

POPs EMISSIONS FROM A LARGE SINTER PLANT IN SOUTHERN ITALY OVER A FIVE-YEARS PERIOD FOLLOWING ENFORCEMENT OF NEW LEGISLATION

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Introduction

Starting from mid-2007¹ the Environment Protection Agency of Apulia has performed several measurement of Persistent Organic Pollutants (POPs) stack emissions for a number of industrial plants located in the large industrial area near Taranto. Although information and estimates of a significant yearly mass flow for dioxins and PCBs from the local integrated steelwork were already available and published in relevant European inventories since year 1993^{2,3}, the actual measurements were in exceedance of those estimates and prompted the need of a more in-depth investigation of the fate and transport of POPs from emissions and release to the various environmental compartments and ultimately to transfer to the food-chain.

In early 2008 high levels of dioxin and dioxin-like PCBs were found in food samples of animal origin that were collected from farms located in the immediate surroundings of the industrial area⁴, causing immediate alarm among citizens and authorities. As an immediate response to the events, as soon as December 2008 a Regional regulation (LR 44/2008) enforced more stringent limits on dioxin stack emissions for plants operating in the metal sector. In fact, the existing Italian emission limits were inadequate to prevent POPs accumulation in the environment and not aligned to relevant regulation already into force in other European countries⁵. The new limits were set to 2,5 ng I-TE/Nm³ starting from 1st July 2009 and 0,4 ng I-TE/Nm³ starting from 1st January 2011.

In addition, and in order to investigate the extent of the contamination, an extensive monitoring plan was set up and performed throughout the period 2008 –2011 during which time more than 100 atmospheric deposition monthly samples, 50 soil and groundwater samples were collected and analysed⁶. As a result of the monitoring the Local Health Authority enforced the ban on grazing over wasteland within 20 km from the industrial area and a ban on the consumption of goat and sheep liver originating from animals grown in the same area, together with the stamping out of over 2000 sheep and goats.

As an outcome of the above actions we observed the reduction of the yearly mass flow of POPs emitted to the atmosphere as stack exhaust gases, as demonstrated by the latest emission measurements. Nevertheless, diffuse and fugitive emissions are arguably contributing to the overall impact on the surroundings resulting in a measurable POPs atmospheric deposition of both wet and dry matter on soils and other urban surfaces⁶.

This papers presents the results of dioxin and PCBs monitoring in stack emissions during a five-year period.

Materials and methods

Stack emission samples were collected according to Method EN 1948-1 (filter condenser method) by using an Isostack apparatus (TCR Tecora, Corsico Milan, Italy). Sample extraction was performed by Accelerated Liquid Extraction (Dionex, Sunnyvale CA USA) with Toluene. Extracts aliquots for the determination of PCDD/Fs and PCBs by method EN 1948 -2-3-4 were purified/fractionated by means of an automated clean-up process with a PowerPrep system (Fluid Management System, Waltham, Massachusetts) using disposable columns (multilayer silica, alumina and carbon). Extract aliquots for the determination of PAHs were purified over silica gel. Labeled standards were purchased from Cambridge Isotope Laboratories (Andover MA USA) and used according to Method EN 1948 1-2-3-4 for PCDD/Fs and PCBs and ISO 11338 1-2 for PAHs. PCDD/Fs were separated by high resolution gas chromatography (HRGC) on a DB-5 MS capillary column (60 m x 0.25 mm, 0.25 μ m film thickness, J&W Scientific, California). Isotope-dilution high-resolution mass-spectrometry determinations (HRMS) were carried out on a DFS High Resolution system (Thermo Fisher, Bremen, Germany) at a resolution of 10000 operating with electron ionisation (EI) at 45 eV in the selected ion monitoring (SIM) mode. PCBs, dl-PCBs and PAHs were separated by HRGC on a DB-5 MS capillary column (30 m x 0.25 mm,

0.25 µm film thickness, J&W Scientific, California) and determined by HRMS, in the same operating conditions used for PCDD/Fs. For each batch of seven samples a laboratory blank and a control sample were analysed. Toxic equivalent (TEQ) values for PCDD/Fs were calculated using NATO Toxic Equivalency Factors (I-TEFs, 1989) as required by Italian legislation on stack emissions and expressed as lower-bound concentrations. Toxic equivalent (TEQ) values for PCBs were calculated using OMS Toxic Equivalency Factors (WHO-TEFs, 1998).

