LEVELS OF PRIORITY ORGANIC MICROCONTAMINANTS IN URBAN AIR, SOIL, AND BUTTER SAMPLED IN ITALY

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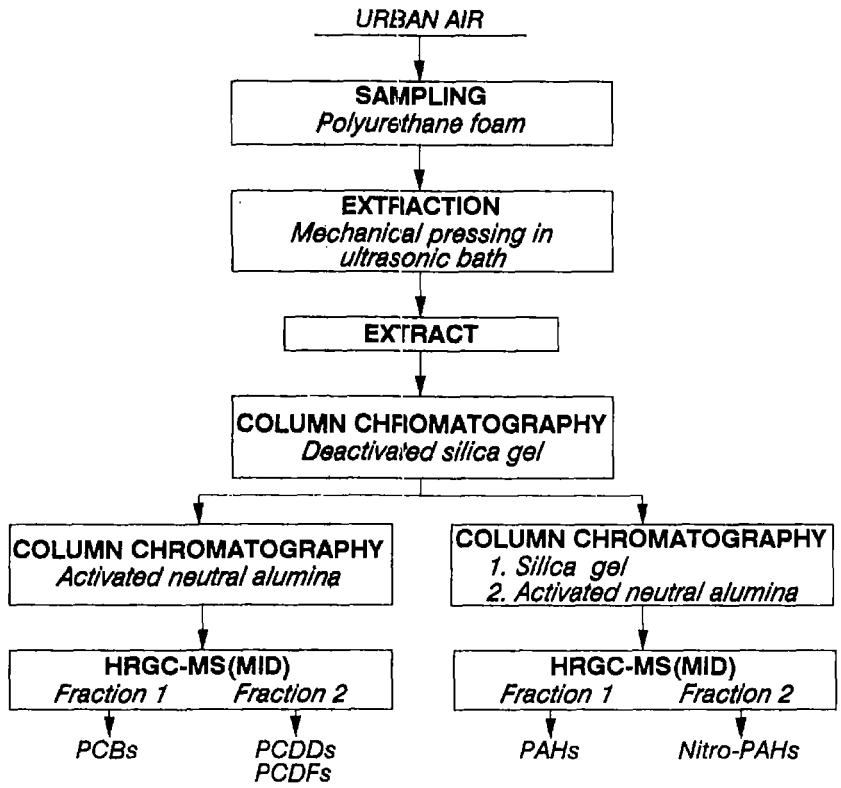
Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), and dibenzofurans (PCDFs), and polynuclear aromatic hydrocarbons (PAHs) and their nitroderivatives (nitro-PAHs) are well-known environmental trace contaminants. Each family consists of a large number of analogs, several of which are severely toxic. The toxic potential includes carcinogenicity at very low chronic exposures. Aside from PCBs which have been produced industrially, PCDD, PCDF, PAH, and nitro-PAH occurrence is unwanted and associated with natural causes and, indirectly, anthropogenic activities. Therefore, when the above chemicals and, specifically, their toxic terms are detected in the environment and in food matrices it is of great relevance to the assessment of human health risks, since man experiences a multimedia exposure to such compounds.

On these premises, our laboratories have been engaged in assaying many different matrices for several years, also by developing appropriate detection procedures (see Berlincioni et al.[1] and the literature cited therein). Further appraisal of the procedure adopted and additional analytical data are reported here. A description of the procedure is in preparation.

The diagram shows the combination of steps used to assay urban air and the changes recently introduced. Sampling was carried out by a high-volume sampler equipped with polyurethane foam septa.[1] The latter were extracted by mechanical pressing and a mixture of n-hexane (40%) and dichloromethane in an ultrasonic bath at room temperature. The extract was subjected to chromatographic cleanup to separate the chemicals under assessment into four different fractions. Urban soil was sampled and extracted as reported.[1] The butter used was a normal commercial product: three brands were tested taking samples of 100 g from each and by dissolving them in 200 ml n-hexane prior to cleanup. The same cleanup steps (see diagram) were adopted for all samples. Destructive techniques, such as treatment with concentrated sulfuric acid,[1] were avoided. Quantitation was carried out by HRGC-MS(MID).



Tables 1-3 summarize the results from this investigation. In general terms, the following may be observed. Aside from those missing, in air PCB congeners with a lower degree of chlorination reach concentration levels greater than PCBs with a higher number of chlorine atoms. As would be expected, this pattern seems to be reversed in the soil, which was collected near the high-volume sampler. In the three butter samples, congeners with a high degree of chlorination [118, 137, 153, 180] exhibit concentration levels somewhat more stable than the other congeners. In terms of 2,3,7,8-T_4CDD equivalents (TE units), the load of PCDDs and PCDFs in air is estimated at 0.064 pg/m^3; however, due to shortcomings in the congener-specific assessment of P_5CDFs, such a figure may be overestimated by up to 30%. In the butter, PCDDs and PCDFs range from 1.1 to 8.4 ngTE/kg, figures that agree with data reported in the literature[5] but are possibly overestimated. Data concerning carcinogenic PAHs show these compounds to be present in all the matrices analyzed; nitro-PAHs were determined only in air. The concentration levels found of these chemicals match the literature data.[4]

All matrices were tested for recovery yield by using large sets of tracers (often, isotopically-labeled compounds) per

Table 1 Uncorrected congener-specific PCB levels detected in urban air and soil and in commercial butter.

