Persistent Organochlorine Microcontaminants in Bottom Sediments of the Northern Adriatic Sea

Roberto Miniero, Elena Dellatte, Silvia De Luca, Anna Rita Fulgenzi, Nicola Iacovella, Anna Maria Ingelido, Fabiola Ferri, and Alessandro di Domenico*

Istituto Superiore di Sanità, Viale Regina Elena 299, 00161 Rome, Italy
E-mail: addeke@iss.it

Introduction

PAHs, PCBs, PCDDs, PCDFs, DDTs, and HCB are organic microcontaminants included in the list of the Persistent Toxic Substances (PTS).[1] The worldwide distribution of these chemicals has prompted a great deal of monitoring activities, essentially aimed at evaluating the amount of exposure of humans and/or organisms in the environment. Recently, in the Mediterranean region a PTS assessment was carried out in the framework of a worldwide UNEP project.[2]

In the north-eastern Mediterranean, the Venice lagoon and the neighboring Adriatic sea are areas of interests for their chemical contamination levels and the level of risk. The large but shallow Venice lagoon is exposed to urban sewage and industrial waste, whereas the northern Adriatic sea appears particularly sensitive to dumping due to morphological and hydrological features (e.g., average depth, 35 m).[3] Since 1990, our laboratory set out a number of studies in the Venice lagoon with financial support granted by the Ministry of the University and Scientific Research, the State Attorney-General in Venice, and the Ministry of the Environment. In the last project, an extensive investigation was carried out on lagoon and marine matrices, including bottom sediments, focused on risk evaluation for lagoon residents.[4] Previous research showed the presence of a large dumping area in the northern Adriatic sea at approximately 8 km from the coast. In this area, stretching north-to-south roughly between the latitudes of the Lido and Chioggia portmouths, unexpected high concentrations of organic microcontaminants and heavy metals, also typical of some activities of the Porto Marghera industrial district, were detected.

This paper provides the results of an additional number of determinations in bottom sediments from samplings off the coast, carried out to consolidate the data already available.

Experimental

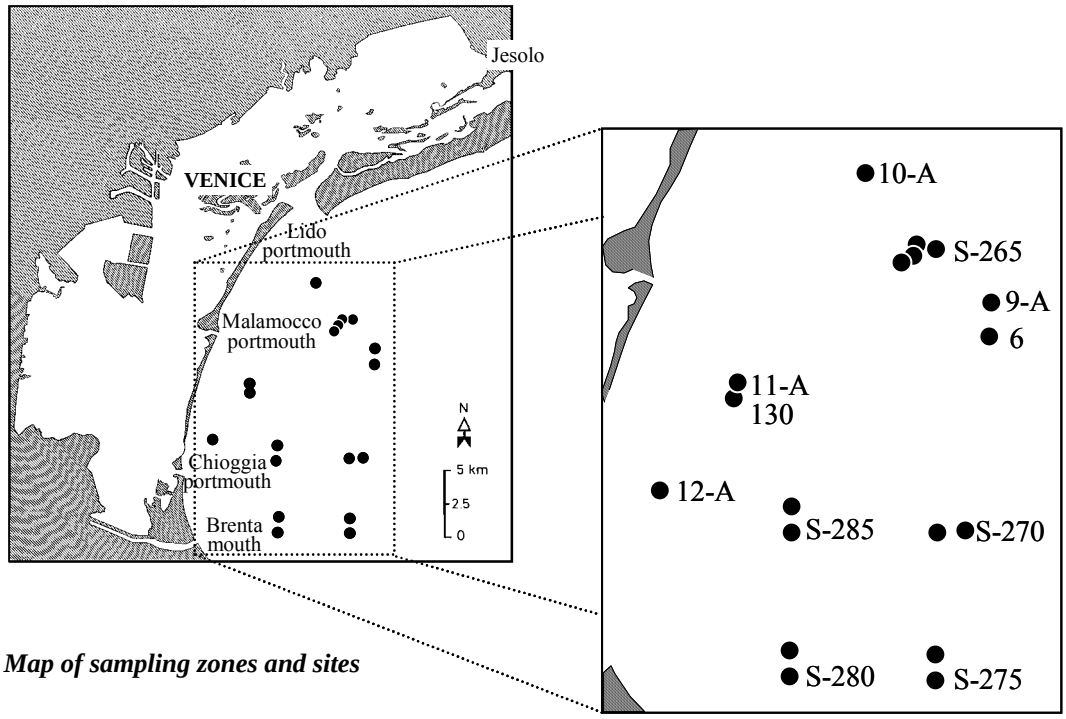
Sediments were collected from five different zones (S-265, S-270, S-275, S-280, and S-285) by a standard Van Veen grab due to the prevailing sandy composition of the bottom. Sampling zones were selected on the basis of the available experimental and historical information, integrated with indications from local experts and bathymetric maps. Each zone was represented by two to four sampling sites (see geographic layout).[4] The position of each site was GPS-determined (Table 1). Once on board, grab specimens were transferred to polyethylene bags for food storage and carried to the laboratory; here, they were stored at 4 °C in view of analytical processing.[3–5]

