

A GENERAL-PURPOSE METHODOLOGY TO DETECT PRIORITY ORGANIC MICROPOLLUTANTS IN THE ENVIRONMENT

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INTRODUCTION

Polychlorobiphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), polychlorodibenzo-p-dioxins (PCDDs), and polychlorodibenzofurans (PCDFs) are well-known families of widespread persistent micropollutants. Each family consists of a large number of analogs, some of which exhibit an extremely high toxic potential—including carcinogenicity at very low chronic exposure. PAH, PCDD, and PCDF occurrence is associated mainly with natural sources or incidental anthropogenic formation. PCBs have been produced industrially for a long time; their commercial mixtures are still available for specific use, generally under restricted conditions. The toxicity of PCB mixtures is often enhanced by the presence of PCDDs and PCDFs.¹

Therefore, the environmental detection of the above compounds is of great interest for human health protection. Indeed, the multimedia, multicomponent assessment of risk entails that the hazardous chemicals present in the environment be investigated and quantitated. This may be a very difficult task since, owing to their toxicologic properties, some of the chemicals must be detected at levels so low that the complexity of the matrix may determine severe interferences and impair the reliability of findings. The set of analytical techniques reported in this preliminary paper—some of which are quite well established, whereas others are still being developed—may be adopted to investigate many different environmental situations. As they allow detection of the analytes of interest starting from the same extract, particular emphasis is placed upon those techniques still under development.²

EXPERIMENTAL

Sampling Topsoil was sampled with a steel corer sunk to a 7- to 20-cm depth.³⁻⁶ After positioning a square metal frame on the soil surface to delimit the sampling area, grass and similar vegetation was cut at its base;²⁻⁴ any vegetables and fruit were simply plucked.² A water sample was obtained from a common potable water faucet;² alternatively, a 1-m³ water volume was allowed to percolate (ca. 60 ml/min) through a sorbing material.^{3,4} Urban air was monitored with a high-volume sampler whose sampling probe contained polyurethane foam.² Cotton swabs, doused with an organic solvent, were used to collect chemicals from smooth, solid, nonsorbing surfaces.²⁻⁴

Extraction Soil was hand-crushed, dried, and removed of any large stones and aggregations; if necessary, the soil was sifted (10 mesh) prior to manual or mechanical extraction with dichloromethane or hexane-acetone mixture.^{1,3-6} Vegetation was chopped or minced and manually extracted, or mechanically homogenized, with dichloromethane.²⁻⁴ Water subsamples were individually extracted with dichloromethane; extraction phases were later combined to yield a pool.²⁻⁴ The matrix obtained from air sampling or surface wiping was transferred to a Soxhlet apparatus and subjected to 300 toluene cycles;^{2,5} alternatively, wipe-test samplings were manually extracted with a hexane-acetone mixture.^{3,4}

Cleanup Any one of Cleanup Steps A through C (see below) was selected to clean up the extraction product. Step A consisted mostly of treatment with concentrated sulfuric acid.¹⁻⁶ Step B involved a chromatographic passage through silica gel.² Step C was a chromatographic

Table 1 Recovery rates at a spiking level of 200 ng/sample for a PCB mixture (Aroclor 1254) and 20.0 ng/sample for each individual PAH.

Matrix	Recovery yield (%)												
	PCB substratum ^a			PAH substratum ^b									
	T ₄ CB	P ₅ CB	H ₆ CB	Phe	Ant	Flu	Pyr	BenAa	Chr	BenEp	BenAp	Per	
Wipe Test ^c	77.5	90.0	125	80.0	90.0	108	121	102	75.5	121	69.5	57.0	
1.	67.5	95.0	100	46.0	15.0	95.0	97.0	98.0	98.0	120	73.0	77.0	
2.	55.0	93.3	122	88.0	44.5	126	112	97.5	101	96.0	54.0	47.5	
3.	77.5	80.0	120	50.0	14.0	75.0	115	88.0	99.0	42.0	26.0	20.0	
4.	107	118	140	75.0	18.5	124	113	121	98.0	111	59.5	45.0	
Potable water ^e	60.0	65.0	100	75.0	30.5	86.0	114	67.0	89.0	85.0	43.0	35.5	
1.	77.5	71.5	100	50.0	14.0	75.0	115	88.0	94.5	42.0	26.0	20.0	
2.	100	113	133	75.0	18.5	124	113	121	135	111	59.5	45.0	
3.	107	118	140	88.0	90.0	126	121	121	135	121	73.0	77.0	
Range	UL ^f	107	118	140	88.0	90.0	126	121	121	135	121	73.0	77.0
	LL ^f	55.0	65.0	100	46.0	14.0	75.0	97.0	67.0	75.5	42.0	26.0	20.0

