PRIORITY MICROCONTAMINANTS IN SEDIMENT SAMPLES FROM THE VENICE LAGOON: EXAMPLES OF VERTICAL AND HORIZONTAL DISTRIBUTIONS AND INTRA-SITE VARIABILITY

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INTRODUCTION

In October 1995, several sediment samples were collected from the bottom of the Venice lagoon and the neighboring Adriatic sea, within a framework of inquiries conducted by the State Attorney-General in Venice [1,2]. Matrices were assayed for several priority toxic microcontaminants selected from the families of PAHs (polycyclic aromatic hydrocarbons), PCBs, PCDDs and PCDFs, chlorinated pesticides, and heavy metals. On the whole, the design of the investigation was expected to provide a knowledge of microcontaminant distribution in lagoon compartments more reliable than that already available [3]. Indeed, a number of goals were sought after, including a more dependable assessment of risks for residents and a circumstantial description of anthropic impact scenarios with related releasing sources. Of a total of 49 samples, 24 were obtained from the bottom top layer in direct contact with the overlying water. All the remaining ones came from greater depths, with the aim of assessing the vertical distribution of contamination.

EXPERIMENTAL DESIGN AND METHODS

At Sites 1A–13A (Figure 1), bottom sampling was carried by utilizing a 4.0-cm- \emptyset_i cylindrical Perspex-lined steel corer where the contamination pattern as a function of depth was investigated; however, where only the top sediment layer was the target, samples were scooped up from the bottom directly by a scuba diver. To allow independent analytical replicates by the three laboratories involved (as per the authors' affiliations), at any given site two close samplings were carried out, yielding paired matrices for analysis; the two samplings were within 5 m (estimated) from one another. Sediment cores were extruded from corers, made into layer-specific samples, and stored at -20 °C in plastic bags for food use, awaiting further processing. In the end, two almost fully parallel sets of samples were available (N = 26; N_{bis} = 23).

For two laboratories, preparative pretreatment included natural drying of the wet matrices, followed by 10- or 20-mesh sifting and extensive homogenizing of each dry matrix; for the third laboratory, the frozen matrices were first coarsely ground and freeze-dried, and then sifted and homogenized. Diverse aliquots of each matrix were used for assessment of the different analytes [1,2].

For the assessment of organic chemicals, each matrix aliquot was spiked with fully ¹³Cand ²H-labelled standards (for chlorinated and PAH analytes, respectively). Extraction was carried out by utilizing Soxhlet apparatuses; alternatively, the techniques known as supercritical fluid (SFE) and accelerated solvent (ASE) extraction were also used to determine, respectively, (*a*)

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PAHs, PCBs, and chlorinated pesticides, and (b) PCDDs and PCDFs [1,2]. Cleanup steps were rather

Figure 1. Venice lagoon layout. The smaller frame offers an oversimplified view of the complex hydrological system known as the Venice lagoon (≈ 550 -km² wide, with an average < 2-m depth). An intricate network of deeper navigable waterways underlies generally unseen the water surface. The lagoon has a limited water exchange with the neighboring northern Adriatic sea, identified by sampling Sites 9A–12A, and is under the impact of several different and important local pollution sources. In the map, the City of Venice is identified by Site 13A whereas the inset comprises the industrial area of Porto Marghera, depicted in the larger frame with a number of topographical details. In previous studies, the lagoon and nearby sea environments were subdivided into exposure AREAS 1–6, formally identified on the basis of the anthropic impact(s) locally presumed predominant and therefore referred to as "virtual risk areas". The latter are not topographically defined; however, most of AREA 1 is made up by the Porto Marghera setting. The enlargement exhibits all the sites of the October 1995 sampling campaign and sampling Zones 30, 40, 60, and 70, previously used and relevant to this study.

canonical procedures based essentially on chromatographic columns. Analytes were quantitated by HRGC-LRMS(SIM) or -HRMS(SIM) [1–3]. GLP protocols were applied throughout.

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Heavy metals were measured by a canonical AAS technique after acid digestion of matrix aliquots [1–3]; prior to that, matrices were subjected to additional grinding and homogenizing. Measurements were replicated at least thrice.

