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Benthic fluxes of trace metals in the lagoon of Venice☆

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Abstract

To assess the exchange and the mobility of trace metals between sediments and water and their geochemical behaviour, experiments were carried out within the sphere of the CORILA project for the safeguarding of the Venice lagoon. Trace element exchanges were examined for approximately 60 h at two sites in the central part of the Venice lagoon (Italy): the first one is located in front of the industrial area of Porto Marghera (Tresse) and the second one in front of Campalto, near the causeway (Campalto). The experiments were carried out using a benthic chamber monitored for pH, dissolved oxygen, salinity, and temperature. The temporal trend of metals inside the benthic chamber was examined in relation to changes of pH and dissolved oxygen. Diffusive metal fluxes were also assessed by determination of the vertical distribution of metals in pore water.

Al, As, Cd, Cu, Fe, Mn, Mo, Sb, U, V and Zn were determined by ICP-SFMS. The metal concentrations for the lagoon samples were in agreement with expected values; the concentration ranges (min–max in ng/ml) were: Al 0.24–0.61, As 1.42–2.27, Cd 0.050–0.182, Cu 0.81–2.46, Fe 0.25–1.66, Mn 11.59–31.66, Mo 6.50–10.62, Sb 0.139–0.516, U 1.7–3.3, V 0.69–3.21, Zn 5.20–21.51.

Positive fluxes for the Tresse and Campalto experiments were determined for Cd (0.21 and 0.18 pmol/cm^2/h), Zn (62 and 67 pmol/cm^2/h), Cu (0.29 and 0.50 pmol/cm^2/h) and Mn (19 and 12 pmol/cm^2/h), while negative fluxes were determined for iron (−3.5 and −6.3 pmol/cm^2/h). Other elements showed differences in behaviour for the two experiments; the fluxes, for the Tresse and Campalto experiments, respectively, were 5.1 and −6.9 pmol/cm^2/h for molybdenum, 0.25 and −0.18 pmol/cm^2/h for arsenic and 1.3 and −8.4 pmol/cm^2/h vanadium. Therefore, the different characteristics of the two areas affect the mobility of trace elements, which can derive from differences in the environmental characteristics of the two areas or seasonal difference in which the experiments were carried out.

Keywords: Benthic fluxes; Trace metals; Venice

1. Introduction

The Venice lagoon, located in Northern Italy, is an open system, and it is important to know the exchanges through all its boundaries to understand the fate of elements that arrive into the lagoon from all the surrounding areas. The lagoon has been subjected to important anthropogenic inputs: domestic sewage, agricultural drainage and various wastes from the industrial area. These inputs have progressively deteriorated the quality of the lagoon ecosystem. Significant amounts of these pollutants are accumulated in sediments, which may constitute a potential source of secondary pollution: chemicals may be recycled many times through the sediment–water interface before being permanently buried or removed through the lagoon inlets. Diagenetic processes contribute to the remobilisation of elements, which are temporarily stored in sediments and may be dissolved in pore water and then diffuse to the overlying bottom water. In this context, the sediment–water interface represents an important exchange surface, which presents the greatest gradient in chemical and physical properties. Fluxes of elements through this interface, named "benthic fluxes", affect element concentrations in both pore water and the overlying bottom water [1]. With the aim of

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understanding and quantify the inputs of trace metals in the waters of the Venice lagoon, the processes of remobilisation of these elements from sediments to overlying waters, related to oxygen concentrations, were studied using a benthic chamber [1–4].

A benthic chamber is a device based on a simple principle to estimate fluxes at the sediment water interface: a known seawater volume and known sediment surfaces are isolated inside the chamber during the experiment period. Concentration changes in the enclosed water over time are used to calculate fluxes of elements into or out of the sediment [5]. Parameters such as pH and oxygen give important information about the changes inside the chamber. Water samples were periodically collected and analysed to follow the temporal trend of the studied trace elements; benthic fluxes were estimated from changes in concentration over time.

The use of a benthic chamber to determine the flux of trace elements at the sediment–water interface is very useful in understanding and quantifying the changes of trace element concentrations from an oxygenated to an almost anoxic environment, and in knowing the fate of trace metals and nutrients when low oxygen conditions occur in bottom waters; this phenomenon frequently occurs in the lagoonal organic rich waters [2].

