

CHARACTERIZATION OF PCDD/F IN AIR IN THE PROVINCE OF TRENTO

M. RAGAZZI*, M. MARCONI*, E.C. RADA*, A. CHISTÈ*, (S. FEDRIZZI**)

* *DICA, Department of Civil and Environmental Engineering, University of Trento – Via Mesiano 77, 38123 Trento, Italy*

** *Municipality of Trento (expected co-author of the final version of the paper)*

SUMMARY: This paper shows an overview on provincial scale with particular reference to PCDD/F measurements in air, detected in several campaigns carried out over a period of ten years (from 2002 to 2012). This in order to obtain a comparison between the results found in the Borgo Valsugana and surroundings and those related to other provincial sites. In particular, in the year 2002 and .in the years 2005 to 2010 there have been some measurement campaigns aimed at obtaining a background reference in terms of micro-pollutants in view of the possible construction of the MSW incinerator of Trento. In 2009, also, a measurement campaign was carried out, by the Provincial Agency of Environment Protection, to achieve environmental characterization in Valsugana, as well as in the town of Trento and its surroundings, in order to assess the impact of a steel making plant. In 2012, finally, a campaign of air monitoring was carried out with the objective of monitoring the area around the plant in Borgo Valsugana.

1. INTRODUCTION

PCDD/Fs are found as a trace element in almost all environmental compartments. In nature they are produced by incomplete combustion of organic material in the fires and volcanic activities. Most emissions come from human activities, however, unlike other pollutants, such as PCBs, PCDD/Fs are never produced intentionally but are formed as secondary products of some industrial activities and all combustion processes. They are considered among the most dangerous pollutants for health, exceeded certain threshold limits. The exposure of the population concerns a multipath: inhalation, ingestion, dermal contact, diet. To contribute to a better understanding of the exposure to PCCD/F in the province of Trento campaigns of measures to characterize the presence of these pollutants in the atmosphere were organized.

To contribute to a better understanding of the PCDD/F's exposure in Trento's province some monitoring campaign were carried out in order to characterize the presence of these pollutants in air. A first characterization concerned the years 2002 and 2003 in the area of the town of Trento (DIIAR, 2003). In particular, it was performed two measurement campaigns in the atmosphere after one year of each other with the aim of determining a background reference in anticipation of the construction of a MSW incinerator in the town of Trento (DICA, 2006; DICA, 2007) and on the presence of the motorway as a likely source of PCDD/F in the atmosphere (Caserini, 2002). The measurements were carried out in order to find a correlation with both the presence of significant potential sources of emission, and with variations of the pollutant PM10 measured during sampling at fixed stations of air quality in the Province of Trento.

In the summer of 2009 and winter of 2010 a study was made to continue the characterization of

the environmental situation near Trento, in order to depict the current situation (DICA, 2010).

During 2009-2010's winter the Provincial Agency of Environment Protection conducted an environmental control campaign, in order to monitor the input of pollutants by the industrial plant emissions in Valsugana valley and in Trento surroundings.

During 2012's spring another PCDD/F measurements' campaign in environment air of Borgo Valsugana was carried out (Istituto Mario Negri, 2012).

2 MATERIALS AND METHODS

During the monitoring campaign 2002/2003 air samples were carried out at three sites representative of the local context and emissivity (Cadine, urban and peripheral urban area of Trento, the area of maximum impact expected for the MSW incinerator plant) and in two periods of time representative of the regime meteorological winter and summer in the area of Trento (DIAR, 2003).

