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Atmospheric bulk deposition to the lagoon of Venice Part I. Fluxes of metals, nutrients and organic contaminants

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Abstract

First available data on atmospheric fall-out were provided by sampling monthly bulk depositions in four sites inside the Lagoon of Venice (550 km^2). Sampling was carried out monthly during the period July 1998–July 1999, in one site near an industrial area (Porto Marghera; site D), another site in the city of Venice (site A), and the remaining two in the southern- and northernmost ends of the Lagoon (Valle Figheri, site C; Valle Dogà site B).

The following determinations were carried out for each samples: pH, conductivity, grain-size, particulate load, and dissolved nutrients (N, P). Samples were then subdivided into soluble and insoluble fractions, and Al, Ca, Na, K, Mg, Si, Mn, Fe, Zn, Ni, Cr, Cu, Pb, Cd, As, Hg, Ti, V, S, P, Se and Sb were analysed on both fractions. Total organic micropollutants (PAH, PCB, HCB, DDT, PCDD/F) were measured.

As regards particle size distribution, there was great variability among sampling sites. The percentage of the ≤ 2 μm grain-size fraction was higher in the southern and northern ends of the Lagoon.

Small differences were found among sites for major elements, whereas higher variability was observed for inorganic and organic micropollutants, with standard deviations between 20% and 60% of the fluxes measured. Major differences in annual fluxes between the most polluted sites (mostly D and A) and background (site B) were seen for Cd (0.26 vs. 0.06 mg m^{-2} $year^{-1}$), Hg (41 vs. 15 μg m^{-2} $year^{-1}$), PCB ($\sim$2500 vs. $\sim$500 ng m^{-2} $year^{-1}$) and HCB ($\sim$8000 vs. $\sim$1000 ng m^{-2} $year^{-1}$). Comparisons with previous data, collected in the periods 1993–1994 and 1995–1997, were only available for a few trace metals. A definite decline in the annual Pb flux in the city of Venice was detected, from 18 to 13 mg m^{-2} in 1996/1997 and 1995/1996 respectively, to $\sim$5 mg m^{-2} in the present study.

Total annual deposition was calculated by means of two different methods, which gave very similar results: (i) the mean value of deposition in the four sites was multiplied by lagoon area (550 km^2); (ii) the monthly rain isopleths were combined to normalize deposition values. The figures are: 15–34 kg of Hg and Sb, $\sim$200 kg of As, $\sim$100 kg of Cd and PAH, 0.7–1.3 tons of Cr, Ni and V, more than 2 tons of Cu and Pb, 17 of Zn, 55 of total P, $\sim$200 of Al, and 3900 of DIN.

Total fluxes of organics inside the lagoon were: PAH $\sim$100 kg; HCB $\sim$1 kg; DDT $\sim$0.4 kg. PCB and PCDD/F fluxes were $\sim$500 g and $\sim$10 g, corresponding respectively to 0.1 and 0.4 g I-TE.

The correlations between fluxes of inorganic micropollutants and grain-size were significant. Multivariate statistical analysis was applied to investigate more accurately relationships between the insoluble and dissolved fractions of inorganic micropollutants and grain-size fractions. In particular, significant correlations were highlighted between the dissolved fraction of As and the ≤ 1 μm particle size fraction. Relations between levels of ΣPCDDF, ΣPCDD, PCB and PAH congeners and grain-size revealed significant correlation coefficients for the remote sites (B, C), and none in the urban and industrial sites (A, D). In particular, significant correlations were highlighted between ΣPCDDF, ΣPCDD and particle size fraction ≤ 2 μm, and between benzo(*a*)pyrene and PCB 167 and particle size fraction 4–8 μm.

Keywords: Bulk deposition; Lagoon of Venice; Metals; Nutrients; Organic contaminants

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1. Introduction

In the last few decades, it has been demonstrated that the atmosphere is a significant pathway for the transport of many natural and polluting materials from continents to oceans. Therefore, actions aimed at safeguarding the Lagoon of Venice have mainly been addressed to geomorphological and hydraulic interventions, almost completely neglecting the contribution of atmospheric deposition to the decrease in environmental quality.

Some atmospheric pollution surveys were conducted by Bertolaccini and Gucci (1985, 1986), who measured Fe, Mn, Pb, V and Cd contents in atmospheric aerosol suspended particulate collected at three sampling sites in the Venice area over a 2-year period between 1973 and 1977. Other works were undertaken on a regional scale in order to assess the quality of rain (Zilio Grandi and Szpyrkowicz, 1991a,b).

