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Sulphate reduction in the sediment of the Venice canals (Italy)

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Abstract

The sulphur cycle in the sediment of the Venice canal network was investigated by considering the sulphate reduction rate (SRR) and the distribution of sulphur compounds, in both pore water and sediment. Sulphate reduction (SR) is the main process in the metabolism of the organic matter supplied to the network by untreated urban effluents. Although it might account for the decomposition of only a limited percentage of the total organic-C inputs, the estimated rates are among the highest observed in coastal sediments. Measured rates range from 0.26 to 0.99 $\mu mol\ cm^{-3}\ d^{-1}$, while mean annual values, estimated by a diagenetic model, vary from 0.16 to 0.43 $\mu mol\ cm^{-3}\ d^{-1}$. The speciation of S in the sediment reveals that pyrite-S is the most abundant component of the total reduced S pool, whereas acid volatile sulphides and elemental sulphur together account for less than 45%. A preliminary budget indicates that the rate of burial of solid-phase S is small compared to the S produced by SR (from 10 to 25%). A large amount of reduced S is then lost from the canal deposits to be re-oxidised at the sediment-water interface or in the overlying water column.
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Keywords: Anoxic sediment; Sulphate reduction; Sulphur speciation; Venice

1. Introduction

Throughout history, people have been required to live in the vicinity of the coasts due to the relative ease of access to a large variety of resources. The industrial age has increased human presence in many coastal areas. It is therefore expected that the coastal zone will continue to sustain the primary needs of a large proportion of the world's population in the forthcoming years. The coastal environment is vulnerable to anthropogenic threats such as pollution, eutrophication, land use, habitat loss, etc. The increased flux of organic matter, which is intimately associated with the expansion of urban settlements, is one of the most severe threats affecting quality of life, and the sustainability of coastal development (Crossland et al., 2005).

The presence of large amount of organic matter in coastal sediments typically results in oxygen depletion, which is followed by the production of sulphide by sulphate-reducing bacteria (Heijs and van Gemerden, 2000). Particularly in sheltered areas, sulphate reduction (SR) and associated fermentation reactions are the major anaerobic decomposition processes (Capone and Kiene, 1988; Jørgensen, 1989; Giblin and Wieder, 1992). Where budgets are available, they are predominant in the organic-C degradation, sometimes exceeding aerobic respiration (Howarth, 1984).

The hydrogen sulphide produced by SR may then chemically react with metals to form insoluble sulphides, such as FeS, FeS_2, as well as a variety of sulphides of other metals (Luther III et al., 1986; Canfield, 1989; Zaggia and Zonta, 1997; Rickard and Morse, 2005). These are accumulated in the sediment, thereby limiting the release of free sulphide (S^{2-}) into the overlying water. Metal-sulphides can also be precipitated by metabolic pathways of micro-organisms, as a detoxification reaction in response to the build-up of dissolved S^{2-} and high levels of heavy metals in pore waters (Baldi et al., 1993).

The reduced sulphur compounds produced in the sediment by anaerobic metabolism present a major risk when polluted sediments have to be dredged, as periodically required in the Venice canal network (Collavini et al.,

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2000). In this framework, the anaerobic metabolism in the sediment of the canal network was investigated to evaluate its importance in the basic geochemical cycles of organic matter, S and Fe. Sulphate reduction rate (SRR) was measured by SO_4^{2-} depletion in incubated sediment samples from representative sites to obtain preliminary indications on the spatial variability of the process. The experiments were repeated during three different periods of the year to investigate the effects of temperature change. The distribution of dissolved SO_4^{2-} and S^{2-} in pore waters, and the speciation of the S pool in the sediment were also determined, in order to estimate the amount of S that is accumulated in the system by precipitation of elemental sulphur and metal-sulphides. The vertical profiles of SO_4^{2-} concentration in pore waters were explained with diagenetic equations, obtaining mean annual SRR to be compared with values obtained by the incubation technique.

2. The study area

Founded in the fifth century, the city of Venice (Fig. 1) is one of the first examples of an urban settlement in a semi-closed coastal ecosystem (i.e. the Venice Lagoon). For many centuries the expansion of this community had a major impact on the lagoon environment, and particularly on the 40 km-long city canal network. The present city, which covers a surface area of about 6.3 km^2, has a population of about 62,000 inhabitants, additional presences of about 10,000 overnight stay tourists, 20,000 day tourists, and a net daily flux of about 46,000 commuters.

