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ORGANIC AND INORGANIC TRACE POLLUTANTS AROUND MUNICIPAL SOLID WASTE INCINERATORS: RESULTS FROM AIR QUALITY MONITORING CAMPAIGNS IN NORTHERN ITALY

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Abstract: In this work the results of monitoring campaigns for air quality around a number of municipal solid waste incineration plants in Northern Italy are presented. As part of the monitoring protocol of each plant, the campaigns were periodically performed at sites characterized by different exposure to the plant's emission, investigating the concentration levels of trace organic pollutants, i.e.: dioxins and furans (PCDD/F) and polycyclic aromatic hydrocarbons (PAHs), of toxic elements (arsenic, cadmium, nickel, lead), of gaseous mercury, of ultrafine particles (UFP, diameter < 100 nm), and of nanoparticles (NP, diameter < 50 nm). Reported data refer to seasonally averaged concentrations of PCDD/F and Cd, resulting from weekly integrated samples collected by means of high volume samplers for the particulate phase, equipped with PUF for the adsorption of the vapour phase of organic pollutants. Overall, data from about 30 campaigns at 20 sites taken during the last 20 years are presented.

Key words: *Air quality, dioxins, heavy metals, waste incineration.*

INTRODUCTION

From the regulatory standpoint the strategy against atmospheric pollution relies on tools with two different goals. The first kind of tools is intended to control the pressure factors that can affect air quality, i.e. to control the release into the atmosphere of pollutants from human activities; the second kind of tools is intended to control the state of air quality, i.e. to monitor the change of air quality as a consequence of regulated and non-regulated activities, in order to prevent the occurrence of harmful conditions for human health and the environment. For industrial plants responsible of atmospheric emissions that can have a significant impact on local air quality, the first control tool is permitting, as the plant activity has to be authorized. Authorization procedures for large plants rely on environmental impact assessment studies, including atmospheric dispersion modelling, to demonstrate that the generated impact on air quality can be considered acceptable. Plant authorizations request the adoption of Best Available Techniques (BATs) and fix emission limits according to national regulations, or even stricter in areas where air quality is a critical issue. Additionally, dedicated air quality monitoring for specific trace pollutants not measured by the air quality monitoring network is usually requested. Actually, the regulatory levels set for air quality control consider a limited number of pollutants, regarded as general tracers for air pollution, but do not take into account source-specific pollutants.

Waste incineration plants are subject to very strict regulations for atmospheric emissions, with emission limits set for both the pollutants typically generated by traditional combustion processes (CO, NOx, SO_2, particulate matter) and for specific pollutants deriving from the combustion of waste (heavy metals, inorganic acids, organic compounds). In particular, an extremely low emission limit is set for the chlorinated organic compounds of the family of dioxins and furans (PCDD/F) due to their toxicity (0.1 ng m^{-3}, as equivalent toxicity). As these pollutants are not considered by air quality regulations and, thus, are not measured at air quality monitoring stations, dedicated campaigns are periodically performed nearby waste incineration plants as prescript by the plant permit.

Our department has been in charge for air quality monitoring campaigns at waste incinerators sites in Northern Italy since 1997 (Caserini et al., 2004). These campaigns were specifically addressed to investigate the concentration levels of trace organic pollutants (PCDD/F and PAHs), as well as of toxic elements (As, Cd, Ni, Pb), of gaseous mercury, of ultrafine particles (UFP, particle diameter < 100 nm), and of nanoparticles (NP, diameter < 50 nm). In this work the results of monitoring campaigns for air quality around three plants are presented: overall, data from about 30 campaigns at 20 sites taken during the last 20 years are reported. The work is focused on PCDD/F and Cd, typically present in the atmospheric emissions of waste incinerators plants.