As said, three laboratories were scheduled to perform the assays. The QA/QC interlaboratory program to improve comparability and harmonize analytical outputs was based on canonical intercalibration and reciprocal cross-check operations through reference and fortified matrices. However, the double set of sediment samples was also originally intended to provide an additional form of interlaboratory QA/QC. As only sampling duplicates were available, each laboratory was planned to assay (approximately) two-thirds of the matrices available [1], as per the following exemplifying scheme applied to nine sample pairs: AB, AB, AB, AC, AC, AC, BC, BC, and BC, where A, B, and C are general laboratory labels.

RESULTS AND DISCUSSION

Let us introduce C_1 and C_2 ($C_2 \ge C_1$) as the parallel numerical outcomes from two laboratories for a given sample pair or replicate analysis. For congruent matrices, the quantity

$$I_{D} = C_{2} \times C_{1}^{-1}$$

may be taken as an indicator of the interlaboratory agreement, at its maximum when $I_D = 1$ ($C_2 = C_1$) and decreasing with increasing I_D values. I_D is correlated to the relative deviation between outcomes

$$\Delta = [C_2 - C_1] \times [(C_2 + C_1) \ 0.5]^{-1}$$

by the following relationship:

$$\Delta\% = 100 \times [I_D - 1] \times [(I_D + 1) \ 0.5]^{-1}$$

As the interlaboratory trials and analytical determinations proceeded, it became clear that the paired samples from Sites 1A–13A should not be used as a tool to control and harmonize laboratory outputs due to the significant amount of intrinsic intra-site variability possibly affecting the samples (i.e. they were not congruent). In fact, I_D often exceeded 2.0 ($\Delta\% = 67\%$) and 1.5 ($\Delta\% = 40\%$), the C₁-C₂ agreement threshold values (V_Ts) tolerated as "physiological" for, respectively, the organic and inorganic analytes on the basis of the results from the canonical QA/QC interlaboratory program implementation.

A close examination of the data gathered [1] reveals that the organic analyte V_T is exceeded by approximately 1/3-2/3 of the paired outcomes available for PAHs, PCBs, and PCDDs and PCDFs, whereas the corresponding I_D incidence for the heavy metals is somewhat less (1/4–1/2); the situation is less clear for the pesticides assessed, partly due to the reduced number of replicates carried out (a discussion of this specific point goes beyond the scope of this report). An additional evidence of the more uniform elemental distribution with respect to that of the organic compounds is also offered by the incidence of I_D values >10 (N = 9 and N = 11 + 4, respectively) and >100 (N = 0 and N = 4). Finally, Table 1 presents a summary of statistical indicators that characterize the analytically homogeneous results available: again, the heavy metal distribution appears to be less spread out than that of the organic compounds by an average factor of ≈ 2 . It may be pointed out that the analytes with the larger confidence intervals (HCB and Hg) are also the most volatile in the laboratory. Examples of intra-site analyte concentration variability are available from Figure 2.

The statistical analysis whose outcomes have been summarized in Table 1 also allows evaluation of the probability P of a given analyte-specific concentration level in virtual risk