The 12 wet specimens were transferred to as many new glass crystallizing dishes, previously cleansed with concentrated HNO_3, bi-distilled water, and high purity *n*-exane. Water was removed by natural evaporation; the 12 dry sediment matrices were then hand-sieved (25 mesh) to separate coarse materials, and homogenized. Five pooled matrices were then obtained by homogenizing equivalent weight portions of zone-related sediment matrices, as per the workplan.[4] Then, each

matrix was divided into four portions ("samples"), as required to determine the different groups of analytes. Before extraction, samples were spiked with internal standards (^{2}H-labeled PAHs and ^{13}C-labeled PCBs, PCDDs, PCDFs, *p,p'*-DDE, *p,p'*-DDT, and HCB), as appropriate.

Spiked samples were exhaustively Soxhlet-extracted with toluene for PCDDs, PCDFs, and non-*ortho* PCBs, or with a *n*-hexane-toluene mixture for the remaining analytes.

For the assessment of non-*ortho* PCBs, PCDDs, and PCDFs, extracts were purified with chromatographic filtrations through a column of Extrelut impregnated with 96% H_2SO_4 followed by a multilayer column and an adsorption-activated neutral alumina column. Cleanup was followed by HRGC-HRMS(SIM) quantitation. PAHs, *ortho* PCBs, and chlorinated pesticides were eluted on a silica gel column and determined by HRGC-LRMS(SIM). Final results were corrected for recovery and estimated according to the medium bound approach. Estimated uncertainty on single measurements, < | ±10 % |.



Map of sampling zones and sites

Layout of 1992, 1995, and 1998 sampling zones and sites in the Venice lagoon and neighboring north sector of the Adriatic sea.

Results and discussion

Table 2 summarizes PAH, B[a]P, PCB, PCDD+PCDF, *p,p'*-DDE, *p,p'*-DDT, and HCB levels measured in the northern Adriatic sea bottom sediments collected between 1992 and 1998 (Table 1). The geographic layout shows details of sampling zones and sites, and coarsely indicates the

boundaries of the area assessed: between northern latitudes 45° 10' 58'' (Zone S-275) and 45° 22' 33'' (Site 10-A), and between eastern longitudes 12° 20' 12'' (Site 12-A) and 12° 30' 55'' (Site 9-A). All samples were collected in the open sea, distant from direct contamination sources.

Six zones/sites (6, 9-A-1, 12-A1-1, S-265, S-270, and S-275) exhibit contamination levels close to or as low as the background measured in remote areas of the world. For example, in Arctic marine sediments PCB levels are generally below 1 ng/g, dry weight (*dw*);[6] in sediments of the North Sea, PAHs cover the range <0.01−20 ng/g *dw*.[7] Furthermore, HCB levels of 0.09−1.8 ng/g *dw* were detected in sediments from remote lakes in northern Canada,[8] and PCDD+PCDF levels below 0.003 pgI-TE/g *dw* were found in Scandinavian remote areas.[9]

On the contrary, five zones/sites (130, S-280, S-285, 10-A1-2, and 11-A2-1) exhibit greater contamination levels and visibly high [PCDFs] × [PCDDs]$^{-1}$ ratios (> 1). In addition, they also have analyte-specific features: for instance, high concentrations of PCDDs+PCDFs and HCB were detected at Zone S-285, PAHs and PCBs appear to be particularly relevant at Site 10-A1-2, whereas PCB, PAH (and similarly PCDD+PCDF), and HCB levels at Site 130 are respectively one, two, and three orders of magnitude higher then the local background levels (see above).

The concomitant presence of higher concentrations of HCB, a reaction by-product in the manifacture of chlorinated solvents,[10] and the prevalence of PCDFs on PCDDs[11] are the industrial fingerprint at Zones S-285 and S-280 (1998 sampling campaign). These recent findings provide a general confirmation of previous results obtained from the assessments of Sites 10-A1-2, 11-A2-1, and, in particular, 130. The remaining zones/sites have altogheter different characteristics. Therefore, the overall picture provides reasonably consistent indications of the presence in the open northern Adriatic sea of a more contaminated area: is origin might be ascribed to transfer of lagoon bottom materials removed from the Porto Marghera industrial district.

Acknowledgements
Research project co-financed by the Italian Ministry of the Environment, Grant No. ISS A-80. The authors are indebted to Mr. Dario Smania of Biotecnica s.r.l and to Magistrato alle Acque, both in Venice, for their kind assistance in the sampling operations.

Table 1. Overview of north Adriatic sea sampling campaigns in the years 1992, 1995, and 1998.

