PCDD, PCDF, PCB AND PAH IN OUTDOOR AIR IN ROME: COMPARISON WITH A REMOTE AREA AND INDOOR LEVELS

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Introduction

Organic micropollutants such as PCDDs, PCDFs, PCBs and carcinogenic PAHs have a much higher density than air and are mostly associated with particulate matter, so that their presence in air should be affected by the height; as a consequence people living or working at higher floors of buildings may have lower exposure for the time spent there. The PCB air contamination varies considerably from winter to summer as these compounds can be found in the vapor phase.

A study jointly funded by the ministry of the Environment and the Istituto Superiore di Sanità investigates exposure of the general urban population to organic micropollutants. Relevant variables influencing exposure included in the study are: the difference between indoor and outdoor levels (for PAHs and PCBs), the difference at different floors in the same building (for PCBs and PAHs) and the difference between urban and remote sites (for PCDD/F, PCBs and PAHs). The partition between vapor and particulate phase for PCBs and PAHs is also investigated as an important factor influencing the bioavailability of the substances.

During a whole year two high volume (HV) samplers were operating in a central site in Rome and in a remote site in the Simbruini Natural Park, about 60 km air distance from Rome; PCDD/Fs, PAHs and PCBs were determined. Moreover, contemporary indoor and outdoor samplings were performed in turn in another Rome area. At each time four different low volume (about 300 m^3) samples were taken: two outdoor, at street and terrace level, and two indoor, at a low and a high floor respectively; PAHs and PCB were determined. All samplings were performed with both filter and polyurethane foam in order to discriminate the particle bound compounds from the vapor-phase ones.

At the moment only a little part of the data collected is available, but it is expected that by the symposium time all of the data will be processed.

Methods and Materials

Sampling: two high volume samplers with a PM10 probe and polyurethane foam (PUF) plugs were located, respectively, in Rome and in a remote site in the Simbruini Park and operated contemporarily twice a month. In the same day, on four occasions, four low-volume samplers, also equipped with filter and PUF plug, were placed in one single building (during the study 3 different buildings were visited), taking two indoor and two outdoor samples at different floors.

Extraction: both the low and high volume quartzfiber filters were extracted with dichloromethane in an ultrasonic bath. The HV PUF plugs were extracted in a soxhlet apparatus with a 9/1 n-hexane/ethylether mixture; the low-volume PUF were extracted in the ASE with a 1/1 n-hexane/acetone mixture.

Clean-up: for the dioxin analysis the extracts were concentrated and then eluted on a column packed with concentrated sulfuric acid coated on an inert support (Extrelut, Merck) with 150 mL

of n-hexane. The concentrated residue was further purified on an allumina column followed by a carbon column.
The extracts from the filters were purified by means of TLC[2] for PAH analysis; for PCB analysis the sample was purified by supercritical fluid extraction (SFE) on a HP model 7680 T[3]; on occasion, the analysis of both PCBs and PAHs was performed by SFE[4].
Determination: The dioxin quantification was carried out on an Autospec GC-HRMS system equipped with a BPX-5 column 50 m long, 0.32 mm i.d. The PAH and PCB determination was carried out on a Thermoquest Trace MS equipped with a HT5 column 25 m long, 0.25 id; 60 CB congeners and 9 PAH were analyzed[4].
The analytical methods for PAHs and PCBs were applied successfully to urban dust (NIST 1649a)

Results and Discussion

Most of the data relative to the comparison of indoor and outdoor contamination, with the exception of PAHs, are still being processed, together with many data relative to the high volume samplers. At this time only a few, preliminary results can be shown and a selection of the most meaningful existing data is presented.

Table 1: Dioxin concentration (fg/m^3) in the Urban and Remote sites.

