

ENVIRONMENTAL LEVELS AND TRENDS

WATER QUALITY ASSESSMENT OF THE VENICE LAGOON: SPATIAL DISTRIBUTION OF POPs BY HIGH VOLUME SAMPLER

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Introduction

The Venice lagoon has been originated more than 6000 years ago by the counteracting effects of the force of the sea and the solid transport of the rivers. In the middle of the lagoon lies the city of Venice, an important tourist city, characterised by elevated boat traffic and the absence of a modern sewage system. At the north-west edge there is the industrial area of Porto Marghera, with important petrochemical factories including chlorinated hydrocarbons production plants and refinery. Many studies have been published on the contamination of the sediments of the lagoon by PCDD/F's and the other POP's^{1,2,3}. On the other hand, no data have been yet published about the levels of contamination of the water of the lagoon by such contaminants, mainly due to the low levels of concentrations which makes these compounds hardly detectable by the traditional analytical methods. In order to verify the concentration limits of the quality objectives for the water of the lagoon given by the april 23th, 1998 Italian Ministry Decree⁴ a new sampling system was tested for the detection at ultratrace levels of PCDD/F's, PCB's, HCB and PAH's⁵.

In the present work the results of the spatial campaign of measurements of POP's made by Magistrato alle Acque, the Water Venice Authority, by using high volume sampling system are presented.

Methods and materials

All the samples have been collected during year 2001 in the sampling stations represented in Fig. 1. The high volume sample system used allowed to preconcentrate the compounds of interest on a glass fiber filter combined with an absorbing resin cartridge⁵. The water samples were collected in each sampling stations also by 4 liter syranized glass bottles in order to compare the different sampling techniques. The samples were spiked with a series of 15 ¹³C₁₂-labeled 2,3,7,8 PCDD/F (EDF8999), 12 ¹³C₁₂-labeled PCB (EC4937), with ¹³C₁₂-HCB (CLM351) substituted isomers and 5 deuterated PAH (Acenaphtene-D10, Chrysene-D12, Naphtalene-D8, Perylene-D12, Phenanthrene-D10,) internal standards, and then extracted with dichloromethane and cleaned up. The HRGC/HRMS analyses were conducted using a HP 6890 plus gas chromatograph coupled to a Micromass Autospec Ultima mass spectrometer operating in EI mode at 35 eV and with a resolution of 10.000 (5 % valley). The recovery always ranged between 55% and 105%. Reproducibility were 15% for lover value or better. The laboratory blank, repeated twice, where lower than 8% respect to the minimum concentration found⁶.

Results and discussion

The high volume system allowed monitoring for the first time the concentration of POP's in the Venice lagoon water. The 35 liters samples collected by INFILTREX system allow the following detection limits (S/N > 3):

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TCDD/F	0,02 pg/L –
OCDD/F	0,05 pg/L
HCB	0,01 ng/L
PCBs	0,5 pg/L (for each congener) 0,05 ng/L (as aroclor)
PAHs	0,01 ng/L

Samples showed the yields reported below, referred to the extraction, purification and analysis:

PCDD/Fs	35%~121%
HCB	54 %~72 %
PCBs	41 %~101 %
PAHs	35 %~94 %

The results were compared with those of the samples collected in the same stations during the same time by the standard method (EPA 1613B/94) and confirmed an average improvement of the detection limits of about 30 times for the new high volume sampling method. The total POP's concentration of the sampling stations are reported in Table 1.

Table 1. Concentrations of POP's in the different stations of the Venice lagoon

Station	PCDD/Fs pg/l I-TE	PCBs Arochlor pg/l I-TE	PCB ng/l	HCB ng/l	PAH Ng/l
A Canal Grande	0.258	0.036	2.48	0.09	190.41
B Fondamenta Nuove	0.074	0.005	0.39	0.02	26.30
C Punta della Salute	0.035	0.004	0.31	0.07	52.98
E Canale Industriale Ovest	0.176	0.013	2.56	0.31	173.80
F Punta Fusina	0.265	0.008	0.73	0.29	32.15
G S.M. Elisabetta	0.051	0.004	0.30	0.03	20.01
H Pellestrina	0.117	0.007	0.52	0.04	82.10
I Chioggia Vigo	0.036	0.004	0.47	0.02	116.13
L Chioggia Lusenzo	0.0002	0.002	0.21	0.02	6.59
M Canale Perognola	0.028	0.001	0.09	0.02	7.76
O Murano	0.102	0.011	0.72	0.02	113.05
P Burano	0.046	0.004	0.35	0.03	68.16
Q Ca' Savio	0.052	< 0.001	0.04	0.01	7.11

The highest concentrations were found in the industrial area (Stations E, F) and in the Canal Grande of the city of Venice (Station A). The concentration of POP's decreased by increasing the distance from these sources. The minimum levels were found in Station Q and in Station M, far from the city and the industrial area. The POP's concentrations detected with standard method were always in agreement with those detected by the high volume system, confirming the experimental work previously conducted⁵. The analysis of the PCDD/F's congeners distribution showed three different patterns: the first is typical of the industrial area of Porto Marghera and is characterised by OCDF/OCDD \cong 4.5 and HpCDF/OCDD \cong 1, the second is located around the urban area of the city of Venice and is