MATERIALS AND METHODS

Monitoring sites and campaigns

Monitoring campaigns were performed for the municipal waste incineration plant of Milano (1350000 residents), Cremona (70000 residents) and Schio (40000 residents), all located in the river Po valley in Northern Italy. All these plants are quite recent WtE (Waste-to-Energy plants) with combined heat and power recovery and adopt state-of-the-art technologies for flue gas treatment, including electrostatic precipitation of dust, activated carbon injection for the adsorption of organic pollutants, fabric filtration and tail-end catalytic treatment for NOx abatement. Currently, the Milano plant has an annual waste throughput of about $500 \cdot 10^3$ tons $year^{-1}$, whereas the other two plants have a smaller size, with a waste throughput of about $75 \cdot 10^3$ tons $year^{-1}$. Nearby each plant (a few kilometres as crow-fly distance) a number of monitoring sites were selected, based on the suggestion on the location of the most impacted receptors resulting from air dispersion modelling for plants' emissions. However, the selection of the monitoring sites was also intended to collect representative data for areas characterized by different land use (i.e.: urban areas, rural areas, industrial areas). Additionally, receptors likely not affected by plants' emission were also considered in order to have background reference values for data interpretation. More in details, data from 5 sites collected during 12 campaigns since 2004 were available for Milano plant, data from 10 sites during 11 campaigns since 2000 for Schio plant, and data from 6 sites during 8 campaigns since 1997 for Cremona plant.

Air sampling

Air sampling was performed by means of medium-/high-volume samplers for about one week, in order to collect a mass of pollutants suitable for analytical determinations. Particulate matter (PM) was collected onto quartz fiber filters, whereas vapour phase pollutants were adsorbed onto polyurethane foam (PUF) plugs. In the first campaigns PM samplers were not equipped with any sampling head, thus collecting samples of the total suspended particles; more recently, depending on the site and campaign, samplers were equipped with PM size-selective inlets, in order to collect PM10 samples. Heavy metals in PM samples were determined by means of inductively coupled plasma-mass spectrometry. Total PCDD/F concentrations were determined by means of high-resolution gas chromatography coupled with high-resolution mass spectrometry after Soxhlet extraction from both PUF and filter. Based on the concentration data for the 17 toxic congeners, the total PCDD/F concentrations have been calculated as equivalent toxicity concentration by means of the toxicity equivalent factors proposed by the World Health Organization (WHO-TEFs). For computation purpose, for the congeners below the detection limit a concentration value equal to half of the detection limit was assumed.

RESULTS

Dioxins and furans

The average and the min-max range values for the seasonal concentrations of PCDD/F measured during all the campaigns are presented in Figure 1. Summary statistics for the cold season (Oct. to Mar.) and the warm season data (Apr. to Sep.) are separately reported in Table 1. In some seasons, data show a rather large dispersion, mainly as a consequence of the two following factors: i) seasonal data sets have different size and can include data from different monitoring areas; ii) the monitoring campaigns were not concurrent and the meteorological conditions can have been more or less favourable for atmospheric dispersion. In general, cold season levels are in the 10-100 fg_{TEQ} m^{-3} range, with only a few data up to 200 fg_{TEQ} m^{-3}; data for the winter 2003 campaign are in the 1-10 fg_{TEQ} m^{-3} range because the weather was highly perturbated and not at all representative of the atmospheric stability condition, typical for the Po valley area in wintertime. The data set analysis shows that the local conditions strongly affect the concentration levels: actually, data from the monitoring sites around Milano plant, all located in a densely populated and highly trafficked area, are generally higher than those from the neighbourhood of the other plants. Warm season levels usually are in the 1-50 fg_{TEQ} m^{-3} range, with only a few data in the same orders of the wintertime concentrations. Differently from wintertime conditions, warm season data do not show any relevant difference among the monitoring areas. On the average, cold season levels are about three times higher than those of the warm season (61 fg_{TEQ} m^{-3} vs. 23 fg_{TEQ} m^{-3}); such a ratio is consistent with the cold/warm season ratio observed for criteria pollutants over the Po valley and is mainly due to the greater atmospheric dispersion in summertime, thanks to a slightly stronger ventilation and to the higher vertical evolution of the planetary boundary layer. However, the higher wintertime concentrations are also due to the contribution of PCDD/F emission from domestic heating (Hübner et al., 2005), still largely based on biomass combustion in single domestic heating stoves.

