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POP emissions from a large sinter plant in Taranto (Italy) over a five-year period following enforcement of new legislation

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HIGHLIGHTS

- Sinter plant is a major emitter of PCDD/F to air due to high pollutants content and high exhaust gas flow
- Drastic reduction of pollutants emission was enforced by legislation
- Active carbon injection proved effective in PCCD/F removal from sinter exhaust gas
- Yearly mass release of PCDD/F to air still in the multigram-per-year range for Taranto plant

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ABSTRACT

PCDD/F in exhaust gas emission samples was determined by the Environmental Agency of Apulia for a sinter plant located in Taranto (Italy) starting from June 2007 following an Agreement Act between plant owners and the Regional Government with the aim to assess and improve the environmental performances of the plant. The first two sampling campaigns yielded results ranging between 3.42 and 8.34 ng I-TE/Nm^3 that were soon considered revelatory of a high potential impact on the surrounding environment and the public, prompting for immediate action. As a first outcome, a Regional Regulation (LR 44/2008) was enforced in order to reduce PCDD/F emissions by plants operating in the metal sector, including sinter plants. After installation of a urea addition plant to the sinter mix as a process-integrated abatement technique the emissions ranged from 0.86 to 3.59 ng I-TE/Nm^3. In order to reach compliance to the newly introduced emission limit value of 0.4 ng I-TE/Nm^3 the urea plant was removed in favour of active-carbon injection as an end-of-pipe technique. Subsequently, during year 2011 emission values ranged from 0.095 to 1.97 ng I-TE/Nm^3, while in 2012 the observed range was 0.058 to 0.91 ng I-TE/Nm^3. As a better evaluation of the potential impact of the sinter plant emissions, a yearly mass-flow was estimated using exhaust gas PCDD/F concentrations and plant operational parameters (3.4 M Nm^3/h). Mass-flow was estimated to be as high as 165 g I-TE/year for 2007 using yearly average concentrations or 248 g I-TE/year using the peak-value of 8.34 ng I-TE/Nm^3.

1. Introduction

Starting from mid-2007 (Esposito et al., 2012; Primerano et al., 2007) the Environment Protection Agency of Apulia has performed several measurements of Persistent Organic Pollutant (POP) stack emissions for a number of industrial plants located in a large industrial area near Taranto. Although information and estimates of a significant yearly mass flow for dioxins and PCBs from integrated steelworks were already available and published in relevant European inventories since year 1993 (Lahl, 1993, 1994; Kinzel et al., 1994; Broker et al., 1999; Anderson and Fisher, 2002), 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 in the Taranto area and ultimately transfer to the food-chain through animal farming and fishery, as well as the evaluation of available abatement techniques to be applied to the existing plant in order to reduce the overall impact (Anderson et al., 2001; Buekens et al., 2001).

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 area (Diletti et al., 2009) causing immediate alarm among citizens and authorities. As an immediate response to the events, as soon as December 2008 a Regional

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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 POP accumulation in the environment and not aligned to relevant regulation already into force in other European countries (Francois et al., 2000, 2001). The new limits were set to 2.5 ng I-TE/Nm^3 starting from 1st of July 2009 and 0.4 ng I-TE/Nm^3 starting from 1st of January 2011 in order to allow a reasonable, although short, amount of time to adopt technologies on such a large scale, the sinter plant being among the largest known with a total sinter bed surface of 472 m^2.

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 analysed (Esposito et al., 2010, 2012). 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 the 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 enforcement of legislative and monitoring actions a significant reduction of the yearly mass flow of POPs emitted to the atmosphere as stack exhaust gases was observed, 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 POP atmospheric deposition of both wet matter and dry matter on soils and other urban surfaces (Esposito et al., 2012).

This paper presents the results of PCDD/F, PCB, and PAH emission control in stack emissions during a five-year period with respect to the enforcement of stricter legislation and adoption of process-integrated and end-of-pipe techniques.