(a) T₄, tetra-; P₅, penta-; H₆, hexachlorobiphenyl. (b) Phe, phenanthrene; Ant, anthracene; Flu, fluoranthene; Pyr, pyrene; BenAa, benzo(a)anthracene; Chr, chrysene and triphenylene; BenEp, benzo(e)pyrene; BenAp, benzo(a)pyrene; Per, perylene. (c) PCBs and PAHs added to unused cotton swab in a toluene medium. (d) PCBs and PAHs added to unused polyurethane foam in a toluene medium. (e) PCBs and PAHs added to tap water in a dichloromethane medium. (f) Range upper limit, range lower limit.

filtration through an activated alumina column.²⁻⁶ Individual steps, or combinations thereof, were chosen as a result of experience acquired. Soil extracts were generally purified through Steps A and C; ^{1,3-6} cleanup of vegetation extracts also included the same steps.²⁻⁴ Water extracts normally underwent Steps B and C.² Extracts from air and wipe-test samples went through two Steps B and two Steps C—in that sequence.²

Instrumental determination The residue from cleanup was injected into the instrumental apparatus utilized. Gas chromatographic units equipped with capillary columns and flame ionization (GC/FID) or electron capture detectors (GC/ECD) were employed; in addition, most quantitative determinations were carried out by combining gas chromatography with mass spectrometry (GC-MS; quadrupole and magnetic sector units available) via the Selected Ion Monitoring (MS/SIM) technique. The following reference materials were used: (a) PCBs: Aroclor 1254; (b) PAHs: phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene and triphenylene; benzo(e)pyrene; benzo(a)pyrene; perylene; (c) PCDDs: 2,3,7,8-tetra-, 1,2,3,7,8-penta-, 1,2,3,6,7,8- or 1,2,3,7,8,9-hexa-, 1,2,3,4,6,7,8-hepta-, and 1,2,3,4,6,7,8,9-octachlorodibenzo-p-dioxin; (d) PCDFs: 2,3,7,8-tetra-, 1,2,3,7,8-penta-, 1,2,3,4,7,8- or 2,3,4,6,7,8-hexa-, 1,2,3,4,6,7,8-hepta-, and 1,2,3,4,6,7,8,9-octachlorodibenzofuran.^{2,5,6}

RESULTS AND DISCUSSION

Tables 1 and 2 summarize the results of several recovery studies. Spiking levels were such as to broadly match detection thresholds for real determinations (Table 3), although in some cases matrices cannot compare with the real ones. The findings from the set of techniques still being developed²—specific for wipe test, air, and water matrices—are exhibited together with those of consolidated procedures to detect PCDDs and PCDFs in vegetable and soil samples.^{1,3-7} Although a full evaluation of the applicability and reliability of the developing set appears to be premature, it should be pointed out that the pertinent recovery rates assessed for all the polychlorinated compounds investigated are in good agreement with those

Table 2 Recovery rates at spiking levels of 5.00, 15.0, and 25.0 ng/sample for tetra- and penta-, hexa- and hepta-, and octachloro substituted PCDDs and PCDFs, respectively.

Matrix	Substratum ^a	Recovery yield (%)									
		T ₄ CDD	T ₄ CDF	P ₅ CDD	P ₅ CDF	H ₆ CDD	H ₆ COF	H ₇ CDD	H ₇ COF	O ₈ CDD	O ₈ COF
Wipe test ^b		106	78.0	106	120	123	125	140	133	121	109
Air ^b	1.	100	98.0	100	96.0	107	99.3	105	107	90.0	104
	2.	112	116	112	114	123	113	111	117	108	106
	3.	78.0	64.0	66.0	92.0	88.7	106	89.3	103	93.6	100
	4.	100	86.0	98.0	98.0	103	105	102	112	101	114
Potable water ^b	1.	128	114	126	110	90.7	123	108	119	110	122
	2.	78.0	64.0	66.0	92.0	88.7	106	88.7	103	93.6	100
	3.	100	86.0	98.0	98.0	103	105	102	112	101	114
	4. ^c	82.0	62.0	101	92.0	126	104	134	118	102	108
Vegetation, RUL ^e	129	116	115	112	120	115	107	119	113	115	
N = 7 ^d	RLl ^e	63.0	69.0	64.0	60.0	68.7	61.3	54.7	56.0	43.2	40.0
Soil, RUL	129	133	120	123	160	140	150 ^g	150	143	137	
N = 19 ^f	RLl	72.9	70.6	64.8	66.7	53.3	57.8	57.8 ^g	48.9	44.7	49.4
Range	UL ^e	129	133	126	123	160	140	150	150	143	137
	LL ^e	63.0	62.0	64.0	60.0	53.3	57.8	54.7	48.9	43.2	40.0