In general, the observed concentration levels are coherent with the emissive features of the monitoring areas, characterized by both residential and industrial settlements and, above all, of a dense road network including stretches and junctions of great communication, also frequented by heavy traffic. Concentration levels are in good agreement with data reported in literature: according to the OSPAR Commission report (OSPAR Commission, 2007), background levels in rural and unpolluted areas in Europe are in the 10-50 fg_{TEQ} m^{-3} range and typical concentrations for the larger cities are in the 50-100 fg_{TEQ} m^{-3} range; ambient concentrations in excess of 300 fg_{TEQ} m^{-3} are indicative for local emission sources. Vilavert et al., 2015 and Rovira et al., 2010 report concentration levels around 10 fg_{TEQ} m^{-3} in the vicinity of a municipal waste incinerators in Spain; referring to Northern Italy, Colombo et al, 2013 report concentration levels in the 10-20 fg_{TEQ} m^{-3} range, Mosca et al., 2012 values in the 5-40 fg_{TEQ} m^{-3} range. A recent work from the local Environmental Agency for the area of the Schio plant reports warm season levels in the 3-4 fg_{TEQ} m^{-3} range and cold season levels in the 11-22 fg_{TEQ} m^{-3}.

Abnormally high concentration levels were observed in Milano plant area during some sessions of both the warm and cold season campaign in 2004. Concurrent measurement taken at the monitoring sites at the beginning of July resulted in concentration levels in the 148-275 fg_{TEQ} m^{-3} (i.e.: 6-10 times higher than the average for summertime) and in the 1340-2360 fg_{TEQ} m^{-3} range on the end of December in concentration levels, that is almost 40 times higher than the average for wintertime and 10 times higher than the maximum value. On both these periods, the occurrence of uncontrolled fire of warehouses storing plastic materials and waste were reported by the fire department nearby the monitoring area. Other than by the concentration levels, the impact of this source is also highlighted by the different congeners profile, as shown in Figure 2 for the summer event.

Table 1. Summary statistics for seasonal PCDD/F weekly concentration data

Season	N° of samples	Mean	St. deviation	Minimum	Maximum	Median	IQR
Cold season	121	61,7	43,9	1,3	221,2	52,7	48,9
Warm season	114	23,1	23,2	0,7	124	16,0	20,0

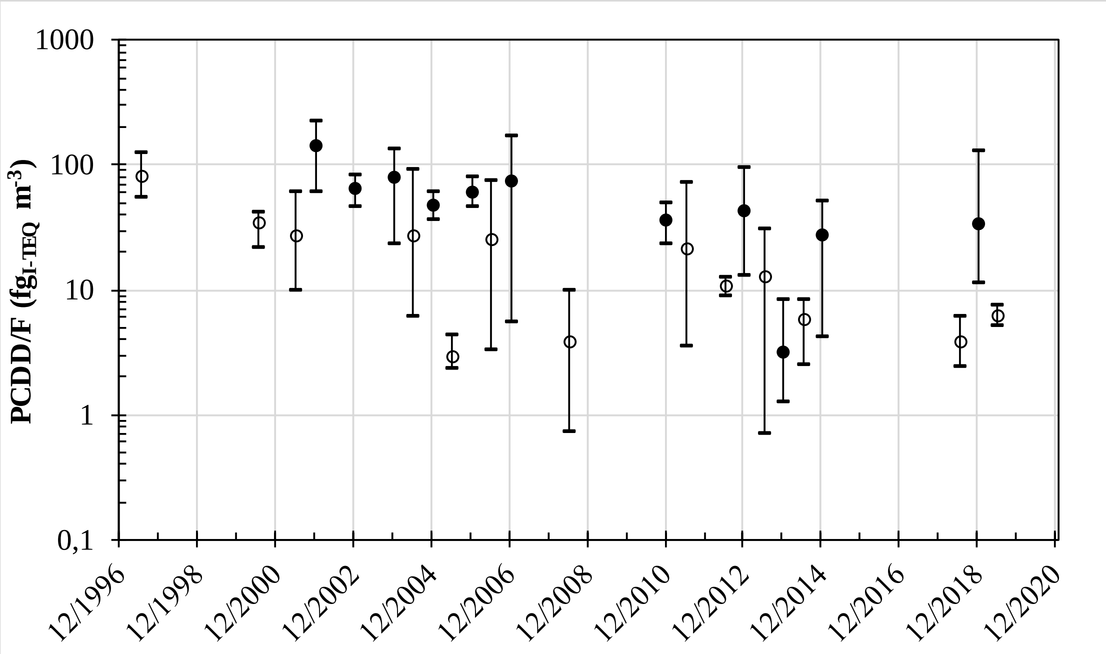

Figure 1. Seasonal average and min-max range for PCDD/F concentrations (fg_{TEQ} m^{-3}); (white markers: warm season; black markers: cold season)