Table 1. Results for stack emission measurements at Taranto sinter plant

Date	PCDD/Fs <i>pg I-TE/Nm³</i>	Dioxin-like PCBs <i>pg WHO-TE/Nm³</i>	Total PCBs <i>ng/Nm³</i>	Benzo(a)Pyrene <i>ng/Nm³</i>	Sum PAHs * <i>mg/Nm³</i>
12/06/07	2395	127	576	428	0,0072
14/06/07	4315	221	1292	888	0,013
16/06/07	4938	284	1032	431	0,015
26/02/08	4443	293	846	917	0,0096
27/02/08	8344	520	1242	1338	0,019
28/02/08	8082	478	1236	2817	0,031
23/06/08	2136	156	947	431	0,0081
24/06/08	3372	291	1163	1039	0,017
26/06/08	1942	181	928	310	0,0078
21/07/09	514	19	380	154	0,0020
22/07/09	469	19	554	177	0,0019
23/07/09	808	29	809	279	0,0033
17/11/09	807	61	755	97	0,0028
18/11/09	706	56	828	140	0,0036
19/11/09	1161	73	837	618	0,015
11/01/10	1963	97	699	666	0,022
12/01/10	498	36	305	453	0,011
13/01/10	2298	147	508	1803	0,035
01/02/10	956	84	535	409	0,014
02/02/10	867	84	432	298	0,011
03/02/10	994	84	390	273	0,015
16/02/11	885	102	580	248	0,0050
17/02/11	1020	107	428	645	0,0064
18/02/11	1258	124	509	479	0,0078
16/05/11	927	99	247	850	0,0079
18/05/11	815	80	245	1059	0,0091
19/05/11	1507	141	420	2469	0,019
14/11/11	196	20	66	10	0,00017
15/11/11	191	20	60	9,0	0,00015
16/11/11	132	19	58	8,7	0,00015
12/12/11	89	8,6	48	0,7	0,000023
13/12/11	70	7,8	51	2,8	0,000043
14/12/11	95	11	73	5,7	0,00013
18/07/12	305	39	126	6,5	0,00024
19/07/12	600	73	174	31	0,0011
20/07/12	501	53	147	46	0,0015
15/10/12	95	10	58	4	0,00011
16/10/12	114	11	62	6	0,00012
17/10/12	201	22	69	5	0,00019
13/12/12	412	34	123	270	0,00513
14/12/12	29	2	22	13	0,00024
15/12/12	237	21	118	65	0,00095

* Sum of selected PAHs as regulated by Italian legislation: Benzo(a)anthracene, Benzo(b+k+j)fluoranthene, Benzo(a)pyrene, Indeno(123-cd)pyrene, Dibenzo(ah)anthracene, Dibenzo(al)pyrene, Dibenzo(ae)pyrene, Dibenzo(ai)pyrene, Dibenzo(ah)pyrene.

Results and discussion

A total of 42 stack emission samples were collected at the sinter plant in Taranto over the period 2007-2012. Results for PCDD/Fs, total PCBs (mono- to deca-CB), dioxin-like PCBs, Benzo(a)pyrene and other selected PAHs are presented in Table 1.

It has to be noted that the new legislation requires a 35% reduction to be applied to PCDD/F measured values as listed in the Table 1 in order to take into account measurement uncertainty and that the reduction is applied irrespectively of the compliance to the emission limit. In addition, O₂% in flue gas is not used to normalize measured values (measured O₂ values ranged from 16% to 18.5%). Emission Limit Values (ELV) are yearly-average of a minimum of nine measurements grouped in a minimum of three campaigns.

The enforced ELV prompted sinter plant operators to adopt primary and end-of-pipe abatement techniques that would allow compliance to the new standards. For the period starting from July 2009 to december 2010 (emission limit equal to 2.5 ng I-TE/Nm³) a Urea addition device was used to add the known organic-nitrogen PCDD/F suppressant to the feed material⁷ together with the existing electrostatic precipitators (ESP+MEEP). Starting from January 2011 plant operators switched from urea addition (dismantled) to activated carbon injection ahead of ESP³. Those measures have allowed compliance to the limits, although up to May 2011 values in excess of 1 ng I-TE/Nm³ were still measured. Figure 1 illustrates PCDD/Fs in stack emissions relative to abatement techniques and new legislation enforcement (red).

