

RISK ASSESSMENT

SELECTED CARCINOGENIC ORGANIC MICROCONTAMINANTS AND HEAVY METALS IN THE VENICE LAGOON.

I. CONTAMINATION LEVELS OF BOTTOM SEDIMENTS

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ABSTRACT

Twenty sediment samples, collected in 1992 and 1995 from the top layers of Venetian lagoon bottom, were assayed for an array of highly toxic microcontaminants. Insufficient to provide a detailed contamination map, the data obtained depict, however, a lagoon scenario where vast areas with relatively low or negligible levels of contamination neighbor zones — under industrial or urban anthropic impacts — characterized by much higher levels.

INTRODUCTION

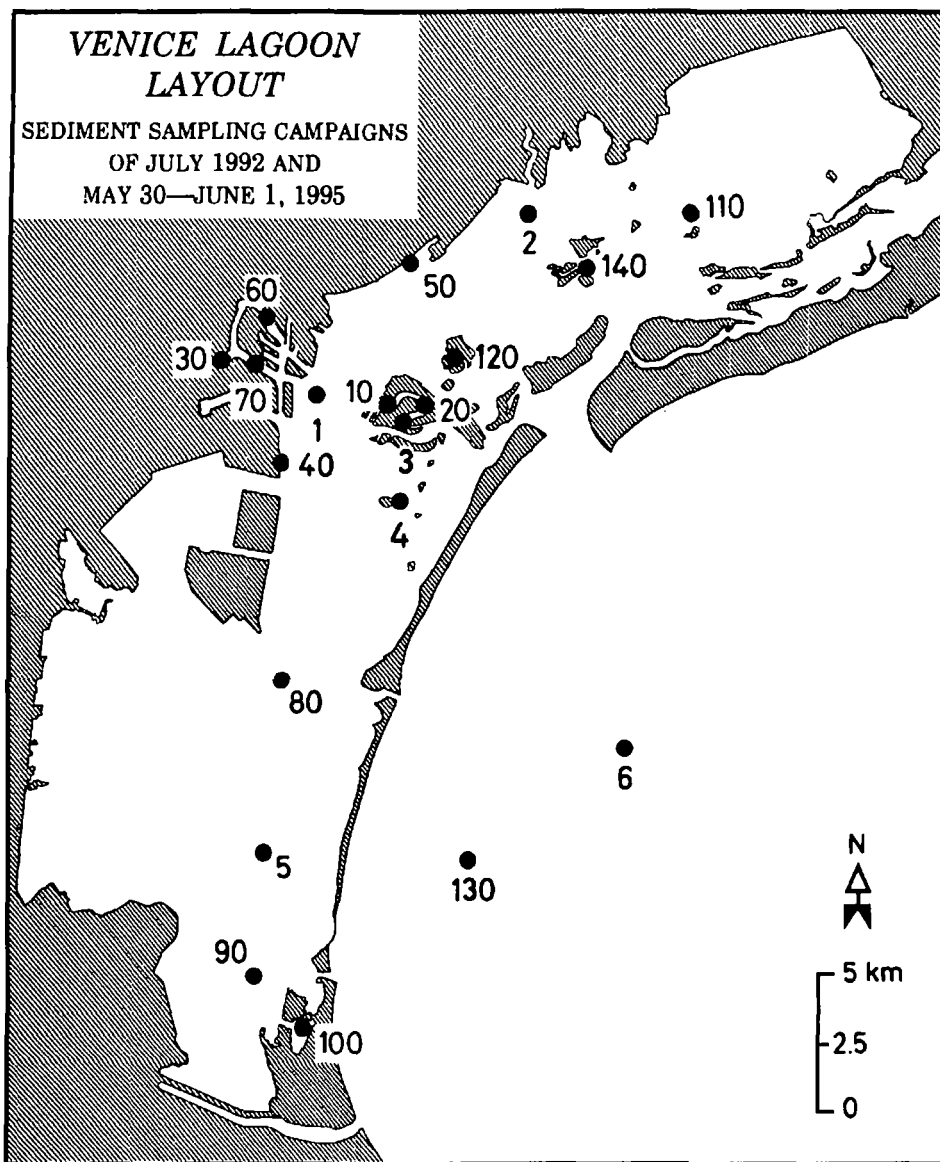
The assessment of toxic microcontaminants in bottom marine sediments from the Venice lagoon (northern Adriatic sea) became a matter of interest for the authors in 1992.¹⁻³ The chemicals to be determined were selected — primarily on the basis of their toxic properties and environmental persistence — from the families of PAHs (polycyclic aromatic hydrocarbons), PCBs, PCDDs and PCDFs, chlorinated pesticides (DDE, DDT, and HCB), and heavy metals (Cd, Cu, Hg, Pb, and Zn). The results of 1992 preliminary study indicated that contamination was quite unevenly distributed,¹⁻³ eventually reflecting the anthropic impacts prevailing locally. In 1995, within a framework of investigations promoted by the State Attorney General in Venice, the study was resumed in order to (a) integrate the existing results, (b) acquire a better knowledge of the microcontaminant distribution in sediments (contamination map), (c) evaluate and characterize the different anthropic impacts and possible sources of contamination, and (d) suggest practicable measures to improve environmental quality and reduce human health risks. What follows is a first account of the major findings from both studies, condensed from the 1996 report to the AG.⁴