During the 2006's measurement campaign some points were identified for a representative air sampling of the interested area; the samples were made by US.EPA specifications, Compendium Method TO-9A, (U.S.EPA, 1999),(DICA, 2006):

1. **Measurement campaign n. 1:** Trento Nord –PCDD/F's measurement at a period of PM₁₀ peak (average value > 90 µg/m³); distance of about 100 m from motorway axis (A22) (cod. I1).
2. **Measurement campaign n. 2:** Trento Nord – research of PCDD/F's gradient by increasing the A22 distance at a period of low values of PM₁₀ (30 µg/m³ < average value < 50 µg/m³). Two points of measurements: at 100 m (cod. I2) and at 760 m (cod. T2) from A22.
3. **Measurement campaign n. 3:** Trento Sud – research of PCDD/F's gradient by increasing the A22 distance at a period of very low values of PM₁₀ (average value < 30 µg/m³). Two points of measurements: at 60 m (cod. MS1) and at 530 m (cod. MS2) from A22.
4. **Measurement campaign n. 4:** Trento Sud – research of PCDD/F's gradient by increasing the A22 distance at a period of moderate values of PM₁₀ (50 µg/m³ < average value < 90 µg/m³). Two points of measurement: at 60 m (cod. MS3) and at 530 m (cod. MS4) from A22.
5. **Measurement campaign n. 5:** Trento Nord e Trento Sud – research of PCDD/F's values at analogues distance from A22 in different sites at a period of moderate values of PM₁₀ (50 µg/m³ < average value < 90 µg/m³). Trento Nord and Trento Sud at 550 m (cod. F6) and at 240 m (cod. MS7) from A22 respectively.
6. **Measurement campaign n. 6:** Centralina di Gardolo (cod. G2) – PCDD/F's measurement at a period of very low PM₁₀'s values (average value < 30 µg/m³).
7. **Measurement campaign n. 7:** Centralina del Parco S.Chiera (cod. SC2) – PCDD/F's measurement at a period of very low PM₁₀'s values (average value < 30 µg/m³).

As regards the values of the pollutant PM₁₀ the measurements performed at the fixed control units of air quality of provincial agency for the environment protection have been taken in consideration. For the measurement campaign of Trento Nord the reference control unit is that of Gardolo, while for Trento Sud is that of Parco S.Chiera (urban background), (APPA, 2006).

During 2007 field monitoring campaign further investigation of PCDD/Fs in air was carried out in the same sampling sites of 2006 measurement campaign (DICA, 2007).

During summer 2009 and winter 2010 some sites in Trento surroundings were carried out: a public park in Lavis, a public park in Terlago and the primary school of Zambana. (DICA, 2010).

For finding PCDD/F's values in air of Borgo Valsugana during the measurement campaign conducted in 2009 by the Provincial Agency of Environment Protection two sites were selected for sampling. The first site is located 888 meters west from a steel plant at a fish farm, while the second

site 1475 meters east from the plant, in the yard on the way to Olle street. Two monitoring campaigns were conducted in order to check the presence of PCDD/F in the air: the first sampling campaign, in a period of suspension of the steel plant was made from the 4th of January 2010 to the 8th of January 2010; the second sampling campaign was carried out from the 1st of February 2010 to the 5th of February 2010 during the operation of the steel plant (APPA, 2010).

3 RESULTS AND DISCUSSION

The background levels of PCDD/F acquired during the monitoring campaign of 2002 (see Tab.1) appear generally mild, with attendances lined up at the intervals characteristic of geographical areas similar to those of the Trento region. The concentrations of PCDD/F in terms of toxic equivalency are between 11 and 110 fg_{I-TEQ} m⁻³ with the only acquisition that winter, in line with the emission and dispersed characteristics of the atmosphere expected in this regime, it is placed into the upper end of the range detected. The results, completely aligned with those available for urban areas similar to that of Trento did not show significant differences related to the localization of the sites of sampling, in agreement with the substantial uniformity of the emissivity of the same area (DIIAR, 2003).

