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Marine Geology 230 (2006) 29 – 51

MARINE GEOLOGY
INTERNATIONAL JOURNAL OF MARINE GEOLOGY, GEOCHEMISTRY AND GEOPHYSICS

www.elsevier.com/locate/margeo

Anthropogenic markers in the Holocene stratigraphic sequence of the Gulf of Trieste (northern Adriatic Sea)

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Received 19 October 2005; received in revised form 18 March 2006; accepted 28 March 2006

Abstract

The Gulf of Trieste is a shallow semi-enclosed marine basin in the northernmost part of the Adriatic Sea that has been affected by the relative rise in sea-level during the Holocene. The sedimentary sequences in three cores, ranging in length from 130 to 320 cm, were investigated through the variability in grain-size parameters, major (Al, Fe, S, N, Ca and Mg) and trace (Ti, Mn, Cr, Ni, Cu, Zn and Hg) elements, organic and inorganic C, $\delta^{13}C$ and ^{14}C dating in order to obtain information on paleoenvironmental evolution and the historical development of heavy metal contamination. The potential sources of pollution are: urban sewage from nearly 400,000 inhabitants, industrial effluents, and 500 yr of Hg mining activity in the Idrija region (western Slovenia), located in the upper basin of the Isonzo river, the main freshwater input to the coastal zone. The conventional ^{14}C ages of bulk sedimentary OC in the basal part of the three cores were 9030 ± 70 (GT1), 8270 ± 50 (GT2) and 9160 ± 120 (GT3) yr BP. An upward increase in highly negative $\delta^{13}C_{org}$ values from the core bottoms indicates that lacustrine-swamp conditions in the study area were rapidly followed by a typical marine depositional environment. Cluster analysis performed on the geochemical data for all subsamples of the three cores identifies several groups with a clear stratigraphic meaning. Factor analysis of the data shows related element groups that can be interpreted as being related to, for instance, the natural contribution from aluminosilicates and carbonates, from organic matter (peat) and the more recent anthropogenic "impact". Predicted natural linear relationships for metal-Al were obtained from the core subsamples and they can be used as a baseline to evaluate metal enrichments on a regional scale. Results show that more recent sediments in the central sector of the Gulf of Trieste are slightly enriched in Cu (max Enrichment Factor EF = 2.1) and Zn (max EF = 1.6), and noticeably contaminated by Hg (up to 23.32 $\mu g\ g^{-1}$) to a maximum depth of 90 cm and up to 60 times above the estimated regional background (0.13 $\mu g\ g^{-1}$). The Hg historical trend is well correlated with extraction activity at the Idrija mine, thus allowing indicative sedimentation rate estimation and tentative assessment of the rate of Hg accumulation in bottom sediments (from 1.77 to 31.49 mg $m^{-2}\ yr^{-1}$ at the surface). The large inventory of Hg in the core GT2 appeared to be the result of proximity to the fluvial source, which is still active in supplying Hg to the coastal areas and makes the Gulf of Trieste one of the most Hg contaminated area in the whole Mediterranean basin.

Keywords: marine sediments; marine geochemistry; metals; mercury; Holocene; Adriatic Sea

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doi:10.1016/j.margeo.2006.03.013

1. Introduction

Human activity has enhanced the delivery and cycling of heavy metals to coastal zones. Many of these contaminants are toxic to aquatic biota and could have an important impact on the whole ecosystem. Hence, it is important to track the influence of anthropogenic activities on the concentration levels of these contaminants and to understand the processes affecting their changes. Interpretation of human influences requires knowledge in natural baseline concentrations. Most contaminants are associated with the surface of particles and are preferentially transported, accumulated and buried within fine-grained sediments. Cores carefully dated through sedimentary deposits can provide chronologies of contaminant concentrations and input in areas of net sediment accumulation. In the coastal zone, the core chronologies are mostly restricted to sediments in anoxic and abiotic environments where resuspension and bioturbation are minimal (Huh, 1996; Hornberger et al., 1999). In bioturbated sediments such studies are less common.

In this study, variations in sedimentological and geochemical features in radiocarbon dated Holocene stratigraphic sequences from the northern and central part of the Gulf of Trieste, which is affected by several potential pollution sources, were investigated. These variations were placed in a paleoenvironmental context and correlated with results obtained in the southern littoral zone of the gulf (Ogorelec et al., 1981, 1984, 1987, 1997; Faganeli et al., 1991).

Special attention was given to providing pre-industrial background levels of heavy metals for the Gulf of Trieste, particularly for mercury (Hg) because of the long-term mining activity in the Idrija region located in the upper Isonzo river drainage basin, the main freshwater input (Faganeli et al., 1991; Gosar et al., 1997; Covelli et al., 1999, 2001). Sedimentary records of this geochemical tracer were compared with the records of 500 yr of ore extraction in order to reconstruct the Hg depositional history, determine the accumulation rate and calculate the cumulative metal inventory.

2. Environmental setting

The Gulf of Trieste, covering an area of about 500 km^2 in the northernmost part of the Adriatic Sea, is an epicontinental semi-enclosed shelf basin characterised by a very low bathymetric gradient in the northern and central part (40 m/100 km). The main water and sediment supplies to the gulf of Trieste are related to the Isonzo river. Its drainage basin covers about 3400 km^2, extending into both Italy and Slovenia. The average annual flow rate at the river mouth is estimated to be 196.8 m^3 s^{-1}, ranging monthly from 43.1 to 665.9 m^3 s^{-1} (Interreg II, 2001). The rate of flow can exceed 2500 m^3 s^{-1} during the autumn floods (RAFVG, 1986). The mean annual solid discharge is 150 g m^{-3}, with peaks of 1000 g m^{-3} during extreme events (Mosetti, 1983).

Sediments vary from medium to fine sands along beaches and the delta front to prodelta muds in mid-Gulf (Brambati et al., 1983). Mesozoic limestone and Eocene flysch are the two prevalent lithologies cropping out in the catchment area. The former prevails in the northernmost alpine chains, the latter outcrops in the hilly and pre-alpine areas bordering the alluvial plain (Stefanini, 1976). Carbonate sediments dominate the marine area near the river mouth. Only the southeasternmost sector of the Gulf, affected by low terrigenous inputs from secondary streams (the Rosandra, the Rizana, and the Dragonja rivers), shows significant amounts of quartzo-feldspathic material (Brambati, 1970), while the carbonate component decreases seawards according to grain-size reduction (Ogorelec et al., 1991).

The Gulf of Trieste is affected by many potential sources of organic and inorganic pollutants, discharged not only by rivers but also by sewers, industrial developments, and activities related to the oil-pipeline terminal in the Trieste harbour area (Olivotti et al., 1986; Adami et al., 1996, 1998).

3. Materials and methods

3.1. Samples collection and analytical procedures

Three sediment cores (10 cm diameter) at sites GT1 (245 cm length; 23 m depth), GT2 (320 cm length; 15 m depth) and GT3 (130 cm length; 25 m depth) (Fig. 1) were collected in 1996 and 1997 from R/V OGS Explora with a gravity corer, sealed on board and stored at +4 °C in a cold room prior to subsampling.

After splitting, the cores were photographed and described macroscopically for lithology and colour variability (Munsell Soil Color Charts, 1975) and for sedimentary structures along with macrofossil content. A half core was examined by X-ray photography to identify faint structures and slight changes in density, texture and mineralogical composition.

Subsampling for water content, grain-size and geochemical analysis was performed by cutting 1-cm-thick slices. Analyses were performed in every 1 cm of the first 25 cm of the cores, every 2 cm (25–50 cm