

PRIORITY MICROCONTAMINANTS IN THE VENICE LAGOON: THE JOINT EFFORT OF THE ITALIAN MINISTRY OF THE ENVIRONMENT AND THE NATIONAL INSTITUTE FOR HEALTH TO DEFINE EXPOSURE AND RISK SCENARIOS

Terri Ballard, Massimo Cardelli, Alessandro di Domenico, Elena De Felip, Fabiola Ferri, Anna Rita Fulgenzi, Nicola Iacovella, Roberto Miniero, Luigi Turrio Baldassarri, Giovanni A. Zapponi, Giovanni Ziemacki

Istituto Superiore di Sanità, 00161 Rome, Italy

INTRODUCTION

In the early 1990s, our laboratory set out a number of studies to characterize contamination of the Venice lagoon, with a specific focus on several heavy metals and a number of persistent organic pollutants (POPs) selected from the chemical families of polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs), and chlorinated pesticides. In the past, our work received additional financial support from the Ministry of the University and Scientific Research as well as by the State Attorney-General in Venice, the latter within the framework of specific investigative interventions. The load of the aforementioned toxic chemicals in marine food from the lagoon was also examined in response to a request from the Ministry of Health to analyze the toxicological risks for the residents exposed to local food. An outcome of this work was a provisional contamination map of the Venice lagoon. The contamination scenario obtained from the assay of sediment and biota samples showed a strong correlation between contamination and anthropic impact [1–4].

At present, within the framework of a three-year (1998–2000) research project co-financed by the Ministry of the Environment, we are focusing on risk evaluation for lagoon residents by describing an exposure scenario based on analyses of sediment, biota, water, suspended particulate, and human milk samples. In order to obtain a more complete risk characterization, the study has been extended to also include the assessment of some radionuclides and organometals of toxicological concern in fish and human milk. What follows is a brief account to highlight the major goals of the project, in line with the aforementioned traditional activities.

GOALS AND STRATEGY

The main goal of the study is the evaluation of the multipathway exposure to several chemical risk factors in the lagoon, using relevant chemical data already available and new data to be obtained from the planned surveys. To this aim, known and validated methods and models will be used together with updated toxicological information. Four surveys have been planned, focusing on the evaluation of contaminant levels in five matrices. Each of these surveys is related to a specific goal, based on priority criteria such as the intrinsic hazardous properties of the chemicals of interest, the specific characteristics of the study environments, and the relevance of the more important substrata and exposure pathways. The surveys cover:

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- water and suspended particulate in two zones of the Venice lagoon, identified as *Alfa* and *Beta* (see map) and characterized by markedly different exposure patterns;
- edible bivalves and fish;
- sediment from the lagoon and from the sea sector outside the lagoon, within 10 km of the coast;
- human milk from donors who are residents in the study area who consume a diet rich in food products from the lagoon, and from non-consumers.

In Zones *Alfa* and *Beta*, the study aims to assess the relationships between the concentration of contaminants in water and on suspended particulate, as well as between the aqueous phase and the sedentary organisms present. The latter have been chosen in order to investigate the transfer of the chemicals of interest through the human food chain and to examine their possible utilization as bioaccumulation indicators.

The study of sediment contamination, including areas not previously sampled (see map), is ongoing. The pragmatic subdivision of the Venice lagoon and neighboring Adriatic sea into six virtual risk areas (Table 1) based on locally relevant anthropic impacts was made in previous studies in order to have a handy criterion for sample and data treatment. Due to the size of the lagoon it was chosen not to carry out randomized sampling, and the data obtained have been and will be used primarily to outline low resolution contamination scenarios.