Location	Site 1	Site 2		Site 3	Site 4
Year	2002	Summer 2002	Winter 2002/2003	Summer 2002	Autumn 2002
Units	fg m ⁻³				
2378-TCDF	80.5	16.6	44.7	9.1	21.3
12378-PeCDF	64.6	9.3	28.4	5.0	9.3
23478-PeCDF	99.7	21.5	56.6	8.0	18.1
123478-HxCDF	51.6	16.6	40.2	6.8	10.8
123678-HxCDF	49.1	13.6	38.1	5.8	11.0
123789-HxCDF	77.9	23.6	50.4	7.9	14.7
234678-HxCDF	30.5	10.5	19.5	3.4	4.1
1234678-HpCDF	112.7	53.0	122.6	24.2	33.9
1234789-HpCDF	36.7	9.7	22.0	5.0	4.9
OCDF	81.1	72.4	65.9	38.9	36.0
2378-TCDD	< 10.1	<1.6	<6.5	0.6	0.6
12378-PeCDD	20.4	2.2	16.1	1.0	4.2
123478-HxCDD	16.8	2.3	14.9	1.0	4.4
123678-HxCDD	35.9	47.7	29.4	13.3	8.6
123789-HxCDD	29.5	4.5	27.3	1.5	6.2
1234678-HpCDD	267.3	67.0	261.7	20.5	66.1
OCDD	613.6	576.6	616.0	117.8	197.5
I-TEQ (NATO/CCMS) (NR=LR/2)	110.4	28.6	72.2	10.9	21.6
PCDD/F/I-TEQ	37.6	58.6	35.6	51.0	43.6

Tab.1: measures of PCDD/F in air (DIIAR, 2003).

The results of laboratory tests in measurement campaigns between 2005 and 2007 (see Tab.2) show levels of I-TEQ sites investigated quite consistent with values between 10 and 75 fg_{I-TEQ} m⁻³. Two exceptions are detected for the first sample I1, which has a value of 115 fg_{I-TEQ} m⁻³ and for the measurement performed at the control unit of air quality of Gardolo (queues AD02) with a value of

138 fg_{L-TEQ} m⁻³: The fact that these values are not confirmed by other levies can be connected to the fact that we are in the presence of particularly unfavorable environmental conditions, as confirmed by the values of PM₁₀ detected by the control units of air quality in the same period (96 and 86 µg m⁻³ respectively). From the available data a significant correlation between PCDD/F and PM₁₀ doesn't seem evident. However, differentiating the measurements carried out in Trento Nord from those carried out in Trento Sud, it emerges that in the first case there is a certain correlation, unlike the second case in which the correlation is irrelevant. This may either be due to the fact that the correlation between the values of PM₁₀ and the values of PCDD/F is detectable during periods of peak PM₁₀ (measured in Trento Nord) and is not significant for lower values of PM₁₀ (such as those measured in Trento Sud) and to the fact that the air quality in Trento Nord (mostly affected by vehicular traffic and human activities) differs from that of Trent Sud (urban-rural background) (DICA, 2006). During the campaign 2006/2007 the correlation found between PCDD/F and PM₁₀ pollution seems significant and represents an important in understanding the dynamics of transport of PCDD/F in the atmosphere (DICA, 2007).

Site name	Trento Nord – interporto offices			Trento Nord via Bepi Todesca	Trento Sud – cabina ECA			Trento Sud – Maso Stella		Trento Sud – cabina Trenta		Trento Nord – scalo merci interbrennero		Control unit of Gardolo		Control unit of Parco S.Chiera
Sample code	I1	I2	AD07	T2	MS1	MS3	AD06	MS2	MS4	MS7	AD05	F6	AD08	G2	AD02	SC2
Sample period	16-19 feb 06	23-26 feb 06	19-21 feb 07	22-28 feb 06	6-9 mar 06	14-17 mar 06	13-15 feb 07	6-12 mar 06	13-20 mar 06	25-28 mar 06	05-07 feb 07	23-30 mar 06	27 feb - 01 mar 07	4-7 apr 06	18-19 jan 07	10-13 apr 06
Distance from A22 (meters)	100	550	100	760	60	60	60	530	530	240	240	550	550	1500		1200
Control unit nearest	GAR			GAR	SCH			SCH		SCH		GAR		GAR		SCH
Distance from Control unit (meters)	1,700			990	3,700			3,500		3,700		1,300		0		0
PM _{10s} average value (control unit) (µg m ⁻³)	96	35	26	37	17	61	29	21	59	63	61	54	38	21	86	16
PM _{10s} average value (3 control units) (µg m ⁻³)	83	30		33	20	66		25	63	74		50		19		19
I-TEQ (fg m ⁻³)	115	58	23	69	17	33	31	49	33	27	75	32	18	17	138	10

Tab. 2: Comparison between the values of PCDD/F and of PM₁₀ in monitoring campaigns 2005/2006 and 2006/2007.