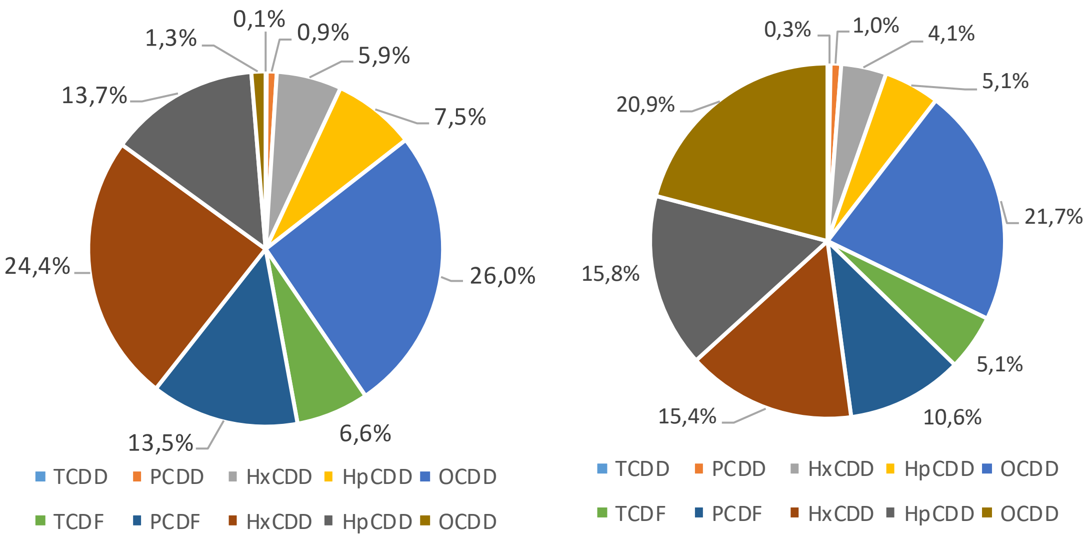

Figure 2. Toxic congeners mass profiles for the fire event in summer 2004 (left panel) and for the rest of summer 2004 campaign (right panel) around Milano plant.

Heavy metals

Heavy metals data refer to concentration levels of arsenic, cadmium, nickel, lead in particulate matter. Actually, these elements are considered by the current EU regulations for air quality, with target values set for the annual average concentration (ranging from 5 ng m^{-3} for Cd up to 500 ng m^{-3} for Pb). As an example, Cd concentrations data measured during all the campaigns are summarized in Figure 3. As for PCDD/F, seasonal data display some dispersion but, with only very few exceptions, concentrations are always below 1 ng m^{-3}, with average levels of 0.26 ng m^{-3} and 0.45 ng m^{-3} for the warm and cold season, respectively.

