



# Establishing geochemical background levels of selected trace elements in areas having geochemical anomalies: The case study of the Orbetello lagoon (Tuscany, Italy)



Elena Romano <sup>a,\*</sup>, Luisa Bergamin <sup>a</sup>, Ian W. Croudace <sup>b</sup>, Antonella Ausili <sup>a</sup>, Chiara Maggi <sup>a</sup>, Massimo Gabellini <sup>a</sup>

<sup>a</sup> ISPR, Italian Institute for Environmental Protection and Research, Via di Castel Romano, 100, 00128 Rome, Italy

<sup>b</sup> GAU-Radioanalytical Laboratories, University of Southampton, National Oceanography Centre, Southampton, SO14 3ZH, UK

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## ABSTRACT

The determination of background concentration values (BGVs) in areas, characterised by the presence of natural geochemical anomalies and anthropogenic impact, appears essential for a correct pollution assessment. For this purpose, it is necessary to establish a reliable method for determination of local BGVs. The case of the Orbetello lagoon, a geologically complex area characterized by Tertiary volcanism, is illustrated. The vertical concentration profiles of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn were studied in four sediment cores. Local BGVs were determined considering exclusively samples not affected by anthropogenic influence, recognized by means of multivariate statistics and radiochronological dating (<sup>137</sup>Cs and <sup>210</sup>Pb). Results showed BGVs well-comparable with mean crustal or shale values for most of the considered elements except for Hg (0.87 mg/kg d.w.) and As (16.87 mg/kg d.w.), due to mineralization present in the catchment basin draining into the lagoon.

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## 1. Introduction

In past years the Italian Authorities identified, through a specific legislation, several sites with a historical pollution legacy, including marine and lagoon areas, such as also Orbetello lagoon, requiring environmental characterization finalized to a clean-up operation, to regain a good environmental status. The anthropogenic pollution in sediments may be evaluated by determining the element concentrations against the geochemical baseline or background value (BGV). The geochemical or natural background is “a relative measure to distinguish between natural concentrations and anthropogenically-influenced concentrations in real samples collectives” (Matschullat et al., 2000). The geochemical background may be considered as a theoretical natural concentration of a substance in a specific environmental sample (or medium), considering the spatial and temporal variables (Galuszka, 2007). In pollution assessment studies, the average shale or the mean crustal value (Turekian and Wedepohl, 1961; Martin and Whitfield, 1983;

Taylor and McLennan, 1995; Li and Shoonmaker, 2003) can be often used as a background or geogenic value (Szefer et al., 1998; Pekey, 2006; Huerta Diaz et al., 2008; Bloundi et al., 2009). However, the BGV depends on many factors related to the specific geological and mineralogical features of an area and it can deviate from the average shale composition. This is particularly true in areas included in volcanic or mineralised districts, where local geochemical anomalies, not due to anthropogenic enrichment, may be present. In this case, local BGVs may be determined from ancient levels deposited in pre-industrial times in sediment cores, or by comparison with a pristine control area in case superficial bottom sediments are studied. Both geochemical and statistical approaches may be applied to the determination of BGV (Zgobicki et al., 2011), but several determinations of the BGV for selected elements in sediments generally used statistical methods (Covelli and Fontolan, 1997; Tobias et al., 1997; Fukue et al., 2006).

The main aim of this research was to establish a reliable method to determine the local geogenic background concentration in case of areas characterized by natural enrichment for some trace elements. The case of Orbetello lagoon was used to define the procedure, applying a statistical approach to geochemical data obtained from four sediment cores, with the support of geochronological

\* Corresponding author.

E-mail address: [elena.romano@isprambiente.it](mailto:elena.romano@isprambiente.it) (E. Romano).

study. The quantification of local background values is necessary to evaluate the contamination status and consequently, environmental quality, in an area with particular geological features. In fact, in the Orbetello area there are many hydrothermal deposits outcropping in carbonate formations which may represent the source of increased element concentration in sediments, supplied by watercourses draining into the lagoon. The applied method was based on the study of vertical concentration profiles of selected elements (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn), taking into account the rate of sediment accumulation to enable a chronological perspective for the anthropogenic inputs. This study may be of interest not only for local pollution assessment, but also as an example of determination of baseline concentration values for selected elements in a volcanic district, where the presence of natural geochemical anomalies have to be considered.

## 2. Study area

The Orbetello lagoon is an enclosed brackish-water coastal basin characterized by very shallow water (1 m mean depth); it is delimited by the southern Tuscan coast to North East and by Monte Argentario to South West and divided in western and eastern basin by a dune cordon (Fig. 1). This is an area of high environmental interest, which was included in the Ramsar Convention in 1976 as an International Relevant Wetland site. In spite of this, the lagoon has been affected by sewage effluents from the town of Orbetello, and wastewater from agriculture and aquaculture, which increased considerably in the second half of 20th century (Lenzi et al., 2003). Additionally, a chemical factory located in the western basin produced granular fertilizers from 1908 to 1985, until final closure in 1991, producing as main waste metal (As, Cd, Pb and Zn) rich pyritic ashes.