To simulate the hypoxic conditions that may occur in lagoon water, in particular due to weather conditions, any water exchange between the exterior and the interior of the chamber must be precluded and the natural decrease in the oxygen content was monitored during the experiments. To describe the processes that control the exchanges and the mobility of trace metals between different environmental compartments with sufficient detail, samples must be collected at an adequate frequency.

Benthic chamber experiments were carried out in two polluted sites in the central part of the Venice lagoon, one close to the industrial area of Marghera and the other close to Campalto, not far from the international airport of Venice and close to the past solid waste unloading area of S. Giuliano. Benthic fluxes were estimated by measurements of changes of concentration of Al, As, Cd, Cu, Fe, Mn, Mo, Sb, U, V and Zn as a function of time.

2. Material and methods

2.1. Chemicals and laboratories

All materials used for sampling, treatment and storage of samples and solutions were carefully chosen, acid-cleaned and conditioned to minimize sample contamination [6,7].

Preparation of all materials, i.e., bottles for sample storage and dilution, standard solutions, and vials for analyses, was carried out in a clean laboratory equipped with a class 100 laminar flow bench available at the Institute for the Dynamics of Environmental Processes, located in the Department of Environmental Sciences-University Ca' Foscari Venice. The laboratories and procedures have been described elsewhere [8,9].

2.2. Sampling and sample handling

Water samples were collected during two benthic chamber experiments carried out in the central part of the Venice lagoon (Fig. 1), one close to the industrial area of Marghera (site A—"Tresse") and the other close to Campalto, not far from the international airport of Venice and close to the solid waste unloading area of S. Giuliano that was used in the past (site B—"Campalto"). The chambers were constituted of a box of 90-l volume (60×60×25 cm), obscured on the top, to minimize light effects, and closed by flexible polyethylene walls to compensate for differences of pressure produced by sampling and tide changes. The chambers were monitored for pH, dissolved oxygen, salinity, and temperature, by a multi-parametric probe (mod. 556, YSI, Ohio, USA), and samples for trace elements were collected every 3–4 h, for approximately 60 h. The sampling was carried out using a pump, the water was filtered using a 0.20-μm filter cartridge (Sartorius Sartobran, Gottingen, Germany); the sampling system and filtration apparatus were previously repeatedly rinsed with an acid solution (ultrapure water with 0.2% ultrapure HCl). After filtration the samples were stored in a freezer at −20 °C until analysis.

Two sediment cores were collected in June 2003, one in the Marghera area and the other in Campalto, to extract the pore water to determine benthic fluxes by an independent method; about 30-cm cores were collected by one piston corer, they were immediately closed and placed in a glove box conditioned by nitrogen to eliminate oxygen. Con-

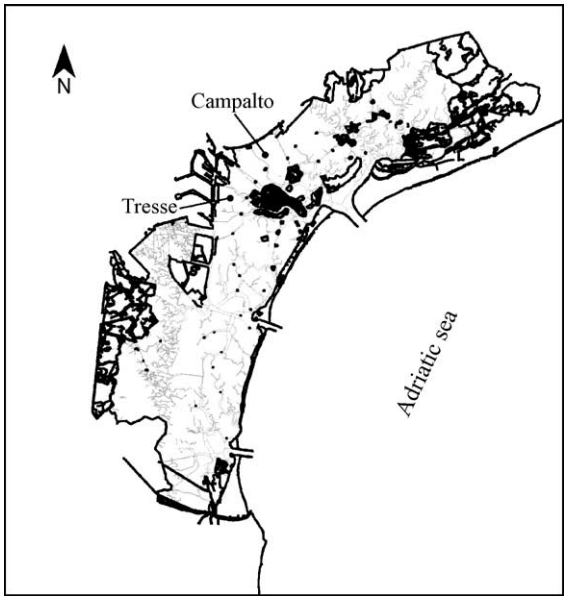

Fig. 1. Venice lagoon map. Locations of benthic chamber experiments.