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	<i>PAHs</i> ng/g	<i>B[a]P</i> ng/g	PCBs ng/g	PCDDs - pg/g	+ <i>PCDFs</i> pgTE/g	<i>DDE</i> ng/g	<i>DDT</i> ng/g	<i>HCB</i> ng/g	Cd µg/g	<i>Cu</i> µg/g	<i>Hg</i> μg/g	<i>Рb</i> µg/g	Zn µg/g	
	4.9 <i>E</i> +3	6.4 <i>E</i> +2	3.1 <i>E</i> +3	8.2 <i>E</i> +3	6.0 <i>E</i> +1	1.1 <i>E</i> +1	2.0 <i>E</i> +0	2.4 <i>E</i> +3	2.00E+0	1.40E+2	7.80E+0	1.30E+2	3.80E+2] 0 cm
IA	5.5E+3	8.5 <i>E</i> +2	6.4 <i>E</i> +3	8.6 <i>E</i> +3	6.2 <i>E</i> +1	1.0 <i>E</i> +1	1.0 <i>E</i> +1	1.1 <i>E</i> +3	1.45 <i>E</i> +0	1.41 <i>E</i> +2	7.56E+0	1.46E+2	4.37E+2	_20
ы	6.9 <i>E</i> +3	8.8 <i>E</i> +2	2.9 <i>E</i> +3	1.0 <i>E</i> +4	7.8 <i>E</i> +1	1.7 <i>E</i> +1	3.1 <i>E</i> +0	3.0E+3	2.00E+0	1.40E+2	1.20E+1	1.50E+2	4.00E+2	1-20
L	8.0 <i>E</i> +3	1.0 <i>E</i> +3	4.1 <i>E</i> +3	4.8 <i>E</i> +3	5.5 <i>E</i> +1	2.0 <i>E</i> +1	1.0 <i>E</i> +1	4.8 <i>E</i> +2	1.37E+0	1.51E+2	7.22E+0	1.55E+2	4.57E+2	10
Ś	7.4 <i>E</i> +3	9.0 <i>E</i> +2	8.3 <i>E</i> +3	4.7 <i>E</i> +3	8.1 <i>E</i> +1	1.8 <i>E</i> +1	2.7 <i>E</i> +0	3.2 <i>E</i> +3	3.00E+0	1.60E+2	1.30E+1	3.60E+2	6.40E+2	1
	7.8 <i>E</i> +3	1.2 <i>E</i> +3	1.7 <i>E</i> +4	3.7 <i>E</i> +3	1.1 <i>E</i> +2	1.5E+1	<5 <i>E</i> +0	8.0 <i>E</i> +2	2.63E+0	1.64E+2	1.59E+1	3.75E+2	7.24E+2	60
,				1		r								
	1.8 <i>E</i> +4	2.7 <i>E</i> +3	5.6E+3	<4.9E+3	4.8E+1	8.8E+0	1.1E+1	4.3E+2	2.31E+0	1 55E+2	7 55E+0	1.80E+2	4 14E+2	0 cm
	4.6 <i>E</i> +4	8.0E+3	9.8E+3	2.1E+3	3.2E+1	1.7E+1	<5E+0	9.6E+2	1.84E-1	1.72E+2	1.64E+1	2.02E+2	8 59E+2	
3A														-30
Ε	9.3 <i>E</i> +4	8.8 <i>E</i> +3	1.4 <i>E</i> +4	5.1 <i>E</i> +4	1.4 <i>E</i> +3	5.6 <i>E</i> +1	1.3 <i>E</i> +1		5.00E+0	3.30E+2	3.20E+2	2.60E+2	2.00E+3	
TI	6.6 <i>E</i> +4	7.7 <i>E</i> +3	2.2 <i>E</i> +4	3.0 <i>E</i> +4	1.4 <i>E</i> +3	5.4 <i>E</i> +1	1.4 <i>E</i> +1	9.7 <i>E</i> +4	5.35E+0	2.68E+2	3.76 <i>E</i> +2	1.55E+2	1.67E+3	
01	A 8 E + A	16E+2	205-4	A 2 E + 5	12512	6551	44511		5 00 5 10	1.405.0	2 70 71 0	0.100.0		-60
	5.2E+4	51E+3	5.5E+4	4.5E+5 4.6E+2	1.3ET3 7 4E+1	$0.5E \pm 1$	4.4 <u>E</u> +1	01515	1.00E+0	1.40E+2	3.70E+2	2.10E+2	1.70E+2	
	5.2014	5.112.5	5.5274	4.0215	7.42+1	4.72+1	1.0272	0.1275	1.065+1	1.002+2	1.002+2	3.87E+2	5.91E+2	-90
	25514	ECE12	4.9511	0.4510	1001	20510		2.45.2	1.77.5.0	1 50 F. 1	1.007.0	1.01.0.0		10 cm
V	3.3E+4	3.0E+3	4.8E+1	8.4E+2	1.2E+1	3.0E+0		3.4E+2	4.77E+0	4.52E+1	1.88E+0	1.01E+2	3.84 <i>E</i> +2	10 cm
5/1	1.0ET4	2.02+3	0.5E+1	9.8E+2	1.4E+1	< <u>5E+0</u>	<5E+0	1.5E+3	2.5/E+0	3.65E+1	2.55E-1	4.72E+1	2.88E+2	-20
E.	2.0E+4	3.4E+3	1.5E+1	3.3E+2	1.5E+0	5.1E-1	1.2E-1	7.3E+0	6.00E+0	3.00E+1	5.00E-1	8.50E+1	5.70E+2	
E	1.2ET4	1.5E+5	$1.5E \pm 1$	4.5E+2	0.2E+0	<5E+0	2.3E+1	3.8E+2	6.10E+0	4.18E+1	4.32E-1	9.91E+1	6.57E+2	-40
S	2.3E+2 4.6E+2	2.5E+1	2.4E+0	9.4E+1	3.0E+0	1.5E-1	<1£-1	2.5E+0	<1.0E+0	8.00E+0	<2.0E-1	1.50E+1	5.50E+1	
	4.0672	0.06+1	1.5671	1.2 <i>L</i> +2	0.02+0	<3E+0	$\leq 5E+0$	9.02+0	<7.8E-1	2.14E+1	< 1.8E - 1	3.11E+1	1.05E+2	60
	1.8E+3	24E+2	9.6E+1	3 5F+3	5.7F+1	1.6F+0	2.7E+0	7.0E+1	4.97E+0	$7.02E \pm 1$	$272E \pm 0$	$0.00E \pm 1$	456E+2	0 cm
¥	1.0E+3	1.1E+2	62E+1	43E+3	5.7E+1	<5E+0	<5E+0	3.3E+1	3 34E+0	5.55E+1	2.72E+0	7.77 <u>5</u> +1	4.30ETZ 5.50E±2	
9	8 8E+2	11E+2	44E+1	3 8F+3	5.0E+1	8 8 F_1	15E 1	1.7E+1	3.00E+0	$2.00E \pm 1$	3.372-1	5.01E+1	2.20E+2	-20
ΤE	4.3E+2	50E+1	1.5E+1	24E+3	3.0E+1	<5E+0	<5E+0	1.75 < 1 1 5F+1	1.61E+0	5.00E+1 5.37E+1	0.00E-1	4 72 E+1	3.20E+2	
Sľ	4.2E+2	5.0E+1	41E+1	2.7E+3	$3.2E \cdot 1$ 3.1E+1	$4.2F_{-1}$	<5E-1	1.5E+0	$2.00E\pm0$	3.00E+1	2.00E 1	4.75E+1	1.00E+2	-40
	3.5E+1	<1E+1	1.5E+1	53E+2	7.0E+0	-5E+0	<5E+1	1.5E+0 1.5E+1	2.00ET0 8.07E 1	2.00E™1 2.24E+1	2.00E-1 7.52E 2	4.00E+1	1.902+2	
	0.00.1	1	1.2011	0.0012	1.02.10	-5610	-5010	1.0411	0.912-1	2.24671	1.J4E-4	J.14671	1.126+2	60