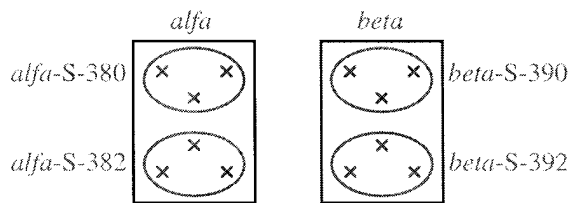
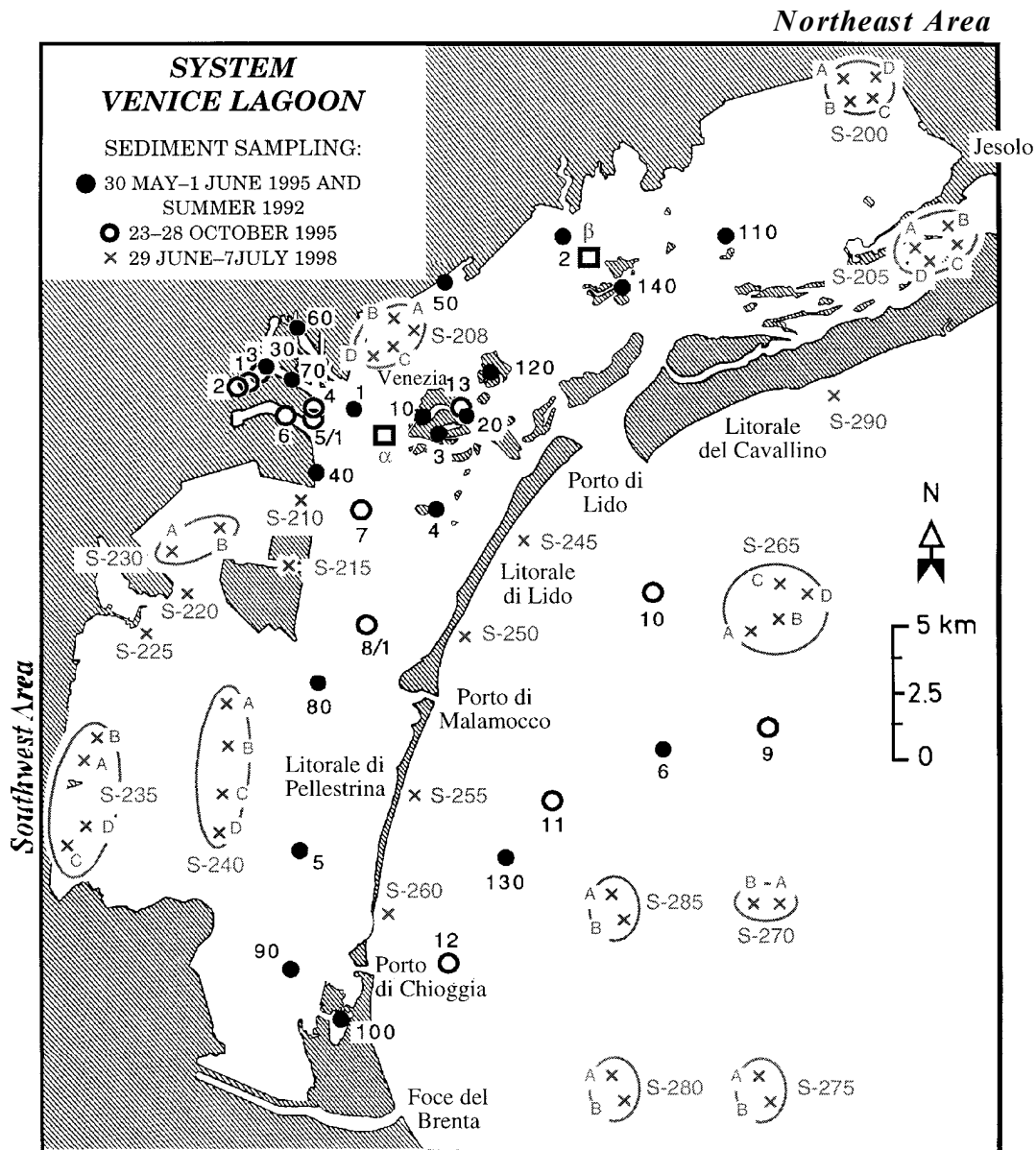
TABLE 1. Identification of Venice lagoon virtual risk areas on the basis of sampling sites or zones used for bottom sediment contamination assessment.

<i>VIRTUAL RISK AREAS</i>	<i>SAMPLING SITES OR ZONES</i>
1 INDUSTRIAL OR PREVAILING INDUSTRIAL EXPOSURE	● 30, 40, 60, 90, ○ 1, 2, 3, 4, 5/1, 6
2 URBAN OR PREVAILING URBAN EXPOSURE	● 3, 10, 20, 120 ○ 13
3 MIXED EXPOSURE	● 1, 2, 4, 50, 100 ○ 7 × 208, 210, 215, 220, 225, 230, 380(α), 382(α), 390(β), 392(β)
4 LOW EXPOSURE, OPEN FISHING AREAS	● 5, 80, 90, 110, 140 ○ 8/1 × 240
5 LOW EXPOSURE, PRIVATE FISHING AREAS	× 200, 205, 235
6 GENERAL ENVIRONMENT, OPEN SEA	● 6, 130 ○ 9, 10, 11, 12 × 245, 250, 255, 260, 290, 265, 270, 275, 280, 285
● Summer 1992 and 30 May–June 1995 ○ 23–28 October 1995	

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Human exposure, whose most relevant contribution comes from food intake, will be evaluated considering different exposure pathways. In addition, the overall estimate(s) will be compared to the contamination levels detected in mother's milk, sampled and analyzed in agreement with guidelines developed and repeatedly utilized for similar studies by WHO. Exposure scenarios will be evaluated according to validated criteria, models, and programmes (McKay models, USES system, etc.), considering both average and worst-case situations. Risk evaluation will take into account the differential toxicity of the compounds of interest; in particular, for PCBs and PCDDs and PCDFs a congener-specific approach will be adopted according to the toxicity equivalency criterion. In addition, more complex risk evaluations may possibly be performed taking into consideration the interactions between chemicals together with the usual estimate of toxicological risk (such as dose-response relationships, NOAEL, safety factors, etc.).