Site	Zambana		Lavis		Terlago	
Sample's date	11 sept 09	24 mar 10	21 sept 09	23 mar 10	28 sept 09	08 apr 10
Sample's code	AD01Z	AD06Z	AD02L	AD05L	AD03T	AD07T
PCDD [fg Nm ⁻³]	103.47	233.46	133.35	223.92	138.07	243.35
PCDF [fg Nm ⁻³]	33.56	206.75	54.26	194.24	68.57	69.19
PCDD/F [fg Nm ⁻³]	137.03	440.21	187.61	418.16	206.64	312.54
PCDD/PCDF	3.08	1.13	2.46	1.15	2.01	3.52
PCDF/PCDD	0.32	0.89	0.41	0.87	0.50	0.28
I-TEQ (NATO) [fg_{I-TEQ} Nm⁻³]	5.60	25.62	6.66	20.02	7.74	10.55
PCDD/F/I-TEQ	24.45	17.18	28.19	20.89	26.69	29.62
Toxic congeners (NR= 0 / NR=LR)	40%	99%	57%	90%	61%	52%
Omologous (NR= 0 / NR= LR)	23%	99%	91%	99%	92%	24%

Tab. 3: PCDD/F's measurea in air – monitoring campaign (2009's spring and 2010's winter) (NR=LR) (DICA, 2010).

During the years 2009-2010 three sites were analyzed in addition to the previous measurement campaigns, as shown in Tab.3 (DICA, 2010). The concentrations of PCDD/F I-TEQ (NATO) recorded during the summer show values between 5.60 and 7.74 $\text{fg}_{\text{I-TEQ}} \text{m}^{-3}$ increasing to between 10.55 and 25.62 $\text{fg}_{\text{I-TEQ}} \text{m}^{-3}$ in winter. The measured values are between 137.03 $\text{fg}_{\text{I-TEQ}} \text{m}^{-3}$ of Zambana and 206.64 $\text{fg}_{\text{I-TEQ}} \text{m}^{-3}$ of Terlago in summer, while ranging from 312.54 $\text{fg}_{\text{I-TEQ}} \text{m}^{-3}$ of Terlago to 440.21 $\text{fg}_{\text{I-TEQ}} \text{m}^{-3}$ of Zambana as concentrations measured in the winter campaign. In the description of PCDD/F is important to determine the ratio between dioxins and furans (PCDF/PCDD) and the profile of homologues. This information is called "fingerprints": indeed, it has been identified as similar thermal processes show fingerprints similar because it is assumed that the mechanisms of formation of some compounds of dioxins and furans is similar in similar processes (Huang and Buekens, 1995). The "fingerprints" from combustion sources are: ratio PCDF/PCDD greater than 1, increasing in weight distribution of homologous to increasing the degree of chlorination for PCDD, and with a maximum at PeCDF or HxCDF for PCDFs. As regards the relationship between PCDDs and PCDFs, PCDDs prevail compared to PCDFs in all sites, with a ratio PCDF/PCDD variable between 0.32 and 0.50 in the summer measurements, while in winter this ratio assumes a value of approximately 0.9 for sites Zambana and Lavis. Also with regard to the relationship between PCDD/F and toxicity equivalent, the values are comparable in all the sites of sampling, and vary between 24.45 and 28.19 in summer, and between 17.18 to 29.62 in winter. These values lead to exclude the origin of PCDD/F from a specific source of ignition. The measured concentrations are therefore the effect of a complex interaction between all the different sources on site. It should also take into account the period in which the analysis were carried out. In summer, as is known, the presence of the main pollutants is reduced by a lower release to the environment of these substances, but above all thanks to the meteorological conditions that facilitate the dispersion and therefore the dilution of the pollutants in the air. The measurements were carried out at the end of winter. Thus it was therefore not possible to characterize the peak of pollutants during winter, which normally occurs during the period from February to March. As regards the toxic congeners it can be noticed a difference between the values registered in winter than in summer campaign. In particular, it can be seen that the samples collected in Lavis and Zambana in winter 2010, showing a relationship between measurements that consider zero compounds below the detection limit of analytical and measures that consider the value of the compound equal to the limit of detection analytical greater than 90%, show different profiles compared to the other samples. It can be seen instead as the profiles of the counterparts are substantially homogeneous in the samples collected in summer. In the analysis of homologous there aren't similarities with known fingerprints of measurements made in industrial plants. The most abundant component (OCDD) is also the least toxic with toxicity value equivalent, according to the indices NATO, equal to 0.001 times that of the component most toxic dioxin 2,3,7,8-TCDD (DICA, 2010).

