PRIORITY MICROCONTAMINANTS IN SEDIMENT SAMPLES FROM THE VENICE LAGOON: A SELECTION OF CONCENTRATION DATA AND PREDOMINANT ANALYTICAL FEATURES

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INTRODUCTION

Thirty-one sediment matrices were obtained from specimens collected in 1992 and 1995 by sampling the top sediment layer of the Venice lagoon bottom. Matrices were assayed for an array of priority toxic microcontaminants including a selection of: PAHs (polycyclic aromatic hydrocarbons), PCBs, PCDDs and PCDFs, chlorinated pesticides, and heavy metals. The assessment of these chemicals in the Venice lagoon (northern Adriatic sea) has become a major research effort for the authors since 1992–1994 preliminary study [1–3]; subsequent investigations (1995–1997) were carried out within a framework of inquiries of the State Attorney-General in Venice [4–7] and following specific requests of the Ministry of Health [5, 7]. Reflecting a three-year agreement with the Ministry of the Environment, our ongoing studies aim at integrating the knowledge on microcontaminant distribution in lagoon compartments, producing more reliable risk estimates for residents, evaluating the different anthropic impacts and possible contamination sources, and identifying practicable measures to reduce environmental and human health risks. This progress report provides an update of results, integrated by a provisional evaluation; a more extensive analysis of the data available is in progress and will be presented elsewhere.

EXPERIMENTAL METHODS

Lagoon sediment sampling and pretreatment processing to produce the matrices for analysis have already been reported upon [2–6]. However, contrary to the past, October 1995 sediment cores were not retrieved in the Rome laboratory by extrusion from corers, but delivered to the laboratory after extrusion [5]. Aliquots of each matrix were used to assess the different analytes [1–7]. For the assessment of organic chemicals, each aliquot was spiked with fully ^{13}C- and ^{2}H-labelled standards (for chlorinated and PAH analytes, respectively). Extraction was formerly carried out by utilizing conventional methods (mechanical aids or Soxhlet apparatuses) [1–4, 6]; however, for the later specimens, the techniques known as supercritical fluid (SFE) and accelerated solvent (ASE) extraction were used to determine, respectively, PAHs, PCBs, and chlorinated pesticides [5, 7, 8], and PCDDs and PCDFs [5, 7]. Cleanup steps were applied as reported in references. Analytes were quantified by HRGC-LRMS(SIM) or -HRMS(SIM) [1–8]. GLP and QA/QC protocols were applied throughout. Heavy metals were measured by a canonical AAS technique after acid digestion of matrix aliquots [2, 4–7]; prior to that, matrices were subjected to extensive grinding and homogenizing. Measurements were replicated at least thrice.

RESULTS AND DISCUSSION

The topographic distribution of sampling sites and zones is visible in the map of Figure 1. A selection of outcomes is contained in the largely self-explanatory table shown in the following pages; PAH, PCB, and PCDD and PCDF data are expressed as cumulative values.

