

## Geochemical and Chemical-Physical Characterization of a Polluted Mud Flat in the Venice Lagoon

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The continual discharge of pollutants in a semi-enclosed body of water as the Venice Lagoon, induces the formation of dystrophic states and causes accumulation of toxic species in water and sediment, particularly in the areas with little tide exchange.

To evaluate in detail the causes of degradation in these areas and to advance solutions to restore it, the study of the environmental conditions can not leave out a multi-parameters analysis of "tracer" variables that permit to establish the availability of nutrients and heavy metals in the sediment to surface water and the biosphere.

On this basis, a study was made on the chemical and physical characteristics of a mud flat inside the Venice Lagoon, that is subject to intense growths of macroalgae, predominantly *Ulva Rigida*. In the last year, in fact, the Venice Lagoon has been particularly afflicted by eutrophication manifestations, at the point of making it necessary to mechanically remove macroalgae during the summer period, to limit the degradation of water and air quality.

The mud flat studied covers a surface area of about 1.5 Km<sup>2</sup>; its mean tide is 50 cm, with mean excursion of about ± 30 cm. Analyses were made on the first 50 cm of sediment. During the period between May 1988 and November 1989, four samplings of sediment cores were taken, using a "syringe-type" corer, hand-made in plexiglass; it allows to extract undisturbed samples with 5 cm diameter. On the collected samples, redox potential E<sub>H</sub>, grain-size distributions and heavy metal (Cr, Cu, Fe, Mn, Ni, Pb, Zn) concentration measurements were performed; the latter for both in the total content and through the application of a selective extraction technique. Further - during two field measurements - the current evolution through the channels delimiting the mud flat was observed in response to tides of quadrature and syzygies, utilizing data acquired by self-recording current meters immersed simultaneously in four places.

For the E<sub>H</sub> measurement a methodology was set-up that permits to obtain representative values of the oxidation-reduction condition in situ from samples practically undisturbed [1].

Instead, the cores to analyse grain-size distribution and heavy metals content were immediately subdivided into ten 5 cm-long cylinders. Grain-size determination was made with a laser-beam particle analyzer [2] (Microtrac mod.7995), obtaining the particles percentage distribution in fifteen dimensional classes of diameter, from 0.7 to 125 µm. Heavy metals were determined in the total content (cold 1N HCl) and for their presence in five geochemical phases [3], [4] corresponding to these metal fractions: extractable, associated with carbonates, bound to Fe and Mn oxides, associated with the organic matter and sulphides, and finally the non-lattice-held residual (obtained for difference).

In the surface layer (the top 5 cm) all measurements made on the samples coming from the nine measurement-sites chosen in the mud flat indicate the existence of three sectors with different characteristics. One is, in fact, able to distinguish a very reduced zone with greater presence of fine grains and heavy metals, where there is the greatest growth of algae in the mud flat. Next, a oxidated zone with a greater presence of larger diameters, poor or no accumulation of heavy metals and scarce algae presence. Finally, a third zone with intermediate characteristics.

As a general rule, the E<sub>H</sub> values decrease along the cores till about 15 cm depth, indicating more reduced conditions in the deeper layers with respect to the surface layers. The upper 15 cm thick-layer has varying redox characteristics, which are sensitive to the hydrodynamical and hydrological conditions of the overlying water, since it is involved in the water interaction processes and bacterial activity. On the contrary, sediment deeper than 15 cm definitely gives negative E<sub>H</sub> values, which are about equal and constant in all the nine sampling-points in the mud flat (≈-170 mV). With the depth, either a general but slight increase of particles with smaller diameters and a remarkable decrease of heavy metal contents (total and fractionated), in the deeper layers with respect to the surface layers. Only Mn does not follow this trend.

Utilizing statistical correlation techniques [5],[6], the existing relations between the three measured variables at the same depth in the mud flat and along the sediment column were finally emphasized. In particular a strong, positive correlation among total heavy metal, the redox condition intensity and particles percentage in the diameter range 10<φ<40 µm is evidenced for the sediment surface layer. Further, the correlation coefficient r values together with heavy metal present in the five extracted geochemical phases permit the formulation of an interpretative picture of the dependence of heavy metal speciation on the intrinsic sediment characteristics.

The authors thank G.Arcari, G.Cogoni, T.Corso, L.Gobbo, G.Magris, M.Meneghin, R.Ruggeri, F.Salviati, F.Simonato, G.Zamperoni and R.V. Zonta for their collaboration given during the field measurements, in collecting the samples and in the analyses by atomic absorption. The research activity was partially financed by the City's Environmental Council.

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