The results of the measurements of PCDD/Fs in the air during the measurement campaign conducted in the winter 2009-2010 by APPA are shown in Tab.4: the values obtained are not critical, but in the period from January 6 to 8 at the fish farming a measured value of PCDD/F equal to 275 $\text{fg}_{\text{I-TEQ}} \text{m}^{-3}$ was found, when the closer steel plant was inactive. An unexpected very low concentration of 0.4 $\text{fg}_{\text{I-TEQ}} \text{m}^{-3}$ was found in the most remote site ("Cantiere comunale"), which may be considered unreliable for the period of study.

Location	“Cantiere comunale”				Fish farming			
	4-6 jan 2010	6-8 jan 2010	1-3 feb 2010	3-5 feb 2010	4-6 jan 2010	6-8 jan 2010	1-3 feb 2010	3-5 feb 2010
PCDD/F I-TEQ (NATO) (fg _{I-TEQ} m ⁻³)	27.1	0.4	9.5	46.0	23.4	275	25.0	5.2

Tab.4: PCDD/F's air concentrations in APPA's monitoring campaigns (APPA, 2010).

The results of 2012's monitoring air campaign will be added in the final version of this paper.

5. CONCLUSIONS

The monitoring campaigns carried out during the years (from 2002 to 2012) in the province of Trento show values of PCDD/F in air relatively low, in line with the values found in other Italian cities, as it can be seen from the values reported in Tab.5. Anomalous results were only detected during the monitoring campaign carried out in the surroundings of the steel making plant: in particular, a very low concentration and an unexpected peak when the plant was not operating were found (0.4 fg_{I-TEQ} m⁻³ and 275 fg_{I-TEQ} m⁻³ respectively). Typical values for agricultural regions were found in rural areas, with an increase during winter, due possibly to biomass burning; typical values for urban areas were found in the urban sites, with higher concentrations with respect to rural sites due to the presence of more combustion sources; however, no critical situations were detected.

Location	PCDD/F I-TEQ [fg _{I-TEQ} m ⁻³]	Caratteristiche dell'area	References
Milano	218.62	Urban area (annual average)	Fanelli, 1997
	126.14	Urban area (spring)	Fanelli, 1997
	39.75	Urban area (summer)	Fanelli, 1997
	230.79	Urban area (autumn)	Fanelli, 1997
	477.79	Urban area (winter)	Fanelli, 1997
Roma	85 (50-280)	Urban area	Turrio-Baldassarri et al., 1994
Cremona	22-124	Urban area close to a sewage treatment plant	DIIAR, 1997; DIIAR, 2000
	36-73	Urban area close to a road with high traffic	DIIAR, 1997; DIIAR, 2000
	39-110	Suburban urban	DIIAR, 1997; DIIAR, 2000
Bolzano	67.4	Suburban area (spring)	DICA, 2001
	9.6	Rural background (spring)	DICA, 2001
	14	Urban area (summer)	DICA, 2001

Tab.5: Examples of measurements of PCDD/F in air detected in Italian characterized areas (DIIAR, 2001).

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