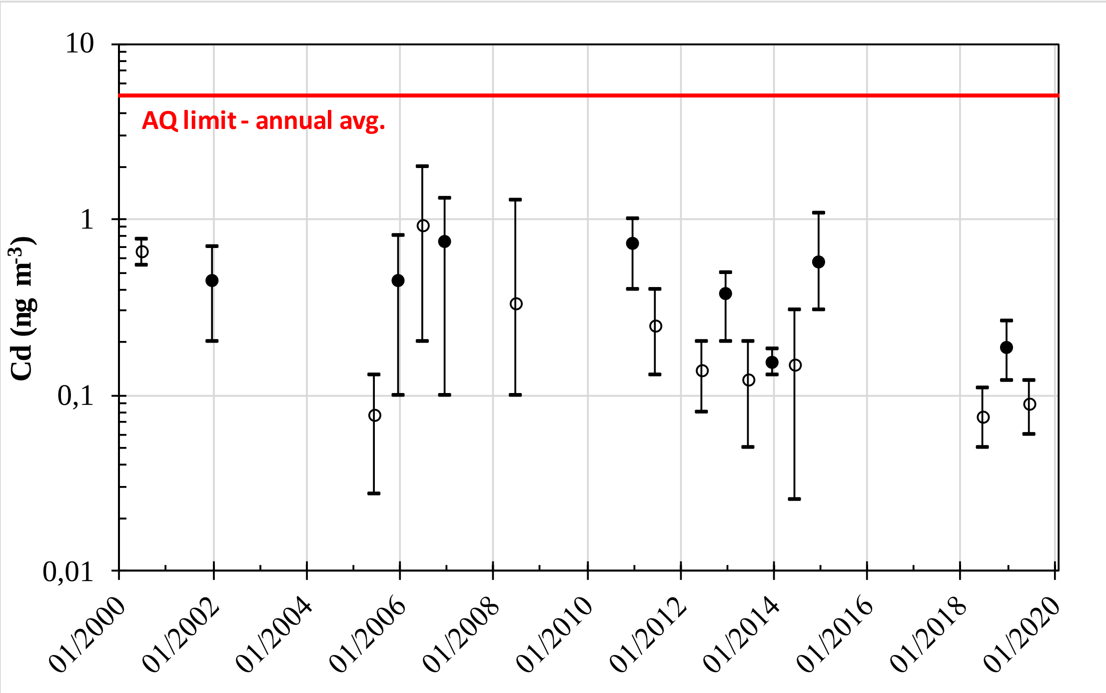

Figure 3. Seasonal average and min-max range for Cd concentrations (ng m^{-3}); (white markers: warm season; black markers: cold season)

CONCLUSIONS

The concentration time patterns of PCDD/F and Cd show both interannual and intraseasonal fluctuations determined by the different meteorological conditions occurring during the campaigns. The cold season is characterized by higher concentration levels reflecting the typical seasonal pattern of atmospheric pollutants in Northern Italy. In general, stable or downward concentration trends have been observed, without a systematic impact of the plants' emission. Additionally, weekly averaged concentration levels for regulated pollutants, such as Cd, are usually well below the air quality regulatory values fixed for the annual average. PCDD/F levels nearby the waste incineration plants are in the same orders reported in literature for urban areas in Europe, thus suggesting that state-of-the-art plants provide an almost negligible contribution to the background levels generated by the complex of anthropogenic activities.

REFERENCES

Caserini S., S. Cernuschi, M. Giugliano, M. Grosso, G. Lonati, P. Mattaini, 2004: Air and soil dioxin levels at three sites in Italy in proximity to MSW incineration plants. *Chemosphere* **54**, 1279-1287

Colombo A., E. Benfenati, S.G. Bugatti, M. Lodi, A. Mariani, L. Musmeci et al., 2013: PCDD/Fs and PCBs in ambient air in a highly industrialized city in Northern Italy. *Chemosphere* **90**, 2352–2357

Hübner, C., R. Boos, T. Prey, 2005: In-field measurements of PCDD/F emissions from domestic heating appliances for solid fuels. *Chemosphere*,. **58,** 367-72.

Mosca S., G.N. Torelli, G. Tramontana, E. Guerriero, M. Rotatori, M. Bianchini, 2012: Concentration of organic micropollutants in the atmosphere of Trieste, Italy. *Environ Sci Pollut Res* **19**, 1927-1935.

OSPAR Commission, 2007: Hazardous substances series: dioxin. *The Convention for the Protection of the Marine Environment of the North-East Atlantic, 2007 update*. Publication Number: 308/2007

Rovira J., M. Mari, M. Nadal, M. Schuhmacher, J.L. Domingo, 2010: Environmental monitoring of metals, PCDD/Fs and PCBs as a complementary tool of biological surveillance to assess human health risks. *Chemosphere* **80**, 1183-1189

Vilavert, L., M. Nadal, M. Schuhmacher, J.L. Domingo, 2015: Two decades of environmental surveillance in the vicinity of a waste incinerator: human health risks associated with metals and PCDD/Fs. *Arch Environ Contam Toxicol*. **69**, 241-253.