CHARACTERIZATION OF PCDD/F AND PCB IN CONIFER NEEDLES FOR SEEKING POTENTIALLY CRITICAL HUMAN EXPOSURE CONDITIONS

Rada E.C., Ragazzi M., A. Chisté

Introduction

Several studies have established that conifer needles are able to accumulate many semi-volatile organic compounds SVOCs (Gaggi et al.,1985; Eriksson et al., 1989), including dichlorodiphenyltrichloroethane DDTs, Hexachlorocyclohexane HCHs (Tremolada et al., 1993), polychlorinated biphenyl PCBs (Jones et al., 1992; Kylin et al., 1994), Polycyclic aromatic hydrocarbons PAHs (Simonich and Hites, 1994; Tremolada et al., 1996), and dioxins (Di Guardo et al., 1999). Conifers, being evergreen species, can accumulate Persistent Organic Pollutants (POPs) for several years compared to broadleaf species because of their longer leaf turnover time (Di Guardo et al., 2003). Gaseous pollutants penetrate needles through the stomata and spread along the intercellular spaces throughout the photosynthesizing mesophyll tissue (Viskari et al., 2000). Thus caution must be exercised when using conifer needles as passive samplers since monitored concentrations presumably depend on a number of factors; among those, some can be listed: species, age of the needles, wax content and nature, aerodynamic factors, temperature and precipitation history, and location of the needles within the forest canopy, as well as ambient concentrations in both gaseous and aerosol phases (Di Guardo et al., 2003). A monitoring of vegetation is a cheapest and best available tool for estimation of the atmospheric contamination levels at remote and poorly accessible locations like the high mountains (Klanova et al., 2009).

The present study proposes a comparison between the values of deposition of polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) and polychlorinated biphenyls dioxin like (PCBs dl) on the needles of spruce trees of four places in the area near a steel making plant in northeast Italy. A total of eight samples of needles were examined, two for tree, referred to two different periods, 2011 and 2005 years. It is significant to consider that the two reference periods are previous and successive to year 2009, when the plant began to operate according to Best Available Technology (BAT).

Materials and Methods

The monitored source point is a steel making plant located in North-East of Italy, into the Alps mountain. This plant works since 1978. Raw materials for this plant are principally ferrous wastes which arrive through heavy vehicles. The final products are billets and bars of iron. Over the years the plant has undergone many changes in order to reduce the emissions. The history of emissions configuration has been reconstructed in order to select needles significant for sampling.

The emissions into the atmosphere from the plant can be primary or secondary. The first come from the raw material combustion into the furnace and from refining furnace, the second from other operations into the plant (spillage, ladle transport operation, etc) and are called diffuse emissions.

Since 1990 the emission suppression system has been characterized by two lines: one for the primary emissions and a part of the secondary, and one only for the secondary emissions. The two lines are connected with two stacks called E1 and E2. Part of the emission control system is composed of a quenching tower (only for the E1 line), a horizontal cyclone and a filter in the end of the line (for both

lines). The chimneys height is 40 m. In the past with the absence of Best Available Techniques (BAT) the abatement system was composed of a basic Air Pollution Control (APC) system characterized by a fabric filter (dust bag), a quenching tower, a vertical cyclone and a bag filter. Since the 2009 year, with the adoption of BAT, this configuration has been improved by a O2 post-burner (oxygen lance), a horizontal cyclone, an increase of the secondary emission aspiration flow and an increase of the bag filter efficiency.
Sampling spruce needles criteria are highly dependent on type of study that has to be conducted. In this case a specify source point of pollution has been monitored and in this way the needles has been sampled from four different points at increasing distance from the source along the main direction of the valley. Sampling sites identified with numbers 1, 2 and 3 are to the east - north east of the plant, number 4 instead to west (Figure 1). Table 1 shows the sampling locations and the distances from the chimneys of the plant.