(a) T₄, tetra-; P₅, penta-; H₆, hexa-; H₇, hepta-; O₈, octachloro substituted PCDDs or PCDFs. For specific isomers, see Instrumental determination. (b) PCDDs and PCDFs added to pertinent matrices (see equivalent calls in Table 1) in a toluene medium. (c) C¹³-labeled PCDD and PCDF isomers (see Instrumental determination). (d) Recovery rates from five samples added with C¹³-labeled PCDDs and PCDFs and two samples spiked with the natural compounds.^{2,7,8} (e) Range upper limit, range lower limit. (f) Recovery rates from ten samples added with C¹³-labeled PCDDs and PCDFs and nine samples spiked with the natural compounds.^{6,8,9} (g) N = 10.

obtained previously for PCDDs and PCDFs in vegetable and soil matrices (Table 2). Further investigation is in progress, also in order to improve the general performance of the procedure for detecting PAHs, and thus avoid an undesired drop in the recovery yield (Table 1). Finally, it may be recalled that the amount of PCDDs and PCDFs in vegetable and soil samples (Table 3)—expressed in 2,3,7,8-T₄CDD equivalents (TE units according to 1987 US EPA ranking¹⁰)—is from 0.047 to 0.066 and from 0.28 to 8.5 ngTE/kg, respectively.³

REFERENCES

- De Felip, E., di Domenico, A., Grande, M., Pazzaglia, R., and Falleni, M. (1990). Intern. J. Environ. Anal. Chem. **38**, 607-616.
- Berlincioni, M., Croce, G., di Domenico, A., and Pupp, M.: Detection of PCBs, PAHs, PCDDs, and PCDFs in the occupational environment, air, water, and vegetables. In preparation.
- di Domenico, A., Silano, V., Viviano, G., and Zapponi, G. (1980). Ecotoxicol. Environ. Safety **4**, 283-297.
- Cattabeni, F., di Domenico, A., and Merli, F. (1986). Ecotoxicol. Environ. Safety **12**, 35-52.
- Berlincioni, M., and di Domenico, A. (1987). Environ. Sci. Technol. **21**, 1063-1069.
- Berlincioni, M., di Domenico, A., Fanelli, R., Palma, S., and Zapponi, G. (1989). Chemosphere **19**, 501-506.
- Berlincioni, M., and Agati, L. (1988). Report for Tuscany Region Health Authorities, November 22.
- di Domenico, A. (1989). Report for Tuscany Region Health Authorities, March 15.

Table 3 Uncorrected levels of PCBs, PAHs, PCDDs, and PCDFs detected in environmental matrices. For detection thresholds (DT), see Notes; for acronyms, see Tables 1 and 2.