Mean width of the canals is 10 m (from 3 to 50 m) and, if regularly dredged, their mean depth is around 2 m. A semidiurnal tide (average spring and neap tide excursions are 80 and 30 cm, respectively) ensures water exchanges with the open lagoon and the Adriatic Sea. Current speed is generally low: from a few cm s^{-1} in the more confined branches up to about 50 cm s^{-1} in larger canals. Salinity (mean value about 30 psu) is affected by the conditions in the surrounding lagoon waters, which in turn are affected by the tide and meteorological conditions. Local physico-chemical variations are induced by the interaction of tidal circulation and the freshwater inputs from urban effluents; their relative importance increases inward.

Due to its peculiar urban structure, Venice has never been provided with a main sewage system and untreated effluents from a large number of inputs are discharged into the canal network. Tidal exchange partially removes the products of organic matter degradation and the delivered contaminants. Nevertheless, these accumulate at the bottom of the canals, adding to materials yielded by weathering of urban surfaces and particulate matter transported by the currents from the open lagoon. The sediment deposited at the bottom of the canal (Zonta et al., 2005a) is a strongly reduced (Eh = -205 ± 28 mV) and organic-rich material (LOI $16.8 \pm 2.7\%$); water content is generally high ($47 \pm 5.5\%$), and the average grain-size distribution is characterised by $7.4 \pm 5.8\%$ of sand, $9.5 \pm 3.2\%$ of fine sand, $33.8 \pm 3.2\%$ of coarse silt, $34.4 \pm 4.8\%$ of fine silt, and $15 \pm 3.3\%$ of clay.

The progressive silting up of the canal bottom and the consequent decay of the hygienic conditions are then major

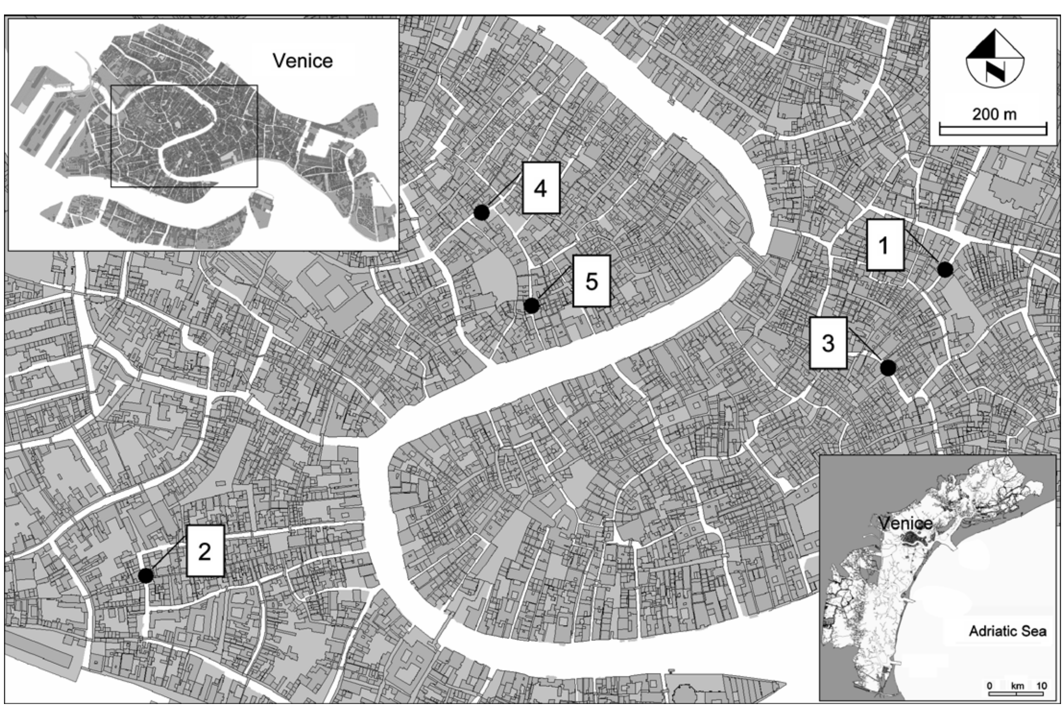

Fig. 1. Map of the study area, sampling sites are indicated (1 = Rio del Piombo; 2 = Rio dell'Avogaria; 3 = Rio di San Zulian; 4 = Rio di San Polo; 5 = Rio della Madonetta). Maps of the Venice Lagoon (lower right) and of the city of Venice (upper left) are show in the insets.

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