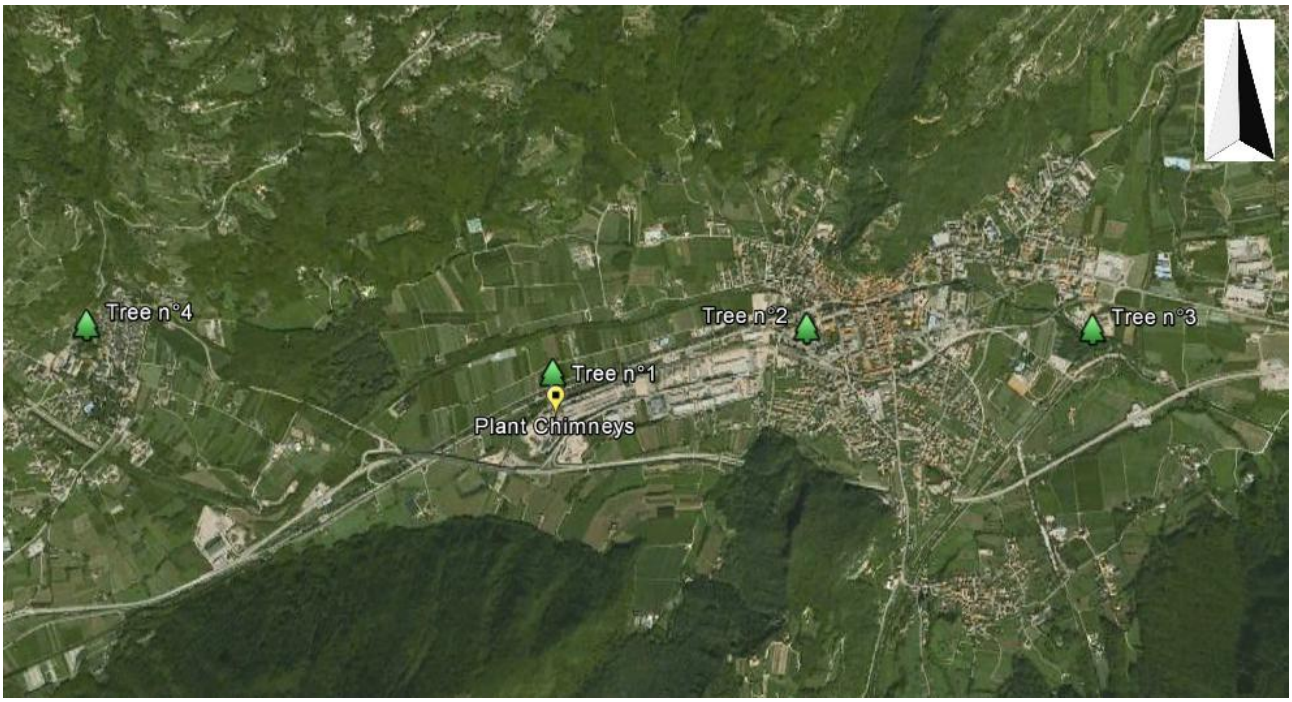

Figure 1. Sampling points location

Sample	Distance from the stacks [m]
1	120
2	1,300
3	2,700
4	2,300

Table 1. Sampling point distances

From the branches of the same tree two different sampling are obtained, in order to have samples of different ages in each location (Di Guardo et al., 2003, Ratola et al., 2011, Urban et al., 2004). The criteria used to obtain two needles samples different of two separate ages is the identification of the nodes on the main branch, from which, by a simple counting, it is possible go back in time finding needles of different periods (Figure 2). Samples collected in this study relate to the years 2011 and 2005.

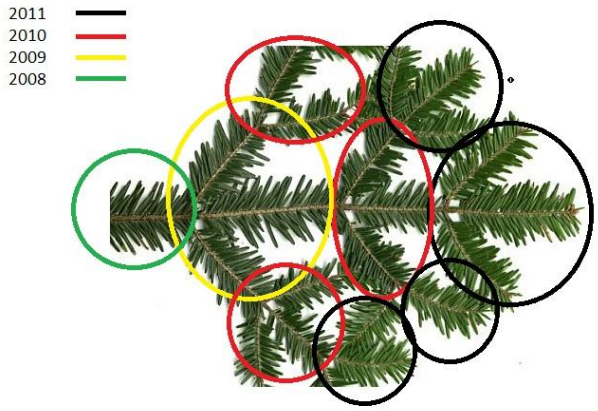

Figure 2. Criteria of dating

Each sample analyzed has a fresh weight of about 250 grams, the sum of the weight of the needles collected from tree at different heights and in different points, in order to ensure a homogeneous sample and a good significance of the sample itself, considering the different exposure that may have branches compared to the source monitored. All samples were immediately packed in an aluminum foil and sealed in a plastic bag, and then shipped to the laboratory. The analysis carried out on samples are of Polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) and polychlorinated biphenyls dioxin like (PCBs dl) concentration. To perform the PCDD/Fs and PCBs dl concentration analysis the United States Environmental Protection Agency (EPA) protocols were followed, respectively EPA 1613 1994 b and EPA 1668 b 2008.