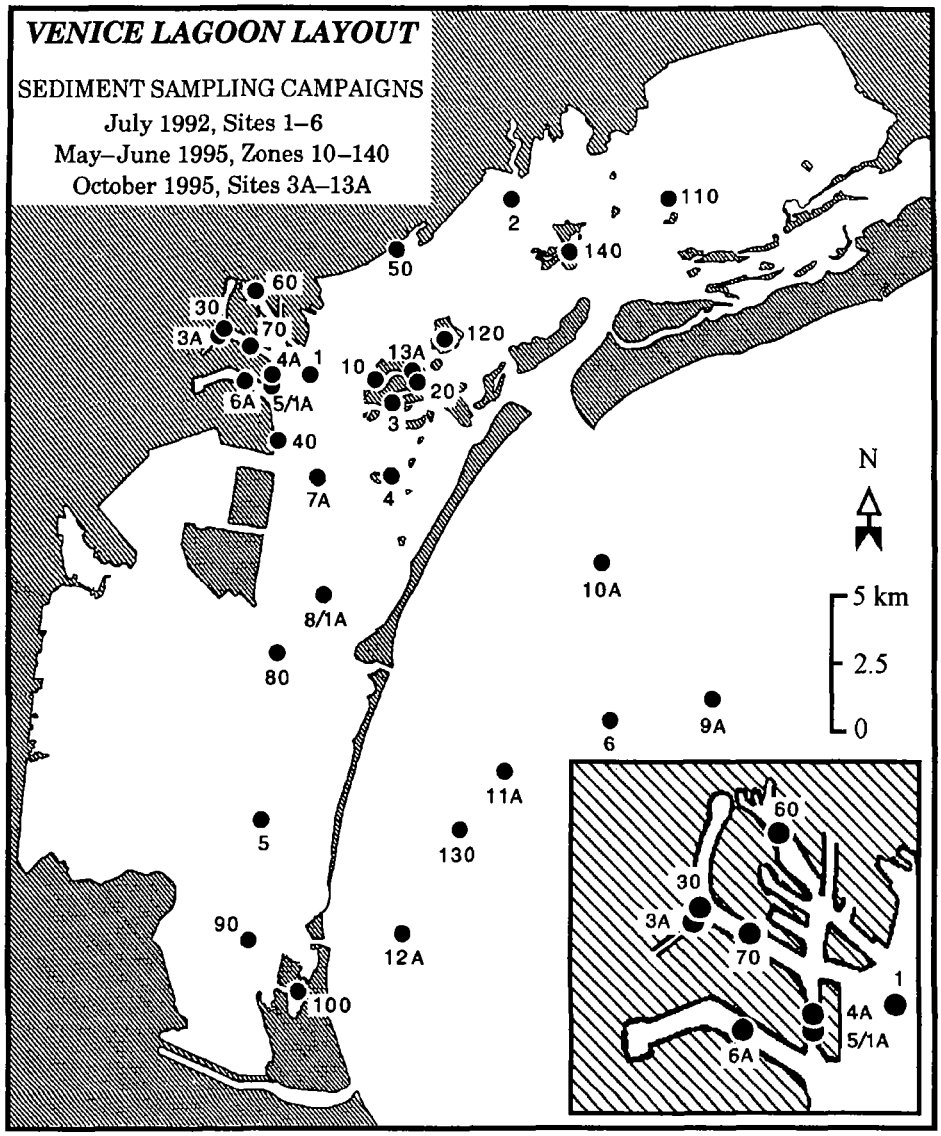

Figure 1. Sediment sampling sites and zones in the Venice lagoon. Specimens were collected from the top 10–30-cm thick bottom layer with a steel dredge or a cylindrical ($Ø_i$, 2.0 or 4.0 cm) Perspex-lined steel corer. Single samplings were performed at Sites 1–6 and 3A–13A; four samplings were carried out at Zones 10–140, with the exception of Zones 30 and 50 (two and three specimens, respectively). Zone samplings were later assayed as zone-specific pooled matrices. The lagoon covers a surface of approximately 550 km^2 and is generally <2-m deep; an intricate network of quite deeper navigable waterways stretches throughout its extension. The lagoon has a limited water exchange with the neighboring sea; to its pollution load contribute several sources including the effluent of water streams and industrial and urban sewage systems, agricultural runoff, and an intense traffic of motorboats. In the map, the City of Venice is identified by Sites 3 and 13A together with Zones 10 and 20; the inset crops out the industrial area of Porto Marghera.

Concentration levels of selected organic microcontaminants and heavy metals in bottom sediments from the Venice lagoon. Specimens were obtained in July 1992 (Sites 1–6), between May 30 and June 1, 1995 (Zones 10–140), and over the October 23–28, 1995, period (Sites 3A–13A). Analyte values are grouped by virtual risk *AREAS 1–6* and expressed per unit dry weight.