Sampling	Urb 1	Rem 1	Urb 2	Rem 2	Urb 3	Rem 3
2,3,7,8-TCDD	< 0,87	< 0,95	< 0,35	< 0,58	< 0,39	< 0,54
1,2,3,7,8-PeCDD	2,02	< 0,79	8,95	< 1,31	< 1,35	< 1,34
1,2,3,4,7,8-HxCDD	2,46	< 1,5	9,96	< 1,2	2,12	0,7
1,2,3,6,7,8-HxCDD	5,06	< 1,2	14,01	2,3	4,75	0,9
1,2,3,7,8,9-HxCDD	5,56	< 1,4	15,29	1,5	3,95	0,8
1,2,3,4,6,7,8-HpCDD	77,5	7,18	125,4	19,40	36,6	5,92
OCDD	263	31,3	296	52,8	96	10,7
2,3,7,8-TCDF	6,28	< 0,63	5,80	2,04	1,74	< 1,03
1,2,3,7,8-PeCDF	5,02	< 1,3	15,15	1,9	4,09	< 1,2
2,3,4,7,8-PeCDF	9,89	< 1,3	32,49	5,1	10,10	< 1,2
1,2,3,4,7,8-HxCDF	7,28	1,15	31,54	5,80	10,39	1,47
1,2,3,6,7,8-HxCDF	6,92	1,23	25,21	4,53	8,25	1,09
1,2,3,7,8,9-HxCDF	< 5,7	< 1,4	< 1,9	< 1,5	< 1,5	< 0,9
2,3,4,6,7,8-HxCDF	10,6	1,50	34,8	6,77	13,7	2,27
1,2,3,4,6,7,8-HpCDF	36,8	5,47	116,4	29,23	45,4	5,35
1,2,3,4,7,8,9-HpCDF	7,52	1,08	17,73	4,30	6,83	< 1,20
OCDF	27,1	4,44	69,9	21,69	30,3	8,21
Sum fg/m^3	476	58,7	820	159,7	276	41,1
TEQ fgI-TE/m^3	12,9	1,90	38,4	6,31	11,4	1,89
TEQ fgWHO-TE/m^3	13,6	2,07	42,5	6,57	11,6	2,21
fg/m^3 Sum PCDD	356	41,5	470	77,5	144	20,0
fg/m3 Sum PCDF	120	17,2	350	82,2	131	21,1

The dioxin data relative to three winter 2000 samplings (February 20 and 29; March 15) are reported in Table 1. Most of the congeners were detectable in the remote site also; the absolute contamination varies markedly in different samplings, while the ratio between the two sites in the same day displays a much smaller bias.

In a summer HV sample, PCBs were totally in the vapor-phase: 836 pg/m^3, as sum of 60 congeners, were found in the PUF of the urban site versus a list of detection limits (making up a sum lower than 3 pg/m^3) on the filter; in the remote site the sum of the 60 congeners in the PUF amounted to 111 pg/m^3, whilst on the filter they were not detected. On the very limited number of data available, total PCB concentration in air varies, as expected, with temperature[1]. In Figure 1 the distribution of the concentration is shown for 60 PCB congener, relative to the mentioned summer HV sample, for both sites.

For PAHs, there was not a constant trend between the outdoor and indoor levels: local situations, such as the use of coal for the central heating in one of the buildings sampled, may have had a relevant influence, as was suggested by the results of a second sampling with the heating off. Indoor and outdoor PCB data are also expected to complement the information obtained from PAHs, as the two classes of compounds have different origin. The Figure 2 reports the temporal trend of benzo[a]pyrene from February to July 2000.