Results

The analysis results are in terms of concentration of PCDD/Fs and PCBs, divided into the main congeners. In addition to the simple concentrations the Toxic Equivalent Concentration (TEQ) can be obtained, using the toxic equivalency factors TEFs. International factors (I-TEFs) are available to this concern, developed by an international scientific committee convened under the auspices of the North Atlantic Treaty Organization (NATO) in 1989 and later extended and updated (NATO/CCMS), while WHO-TEFs refer to those defined by the World Health Organization (WHO) and revised in 2005 (UNEP/POPS/COP.3/INF/27). In the following tables 2 and 3 the concentration values obtained from the different samples are listed, the last line showing the value of TEQ of the sample, calculated using the TEF of each congener. Blue values are those concentrations below the instrumental detection limit (LOD), which were considered to be equal to half of LOD (ISTISAN).

The concentrations obtained are very low, as evidenced by the many values below the LOD, 110 of 136 for PCDD/Fs and 53 of 96 for PCBs dl. This may be due to the fact that the plant after the 90s has a low emission of these compounds and in the area there is not another significant source (the valley is characterized by a rural general appearance). The low concentrations are also demonstrated by a comparison with the depositions measured on a sample of needles collected in Denali National Park (Alaska) and subject to the same analysis. Considering the sample "Alaska" as originating from a typical low air pollution environment, it is noted as the depositions in terms of TEQ are similar to those found in the study area.

	I-TEF	C (ng/kg DM)							
		2005				2011			
		1	2	3	4	1	2	3	4
2,3,7,8 - TCDD	1	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
1,2,3,7,8 - PCDD	0.5	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
1,2,3,4,7,8 - HxCDD	0.1	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
1,2,3,6,7,8 - HxCDD	0.1	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.70
1,2,3,7,8,9 - HxCDD	0.1	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
1,2,3,4,6,7,8 - HpCDD	0.01	0.25	0.25	0.25	0.25	0.25	0.25	0.25	1.20
OCDD	0.001	2.90	3.30	0.50	2.20	0.50	2.00	0.50	3.20
2,3,7,8 - TCDF	0.1	0.20	0.30	0.05	1.80	0.05	0.05	0.10	0.90
1,2,3,7,8 - PCDF	0.05	0.25	0.25	0.25	0.90	0.25	0.25	0.25	1.90
2,3,4,7,8 - PCDF	0.5	0.25	0.25	0.25	0.60	0.25	0.25	0.25	1.10
1,2,3,4,7,8 - HxCDF	0.1	0.25	0.25	0.25	0.25	0.25	0.25	0.25	1.80
1,2,3,6,7,8 - HxCDF	0.1	0.25	0.25	0.25	0.25	0.25	0.25	0.25	2.20
2,3,4,6,7,8 - HxCDF	0.1	0.25	0.25	0.25	0.25	0.25	0.25	0.25	1.30
1,2,3,7,8,9 - HxCDF	0.1	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
1,2,3,4,6,7,8 - HpCDF	0.01	0.70	0.70	0.70	0.90	0.25	1.20	0.25	3.00
1,2,3,4,7,8,9 - HpCDF	0.01	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
OCDF	0.001	0.50	0.50	0.50	0.50	0.50	0.50	1.00	1.70
ng I-TEQ/kg DM		0.523	0.533	0.506	0.892	0.501	0.512	0.507	1.634

Table 2. PCDD/F concentrations in needles

	WHO -TEF	C (ng/kg DM)							
		2005				2011			
		1	2	3	4	1	2	3	4
IUPAC 77	0.0001	47.00	28.00	1.00	81.00	18.10	6.60	3.60	42.00
IUPAC 81	0.0003	0.50	0.50	0.50	1.60	0.50	0.50	0.50	0.50
IUPAC 105	0.00003	128.00	50.00	2.50	108.00	32.00	22.00	21.00	69.00
IUPAC 114	0.00003	4.30	1.90	0.50	3.80	1.70	1.40	0.50	7.60
IUPAC 118	0.00003	164.00	75.00	10.00	260.00	71.00	45.00	30.00	186.00
IUPAC 123	0.00003	12.50	11.50	0.50	14.00	8.20	7.00	4.10	7.70
IUPAC 126	0.1	0.50	1.10	0.50	1.10	0.50	0.50	0.50	0.50
IUPAC 156	0.00003	18.70	7.50	7.50	24.00	7.50	7.50	7.50	7.50
IUPAC 157	0.00003	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
IUPAC 167	0.00003	9.40	5.20	2.50	8.70	2.50	2.50	2.50	2.50
IUPAC 169	0.03	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
IUPAC 189	0.00003	2.50	2.50	2.50	6.90	2.50	2.50	2.50	2.50
ng WHO-TEQ/kg DM		0.080	0.133	0.066	0.146	0.071	0.069	0.068	0.078

Table 3. PCB concentrations in needles

Not always the concentrations of 2005 samples are higher than those of 2011 (tables 4 and 5), as one would expect since the deposition of the first is six years longer than the second.