Figure 2. Analyte-specific vertical distributions in the top layers of the Venice lagoon bottom sediments at four sampling sites of virtual risk AREA 1.

AREA 1 to be exceeded (Table 2). For instance, the *P* values for PCDD and PCDF concentration levels of 740, 2400, and 9300 pgTE/g are, respectively, 5, 1, and 0.1 %. It may be pointed out that a PCDD and PCDF level of 2900 pgTE/g has been indeed reported for the bottom sediments of Canale Brentella (Figure 1, left of sampling Zone 60) [4].

It was anticipated [2] that at two sites in virtual risk *AREA 1* the sediment layers below the top one eventually exhibited contamination levels greater than those in the corresponding top layer specimens. In Figure 2 this is exemplified by the analyte vertical distributions detected at Sites 1A and, above all, 3A. It may be readily observed that distribution patterns are largely analyte- and site-specific. For instance, at Site 1A only the concentration levels of PCB, DDE, Hg, Pb, and Zn exhibit an increasing trend with depth, although not very marked; of the three layers tested, those affected are both the middle one (-20 to -40 cm) and the layer below (-40 to -60 cm). More evident is the situation at Site 3A: with the exception of PAHs, all the organic compounds and, to a lesser extent, the heavy metals Cd, Hg, and Zn appear to undergo a quite visible concentration increase with increasing depth. In at least two cases (PCBs, and PCDDs and PCDFs), the concentration increase hits between one and two orders of magnitude; for HCB, an increase of up to three orders of magnitude is observed. Again, the layers affected are the middle one (-30 to -60 cm) and the layer below (-60 to -90 cm). Two major conclusions were drawn from these (and other) results [1-3]: (a) in the Venice lagoon, the aforementioned chlorinated compounds qualify as probably the best tracers of (historical) industrial activity, and (b) the relatively high