The geological setting of the area is relevant to this investigation because it provides an insight into possible geogenic contributions; in fact, a Palaeozoic basement is overlaid by the Tuscan nappe, characterized by carbonate formations, widely outcropping in the study area, especially in the Monte Argentario and the Ligurian nappe, made up of flysch formations. The carbonate formations

were affected by the intrusion of magmatic bodies from Upper Miocene (Elba island) to Quaternary (Amiata district), due to the extensional tectonics successive to the Alpine orogenesis (Miocene age) (Puxeddu, 1984; Carmignani and Kligfield, 1990; Serri et al., 1993). Geothermal activity currently characterizes the central and southern Tuscan region as a consequence of such volcanism. Several mineralised faults are present around Monte Argentario, mostly containing pyrite ( $\text{FeS}_2$ ) and chalcocopyrite ( $\text{CuFeS}_2$ ), and lesser cinnabar ( $\text{HgS}$ ). The Amiata volcanic district, about 50 km North East of the Orbetello lagoon, is characterized by the presence of large cinnabar deposits which have been exploited since the Etruscan age (Ferrara et al., 1998). Mercury occurs in the catchment basin of the Albegna River, which flows into the Orbetello lagoon, both as mineralization and clastic material within shallow alluvial sediments (Protano et al., 1998; Grassi and Netti, 2000). Due to this geological setting, it appears clear that in this region the determination of local background concentration is needed because the natural concentration of some heavy metals could be considerably higher than mean crustal values.

## 3. Materials and methods

### 3.1. Material collection

Cores of length ranging from 220 to 235 cm were collected in June 2010 from two sites of the western (OR94, OR96) and eastern basin (OR98, OR100) of Orbetello lagoon (Fig. 1). Replicate cores were taken using a Rossfelder vibrocorer fitted with internal PVC liners and samples were acquired for systematic analysis of grain-size, geochemistry and radionuclides for chronological determinations.

### 3.2. Grain-size and geochemical analysis

The sediment cores were sampled at 2-cm intervals and aliquots for grain-size and chemical analysis were taken. The frequency of sampling, from 0 to 22 cm depth, was continuous while it ranged, from 22 to 100 cm depth, every 10 cm and below 100 cm every 20 cm. This strategy ensured a detailed study of the upper potentially contaminated levels and sufficient study of the deeper pre-industrial sample to use as reference conditions.

In grain-size analysis the coarse ( $>63 \mu\text{m}$ ) and fine ( $<63 \mu\text{m}$ ) sediment fractions were separated by wet-sieving, after pre-treatment with  $\text{H}_2\text{O}_2$ . After that, the coarse fraction was sieved while fine fraction was dried at  $40^\circ\text{C}$  then dispersed in hexamethosphosphate and distilled-water solution ( $0.5 \text{ g}/80 \text{ mL}$ ), ultrasonically treated and analysed by laser granulometer Sympatec Helos® (Romano et al., 2009).

A set of metals and trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) was analysed previously dissolving them through a microwave-assisted digestion (Milestone MLS Ethos TC high performance microwave digestion unit). About 0.5 g of oven-dried (48 h,  $35^\circ\text{C}$ ) sediment was digested in Teflon bombs with 3 mL of  $\text{HNO}_3$  and 9 mL of HCl superpure (37%). As and Cd were determined by digesting in a graphite furnace using atomic absorption with Zeeman background correction technique (SpectrAA-220Z, Varian). Chemical modifier used for Cd analysis was palladium solution ( $500 \mu\text{g m L}^{-1}$ ) plus ascorbic acid (1%) as reducing agent, while chemical modifier used for As analysis was nickel nitrate ( $500 \text{ mg/mL}$ ). Cr, Cu, Fe, Zn, Pb and Ni were measured using ICP-OES (Liberty AX, Varian). Hg analysis was carried out using a Milestone DMA-80 (Milestone Direct Mercury Analyzer DMA-80, FKV). The Hg analysis was performed using dried sediment samples ( $35^\circ\text{C}$ , 48 h) without any further sample preparation. The accuracy for total content of metals was evaluated using certified reference materials (PACS-2

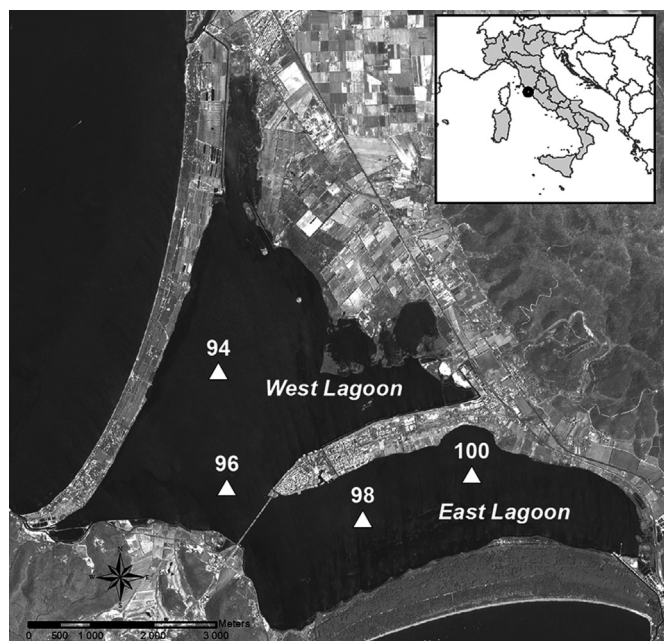


Fig. 1. Orbetello lagoon and core sampling sites.

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