METHODS

Collection of sediments, biota, water, and particulate was carried out between June 29 and July 22, 1998. The map shows the 55 sites where sediments were sampled, including 12 in Zones *Alfa* and *Beta*. Edible biota species were obtained at or near some of the locations shown in the map. In previous studies (Table 2), the biota analyzed showed a trend towards higher contamination levels with increasing anthropic impact (generally speaking, moving from *AREA 4* to *AREA 1*) [1,2]. The amount of microcontaminants found in mussels from *AREA 4* inside the lagoon [1,2] did not appear to be significantly different from that found in mussels collected in breeding areas of the Italian Adriatic coast [3]. These mussels were sampled in areas suitable for bivalve cultivation, not directly exposed to a chemical anthropic impact. In other words, *AREA 4* levels appear to be compatible with low impact areas, or with the chemical concentration levels found in the general environment. As observed in the biota, highest levels of sediment

TABLE 2. Synoptical comparison of organic contamination levels in the Venice lagoon virtual risk *AREAS 1, 2, and 4, [1,2,4,5]* and in mussels collected in previous campaigns along the Italian Adriatic sea coastline [3].

	<i>ANALYTE LEVELS (ng/g except where noted)</i>					HCB
	PAHs	PCBs	PCDDs+PCDFs		DDE	
			<i>pg/g</i>	<i>pgTE/g</i>		
<i>AREA 1 – INDUSTRIAL OR PREVAILING INDUSTRIAL EXPOSURE</i>						
Sediments	1600–48000	53–5500	840–29000	12–570	1.5–9.9	35–470
Biota	62–210	23–170	21–45	1.1–5.3	0.82–39	≈4–18
<i>AREA 2 – URBAN OR PREVAILING URBAN EXPOSURE</i>						
Sediments	7500–45000	71–610	210–1400	4.8–23	1.3–27	0.33–6.4
Biota	26	29	13	0.87	1.2	0.73
<i>AREA 4 – LOW EXPOSURE, OPEN FISHING AREAS</i>						
Sediments	62–630	0.27–8.3	15–160	0.35–3.3	<0.05–1.3	0.059–0.29
Mussels	5.2–17	14–46	3.1–7.6	0.23–0.68	1.5–3.8	<0.08–0.55
Clams	2.8	1.9	1.4	0.079	0.18	0.29
<i>PRISMA PROJECT</i>						
Mussels	—	6.7–45	1.4–3.1	0.11–0.24	1.6–3.0	—

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contamination are found in *AREA 1* followed by *AREA 2*, and lower values are exhibited by *AREA 4* (Table 2) [4,5].

Human milk collection is in the second season of sampling. Milk is being collected between the fourth and eighth week after delivery, with great care to avoid accidental contaminations. Milk sampling will continue until the year 2000, for a total time span of no less than four six-month seasons, collecting a total of 20–30 samples.

Zones *Alfa* and *Beta* were formally divided into two subzones comprising three sampling sites each. On the whole, the water sampling campaign lasted four weeks, each zone being tested every other week, three times a week. In the end, 24 three-sampling pools became available. After collection, samples were taken to the laboratory responsible of the analysis. Each aqueous matrix was filtered off to remove the suspended particulate (to be analyzed separately) and submitted to continuous solvent extraction and the following cleanup passages. The particulate component, held on filters, was kept stored at $-20\text{ }^{\circ}\text{C}$ awaiting further treatment.

Sediment samples were transferred to the Ecotoxicology Unit of the Italian National Institute for Health. Individual samples were allowed to dry, then sieved, and mechanically homogenized. In most cases, when the contamination distribution of the area assayed was likely to be uniform, two to four individual pretreated matrices were made into pools using equiponderal contributions. The final matrices were then delivered to the participating laboratories for specific analytical processing and determination (Table 3).

TABLE 3. Overview of the Venice lagoon and Adriatic sea bottom sediment sampling campaign of June 29 through July 7, 1998, and outcome of pretreatment processes.

<i>PRETREATMENT OF SEDIMENT SAMPLES</i>			
		N	WEIGHT (g)
Drying		55	253–2200
Sieving (25 mesh)		55	137–1970
Homogenization		55	137–1970
<i>Pools</i> of sample aliquots		17	200–800
Single samples		5	355–999
<i>Sample or pool subdivision in portions for the laboratories involved</i>			
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Elements (15g)	PAHs, PCBs, PCDDs, PCDFs, DDE, HCB, etc. (50 g)	Physics Unit (200 cc)	Chemistry Unit (35 g)

COLLABORATIONS

The project described is supported by the following collaborations:

- *Magistrato alle Acque* (Venice), for sampling of environmental matrices;
- *Center for the Study of Environmental Chemistry and Technologies, Italian National Council for Research*, c/o Department of Environmental Sciences, University of Venice

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(Venice), for sampling of water and particulate, pretreatment, and determination of PCBs in water samples;

- *Regional Agency for Environmental Protection and Prevention of the Veneto Region* (Venice), for assessment of radionuclides and organometals in environmental samples;
- *Venice Department of Health Prevention* (AULSS 12), for milk sampling;
- *Italian National Institute for Health* (Rome), for coordination and determination of PAHs, PCBs, PCDDs and PCDFs, chlorinated pesticides, and heavy metals in sediments, biota, particulate matter, milk, and radionuclides in milk.

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