

Geochemical and sedimentological markers in the Holocene stratigraphic sequence of the Gulf of Trieste (N Adriatic Sea)

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The Gulf of Trieste is a shallow semi-enclosed marine basin in the northernmost part of the Adriatic Sea. The coastal area is currently affected by many potential sources of organic and inorganic pollutants: urban sewage from nearly 400,000 inhabitants, industrial effluents, and 500 years of mercury (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. In this study, variations in sedimentological and geochemical features in radiocarbon dated Holocene stratigraphic sequences from three cores from the northern and central part of the Gulf of Trieste were investigated. These variations were placed in a paleoenvironmental context and correlated with results obtained in the southern littoral zone of the gulf. All of our data fit the scenario that the terrestrial component of organic carbon decreases with distance offshore. Sediments at the mouth of the river Isonzo are calculated to contain more than 90% of terrigenous OC today. Analyses of different size fractions indicate that smaller particles are consistently more organic-rich on a mass basis and tend to be transported further from the river mouth depending on river discharge. The deposition of almost entirely marine (phytoplanktonic and microphytobenthic) organic matter is restricted to a narrow strip in the central part of the Gulf located between two areas affected by increasing contribution of terrigenous OC. The natural abundance of ¹³C and ¹⁴C tracers suggests a two-component mixture of ancient and modern C in the sediments down to approximately 60 cm sub-bottom, with an estimated ~45% of sedimentary OC probably being derived from ancient sedimentary OC (kerogen). This observation will change our previous estimation of the OC budget in the sediments influencing mostly recycling efficiency. The ¹⁴C ages of bulk sedimentary OC in all three studied cores reaches the age of 9030 ±70 yrs BP (140 cm, GT1), 9380 ±40 yrs BP (215 cm, GT2) and 9160 ±50 yrs BP (120 cm, GT3), respectively. There is a significant change in the source of organic material at these depths. The data as well as geological parameters indicate the complete terrestrial environment, in particular soils present at that time. Paleoenvironmental reconstruction of P burial,

reflecting past phytoplanktonic and microphytobenthic production, revealed that a marked increase in P_{tot} and P_{org} (about 25%), as well as C_{org} (about 30%) and N_{tot}, (about 50%) contents appeared after 1950, most probably due to the increased use of inorganic fertilizers and detergents in this area. Special attention was given to providing pre-industrial background levels of heavy metals for the Gulf of Trieste, particularly for Hg. Sedimentary records of this geochemical tracer were compared with the records of 500 years of ore extraction in order to reconstruct the Hg depositional history, determine the accumulation rate and calculate the cumulative metal inventory. 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. Whereas moderate contamination of Cu and Zn was detected at the core top, significant Hg enrichment, far above the average estimated background value for the Gulf (0.13 µg g⁻¹), occurred upcore, especially in front of the Isonzo River mouth, as a consequence of the long-term mining activity. 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 y⁻¹ at the surface) that is from one to two orders of magnitude higher than the Po river's, the main freshwater supply of sediments in the Adriatic sea. The cumulative Hg inventory allowed to estimate roughly the amount of metal buried in the sediments of the gulf, which can be considered as an important "reservoir" for the metal. However, the results seem to indicate that only a small part of Hg extracted and lost in the environment is stored within marine sediments, suggesting that large amounts of Hg are still present in the drainage basin of the Isonzo River. As a consequence, although Hg fluxes into the Gulf have decreased in recent times, natural attenuation as a passive decontamination approach for sediment remediation seems to be the only long-term solution since Hg inputs will be supplied by river waters during flood events.