SAMPLING SITE OR ZONE[a]	*ORGANIC MICROCONTAMINANTS (ng/g, except where noticed)*[b]								*HEAVY METALS (μg/g)*[c]				
	PAHs[d]	B[a]P	PCBs[e]	PCDDs+PCDFs[f] *pg/g*	*pgTE/g*	DDE	DDT	HCB	Cd	Cu	Hg	Pb	Zn
AREA 1 - INDUSTRIAL OR PREVAILING INDUSTRIAL EXPOSURE													
3A	17 000	2700	5500	≤4900[g]	48	8.8	11	430	2.31	155	7.55	180	414
4A	10 000	950	2700	7000	130	6.0	—	460	6.56	100	48.5	158	590
5/1A	35 000	5600	53	840	12	3.0	—	340	4.77	45.2	1.88	101	384
6A	1800	240	97	3500	57	1.5	2.7	69	4.97	70.2	2.72	99.9	456
30	9800	1300	720	2500	32	10	<0.3[h]	470	2.56	149	3.77	58.1	248
40	1600	200	230	1400	23	5.1	2.9	49	9.63	97.1	1.52	73.8	1270
60	48 000	7500	220	29 000	570	9.9	5.2	110	22.9	247	14.2	282	1820
70	16 000	2300	540	3100	52	3.4	<0.3	35	3.83	159	3.51	110	312
AREA 2 - URBAN OR PREVAILING URBAN EXPOSURE													
3	45 000	9300	290	590	15	7.0	20	1.7	2.22	140	1.52	62.2	440
10	19 000	3000	380	840	18	14	2.4	3.7	5.03	217	2.01	109	592
13A	14 000	2500	490	890	12	15	—	6.4	4.57	176	3.78	146	573
20	30 000	4800	610	1400	23	27	24	5.0	5.69	297	2.08	97.1	591
120	7500	1300	71	210	4.8	1.3	0.51	0.33	0.723	36.2	0.531	47.8	104
AREA 3 - MIXED EXPOSURE													
1	240	43	13	490	7.8	1.0	0.72	6.2	1.87	24.9	1.94	15.3	136
2	430	77	3.1	14	0.48	1.1	10	0.097	1.81	18.2	0.0820	7.22	46.4
4	140	26	7.2	75	1.9	0.78	0.63	0.26	1.42	31.8	0.0230	7.29	70.1
7A	390	47	23	1100	20	0.057	0.080	0.28	2.06	42.8	2.38	45.4	341
50	410	54	77	670	8.5	19	<0.3	2.2	1.39	42.3	0.268	37.4	240
100	1300	190	9.2	53	1.0	1.5	0.48	0.064	0.184	10.7	0.263	12.8	2.31

(Continued on following page)

(Table, continued)

AREA 4 - LOW EXPOSURE, OPEN FISHING AREAS													
5	62	11	2.0	38	1.1	1.1	0.059	0.17	1.73	33.2	3.44	11.1	64.6
8/1A	130	13	10	160	3.3	<0.05	<0.05	<0.05	0.614	23.5	0.598	28.8	176
80	60	3.3	≈0.3[i]	15	0.35	0.70	0.50	0.10	0.139	11.4	0.194	16.1	15.7
90	220	24	8.3	130	1.8	0.93	<0.3	0.29	0.429	15.2	0.222	20.3	58.7
110	180	14	≈0.5[i]	21	0.43	0.55	0.31	0.059	0.133	9.99	0.294	9.44	2.03
140	630	82	4.1	41	0.80	1.3	1.3	0.072	0.0990	13.1	0.286	11.4	2.22
AREA 5 - LOW EXPOSURE, PRIVATE FISHING AREAS													
No data available from survey													
AREA 6 - GENERAL ENVIRONMENT, OPEN SEA													
6	94	17	2.5	1.0[j]	0.16[j]	0.59	0.50	0.039	0.488	9.09	0.0210	10.4	10.1
9A	3.1[j]	<1	0.62	2.4	0.073[j]	<0.05	<0.05	<0.05	0.0679	2.82	0.0525	5.43	16.2
10A	590	86	27	38	0.60	<0.05	<0.05	<0.05	0.0595	7.70	0.197	15.9	35.5
11A	2300	330	15	540	10	0.98	0.74	17	0.769	17.2	2.28	24.7	102
12A	250	33	6.3	150	2.3	<0.05	0.055	<0.05	0.296	11.8	2.55	20.2	63.1
130	2400	340	27	910	17	0.94	0.52	44	0.721	13.9	0.534	26.2	90.2