Substratum	Wipe test ^a (ng/m ²)	Air ^b (ng/m ³)	Potable water ^c (ng/m ³)	Vegetation ^d (ng/kg)		Soil ^e (ng/kg)		
				Min	Max	Min	Max	
PCBs ^f	T ₄ CB	4.1 E+3 ^g	1.1	3.8 E+3				
	P ₅ CB	6.5 E+3	4.9 E-1	3.3 E+3				
	H ₆ CB	1.3 E+4	6.3 E-1	9.2 E+3				
	Phe	1.2 E+5	2.1 E+2	1.4 E+4				
	Ant	5.1 E+3	1.7 E+1	2.0 E+1				
	Flu	5.2 E+4	1.1 E+2	5.7 E+3				
	Pyr	1.1 E+5	1.6 E+2	3.0 E+1				
PAHs	BenAa	1.8 E+4	2.3	8.0 E+2				
	Chr	6.1 E+4	1.5	8.0 E+3				
	BenEp	7.9 E+3	1.8	1.2 E+3				
	BenAp	4.5 E+3	3.9 E-1	8.0 E+2				
	Per	1.5 E+3	<1.0 E-1	1.1 E+3				
PCDDs ^h and	T ₄ CDD	<8.0	1.2 E-5 (3.0 E-6)	<2.0	<5.0 E-1	<1.0	1.6 E+1	
	T ₄ CDF	<8.0	2.6 E-4 (6.6 E-6)	<2.0	<5.0 E-1	1.5	<1.0	7.0 E+1
PCDFs ^h	P ₅ CDD	<8.0	3.0 E-5 (6.0 E-6)	<2.0	<5.0 E-1		1.0	7.5 E+1
	P ₅ CDF	<8.0	2.4 E-4 (2.5 E-5)	<2.0	<5.0 E-1		<1.0	6.6 E+1
	H ₆ CDD	<2.4 E+1	4.1 E-5 (9.2 E-6)	<5.0	<5.0 E-1	5.0 E-1	1.0	1.0 E+2
	H ₆ CDF	<2.4 E+1	1.3 E-4 (4.0 E-5)	<5.0	<5.0 E-1	1.0	<1.0	5.1 E+1
	H ₇ CDD	1.6 E+2	1.3 E-4 (7.0 E-5)	<5.0	1.0	1.2 E+1	8.8	2.2 E+2
	H ₇ CDF	<2.4 E+1	1.4 E-4 (9.5 E-5)	<5.0	1.0	5.8	<2.0	1.9 E+2
	O ₈ CDD	5.0 E+3	2.2 E-4	2.0 E+1	1.0	5.0 E+1	1.3 E+1	4.2 E+2
	O ₈ CDF	3.5 E+2	2.2 E-5	<8.0	1.0	2.5	2.0	2.2 E+2

(a) Occupational environment: surface (N = 1; 50 x 50 cm) near a lathe and a milling machine. From the surface, 3.2 g of greasy matter were collected. DT, ng/m²: PCBs, 5.0 x 10²; PAHs, 50; PCDDs and PCDFs, 8.0 for tetra- and penta-, 24 for hexa- and hepta-, 40 for the octachloro derivatives.² (b) Urban environment air (N = 1; sample size, 1118 m³; sampling rate, 60 l/min), 1.8 m from ground level and 3 m from the side of a city street; traffic rate, 1000 vehicles/h. DT, ng/m³: PCBs, <0.50; PAHs, <0.10; PCDDs and PCDFs, 3.0 x 10⁻⁶.² (c) Chlorinated water for drinking from a house faucet: ten 20-liter subsamples, individually extracted, provided a single extraction pool (N = 1). DT, ng/m³: PCBs, 2.5 x 10²; PAHs, <50; PCDDs and PCDFs, 2.0 for tetra- and penta-, 5.0 for hexa- and hepta-, 8.0 for the octachloro derivatives.² (d) Vegetable (potatoes, cabbage, salad) and corn samples (N = 5; 0.4-0.9 kg) from a farming area outside the City of Florence. DT, ng/kg: 0.50 for tetra-, penta-, and hexa-, and 1.0 for hepta- and octachloro derivatives.^{2,7,8} (e) Soil samples (N = 48; 0.4-1 kg) from the same farming area as that in (d): topsoil cored with a 7-cm-i.d. steel cylinder sunk to a 7-cm depth. DT, ng/kg: 1.0 for tetra-, penta-, and hexa-, and 2.0 for hepta- and octachloro derivatives. The area had been exposed to fallout from an urban incineration plant for several years.^{5,6,8,9} (f) Each congener group was determined by assessing three individual isomers of that group, the three independent findings were averaged to yield a single datum.² (g) 4.1 E+3 = 4100. (h) All findings are congener-specific, except for the right section of the air column where specific isomers have been reported (see Instrumental determination: as to H₆CDD and H₆CDF, reference is made to 1,2,3,6,7,8-H₆CDD and 1,2,3,4,7,8-H₆CDF only).

9. Berlincioni, M., and Casadonte Piccinini, M. (1988). Report for Tuscany Region Health Authorities, August 30.
 10. di Domenico, A. (1990). Regul. Toxicol. Pharmacol. **11**, 8-23.