	I-TEF					2011 vs 2005 (red = 2011>2005) (green = 2011<2005) (n.a. = not assesseable)			
						1	2	3	4
2,3,7,8 - TCDD	1					n.a	n.a	n.a	n.a
1,2,3,7,8 - PCDD	0.5					n.a	n.a	n.a	n.a
1,2,3,4,7,8 - HxCDD	0.1					n.a	n.a	n.a	n.a
1,2,3,6,7,8 - HxCDD	0.1					n.a	n.a	n.a	0.70
1,2,3,7,8,9 - HxCDD	0.1					n.a	n.a	n.a	n.a
1,2,3,4,6,7,8 - HpCDD	0.01					n.a	n.a	n.a	1.20
OCDD	0.001					0.50	2.00	n.a	3.20
2,3,7,8 - TCDF	0.1					0.05	0.05	0.10	0.90
1,2,3,7,8 - PCDF	0.05					n.a	n.a	n.a	1.90
2,3,4,7,8 - PCDF	0.5					n.a	n.a	n.a	1.10
1,2,3,4,7,8 - HxCDF	0.1					n.a	n.a	n.a	1.80
1,2,3,6,7,8 - HxCDF	0.1					n.a	n.a	n.a	2.20
2,3,4,6,7,8 - HxCDF	0.1					n.a	n.a	n.a	1.30
1,2,3,7,8,9 - HxCDF	0.1					n.a	n.a	n.a	n.a
1,2,3,4,6,7,8 - HpCDF	0.01					0.25	1.20	0.25	3.00
1,2,3,4,7,8,9 - HpCDF	0.01					n.a	n.a	n.a	n.a
OCDF	0.001					n.a	n.a	1.00	1.70

Table 4. PCDD/F comparison: 2011 vs 2005

	WHO –TEF					2011 vs 2005 ((red = 2011>2005) (green = 2011<2005) (n.a. = not assesseable)			
						1	2	3	4
IUPAC 77	0.0001					18.10	6.60	3.60	42.00
IUPAC 81	0.0003					n.a	n.a	n.a	0.50
IUPAC 105	0.00003					32.00	22.00	21.00	69.00
IUPAC 114	0.00003					1.70	1.40	n.a	7.60
IUPAC 118	0.00003					71.00	45.00	30.00	186.00
IUPAC 123	0.00003					8.20	7.00	4.10	7.70
IUPAC 126	0.1					n.a	0.50	n.a	0.50
IUPAC 156	0.00003					7.50	n.a	n.a	7.50
IUPAC 157	0.00003					n.a	n.a	n.a	n.a
IUPAC 167	0.00003					2.50	2.50	n.a	2.50
IUPAC 169	0.03					n.a	n.a	n.a	n.a
IUPAC 189	0.00003					n.a	n.a	n.a	2.50

Table 5. PCB comparison: 2011 vs 2005

In fact the limit of air quality monitoring with spruce and conifer needles are those characteristic of all passive system of monitoring, due the bounce during primary deposition since the monitoring surface can interrupt its interaction with environment after the accumulation (Lehndorff et al., 2004), due the wash off by rain and wind removal (Lehndorff et al., 2004, Lehndorff et el., 2006, Urban et al., 2004) or of chemical and physical alterations of the needles surface itself, such a degradation or new production of epicuticular wax (Lehndorff et al., 2006).
In this study the most significant concentration values, however, are those found in the number 4 sample. For both years, 2005 and 2011, concentrations of the samples expressed as TEQ are resulted greater than those of the other selected trees. It is also significant to note that number 4 spruce is the only one who stands to the west of the plant.

CONCLUSIONS

In this study several samples of spruce needles were analyzed, subjecting them to tests on the concentration of PCDD/Fs and PCBs dl. The primary objective was to verify the incidence of a steel making plant on local air quality, in particular the use of spruce needles allows going back to values of pollution not only of the present, but also of the past. This fact is very important and allows, in this case, verifying whether the introduction of BAT by the facility has produced significant changes in the values of deposition of pollutants in the area. A comparison between the value of deposition on the needles dating back to 2005 and 2011 made it possible to say that there are not big differences, and this contributes to say that the plant activity was not critical also few years before the BATs (2005-2009).

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