EXPERIMENTAL METHODS

Samplings of bottom marine sediments were carried out at Sites 1—6¹⁻³ and Zones 10—14⁴ in two different periods (see map). The coring apparatus for zone sampling was made of a heavy tubular steel holder lined with a Perspex cylinder; the holder was freshly and carefully cleansed any time it was used. Each sampling was performed by letting the apparatus drop freely from the boat, to have it sunk vertical into the sediment bed underneath. The apparatus was then retrieved, deprived of loose water, and opened to release the cylinder with its sediment core.

For pretreatment, each site specimen was allowed to warm up and then transferred to a glass dish;¹⁻³ similarly, each zone sediment core was extruded into a glass dish by gently applying air pressure to the empty end of the Perspex cylinder.⁴ All specimens were allowed to dehydrate by natural evaporation under hood; the dry sediment matrices were sifted through a 10- or 20-mesh sieve and homogenized. Site matrices were used as such; the matrices from a same zone were combined in equiponderant contributions, mixed thoroughly, and homogenized anew.⁴

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Venice lagoon layout. Sediment specimens at Sites 1–6 were collected with a steel dredge in 1992; they were transferred in PE bottles to the laboratory in Rome, and maintained at $-20\text{ }^{\circ}\text{C}$ until pretreatment (see text).¹⁻³ Zone 10–140 samplings were performed in 1995 by coring the top sediment layer with 2-cm- \varnothing ; Perspex cylinders; at each sampling, a new cylinder was used. Once used, a cylinder was sealed at both ends with plastic foil for food use and stored at $\approx 4\text{ }^{\circ}\text{C}$ until pretreatment. Aside from Zones 30 and 50 (two and three specimens, respectively), the 12 remaining zones yielded four specimens each, for a total of 53.⁴ All samplings were from the top 10–20-cm thick bottom layer. The 550-km² lagoon is generally <2-m deep, although navigable waterways may exhibit quite greater depths. The lagoon has limited water exchange with the neighboring sea; it also receives the effluent of many water streams and industrial and urban sewage systems, agricultural runoff, and pollution from an intense traffic of motorboats.

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An aliquot (<200 g) of each pretreated matrix (sample) was used for the analytical assessment of organic chemicals; before extraction, aliquots were spiked with known amounts of tracers (fully C¹³- and H²-labelled standards for quantitation of chlorinated and PAH analytes, respectively). Extraction was carried out by utilizing a 1:1 (v/v) mixture of *n*-hexane-acetone either with a mechanical aid¹⁻³ (site samples, N = 6) or with a Soxhlet apparatus^{4,5} (zone samples, N = 14). Acetone was removed from extracts by gentle evaporation to almost dryness; extracts were then taken up to known volumes with *n*-hexane, eventually adding small amounts of dichloromethane to avoid separation of organic matter. Two portions of each extract were utilized, respectively for the parallel assessment of PAHs^{1-4,6-8} and the chlorinated compounds.^{1-4,8-13} The organic analytes were quantitated by HRGC-LRMS(SIM) or -HRMS(SIM), the latter being used to measure PCDDs and PCDFs or as a confirmatory technique.^{1-4,13-15} GLP and QA/QC protocols were applied throughout; procedural blanks were run repeatedly during a daily assessment sequence.

Heavy metals were measured by a canonical AAS technique¹⁶ after appropriate acid digestion of portions (≤ 0.15 g) of the pretreated matrices; prior to that, the latter were subjected to additional grinding and homogenizing. Measurements were replicated at least thrice.

