

RELIABILITY ASSESSMENT OF A METHOD FOR DETECTING PRIORITY ORGANIC MICROCONTAMINANTS IN URBAN AIR

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Polychlorinated dibenzodioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs), and polynuclear aromatic hydrocarbons (PAHs) and their nitrosubstituted derivatives (nitro-PAHs) are widespread trace-level environmental contaminants which mostly arise from combustion processes. Each family consists of a large number of analogs, some of which are highly toxic. Since the relevance of these compounds to human health is widely recognized, a few years ago our laboratories started a multimedia monitoring program of the environment which also entailed development of specific assessment procedures.¹⁻⁵ In this report, our focus is particularly on the assay of urban air samples and the appraisal of the latest developments of this procedure. For the appraisal, the matrices were fortified by the laboratory in Rome, and later delivered without indications to the laboratory in Florence³ for sampling and analysis.

In-field samplings (outcomes^{3,5} not considered in this report) were performed close to roads with medium-to-high traffic, at a height of ≈ 2 m from the ground, and for up to a total of 4,000 m³. TSP Andersen-Tecora high-volume samplers, modified to accommodate a trapping set (TS) of three contiguous polyurethane foam cylindrical septa ($\phi = 12$ cm; height = 4 cm each; weight = 10 g each), were utilized at an air flow rate of 60-70 m³/h. Prior to use, the septa were extensively washed with dichloromethane and dried. In the reliability checks dealt with in this report, the outer septum of each set was spiked by dispersing droplets of volatile solutions of tracers on the surface. Sampling was real for PCDDs and PCDFs; otherwise, it was simulated in a protected contamination-free space.

After sampling, each trapping set was removed and treated five times with dichloromethane in order to extract the organic

vapors (or the tracers) directly sorbed on the foam and the organic compounds present on the blocked air particulate. Each extraction was carried out by mechanical pressing in an ultrasonic bath at room temperature. Fractions were pooled, gently evaporated to a small volume, and purified following the clean-up scheme previously shown⁵ and described briefly below.

The concentrated extract was first subjected to silica column chromatography ($\phi_i = 4$ cm; height = 11 cm) by eluting with 400-ml n-hexane (**Fraction A**) followed by a 600-ml n-hexane-toluene (80:20, v/v) mixture and 400-ml toluene, pooled together to form **Fraction B**. Both fractions were reduced to small volumes by gentle evaporation. Prior to use, the adsorbent (100-200-mesh Bio-Sil A from Bio-Rad Laboratories, Richmond, California) was incorporated with water (4 % of silica weight) and allowed to stabilize overnight at 105 °C.

Fraction A—which contained PCDDs, PCDFs, and PCBs—was eluted on a chromatographic alumina column ($\phi_i = 1$ cm; height = 9.5 cm) with 50-ml n-hexane containing 0.6% (v/v) dichloromethane (**Fraction A1**) followed by a 50-ml n-hexane-dichloromethane (90:10, v/v) mixture (**Fraction A2**). Prior to use, the adsorbent (100-200-mesh Basic Alumina AG 10 from Bio-Rad) was activated at 220 °C for at least 24 h.

Fraction B, containing PAHs and their nitroderivatives, was transferred to a chromatographic column of untreated silica ($\phi_i = 2$ cm; height = 11 cm) and eluted first with a 200-ml n-hexane-toluene (80:20, v/v) mixture (**Fraction B1**) and then with a 150-ml mixture of the same solvents combined in equal volumes (**Fraction B2**).

The four eluates from cleanup were gently dried and taken up to known volumes with iso-octane. Quantitation was carried out by HRGC(FID) followed by HRGC-LRMS(MID) confirmation for **Fractions B1** and **B2**, and directly by HRGC-LRMS(MID) for **Fractions A1** and **A2**. When assays of in-field samples were carried out, HRGC(ECD) was also used on occasions for screening the latter two fractions. In all cases, HRGC-HRMS(MID) was employed when required for further confirmation.

Results of the reliability assessment study are summarized in Tables 1-3. These are largely self-explanatory; however, some aspects should be pointed out. For PCDDs and PCDFs, most recovery rate means are ≥ 90 % and all are > 70 %, regardless of the spiking level. For PCBs, most means are ≥ 70 % and all are in the 54-90% range, regardless of the degree of chlorination of the tracer. For PAHs and nitroPAHs, recovery rate means show a greater variability when compared to those of the chlorinated compounds; however, almost all of them are within 50 and 91 %. The spiking levels (pg/m^3) employed correspond to (trapping efficiency assumed to be 100 %): 0.075, 0.15, 0.30,

and 0.625 for any one tetra- or pentachloro congener of PCDDs and PCDFs; 2.5 for any one PCB tracer; 12 for any one PAH isomer; 100 for any one nitroPAH compound.