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contamination levels of the same compounds detected in the deeper sediment layers at Sites 1A and 3A are likely to date back several to many years ago. Although also located in virtual risk *AREA 1*, but possibly because less exposed to industry's direct heavy impact in the past, bottom sediments at Sites 5/1A and 6A exhibit a top layer on the whole more contaminated than the lower ones. This latter observation is in agreement with the results of the depth trend studies carried out at other non-*AREA 1* sites (7A, 8/1A, 11A, and 13A).

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1. Estimates of the statistical indicators (SI) used to characterize the 13 data sets built with the concentration levels a of the es of interest measured in the bottom sediments of Venice lagoon virtual risk *AREA 1*.

	ORGANIC MICROCONTAMINANTS $(ng/g)^b$ PAHs B[a]P PCBs PCDDs + PCDFs DDE DDT HC $5.9E+3$ $7.4E+2$ $5.0E+2$ $3.0E+3$ $4.5E+1$ $5.9E+0$ $2.4E+0$ 2.11 $3.5E+1$ $<1E+1$ $2.4E+0$ $5.4E+1$ $1.0E+0$ $1.5E-1$ $<1E-1$ 1.51 $9.3E+4$ $8.8E+3$ $5.5E+4$ $4.3E+5$ $1.4E+3$ $6.5E+1$ $1.6E+2$ 8.11 $2.9E+3$ $3.7E+2$ $1.8E+2$ $1.5E+3$ $2.4E+1$ $3.5E+0$ $1.2E+0$ 6.91 $1.2E+4$ $1.5E+3$ $1.4E+3$ $5.9E+3$ $8.4E+1$ $1.0E+1$ $4.9E+0$ 6.61								HEAVY METALS (µg/g)					
PAHs	B[a]P	PCBs	PCDDs - pg/g	+ <i>PCDFs</i> pgTE/g	DDE	DDT	НСВ	Cd	Cu	Hg	Pb	Zn		
5.9E+3 7	7.4 <i>E</i> +2	5.0 <i>E</i> +2	3.0 <i>E</i> +3	4.5 <i>E</i> +1	5.9 <i>E</i> +0	2.4 <i>E</i> +0	2.1 <i>E</i> +2	2.62 <i>E</i> +0	9.34 <i>E</i> +1	3.91 <i>E</i> +0	1.05 <i>E</i> +2	4.40 <i>E</i> + 2		
3.5 <i>E</i> +1	<1 <i>E</i> +1	2.4 <i>E</i> +0	5.4 <i>E</i> +1	1.0 <i>E</i> +0	1.5 <i>E</i> –1	<1 <i>E</i> -1	1.5 <i>E</i> +0	1.84 <i>E</i> -1	8.00 <i>E</i> +0	7.52 <i>E</i> –2	1.50 <i>E</i> +1	5.50 <i>E</i> + 1		
9.3 <i>E</i> +4 8	8.8 <i>E</i> +3	5.5 <i>E</i> +4	4.3 <i>E</i> +5	1.4 <i>E</i> +3	6.5 <i>E</i> +1	1.6 <i>E</i> +2	8.1 <i>E</i> +5	2.29 <i>E</i> +1	1.25 <i>E</i> +3	3.76 <i>E</i> +2	3.87 <i>E</i> +2	2.00 <i>E</i> + 3		
2.9 <i>E</i> +3 3	3.7 <i>E</i> +2	1.8 <i>E</i> +2	1.5 <i>E</i> +3	2.4 <i>E</i> +1	3.5 <i>E</i> +0	1.2 <i>E</i> +0	6.9 <i>E</i> +1	1.82 <i>E</i> +0	6.49 <i>E</i> +1	1.63 <i>E</i> +0	7.88 <i>E</i> +1	3.30 <i>E</i> +2		
1.2 <i>E</i> +4 1	1.5 <i>E</i> +3	1.4 <i>E</i> +3	5.9 <i>E</i> +3	8.4 <i>E</i> +1	1.0 <i>E</i> +1	4.9 <i>E</i> +0	6.6 <i>E</i> +2	3.79 <i>E</i> +0	1.34 <i>E</i> +2	9.42 <i>E</i> +0	1.39 <i>E</i> +2	5.87 <i>E</i> +		
32	32	32	32	32	32	30	29	32	32	32	32	32		