RESULTS AND DISCUSSION

The study outcomes are summarized in Tables 1 and 2. For PAHs, PCBs, and PCDDs and PCDFs, data are expressed as cumulative values; in particular, PCDD and PCDF results are also presented after conversion to 2,3,7,8-T₄CDD toxicity equivalents. Tables are largely self-explanatory and, for conciseness, only interpretative hints are provided below.

A substantially low space frequency and a lack of randomness characterize sediment samplings:¹⁻⁴ as a consequence, the contamination distribution layout obtained lacks detail and can only be taken as a general reference. In addition, it may be noticed that large lagoon areas were not assessed: therefore, limited deposits of chemical contaminants might have eluded detection even if highly contaminated ("local contamination peaks").

The lagoon environment was broadly subdivided into six exposure (or risk) areas (AREAS 1-6, see tables),⁴ with theoretically decreasing exposure values. This proved to be a pragmatic criterion for sample (and data) grouping, and provided suggestions on data description and interpretation. As a detailed contamination map was not available, areas were left topographically unidentified — and referred to as "virtual" — but were provisionally defined on the basis of prevailing anthropic impacts they were presumably subjected to. However, from the application of the grouping criterion, area locations are hinted at by the sampling sites and zones assayed.

The aforesaid subdivision find a general support from the analytical scenario obtained. Sediment contamination magnitude varies between the relatively high levels detected in AREA 1 and, second next, AREA 2 — respectively, under industrial (e.g. Porto Marghera) and urban (e.g. Venice) influences — and the low levels exhibited by the fishing zones of AREA 4 (the unassayed AREA 5 is provisionally viewed as an extension of AREA 4). In particular, the overall anthropic impact detected in AREA 4 does not appear to be significantly different from that associated with the medium-to-high values of open sea background range and — at least for the organic compounds — may be assumed to be primarily due to atmospheric deposition. However, not only the levels of contamination but also its quality indicators — congener- or compound-specific profiles, relative levels of all the analytes, etc. — vary significantly from area to area, as an apparent function of anthropic impact changes. These observations apply to AREA 3 as well, according to its postulated mixed exposure. Lastly, open sea AREA 6 features stand out in that — opposite to Site 6 — Zone 130 sediments exhibit unexpected high levels of some analytes.

In general, the microcontaminants monitored appear to work as sensitive indicators of anthropic impact. In particular, some of them — namely: PAHs, PCDDs and PCDFs, HCB, Cd, Hg, and Zn — cover very large ranges of concentration (for the organic compounds, $\Delta \approx 10^3 - 10^4$, where $\Delta = [C_{MAX}] \cdot [C_{MIN}]^{-1}$; for the metals, $\Delta \approx 10^2 - 10^3$). In any case, as suggested by the experimental evidence, contamination composition and magnitude seem to be characterized by a high level of localization or, else, an apparent limited-to-scarce tendency to

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Table 1. Concentration levels of selected organic microcontaminants in bottom sediments from the Venice lagoon. Samples were obtained in July 1992¹⁻³ and between May 30 and June 1, 1995.⁴ Analyte values are grouped by virtual risk areas (AREAS 1-6, see text) and expressed per unit dry weight.

SAMPLING SITE OR ZONE ^a	ANALYTE LEVELS ^b (ng/g, except where noticed)						
	PAHs ^c	PCBs ^d	PCDDs+PCDFs ^e		DDE	DDT	HCB
			pg/g	pgTE/g			
AREA 1 - INDUSTRIAL OR PREVAILING INDUSTRIAL EXPOSURE							
30	10000	720	2500	32	10	<0.3 ^f	470
40	1600	230	1400	23	5.1	2.9	49
60	54000	220	29000	570	9.9	5.2	110
70	17000	540	3100	52	3.4	<0.3	35
AREA 2 - URBAN OR PREVAILING URBAN EXPOSURE							
3	48000	290	590	15	7.0	20	1.7
10	20000	380	840	18	14	2.4	3.7
20	32000	610	1400	23	27	24	5.0
120	8000	71	210	4.8	1.3	0.51	0.33
AREA 3 - MIXED EXPOSURE							
1	240	13	490	7.8	1.0	0.72	6.2
2	460	3.1	14	0.48	1.1	10	0.097
4	150	7.2	75	1.9	0.78	0.63	0.26
50	430	77	670	8.5	19	<0.3	2.2
100	1300	9.2	53	1.0	1.5	0.48	0.064
AREA 4 - LOW EXPOSURE, OPEN FISHING AREAS							
5	64	2.0	38	1.1	1.1	0.059	0.17
80	62	0.27 ^g	15	0.35	0.70	0.50	0.10
90	220	8.3	130	1.8	0.93	<0.3	0.29
110	180	0.47 ^g	21	0.43	0.55	0.31	0.059
140	660	4.1	41	0.80	1.3	1.3	0.072
AREA 5 - LOW EXPOSURE, PRIVATE FISHING AREAS							
No data available from this survey							
AREA 6 - GENERAL ENVIRONMENT, OPEN SEA							
6	99	2.5	1.0 ^g	0.16 ^g	0.59	0.50	0.039
130	2500	27	910	17	0.94	0.52	44

