

TRENDS IN CHLORINATED HYDROCARBONS AND HEAVY METALS IN SEDIMENTS OF VENETIAN CANALS

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Abstract

Sediments of the Laguna Veneta (north-east Italy) sampled around the contaminated area between the industrial zone of Porto Marghera and the city of Venice were analysed for their chlorinated hydrocarbon (DDTs and PCBs) and heavy metal (Cd, Pb, Hg, Zn) content in 1985 and 1995. Comparison demonstrates the overall decline of total DDT, while PCBs, Cd, Pb, Hg and Zn appear to be almost unchanged during this 10 year period.

Key-words: chlorinated hydrocarbons, metals, sediments, Adriatic Sea

Introduction

The distribution of chemical pollutants in sediments of the Lagoon of Venice has been largely studied during the last years (1, 2). The emerging profile shows that the most contaminated area lies in the central part of the lagoon around the industrial zone of Porto Marghera and the city of Venice where the most still canals have mud bottoms ideal for accumulation and preservation of chemical pollutants. In 1985 a survey was carried out at twenty five stations distributed in this area to measure existing concentrations of chlorinated hydrocarbons and heavy metals in sediments (3, 4); ten years later the survey was repeated at eight selected stations with the aim of investigating the spatial and temporal trends for these contaminants. In this paper we describe the results from the latter survey.

Materials and methods

At each station, three samples of surface (top 10 cm) sediments were collected, combined, carefully homogenised and frozen at -20°C until analysis. Extraction of chlorinated hydrocarbons was accomplished by Soxhlet refluxing about 30 g of wet sediment for eight hours, firstly with acetonitrile then with n-hexane. CB-29 was added as internal standard for recovery determinations. Extracts were analysed by ECD gas chromatography (Carlo Erba FV 4160 with a SE-54 fused silica column, 30 m long x 0.32 mm i.d.) following partition into n-hexane, clean-up with sulphuric acid and fractionation on a silica gel microcolumn (3). Identity of the compounds was assumed from their retention times. Quantification was based on peak area measurement and comparison to responses of reference standards: pp'DDE, pp'DDD, pp'DDT, PCB Aroclor 1260 and CB congeners No. 29, 52, 101, 118, 138, 153, 180.

For heavy metal analysis, dissolution was accomplished by refluxing 5 g of dry sediment for 2 hour with HNO_3 (5); Hg was extracted with a mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4$ (6). Instrumental determination was performed using a Perkin-Elmer mod. 372 atomic absorption spectrophotometer equipped with Deuterium Background Corrector. Cd, Pb and Zn were determined directly in an air-acetylene flame, while Hg was measured using cold vapour technique by reduction with NaBH_4 . Organic carbon was determined by the chromate digestion method of FAO (7).

Quality control of the analytical results was based on repeated analyses of the lagoon sediment IAEA-357 and the standard estuarine sediment CRM 277 (BCR/EU) for organochlorine and heavy metals, respectively.

Results and discussion

The stations, plotted in Fig. 1, were selected as representative of a variety of hydrographic and pollution load conditions. Stations 2, 8, 11, 12 and 16 were located in the deepest canals (2-4 m depth) inside and around the city. These stations have a favourable exchange of waters due to tidal currents. Station 18 was fixed on the side of a ship channel (12 m deep) between Porto Marghera and Venice. Stations 23 and 24 were located in the shallow canals (about 1 m depth) interior of the city which receive raw municipal sewage and have limited water circulation.

Sedimentation rates are highly variable within the study area, due to the complex current patterns. Values between 0.23 and 0.41 cm y^{-1} were determined by radiometric analysis on a sediment core taken in the open lagoon near station 18 (8); however, in the most still canals in the interior of the city a sedimentation rate of 2-3 cm y^{-1} may be estimated on the basis of their depth variation over time.

Organic carbon values in sediments sampled in the years 1985 and 1995 are plotted together in Fig. 2 to permit direct spatial and temporal

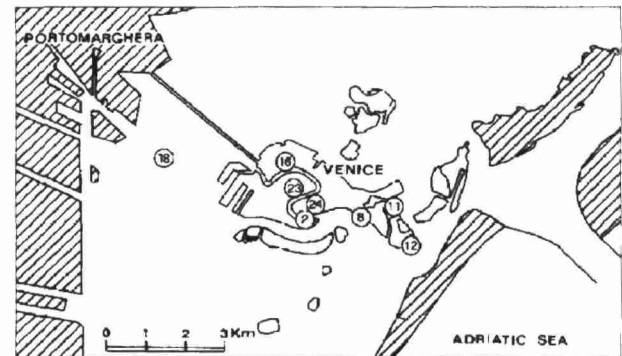


Fig. 1. Sampling stations in the Venice Lagoon.

comparisons: values range from 0.5% (Sta. 12) to 4.5% (Sta. 23) and are generally well correlated with pollutant content of the sediments, and weakly correlated with pelite (silt + clay; $< 0.063 \text{ mm}$) content. Fine-grain size sediments of the most still canals near the inner city, rich in organic matter, are expected to have higher affinity for contaminants. This is evident when the concentrations are expressed on dry weight basis, while the differences between stations greatly diminish when basing the concentrations on organic carbon weight.

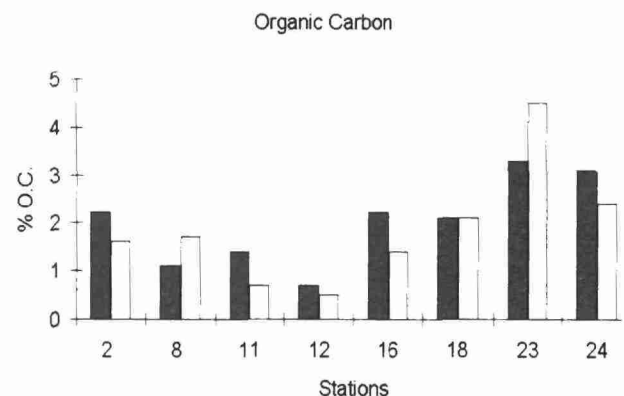


Fig. 2. Organic carbon values (% dry wt.) in sediments sampled in the years 1985 (grey histograms) and 1995 (white histograms).

Distribution patterns are basically similar for total DDT (Fig. 3A) and total PCB (Fig. 3B) which may reflect a common biogeochemical pathway in the lagoon consistent with their low water solubilities and high affinity for organic matter ($r = 0.85$ $p < 0.01$). Our data demonstrate the overall decline of the magnitude of DDT residues in the sediments (Fig. 3) and the increase of the amount of the metabolites DDD and DDE versus the total amount of DDT (not shown). Results also indicate a more severe and persistent contamination by PCB in this area. For DDT and PCB it is likely that the greatest input occurred in the past, before the ban in the use of chlorinated pesticides and polychlorinated biphenyls. However, resuspension of sediment by wave action and transport of fine materials by tidal currents may be responsible of the increase of DDT and PCB in some less contaminated areas (Sta. 2 and 12).