Site or zone	Sampling location[a]		Sampling date
6	Lat. 45° 18' 48" N	Long. 12° 30' 54" E	July 1992
130[b]	Lat. 45° 17' 32"–42" N	Long. 12° 22' 36"–39" E	June 1995
9-A-1	Lat. 45° 19' 30" N	Long. 12° 30' 55" E	October 1995
10-A1-2	Lat. 45° 22' 33" N	Long. 12° 26' 56" E	October 1995
11-A2-1	Lat. 45° 17' 30" N	Long. 12° 22' 36" E	October 1995
12-A1-1	Lat. 45° 15' 15" N	Long. 12° 20' 12" E	October 1995
S-265[b]	Lat. 45° 20' 30"–71" N	Long. 12° 28' 12"–54" E	July 1998
S-270[b]	Lat. 45° 14' 20" N	Long. 12° 30' 00"–12" E	July 1998
S-275[b]	Lat. 45° 10' 58"–11' 31" N	Long. 12° 29' 12" E	July 1998
S-280[b]	Lat. 45° 10' 60"–11' 36" N	Long. 12° 24' 24"–30" E	July 1998
S-285[b]	Lat. 45° 14' 20"–55" N	Long. 12° 24' 27"–28" E	July 1998

(a) GPS coordinates. For pooled samples, range values are reported. *(b)* Pooled samples.

Table 2. Analytical results obtained from dry bottom sediments of the northern Adriatic sea.

Zone or site	PAHs	B[a]P	PCBs	PCDDs+PCDFs		DDE	DDT	HCB
	ng/g	*ng/g*	*ng/g*	*pg/g*	*pgI-TE/g*	*ng/g*	*ng/g*	*ng/g*
6	99	17	2.5	≈1[a]	≈0.2[a]	0.59	0.50	0.039
130	2500	340	27	910	17	0.94	0.52	44
9-A-1	≈3[a]	<1[b]	≈0.5[a]	2.4	≈0.07[a]	<0.05	<0.05	<0.05
10-A1-2	590	86	26	36	0.6	<0.05	<0.05	<0.05
11-A2-1	2300	330	15	540	10	0.98	0.74	1.7
12-A1-1	250	33	6.3	150	2.4	<0.05	0.05	<0.05
S-265	52	7.8	≈4[a c]	37	0.73	<0.2	<0.2	0.83
S-270	12	1.9	≈4[a,c]	29	0.61	<0.2	<0.2	0.20
S-275	22	4.1	≈4[a,c]	48	0.92	<0.2	<0.2	0.13
S-280	260	38	12[c]	330	5.0	0.49	<0.2	2.1
S-285	63	8.4	≈4[a,c]	96	1.6	<0.2	<0.2	1.2

(a) Figures preceded by the sign ≈ are "not representative" as they are formed, mostly or in full, by congener contributions below limit of quantification (<LOQ). *(b)* Figures preceded by the sign < indicate the limit of quantification. *(c)* Figure including non-*ortho* PCBs.

References

1. Buccini J. (1999). *Organohalogen Compounds* **43**, 459–460.
2. UNEP (2002). *Mediterranean Regional Report — Regionally-Based Assessment of Persistent Toxic Substances*. Albaiges J., Regional Coordinator.
3. di Domenico A., Turrio Baldassarri L., Ziemacki G., De Felip E., Ferrari, G., La Rocca C., Cardelli M., Cedolini G., Dalla Palma M., Grassi M., Roccabella V., Volpi F., Ferri F., Iacovella N., Rodriguez F., D'Agostino O., Sansoni R., and Settimo G. (1998). *Organohalogen Compounds* **39**, 199–204.
4. Ballard T., Cardelli M., di Domenico A., De Felip E., Ferri F., Fulgenzi A.R., Iacovella N., Miniero R., Turrio Baldassarri L., Zapponi G., and Ziemacki G. (1999). *Organohalogen Compounds* **44**, 447–452.
5. di Domenico A., De Felip E., Ferri F., Iacovella N., Miniero R., Scotto di Tella E., Tafani P., and Turrio Baldassarri L. (1992). *Microchemical Journal* **46**, 48–81.
6. UNEP (2002). *Arctic Regional Report — Regionally-Based Assessment of Persistent Toxic Substances*.
7. WHO (1998). *Polycyclic Aromatic Hydrocarbons (selected non-heterocyclic)*. Environmental Health Criteria 202. World Health Organization (Geneve).
8. Muir D.C.G., Grift N.P., Lockhart W.L., Wilkinson P., Billeck B.N., and Brunskill G.J. (1995). *The Science of the Total Environment* **160/161**, 447–457.
9. Rappe C., Andersson R., Bonner M., Cooper K., Fiedler H., Howell F., Kulp S.E., and Lau C. (1997). *Chemosphere* **34**, 1297–1314.
10. WHO (1997). *Hexachlorobenzene*. Environmental Health Criteria 195. World Health Organization (Geneve).
11. Wu W.Z., Schramm K.W., Xu Y., and Kettrup A. (2001). *Water Research* **35**, 3025–3033.