(a) To locate sampling sites or zones, see map. (b) All values corrected for analytical recovery and rounded off to two figures. Estimated mean analytical uncertainty, $\langle CV \rangle \approx |\pm 10| \%$ (generally, $CV < |\pm 30| \%$). (c) A, B[a]A, B[b+j+k]Fl, B[a]P, B[ghi]Pe, Chr, DB[ah]A, and IP. B[ghi]Pe and DB[ah]A were not assessed at Sites 1-6. (d) Approximately 50 analytically relevant congeners of the tri- to octachlorosubstituted homologous groups. (e) All 17 2,3,7,8-chlorosubstituted congeners. Cumulative results are expressed in analytical units and as 2,3,7,8-T₄CDD toxicity equivalents (I-TEF system).¹⁷ (f) The sign < indicates below limit of quantification (S/N \approx 3; N \approx 4 σ_N); figures preceded by this sign were entered as half their nominal value in calculations. (g) Lacking representativeness.^{18,19}

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migrate through the water medium from point sources (e.g. the aforementioned local contamination peaks) into contiguous areas. A final observation is that the remarkable presence of microcontaminants in *AREA 1* may be traced back to a number of chemical production processes belonging to the industrial tradition of Porto Marghera: in particular, the PCDD and PCDF profiles detected reflect what is generally known as the "chlorine fingerprint", a typical environmental feature frequently associated with exposure of the environment to releases from industrial plants utilizing massive amounts of the halogen.²⁰⁻²³

Table 2. Concentration levels of selected heavy metals in bottom sediments from the Venice lagoon. Samples were obtained in July 1992¹⁻³ and between May 30 and June 1, 1995.⁴ Analyte values are grouped by virtual risk areas (*AREAS 1-6*, see text) and expressed per unit dry weight.

SAMPLING SITE OR ZONE ^a	ANALYTE LEVELS ^b (µg/g)				
	Cd	Cu	Hg	Pb	Zn
AREA 1 - INDUSTRIAL OR PREVAILING INDUSTRIAL EXPOSURE					
30	2.56	149	3.77	58.1	248
40	9.63	97.1	1.52	73.8	1270
60	22.9	247	14.2	282	1820
70	3.83	159	3.51	110	312
AREA 2 - URBAN OR PREVAILING URBAN EXPOSURE					
3	2.22	140	1.52	62.2	440
10	5.03	217	2.01	109	592
20	5.69	297	2.08	97.1	591
120	0.723	36.2	0.531	47.8	104
AREA 3 - MIXED EXPOSURE					
1	1.87	24.9	1.94	15.3	136
2	1.81	18.2	0.0820	7.22	46.4
4	1.42	31.8	0.0230	7.29	70.1
50	1.39	42.3	0.268	37.4	240
100	0.184	10.7	0.263	12.8	2.31
AREA 4 - LOW EXPOSURE, OPEN FISHING AREAS					
5	1.73	33.2	3.44	11.1	64.6
80	0.139	11.4	0.194	16.1	15.7
90	0.429	15.2	0.222	20.3	58.7
110	0.133	9.99	0.294	9.44	2.03
140	0.0990	13.1	0.286	11.4	2.22
AREA 5 - LOW EXPOSURE, PRIVATE FISHING AREAS					
No data available from this survey					
AREA 6 - GENERAL ENVIRONMENT, OPEN SEA					
6	0.488	9.09	0.0210	10.4	10.1
130	0.721	13.9	0.534	26.2	90.2

(a) To locate sampling sites or zones, see map. (b) Values rounded off to three figures. Estimated analytical uncertainty, $CV < |\pm 3| \%$.

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