ORIGIN OF SEDIMENTARY ORGANIC MATTER AND HUMIC ACIDS IN THE GRADO AND MARANO LAGOON

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Abstract
In the framework of the MIRACLE project (Mercury Interdisciplinary Research for Appropriate Clam farming in Lagoon Environment), sediment cores were sampled in the Grado and Marano lagoon and in the tributary Aussa River in order to quantify and to characterize humic acids (HA) that are recognized to play an important role in complexing heavy metals, mercury included. Stable carbon isotopic composition was used to identify sources and contribution of organic matter from different environments to lagoon sediments.
Keywords: Organic Matter, Lagoons, Carbon, Chemical Analysis

Introduction
A substantial fraction of the so-called refractory organic matter in sediments is constituted by humic substances (HS) which are formed from the decomposition of plant, animal and microbial tissues and tend to be more recalcitrant than their precursors. HS can play an important role as electron transfer in the anaerobic environment [1]. HS they can bind both hydrophobic and hydrophilic species [2] and are electron donors in photo-oxidation reactions in marine environments [3]. The aim of the present work is to investigate the relevance and the origin of humic acids in the sedimentary organic matter of the Grado and Marano Lagoon.

Methodology
The sediments, surface layer (0-1 cm) and a sub-surface layer (5-6 cm), were collected in 16 stations in the Grado and Marano lagoon and in the Aussa River. Organic carbon (C_{org}) was determined in sediments and humic acids extracted by a CHNS-O elemental analyzer after removal of carbonates with HCl 1N [4]. Nitrogen (N) was determined following the same procedure, without acidification. The detection limit of the method was 0.4 micromole for C_{org} and 0.9 micromole for N. The stable isotopic ratio of organic carbon ($^{13}C/^{12}C$) was determined by a CHNS-O analyzer coupled with an Isotope Ratio Mass Spectrometer. The analytical precision of measurements was 0.2%. The extraction of HA from sediments was performed following the methods of the International Humic Substance Society, modified by Moreda-Piñeiro et al. [5] .

Results and discussion
The contribution of humic C to total C_{org} was high both in lagoon and riverine sediments (~ 30 %). The concentrations in riverine sediments were the highest and increased upstream from the river mouth. This relevant amount of humic acid to the sedimentary organic matter points out their important role in the transformation and accumulation of organic material in the lagoon environment. The $^{13}C/^{12}C$ ratios for the sedimentary organic matter showed a prevalently marine/lagoon origin whereas the riverine sediments appeared significantly more depleted in $^{13}C/^{12}C$ (more negative ^{13}C) along with the highest C/N ratios, due to the fluvial and terrestrial origin of the organic matter [Fig. 1].

Extracted humic substances showed similar $^{13}C/^{12}C$ values of the corresponding sediments [Fig. 1], but higher C/N ratios, in particular in the subsurface ones. This increase with depth seems to indicate that different stages of transformation of the organic matter take place during early diagenesis.

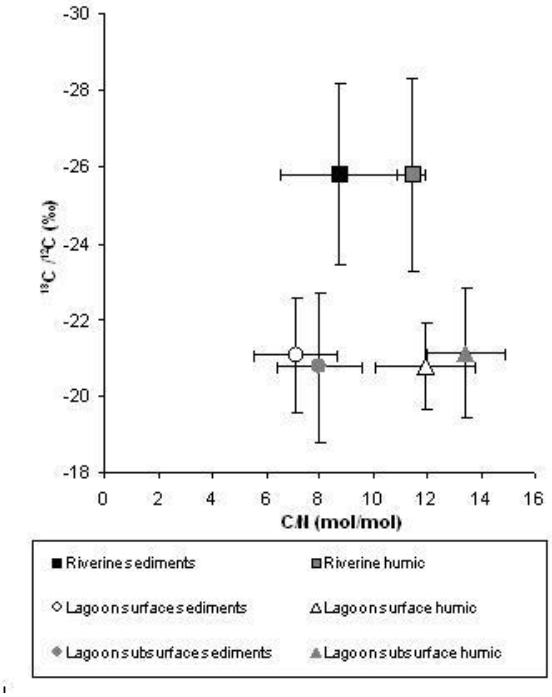

Fig. 1. Stable carbon isotope ratios ($^{13}C/^{12}C$) of organic carbon vs C/N molar ratios in river Aussa, in lagoon surface and subsurface sedimentary organic matter and in corresponding extracted humic acids.

References
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