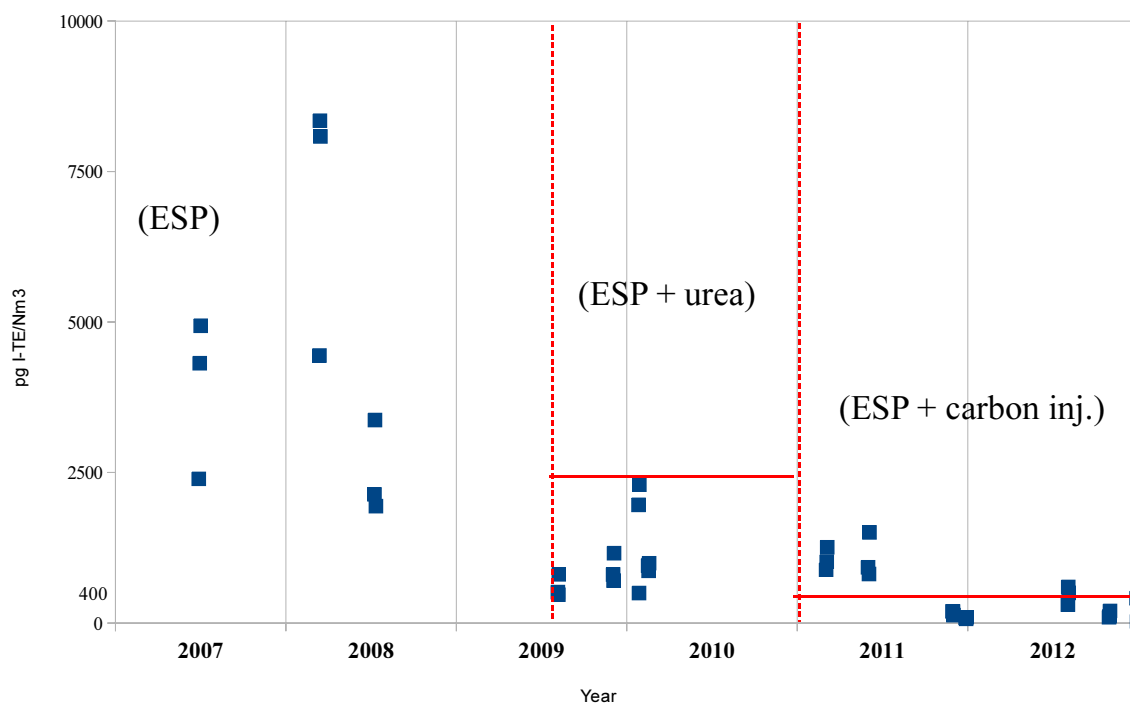


Figure 1. PCDD/F in sinter plant stack emission relative to the adoption of abatement techniques

It is possible to estimate the impact of stack emissions as a yearly mass flow considering a flue gas emission of 3.4 million Nm³/h (the plant operates continuously, maintenance aside) and the average emission value calculated for each year. Results are summarised in Table 2 and show a significant contribution of dioxin-like PCBs to overall TEQ (about 1:20) as well as an emission of BaP still in the order of the tenth of Kg/year. The reduction of the yearly mass flow for PCDD/Fs is evident.

Table 2. Estimated yearly mass flow of selected pollutants for Taranto sinter plant

	PCDD/F	Dioxin-like PCBs	Total PCBs	Benzo(a)Pyrene	Sum PAHs *
Year	<i>g I-TE/year</i>	<i>g WHO-TE/year</i>	<i>kg/year</i>	<i>kg/year</i>	<i>kg/year</i>
2007	116	6	29	17	349
2008	141	10	32	34	459
2009	22	1	21	7	147
2010	38	3	14	19	538
2011	18	2	7	14	140
2012	8	1	3	1	32

* Sum of selected PAHs as regulated by Italian legislation: Benzo(a)anthracene, Benzo(b+k+j)fluoranthene, Benzo(a)pyrene, Indeno(123-cd)pyrene, Dibenzo(ah)anthracene, Dibenzo(al)pyrene, Dibenzo(ae)pyrene, Dibenzo(ai)pyrene, Dibenzo(ah)pyrene.

Conclusions

In 2007 stack emissions measurements performed by the Apulian Environment Protection Agency (ARPA) revealed a high PCDD/F emission at a sinter plant. Since then a stringent monitoring program to prove the efficiency of the new abatement techniques introduced by plant operators and to assess the compliance to newly introduced Emission Limit Values has been carried out in the period 2008-2012. Studies are still ongoing to evaluate if the improvements in stack emissions are having a concomitant positive effect on the observed POPs levels in the surrounding environment.

References

1. Primerano R., Esposito V., Angiuli L., Fanigliulo A., Ficocelli M., Giua R., Menegotto M., Nocioni A., Valenzano B., Bisceglia L., Assennato G. (2007) *Organohalogen Compounds* 69: 966
2. Lahl, U. (1993) *Organohalogen Compounds* 11: 311
3. Francois F, Bernaert P, Baert R. (2001) *Organohalogen Compounds* 54: 115
4. Diletti G, Ceci R, Scortichini, G, Migliorati G. (2009) *Organohalogen Compounds* 38: 2359
5. Francois F, Bernaert P, Baert R. (2000) *Organohalogen Compounds* 45: 352
6. Esposito V, Maffei A, Castellano G, Martinelli W, Conversano M, Assennato G. (2010) *Organohalogen Compounds* 72: 736
7. Anderson DR, Fisher R, Johnston S, Aries E, Fray TAT, Ooi TC. (2007) *Organohalogen compounds* 69:355