Many studies have also focused on the presence of PCDD/F and other organic chlorinated compounds in bottom sediments and aquatic biota in the Lagoon. Sources of contamination are often discharges from the industrial zone of Porto Marghera, untreated domestic sewage from the historical city of Venice, and emissions from motorboats and traffic in the nearby mainland town of Mestre (Di Domenico et al., 1997; Fattore et al., 1997; Marcomini et al., 1997; Wenning et al., 2000). Preliminary available data on atmospheric dioxin fall-out came from bulk deposition sampling (Rossini et al., 2001a,b; Guerzoni et al., 2004), and a dioxin budget showed that atmospheric deposition accounted for one-quarter of the total load in the Lagoon (Marcomini et al., 1999). Data on soils collected around the industrial zone suggested an airborne PCDD/F fall-out effect up to several km downwind (Della Sala et al., 1999).

This paper presents a compilation of data on atmospheric fall-out, provided by sampling monthly bulk depositions in four sites inside the Lagoon of Venice (550 km^2) for 1 year. The purpose of this study was to estimate the importance of atmospheric transport and deposition of inorganic and organic micropollutants inside the Lagoon, in order to provide a comparison with other sources (e.g., inputs from rivers) and updated information useful for environmental risk assessment.

2. Materials and methods

2.1. Sampling

A total of 96 deposition samples was collected monthly over a 13-month period (July 1998–July 1999) in one site near an industrial area (Porto Marghera; site D), one in the city of Venice (site A), and two in the more remote southern (site C) and northern (site B) ends of the Lagoon (Fig. 1).

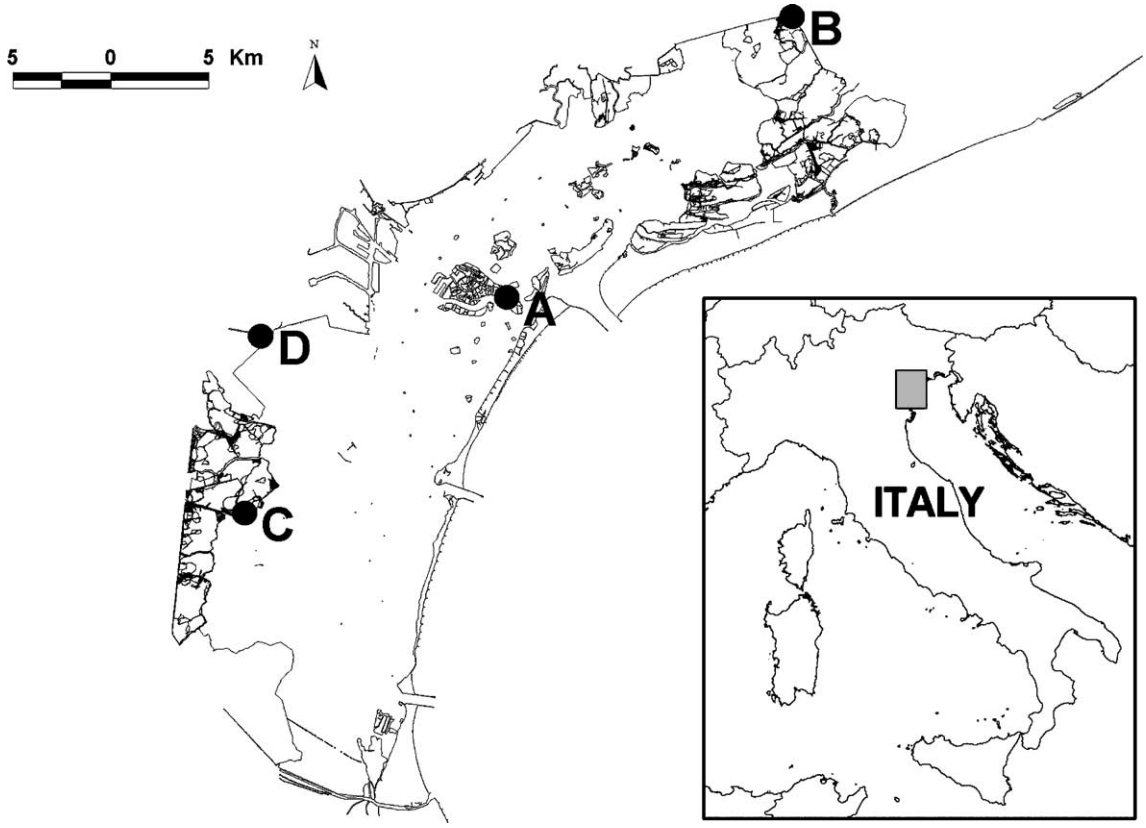

Fig. 1. Location of atmospheric deposition sampling sites. (A=city of Venice; B=Valle Dogà; C=Valle Figheri; D=Dogaletto). Large circle encloses industrial zone of Porto Marghera.