DISTRIBUTION OF TRACE METALS IN THE ARNO RIVER AND ITS ESTUARY

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Abstract
Trace metal (TM) concentrations in water samples collected in the Arno River, its main tributaries and estuarine transect were measured in order to evaluate anthropogenic influence, TM dynamics and a potential impact on the coastal sea. A downstream increase of concentration for most of TM was observed in the river, whereas a (near)conservative behavior was registered for the majority of dissolved TM in estuarine salinity gradient.

Keywords: Trace elements, Estuaries, Mediterranean Sea

Introduction and study site: In order to understand the impact, behavior and fate of trace metals (TM) in natural waters, studies of interactions between TM and other constituents of the water body (particles, organic matter, organisms, etc.) are highly demanded [1,2]. The Arno river is located in the central Italy (Tuscany), with its source in the Northern Apennines and a total length of ~242 km. Through entire flow, the Arno River is altered by various tributaries, natural factors, and sources of anthropogenic contamination [3]. The objectives of this work were to examine the distribution of TM along the Arno river, to evaluate the influence of its major tributaries (Canale della Chiana, Sieve, Bisenzio, Ombrone and Era), to identify the main sources and finally, to assess the behavior of TM in estuarine salinity gradient.

Sampling and analysis methods: During the field campaign organized in September 2015, water samples were taken either by hand grab sampling (in river; 18 sites) or by using Van-Dorn type horizontal water sampler (in estuary; surface and bottom layers; 10+6 sites). Samples were immediately on-site filtered using syringe filters (0.22 µm) and afterwards acidified to pH<2 and UV digested. Hydrolab DS5 multiprobe was used for in-situ profiling of salinity, temperature, pH, dissolved oxygen. Analyses of TM were performed either by HR ICPMS or by stripping. voltammetry.

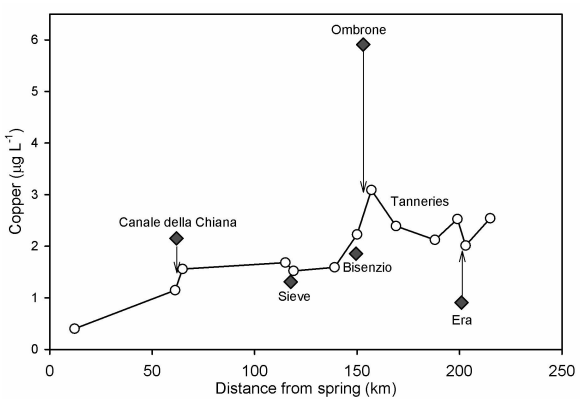

Fig. 1. Distribution of dissolved Cu along the Arno River and its tributaries

Results and discussion: As expected, for most of the metals very low concentrations were measured in samples collected at the first site (12 km from the spring), before any evident anthropogenic inputs, representing the location comparable to other clean freshwater systems [4]. A generally increasing trend of TM concentrations along the entire freshwater part was registered for most of the examined TM (Fig. 1). TM showed a highly variable concentration among the examined tributaries. After merging with the Canale della Chiana, Bisenzio and Ombrone Rivers an obvious increase of TM concentrations was observed in the Arno River. The particular characteristic of the examined 12 km long estuarine segment was a strong salinity stratification (Fig. 2). In the surface layer, seawater-conservative metals (Cs, Li, Mo, Rb, U, Sr) showed a clear linear increase in concentration as a function of salinity (Fig. 2; left inset). TM followed a near-conservative behavior (Cr, Co, Ni, Pb, Sb) or were under the influence of anthropogenic or natural process (As, Cd, Cu, Fe, Mn, Zn), as exemplified by dissolved Cu (Fig. 2), for which an additional input from antifouling paints of the numerous boats was evidenced [4]. Out of the plume, the concentrations of metals reached the range characteristic for clean costal Mediterranean Sea. In the bottom seawater layer, a strong hypoxia was registered in the upper estuary region. In combination with the progressive accumulation and partial TM scavenging, either increase (Co, Cr, Fe, Mn, Ni, Sb) or removal (Cd, Cu, Pb, U, V) of TM was observed in the upstream direction of seawater flow.

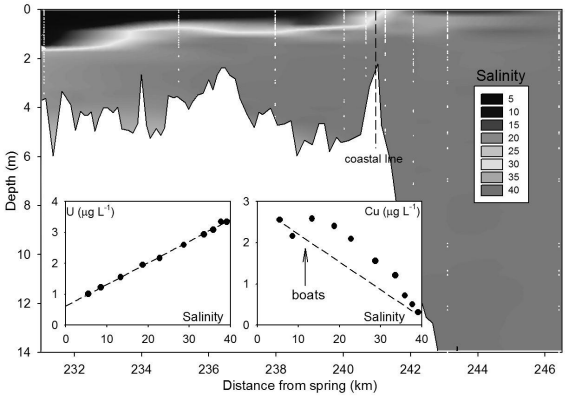

Fig. 2. Salinity distribution along the Arno estuary: Insets: dissolved U and Cu distributions in surface layer

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