POLYCHLORINATED DIBENZODIOXINS (PCDDS) AND DIBENZOFURANS (PCDFS) IN THE URBAN AIR OF FLORENCE, ITALY — A PRELIMINARY EVALUATION

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Introduction

The 17 polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) with a 2,3,7,8-chlorosubstitution pattern are known to elicit severe toxic responses — including carcinogenic effects — in laboratory animals, even at very low exposures. In particular, the most toxic PCDD congener, 2,3,7,8-T_4CDD, was ranked a Class 1 (i.e., human) carcinogen by IARC (1997).

PCDDs and PCDFs are not industrial chemicals; however, many anthropogenic activities, by-and-large related to combustion processes, are at the origin of their undesirable formation and release into the environment, where they become an important environmental and human health risk factor. As vehicular traffic and home heating were recognized sources of PCDD and PCDF contamination, these chemicals were monitored a number of times since the early 1990s in the air of some Italian cities. This paper describes the outcomes of the monitoring campaigns carried out in the city of Florence for a year long in 1995–1996 and during the month of July in 2000.

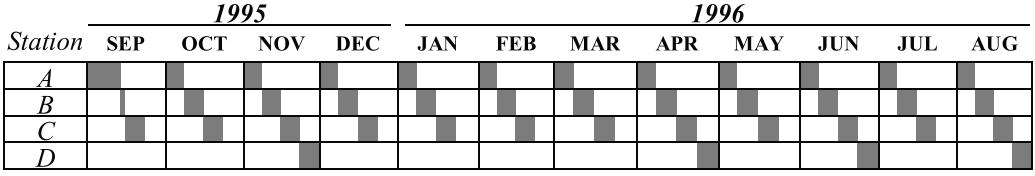
Air Sampling

As per the Italian law, 1995–1996 ambient air samplings were performed at three urban locations (Stations A "Giardino di Boboli", B "Via Bassi", and C "Viale Gramsci"), in ascending anthropogenic and vehicular traffic impacts, and at one extra-urban site (Station D "Castagneto", general environment or background). The latter was some 40 km away from Florence, at an altitude of approximately 700 m. The sampling time scheme adopted is summarized in Table 1: each urban station was activated for a few days a week, in a sequential pattern lasting three weeks a month; each month, the sequence was re-started. Station D was activated four times over the entire observation year.

In July 2000, only an urban station C-type ("Via Ponte alle Mosse") was utilized. Twelve day-long air samplings were performed, at intervals of two to three days.

High-volume samplers for inhalable particulate (Ø, <10 µm) were utilized at a samplig height of some 2 m from ground, with an average flow rate of approximately 60 m^3/h. Each sampler was equipped with a trapping set (face, 10 ´ 10 cm) made of an outer glass-fiber filter followed by a train of three contiguous polyurethane foam (PUF) septa (thickness, 4 cm each). Each sampling episode was organized to last up to 24 continuous hours (minimum sampled volume, 1400 m^3). A filter was replaced with a new one after a 24-h operation or earlier, if the air flow rate decreased too much. To evaluate sampling efficiency/reliability, each filter was spiked by dispersing droplets of volatile solutions containing known amounts of ^{13}C-labelled internal standards (tracers). Prior to use, the septa were extensively washed with dichloromethane and *n*-hexane and dried. The sampling technique was adapted from Berlincioni *et al.* (1993).

Table 1. Sampling time scheme to monitor Florence, Italy, ambient air in 1995–1996.



Analysis

After sampling, each trapping set was extracted several times with dichloromethane: the glass fiber filter and the PUF train were treated together by mechanical pressing in an ultrasonic bath at room temperature. Fractions were pooled, gently evaporated to a small volume, added with a complemental set of tracers (for a total of 16 2,3,7,8-chlorosubstituted congeners), and cleaned up according to a procedure derived from Berlincioni *et al.* (1992, 1993).