2. Materials and methods

Stack emission samples were collected according to Method UNI EN 1948-1 (filter condenser method) by using an Isostack apparatus (TCR Tecora, Corsico Milan, Italy). The filter-condenser method allows sampling of both gas-phase matter and particle-phase matter. The flue gas enters the sampling train through an electrically heated glass lined probe. This is connected to a glass filter casing in which a quartz fibre filter (Munktell, Baresnstein, Germany) is supported on a PTFE filter holder. The filter casing is inside an electrically heated box. It is followed by a water cooled coil condenser and a XAD-2 resin (Supelco, Supelpak, St Louis, MO, USA) filled cartridge. The condensate and the gas pass through the resin to a round bottomed flask in which the condensate is collected. Exhaust gases were drawn in isokinetic conditions from plant stack for a total of 6 h. Sample extraction was performed by Accelerated Liquid Extraction (Dionex, Sunnyvale, CA, USA) with Toluene. Extract 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. Labelled 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 × 0.25 mm, 0.25 μm film thickness, J&W Scientific, California). Isotope-dilution high-resolution mass-spectrometry (HRMS) determinations were carried out on a DFS High Resolution system (Thermo Fisher, Bremen, Germany) at a resolution of 10,000 operating with electron ionisation (EI) at 45 eV in the selected ion monitoring (SIM) mode. PCBs including dioxin-like PCBs (dl-PCBs) were separated by HRGC on a HT8 capillary column (60 m × 0.25 mm, 0.25 μm film thickness, SGE Analytical Science, Australia) and determined by HRMS, in the same operating conditions used for PCDD/Fs. PAHs were separated by HRGC on a DB-5 MS capillary column (30 m × 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 (certified fly-ash from inter-laboratory proficiency tests) were analysed. In addition, every sampling campaign included a field blank, according to UNI EN 1948-1 that was used to ensure that no significant contamination had occurred during all steps of the measurement, and were not subtracted from measured values. Recovery rates for sampling and extraction labelled standards were in compliance with UNI EN 1948 requirements (greater than 50%).

Table 1

Results for stack emission measurements at Taranto sinter plant.

Date	PCDD/Fs[a]	Dioxin-like PCBs[b]	Total PCBs[c]	Benzo(a) pyrene	Sum PAHs[d]
	pg I-TE/Nm^3	pg WHO-TE/Nm^3	ng/Nm^3	ng/Nm^3	mg/Nm^3
12 Jun 07	3421	181	823	611	0.010
14 Jun 07	7192	368	2153	1480	0.022
16 Jun 07	6022	346	1259	526	0.018
26 Feb 08	4443	293	846	917	0.0096
27 Feb 08	8344	520	1242	1338	0.019
28 Feb 08	8082	478	1236	2817	0.031
23 Jun 08	2670	195	1184	539	0.010
24 Jun 08	4215	364	1454	1299	0.021
26 Jun 08	2428	226	1160	388	0.0098
21 Jul 09	857	32	633	257	0.0033
22 Jul 09	711	29	839	268	0.0029
23 Jul 09	1063	38	1064	367	0.0043
17 Nov 09	1552	117	1452	187	0.0054
18 Nov 09	1261	100	1479	250	0.0064
19 Nov 09	2103	132	1516	1120	0.027
11 Jan 10	3166	156	1127	1074	0.035
12 Jan 10	778	56	477	708	0.017
13 Jan 10	3591	230	794	2817	0.055
1 Feb 10	1138	100	637	487	0.017
2 Feb 10	1057	102	527	363	0.013
3 Feb 10	1243	105	488	341	0.019
16 Feb 11	1639	189	1074	459	0.0093
17 Feb 11	1700	178	713	1075	0.011
18 Feb 11	1966	194	795	748	0.012
16 May 11	1159	124	309	1063	0.0099
18 May 11	1019	100	306	1324	0.011
19 May 11	1884	176	525	3086	0.024
14 Nov 11	327	33	110	17	0.00028
15 Nov 11	318	33	100	15	0.00025
16 Nov 11	264	38	116	17	0.00030
12 Dec 11	135	13	73	1.1	0.000035
13 Dec 11	95	11	69	3.8	0.000058
14 Dec 11	136	16	104	8.1	0.00019
18 Jul 12	462	59	191	10	0.00036
19 Jul 12	909	111	264	47	0.0017
20 Jul 12	677	72	199	62	0.0020
15 Oct 12	119	13	73	5.0	0.00014
16 Oct 12	143	14	78	7.5	0.00015
17 Oct 12	251	28	86	6.3	0.00024
13 Dec 12	687	57	205	450	0.0086
14 Dec 12	58	4	44	26	0.00048
15 Dec 12	339	30	169	93	0.0014
17 Jun 13	248	44	178	1.4	0.00018
18 Jun 13	123	13	71	1.3	0.00017
19 Jun 13	149	16	103	1.4	0.00032

All data are normalised to 16% O_2 content for consistency purposes only and not for regulatory compliance.

[a] Sum of seventeen 2378-chlorine substituted congeners.

[b] Sum of twelve non-ortho and mono-ortho PCBs.

[c] Sum of all measurable mono- to deca-CB.

[d] 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, and Dibenzo(ah) pyrene.