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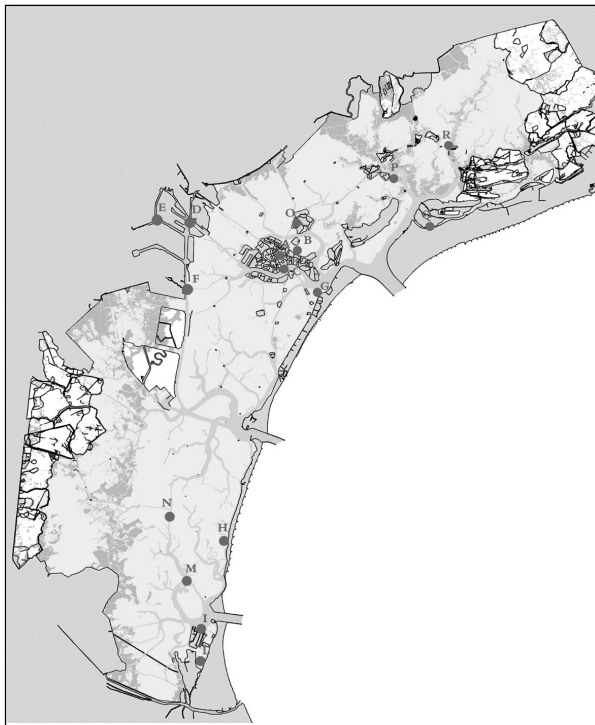


Figure 1. Spatial distribution of the Magistrato alle Acque monitoring stations

characterised by $OCDF/OCDD \cong 1$ and $HpCDF/OCDD \cong 0.7$. The stations which are located far from the industrial area are characterised by $OCDF/OCDD \cong 0.1-0.3$ with the typical congeners distribution of not specific combustion processes (Fig. 2).

Conclusions

The high volume sampling system used allowed to lower the detection limit and made possible to measure, for the first time, the concentration of POP's (PCDD/F's, PCB's, HCB, PAH's) in the waters of the Venice lagoon and to recognise specific sources of contamination of POP's. The results obtained with the preconcentration method were in agreement with those obtained with the traditional method. Magistrato alle Acque will continue to control the water lagoon by measuring the temporal trend of POP's concentration in the different stations and to investigate, also by statistical approach, to find the main sources of POP's in the Venice lagoon.

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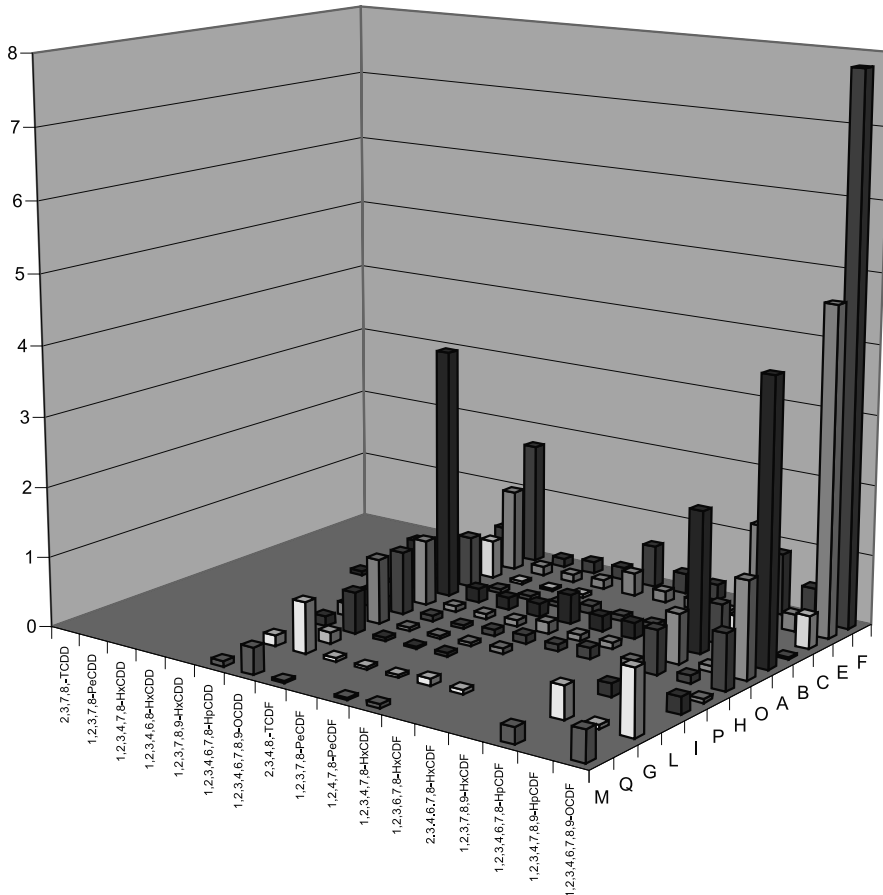


Figure 2. PCDD/F's congeners distribution in the different stations

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