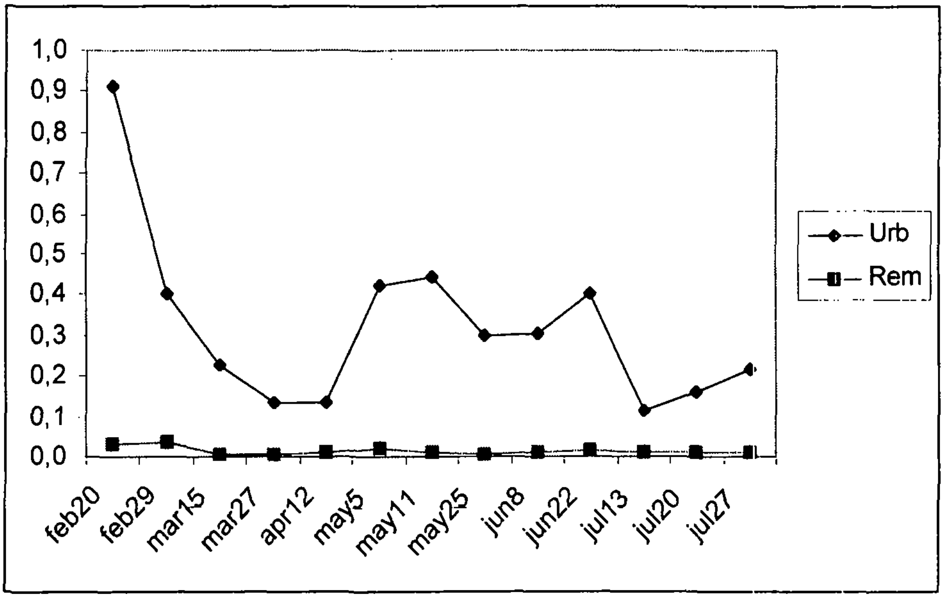

Figure 2: concentration (ng/m^3)of benzo[a]pyrene in the urban and remote site

References

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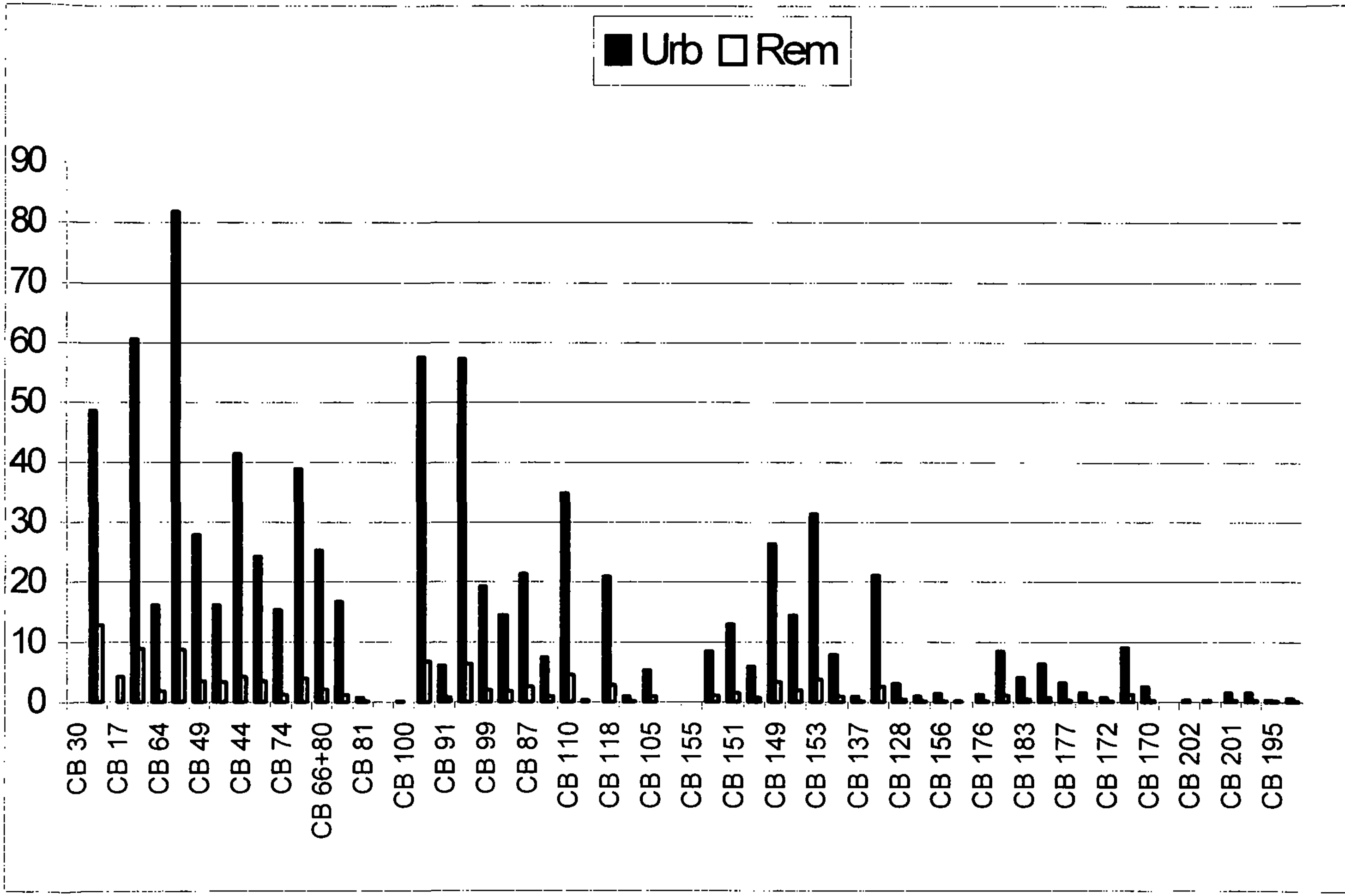

Figure 1: PCB congener concentration (pg/m^3), vapor-phase, of a summer sample in the urban and in the remote site.