Each concentrated extract was first subjected to silica (100–200-mesh Bio-Sil; 4% water, w/w) column chromatography by eluting with *n*-hexane followed by other solvents. The *n*-hexane eluate was reduced to a small volume and filtered through an activated 100–200-mesh basic alumina column by eluting with *n*-hexane containing 0.6% dichloromethane (v/v) followed by a 9:1 (v/v) *n*-hexane-dichloromethane mixture. This fraction, containing PCDDs and PCDFs, was gently dried and taken up to an appropriate volume with *iso*-octane.

Congener-specific quantitation was carried out by high resolution gas chromatography combined with high resolution mass spectrometry utilized in the single ion monitoring mode (HRGC-HRMS(SIM)). GLP and QA/QC protocols were applied throughout. In general tracers were recovered with yields between 60 % and 130 %; recovery yields <20 % were not considered to be adequate: such results were individually checked and, if possible, the analysis was repeated.

Results and Discussion

The outcomes of the 1995–1996 analytical assessments are reported in Table 2 as cumulative analytical, I-TE (NATO/CCMS, 1988), and WHO-TE (van Leeuwen and Younes, 2000) monthly values of the 17 PCDD and PCDF congeners of interest. From the table, the following may be readily observed: *(a)* higher contamination values seem to be broadly associated with cooler environmental temperatures (e.g., winter months), and *vice versa* ([Max] ´ [Min]$^{-1}$ = 2–4); *(b)* the I-TE values are slightly greater than, or coincident with, the WHO-TE ones; *(c)* the year-based mean estimates of the urban monthly concentrations increase steadily when moving from Station A, to B, to C, as expected (e.g., 11.4 ± 3.8, 14.4 ± 3.6, and 19.6 ± 8.2 fgI-TE/m^3, respectively); *(d)* all year-based urban means are significantly higher than the mean value estimated for the general environment (Station D, 6.3 ± 3.3 fgI-TE/m^3). The year-based averaged congener-specific profiles detected at Stations A, B, C, and D (Figure 1) are in excellent agreement with each other, as if PCDD and PCDF contamination were to be traced back to a general common origin, mostly not site-specific. The TE estimates are primarily contributed by PCDFs (80–90 %), the 2,3,4,7,8-P$_5$CDF being the main contributor (30–40 %).

The average contamination levels in July 2000, as estimated from 12 daily determinations, were: 225 ± 81 fg/m^3, 9.8 ± 2.3 fgI-TE/m^3, and 9.7 ± 2.3 fgWHO-TE/m^3. These values are in very good agreement with the 1995–1996 July assessment carried out at Station C "Viale Gramsci" (234 fg/m^3,

10.8 fgI-TE/m^3, and 10.7 fgWHO-TE/m^3). Again, the TE estimates are primarily contributed by PCDFs (more than 90 %) and, in particular, by the 2,3,4,7,8-P_5CDF congener (more than 40 %). Figure 2 exhibits the mean PCDD and PCDF analytical profile, that appears to be consistent with those of the 1995–1996 assessments.

In 1993 the PCDD and PCDF winter levels in Florence ambient air, as estimated by the 95% confidence interval, were 72–200 fgI-TE/m^3 (mean, 120 fgI-TE/m^3): this outcome was obtained by pooling the results from repeated assessments at the canonical Stations A, B, and C (Berlincioni *et al*., 1995). Even considering that in 1993 all the air-borne particulate was sampled, these figures could indicate that a remarkable reduction of PCDD and PCDF presence in Florence air has occurred over time. This phenomenon is likely to be correlated to the substitution of town gas with methane for home heating, to the introduction of "green" gasoline and vehicles equipped with catalytic converters, and in general to the enforcement of regulations to reduce air pollution. Preliminary results seem to provide evidence of a similar trend in Rome ambient air as well.

Table 2. Summary of monthly cumulative analytical, I-TE, and WHO-TE results obtained from Florence, Italy, ambient air monitoring in 1995–1996. Values rounded off to three figures.