gures preceded by the sign < (below limit of quantification) were entered in calculations as half their nominal value. Indicators betained from the log-normal distributions of the original data sets. (b) Except where noticed. (c) P = 95 %.

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2. Analyte-specific probabilities (*P*) to exceed given concentration levels. Estimates based on the outcomes of measurements tom sediment specimens from Venice lagoon virtual risk *AREA* $1.^{a}$

		OR	GANIC MI		HEAVY METALS (µg/g)								
	PAHs	B[a]P	PCBs	PCDDs - pg/g	+ <i>PCDFs</i> pgTE/g	DDE	DDT	НСВ	Cd	Cu	Hg	Pb	Zn
	4.8 <i>E</i> +3	6.1 <i>E</i> +2	6.2 <i>E</i> +2	3.6 <i>E</i> +3	4.2 <i>E</i> +1	4.5 <i>E</i> +0	2.3 <i>E</i> +0	2.3 <i>E</i> +2	2.7 <i>E</i> +0	9.1 <i>E</i> +1	3.8 <i>E</i> +0	1.0 <i>E</i> +2	4.0 <i>E</i> +2
	7.9 <i>E</i> +3	1.0 <i>E</i> +3	1.2 <i>E</i> +3	5.9 <i>E</i> +3	6.5 <i>E</i> +1	6.6 <i>E</i> +0	3.8 <i>E</i> +0	4.9 <i>E</i> +2	3.5 <i>E</i> +0	1.2 <i>E</i> +2	6.7 <i>E</i> +0	1.3 <i>E</i> +2	5.1 <i>E</i> +2
	1.3 <i>E</i> +4	1.7 <i>E</i> +3	2.5 <i>E</i> +3	9.9 <i>E</i> +3	1.0E+2	9.9 <i>E</i> +0	6.5 <i>E</i> +0	1.1 <i>E</i> +3	4.7 <i>E</i> +0	1.6 <i>E</i> +2	1.2 <i>E</i> +1	1.6 <i>E</i> +2	6.4 <i>E</i> +2
	2.5E+4	3.3 <i>E</i> +3	5.8 <i>E</i> +3	1.8 <i>E</i> +4	1.8 <i>E</i> +2	1.6 <i>E</i> +1	1.2 <i>E</i> +1	2.7 <i>E</i> +3	6.5 <i>E</i> +0	2.3 <i>E</i> +2	2.6 <i>E</i> +1	2.1 <i>E</i> +2	8.5 <i>E</i> +2
	5.9 <i>E</i> +4	7.9 <i>E</i> +3	1.9 <i>E</i> +4	4.2 <i>E</i> +4	3.9 <i>E</i> +2	3.1 <i>E</i> +1	2.9 <i>E</i> +1	9.9 <i>E</i> +3	1.0E+1	3.7 <i>E</i> +2	7.1 <i>E</i> +1	2.9 <i>E</i> +2	1.3 <i>E</i> +3
5	1.2 <i>E</i> +5	1.6 <i>E</i> +4	5.0 <i>E</i> +4	8.5 <i>E</i> +4	7.4 <i>E</i> +2	5.4 <i>E</i> +1	5.9 <i>E</i> +1	2.9 <i>E</i> +4	1.5 <i>E</i> +1	5.5 <i>E</i> +2	1.6 <i>E</i> +2	4.0 <i>E</i> +2	1.7 <i>E</i> +3
l	4.6 <i>E</i> +5	6.3 <i>E</i> +4	3.0 <i>E</i> +5	3.1 <i>E</i> +5	2.4 <i>E</i> +3	1.5 <i>E</i> +2	2.2 <i>E</i> +2	2.1 <i>E</i> +5	3.1 <i>E</i> +1	1.2 <i>E</i> +3	7.7 <i>E</i> +2	6.9 <i>E</i> +2	3.2 <i>E</i> +3
1	2.1 <i>E</i> +6	2.9 <i>E</i> +5	2.3 <i>E</i> +6	1.3 <i>E</i> +6	9.3 <i>E</i> +3	4.7 <i>E</i> +2	1.0 <i>E</i> +3	2.0E+6	6.9 <i>E</i> +1	2.7E+3	4.4E+3	1.3 <i>E</i> +3	6.3 <i>E</i> +3
he d.	individua	l data sets	s utilized to	obtain the	estimates	were the s	ame that	provided	the data ba	ase for Ta	able 1. (b) Exce	pt where