According to various observations not reported here, it is emphasized that the cleanup sequence described may be successfully utilized also for extracts of different matrices.

Table 1. PCDD and PCDF congener-specific^a recovery rate (%) ranges and means (N = 3) at four spiking levels^b of the trapping sets. Values rounded off to ± 0.5 %.

TRACER	LEVEL 1	LEVEL 2	LEVEL 3	LEVEL 4
T ₄ CDD	85-94 89	78-118 94	80-108 91	90-104 96
P ₅ CDD	83-105 94	87-97 93	92-96 95	95-107 99
H ₆ CDD ^c	83-100 90	83-98 91	87-104 95	94-100 98
H ₇ CDD	75-118 91	74-102 91	76-107 86	84-119 97
O ₈ CDD	63-108 83	65-116 85	87-106 97	72-78 76
T ₄ CDF	75-108 90	75-109 92	92-104 99	90-101 96
P ₅ CDF ^d	82-108 95	92-110 102	92-104 97	89-98 94
H ₆ CDF ^e	80-97 89	67-80 74	88-95 91	87-93 90
H ₇ CDF ^f	86-95 90	72-100 87	70-88 81	70-85 78
O ₈ CDF	70-92 79	68-90 75	70-97 84	70-82 74

(a) 2,3,7,8-chlorosubstituted C¹³-labelled congeners. (b) Tracer ratios in the spiking solution: [tetras] = [pentas] = 1; [hexas] = [heptas] = 3; [octas] = 5. Spiking levels (pg/TS, reported for any one of the tetra- or pentachloro congeners only): Level 1 300; Level 2 600; Level 3 1,200; Level 4 2,500. (c) 1,2,3,6,7,8-H₆CDD. (d) 1,2,3,7,8-P₅CDF. (e) 1,2,3,4,7,8-H₆CDF. (f) 1,2,3,4,6,7,8-H₇CDF.

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Table 2. Unlabelled PCB recovery rate (%) ranges and means (N = 3) at a congener spiking level of 10 ng/TS. Values rounded off to ± 0.5 %; ID numbers from Ballschmiter and Zell.⁶

TRACER			TRACER		
T ₃ CB [28]	60-112	85	P ₅ CB [118]	81-92	88
T ₄ CB [52]	66-104	82	P ₅ CB [126]	59-79	65
T ₄ CB [81]	43-65	54	H ₆ CB [137]	70-82	77
P ₅ CB [87]	78-90	83	H ₆ CB [153]	48-64	54
P ₅ CB [101]	63-77	70	H ₆ CB [156]	75-101	89
P ₅ CB [105]	68-80	75	H ₆ CB [169]	60-70	65
P ₅ CB [114]	60-92	73	H ₇ CB [180]	77-102	90

Table 3. Unlabelled PAH and nitroPAH recovery rate (%) ranges and means at isomer spiking levels of 48 and 400 ng/TS, respectively. Values were obtained from three (PAHs) or four (nitro-PAHs) trials and have been rounded off to ± 0.5 %.

TRACER			TRACER		
Benz[a]anthracene	61-76	69	1,3-Dinitro-	70-91	82
Benzo[b+j+k]- fluoranthene	46-91	68	naphthalene		
Benzo[g,h,i]- perylene	64-93	77	1,5-Dinitro-	63-88	76
Benzo[a]pyrene	53-93	71	naphthalene	65-90	76
Dibenz[a,h]- anthracene	65-112	82	1,8-Dinitro-		
Dibenzo[a,e]pyrene	60-101	85	naphthalene		
Dibenzo[a,h]pyrene	70-100	85	2-Methyl-1-nitro-	37-44	39
Dibenzo[a,i]pyrene	68-110	87	naphthalene		
Dibenzo[a,l]pyrene	59-121	91	2-Nitrofluorene	69-86	77
Fluoranthene	34-63	50	1-Nitro-	43-49	46
Indeno[1,2,3-cd]- pyrene	64-94	76	naphthalene		
			2-Nitro-	37-68	50
			naphthalene		
			1-Nitropyrene	67-81	71

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