	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG
Station A "Giardino di Boboli"												
fg/m^3	363	416	412	314	288	130	193	333	359	247	280	199
fgI-TE/m^3	10.5	16.6	17.6	16.0	10.9	7.91	7.29	11.9	12.6	11.1	7.53	6.73
Fgwho-te/m^3	10.3	16.4	17.4	15.9	10.8	7.86	7.21	11.7	12.4	12.9	7.37	6.63
Station B "Viale Bassi"												
fg/m^3	342	502	518	607	529	389	323	597	303	214	342	271
fgI-TE/m^3	10.5	16.4	19.1	18.2	11.7	15.0	16.5	18.3	14.4	11.7	13.7	6.95
Fgwho-te/m^3	10.3	16.2	18.9	19.2	11.4	14.8	16.4	18.0	14.3	12.8	13.6	6.79
Station C "Viale Gramsci"												
fg/m^3	352	441	665	680	1840	569	398	361	572	294	238	208
fgI-TE/m^3	18.1	18.1	29.9	39.4	18.6	21.5	16.7	16.0	22.9	13.6	10.8	9.93
Fgwho-te/m^3	18.0	19.2	29.6	39.1	17.2	21.2	16.5	16.9	24.8	14.6	10.7	9.84
Station D "Castagneto"												
fg/m^3			270					126		98.1		136
fgI-TE/m^3			10.5					7.04		5.09		2.63
Fgwho-te/m^3			10.4					7.00		5.05		2.56

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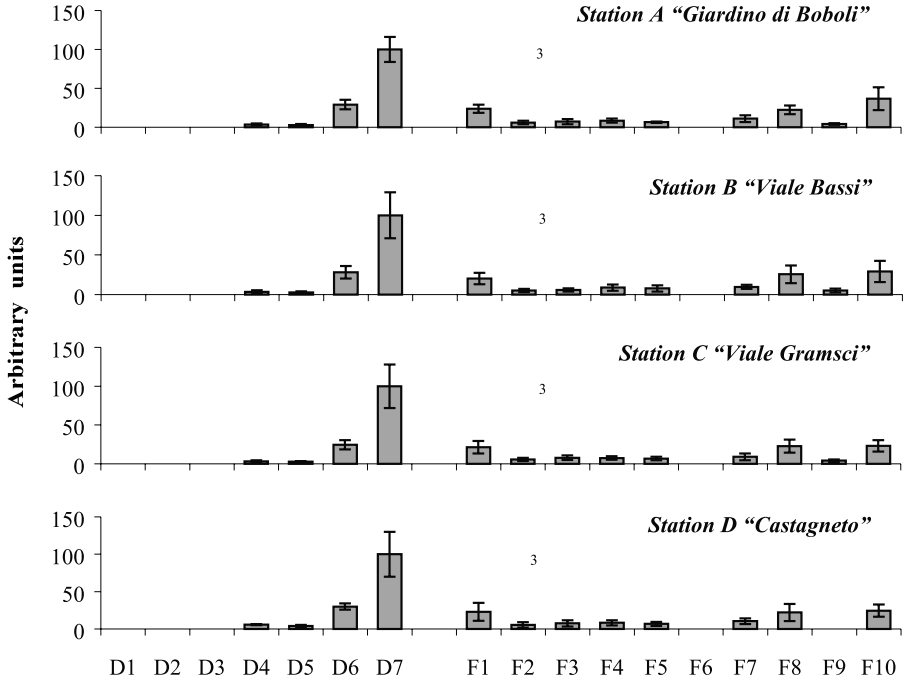

Figure 1. Average PCDD and PCDF profiles detected in Florence ambient air in 1995–1996.

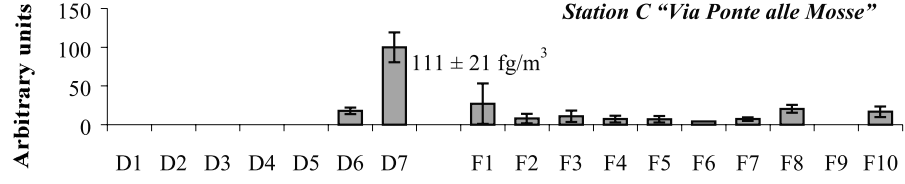

Figure 2. Average PCDD and PCDF profile detected in Florence ambient air in July 2000.

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