(a) To locate sampling sites or zones, see map. *(b)* Values corrected for analytical recovery and rounded off to two figures. Estimated mean analytical uncertainty, $<CV> \approx |\pm 10|$ % (generally, $CV < |\pm 30|$ %). *(c)* Values rounded off to three figures. Estimated mean analytical uncertainty, $<CV> \approx |\pm 3|$ % (generally, $CV < |\pm 10|$ %). *(d)* B[a]A, B[b+j+k]Fl, B[a]P, B[ghi]Pe, Chr, DB[ah]A, and IP; due to its toxicological importance, B[a]P concentration levels have been singled out. B[ghi]Pe and DB[ah]A, normally contributing some 10–30 % to cumulative data, were not assessed at Sites 1–6: therefore, the pertinent analytical figures may be underestimated by up to ≈40 %. *(e)* Approximately 50 analytically relevant congeners of the tri- to octaclorosubstituted homologous groups. O_8CB congeners were not assessed at Sites 1–6, this introducing a minor (<5 %) underestimation in the corresponding cumulative data. *(f)* All 17 2,3,7,8-chlorosubstituted congeners. Cumulative data are expressed in analytical units and as 2,3,7,8-T_4CDD toxicity equivalents (I-TEF system). *(g)* The sign ≤ indicates a possible overestimation due to interferences on O_8CDF signals; however, the eventual extra contribution to the paired TE figure may be considered to be negligible. *(h)* The sign < indicates below limit of quantification ($S/N \approx 3$; $N \approx 4\ \sigma_N$); figures preceded by this sign were entered as half their nominal value to calculate PAH, PCB, and PCDD and PCDF cumulative data. *(i)* The low level approximation reflects background interferences on signals of several congeners, thereby left unassessed, in addition to the presence of many congener findings marked <. *(j)* Lacking representativeness [9].

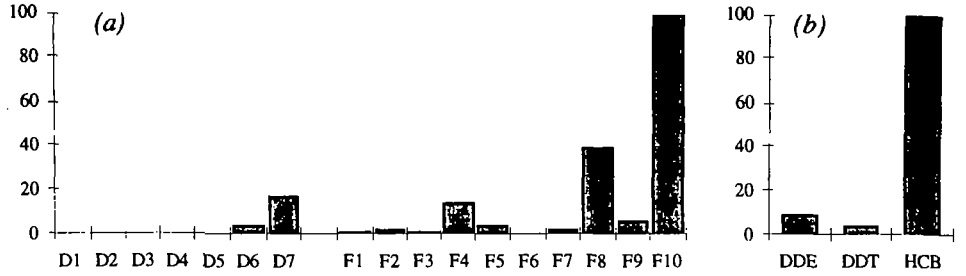

Figure 2. *(a)* Base-congener normalized bar graph of 2,3,7,8-chlorosubstituted PCDD and PCDF congeners measured in a pooled sediment matrix from sampling Zone 60 in *AREA 1* (Series D and F stand for PCDD and PCDF congeners, IUPAC ordered). *(b)* Base-compound normalized bar graph of the chlorinated pesticides measured in the same sediment matrix. The visible predominance of F10 (15000 pg/g), F8, and, next to them, D7 in *(a)*, and that of HCB (110 ng/g) in *(b)* are typical recurring features of lagoon sediments exposed to a prevailing industrial impact.

It is here recalled [4–7] that, due to the limited number of sediment samplings and their lack of randomness, the available data may be used to depict only low resolution contamination scenarios; moreover, as large lagoon areas have not been assessed, limited chemical waste deposits might have eluded detection even if highly contaminated. We also recall that, in order to have a handy criterion for sample and data treatment, the lagoon environment was pragmatically subdivided into six risk areas (*AREAS 1–6*, see table) with theoretically decreasing exposure values. These areas were defined according to the presumed anthropic impact(s) prevailing locally, and may be broadly identified by the sampling sites and zones associated.

