions of high concentrations of PCDD/PCDF in almost all incineration facilities evaluated. Therefore, some improvements should be implemented in incineration plants in order to reach the limit value of 0.1 ng I-TEQ/Nm^3 enforced in countries all over the world.

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