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Table 1. Estimates of the statistical indicators (SI) used to characterize the 13 data sets built with the concentration levels a of the analytes of interest measured in the bottom sediments of Venice lagoon virtual risk *AREA 1*.

SI	ORGANIC MICROCONTAMINANTS (ng/g) b									HEAVY METALS (µg/g)						
	PAHs	B[a]P	PCBs	PCDDs - pg/g	<i>⊦ PCDFs</i> pgTE/g	DDE	DDT	НСВ	Cd	Cu	Hg	Pb	Zn			
<x></x>	5.9 <i>E</i> +3	7.4 <i>E</i> +2	5.0 <i>E</i> +2	3.0 <i>E</i> +3	4.5 <i>E</i> +1	5.9 <i>E</i> +0	2.4 <i>E</i> +0	2.1 <i>E</i> +2	2.62 <i>E</i> +0	9.34 <i>E</i> +1	3.91 <i>E</i> +0	1.05 <i>E</i> +2	4.40 <i>E</i> +			
X _{min}	3.5 <i>E</i> +1	<1 <i>E</i> +1	2.4 <i>E</i> +0	5.4 <i>E</i> +1	1.0 <i>E</i> +0	1.5 <i>E</i> -1	<1 <i>E</i> -1	1.5 <i>E</i> +0	1.84 <i>E</i> -1	8.00 <i>E</i> +0	7.52 <i>E</i> –2	1.50 <i>E</i> +1	5.50 <i>E</i> + 1			
X _{max}	9.3 <i>E</i> +4	8.8 <i>E</i> +3	5.5 <i>E</i> +4	4.3 <i>E</i> +5	1.4 <i>E</i> +3	6.5 <i>E</i> +1	1.6 <i>E</i> +2	8.1 <i>E</i> +5	2.29 <i>E</i> +1	1.25 <i>E</i> +3	3.76 <i>E</i> +2	3.87 <i>E</i> +2	2.00 <i>E</i> +			
LCL ^c	2.9 <i>E</i> +3	3.7 <i>E</i> +2	1.8 <i>E</i> +2	1.5 <i>E</i> +3	2.4 <i>E</i> +1	3.5 <i>E</i> +0	1.2 <i>E</i> +0	6.9 <i>E</i> +1	1.82 <i>E</i> +0	6.49 <i>E</i> +1	1.63 <i>E</i> +0	7.88 <i>E</i> +1	3.30 <i>E</i> +			
UCL ^c	1.2 <i>E</i> +4	1.5 <i>E</i> +3	1.4 <i>E</i> +3	5.9 <i>E</i> +3	8.4 <i>E</i> +1	1.0 <i>E</i> +1	4.9 <i>E</i> +0	6.6 <i>E</i> +2	3.79 <i>E</i> +0	1.34 <i>E</i> +2	9.42 <i>E</i> +0	1.39 <i>E</i> +2	5.87 <i>E</i> +			
Ν	32	32	32	32	32	32	30	29	32	32	32	32	32			

(a) Figures preceded by the sign < (below limit of quantification) were entered in calculations as half their nominal value. Indicators were obtained from the log-normal distributions of the original data sets. (b) Except where noticed. (c) P = 95 %.