Substratum[a]	Urban air[b] (pg/m^3)	Urban soil[c] ($\mu g/kg$)	Butter[d] ($\mu g/kg$)
T_3CB [28]	1.6 E+2[e]	1.6 E-1	<1.0 E-1[f]
T_4CB [52]	1.7 E+2	8.7 E-1	<1.0 E-1—≤1.0 E-1
T_4CB [81]	<1.0	5.7 E-2	<1.0 E-1
P_5CB [87]	4.6 E+1	1.5	≤1.0 E-1—5.0 E-1
P_5CB [101]	2.4 E+1	6.8	3.0 E-1—1.3
P_5CB [105]	2.4 E+1	1.2	<1.0 E-1—6.0 E-1
P_5CB [114]	2.6 E+1	3.2	<1.0 E-1
P_5CB [118]	<1.0	2.3 E-1	1.1—2.5
P_5CB [126]	<1.0	2.0	<1.0 E-1
H_6CB [137]	7.4 E+1	3.3 E+1	2.9—4.6
H_6CB [153]	<1.0	2.8 E+1	3.4—4.3
H_6CB [156]	5.0	4.5	≤1.0 E-1—4.0 E-1
H_6CB [169]	<1.0	<5.0 E-3	<1.0 E-1
H_7CB [180]	<1.0	4.8 E+1	2.2—2.8

(a) From Ballschmiter and Zell.[2] (b) Mean levels, N = 3. (c) Mean levels, N = 6. (d) Ranges, N = 3. (e) 1.6 E+2 = 160. (f) Below ("<") and at ("≤") detection threshold.

Table 2 Uncorrected congener-specific PCDD and PCDF levels detected in urban air and commercial butter.

Substratum[a]	Urban air[b] (pg/m^3)	Butter[c] (ng/kg)
T_4CDD	1.6 E-2[d]	<5.0 E-2[e]
P_5CDD	<1.0 E-2	1.0—5.0
H_6CDD	≤6.0 E-2	1.8—8.2
H_7CDD	1.3 E-1	2.0—1.5 E+1
O_8CDD	4.0 E-1	1.0—1.0 E+1
T_4CDF	1.8 E-1	<5.0 E-2
P_5CDF	3.0 E-2	6.0 E-1—1.0 E+1
H_6CDF	3.0 E-2	3.0 E-1—1.7 E+1
H_7CDF	1.6 E-1	3.0 E-1—7.0
O_8CDF	≤4.0 E-2	6.0 E-1—9.0 E-1
Total[f]	6.4 E-2 $pgTE/m^3$	1.1—8.4 ngTE/kg

(a) Only the 2,3,7,8-congeners or their sum when more than one. (b) Mean levels, N = 3. (c) Ranges, N = 3. (d) 1.6 E-2 = 0.016. (e) Below ("<") and at ("≤") detection threshold. (f) Conversion to International Toxicity Equivalents (I-TEFs)[3] performed by adopting the most conservative approach.

Table 3 Uncorrected carcinogenic[a] PAH and nitro-PAH levels detected in urban air and soil and in commercial butter.

Substratum	Urban air[b] (ng/m^3)	Urban soil[c] ($\mu g/kg$)	Butter[d] ($\mu g/kg$)
Benz[a]anthracene	1.3 E+1[e]	1.8 E+1	1.9—6.4
Benzo[b+j+k]-fluoranthene	2.4	2.0 E+1	1.0 E-1—4.0 E-1
Benzo[a]pyrene	5.4	2.2 E+1	3.0 E-1—8.0 E-1
Dibenz[a,h]-anthracene	8.8 E-2	1.0	≤5.0 E-2—1.0 E-1[f]
Dibenzo[a,e]pyrene	2.1	3.0	<5.0 E-2
Dibenzo[a,h]pyrene	1.0	≤1.0 E-1	<5.0 E-2
Dibenzo[a,i]pyrene	1.1	≤1.0 E-1	<5.0 E-2
Dibenzo[a,l]pyrene	6.4 E-1	5.1	<5.0 E-2—1.0 E-1
Indeno[1,2,3-cd]-pyrene	1.5 E-1	6.9	≤5.0 E-2—1.0 E-1[f]
2-Nitrofluorene	≤1.0 E-2		
1-Nitropyrene	4.0 E-1		

(a) From Menichini and Rossi.[4] (b) Mean levels, N = 3. (c) Mean levels, N = 6. (d) Ranges, N = 3. (e) 1.3 E+1 = 13. (f) Below ("<") and at ("≤") detection threshold. Dibenzanthracene and indenopyrene determined together.

family. Spiking level for individual chemicals was such as to fall in the S/N range from 10 to 20. Set-specific mean recovery yields were >70% for PCBs, PAHs, and nitro-PAHs, and quantitative (>90%) for PCDDs and PCDFs. In Tables 1-3, data have not been corrected for recovery yield.

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