The former analytical scenario [4–7] is strengthened by the new entries associated with Sites 3A–13A. In brief, contamination magnitude spans between the higher levels of *AREA 1* and, second next, *AREA 2* and the lower values exhibited by the fishing zones of *AREA 4* (*AREA 5* is still unassessed): in particular, *AREA 4* contamination levels do not appear to be significantly different from the upper end values of open sea background range. The contamination levels measured in *AREA 3* fit adequately the scenario depicted, in agreement with the postulated mixed exposure of the risk area. Lastly, the new open sea data provide further evidence that *AREA 6* has been an abused receptacle of polluted material, in that significantly contaminated spots (e.g., Zone 130 and Site 11A) come together with background-type Sites 6 and 9A.

PCDD, PCDF, and chlorinated pesticide contamination quality indicators, such as congener- or compound-specific profiles, analyte magnitude and relative magnitude, etc., appear to vary significantly as a function of anthropic impact changes. The outcomes (unreported) of cluster analysis applied to the available data sets show that two types of profiles prevail in lagoon bottom sediments, namely those observed in the industrial zones (Figure 2), associated with the massive use of chlorine ("chlorine fingerprint") [4–6, 10–12], and those detected in the urban environment (Figure 3); other profiles are also present, but in general they may be accounted for by combinations of the two prevailing ones. The quality indicators of remaining analytes seem to be much less sensitive to anthropic impact changes, as will be discussed elsewhere.

With respect to the top sediment layer, the new data are in agreement with the observation that most microcontaminants monitored cover very large ranges of concentration [4–6]; with respect to deeper layers, the same data also provide evidence that the top layer generally presents a higher contamination level. However, it may be anticipated [5] that at two sites within *AREA 1* (unshown in the map) the sediment layers below the top one exhibit contamination values greater than those measured in the corresponding top layer specimens (the type of specimens concerning this report). In particular, in layers between –30 and –90 cm near Site 3A, PCBs, PCDDs and PCDFs, and HCB reach values from one up to three orders of magnitude greater than in the corresponding top layer, thereby hitting the highest levels ever found in our lagoon sediment studies.

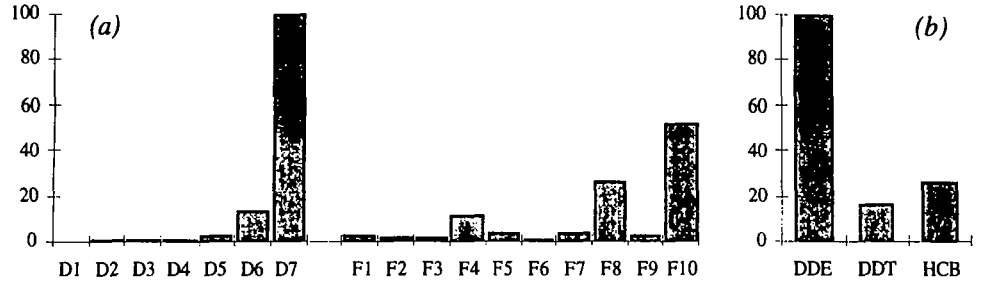

Figure 3. *(a)* Base-congener normalized bar graph of 2,3,7,8-chlorosubstituted PCDD and PCDF congeners measured in a pooled sediment matrix from sampling Zone 10 in *AREA 2* (Series D and F stand for PCDD and PCDF congeners, IUPAC ordered). *(b)* Base-compound normalized bar graph of the chlorinated pesticides measured in the same sediment matrix. The visible predominance of D7 (370 pg/g) and, next to it, F10 and F8 in *(a)*, and that of DDE (14 ng/g) in *(b)* are consistent features of lagoon sediments exposed to a prevailing urban impact or, in general, to local thermal emissions and/or long range transport (such as sediments in open authorized fishing areas). In the pesticide pattern, DDT at times appears to compete with DDE.

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