Table 2. Analyte-specific probabilities (P) to exceed given concentration levels. Estimates based on the outcomes of measurements of bottom sediment specimens from Venice lagoon virtual risk *AREA* 1.^{*a*}

Р		ORC	GANIC MI	CROCONTAMINA	NTS (ng/	g) ^b		HEAVY METALS (µg/g)					
	PAHs	B[a]P	PCBs	PCDDs + PCDFs pg/g pgTE/g	DDE	DDT	НСВ	Cd	Cu	Hg	Pb	Zn	
0.5	4.8 <i>E</i> +3	6.1 <i>E</i> +2	6.2 <i>E</i> +2	3.6 <i>E</i> +3 4.2 <i>E</i> +1	4.5 <i>E</i> +0	2.3 <i>E</i> +0	2.3 <i>E</i> +2	2.7 <i>E</i> +0	9.1 <i>E</i> +1	3.8 <i>E</i> +0	1.0 <i>E</i> +2	4.0 <i>E</i> +2	
0.4	7.9 <i>E</i> +3	1.0 <i>E</i> +3	1.2 <i>E</i> +3	5.9E+3 6.5E+1	6.6 <i>E</i> +0	3.8 <i>E</i> +0	4.9 <i>E</i> +2	3.5 <i>E</i> +0	1.2 <i>E</i> +2	6.7 <i>E</i> +0	1.3 <i>E</i> +2	5.1 <i>E</i> +2	
0.3	1.3 <i>E</i> +4	1.7 <i>E</i> +3	2.5E+3	9.9E+3 1.0E+2	9.9 <i>E</i> +0	6.5 <i>E</i> +0	1.1 <i>E</i> +3	4.7 <i>E</i> +0	1.6 <i>E</i> +2	1.2 <i>E</i> +1	1.6 <i>E</i> +2	6.4 <i>E</i> +2	
0.2	2.5 <i>E</i> +4	3.3 <i>E</i> +3	5.8 <i>E</i> +3	1.8 <i>E</i> +4 1.8 <i>E</i> +2	1.6 <i>E</i> +1	1.2 <i>E</i> +1	2.7 <i>E</i> +3	6.5 <i>E</i> +0	2.3 <i>E</i> +2	2.6 <i>E</i> +1	2.1 <i>E</i> +2	8.5 <i>E</i> +2	
0.1	5.9 <i>E</i> +4	7.9 <i>E</i> +3	1.9 <i>E</i> +4	4.2 <i>E</i> +4 3.9 <i>E</i> +2	3.1 <i>E</i> +1	2.9 <i>E</i> +1	9.9 <i>E</i> +3	1.0 <i>E</i> +1	3.7 <i>E</i> +2	7.1 <i>E</i> +1	2.9 <i>E</i> +2	1.3 <i>E</i> +3	
0.05	1.2 <i>E</i> +5	1.6 <i>E</i> +4	5.0 <i>E</i> +4	8.5 <i>E</i> +4 7.4 <i>E</i> +2	5.4 <i>E</i> +1	5.9 <i>E</i> +1	2.9 <i>E</i> +4	1.5 <i>E</i> +1	5.5 <i>E</i> +2	1.6 <i>E</i> +2	4.0 <i>E</i> +2	1.7 <i>E</i> +3	
0.01	4.6 <i>E</i> +5	6.3 <i>E</i> +4	3.0 <i>E</i> +5	3.1 <i>E</i> +5 2.4 <i>E</i> +3	1.5 <i>E</i> +2	2.2 <i>E</i> +2	2.1 <i>E</i> +5	3.1 <i>E</i> +1	1.2 <i>E</i> +3	7.7 <i>E</i> +2	6.9 <i>E</i> +2	3.2 <i>E</i> +3	
0.001	2.1 <i>E</i> +6	2.9 <i>E</i> +5	2.3 <i>E</i> +6	1.3 <i>E</i> +6 9.3 <i>E</i> +3	4.7 <i>E</i> +2	1.0 <i>E</i> +3	2.0 <i>E</i> +6	6.9 <i>E</i> +1	2.7 <i>E</i> +3	4.4 <i>E</i> +3	1.3 <i>E</i> +3	6.3 <i>E</i> +3	
(<i>a</i>) The noticed.	individua	al data sets	utilized to	obtain the estimates	were the s	ame that	provided	the data ba	use for Ta	able 1. (b) Exce	pt where	