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Compositional analysis and pollution impact assessment: A case study in the Gulfs of Naples and Salerno

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ABSTRACT

This paper presents the results of an environmental geochemical investigation of the Gulfs of Naples and Salerno, near the Campania plain (Southern Italy). Surface marine sediment samples were collected during three field campaigns: 96 from the Gulfs of Naples and Salerno (NaSa); 123 from the Bagnoli site coastal area (BaSi); and 11 from the ports around the Gulf of Naples (PoNa).

Elemental concentrations were determined and their interpolated distribution maps were compiled. Three geochemical sources (or processes) were determined associating elemental distribution with the results obtained from a R-mode factor analysis: 1) geogenic, 2) water kinetics and 3) anthropogenic. The results are presented as raw data single element distributions of eight potential toxic elements (PTEs) (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn) in the forms of raw data and additive log-ratio transformed data. The latter showed advantages in revealing the actual distribution patterns.

Geochemical background reference values of PTEs were determined from the median value of local background reference values. Based on these values, pollution impact analysis was carried out to both BaSi and PoNa samples, indicating most of BaSi and PoNa sediments were affected by moderate to strong Pb, Zn, Cd and Hg pollution. An ecological risk assessment was subsequently carried out on the entire database, pointing a toxic risk ranking in the order Pb > As > Ni > Cd > Hg > Cr.

1. Introduction

Environmental geochemistry illustrates the spatial variation of elements and compounds in the composition of Earth surface, and focuses on potential toxic elements (PTEs) behavior and distribution. Results of environmental geochemical studies can serve to determine background and baseline values of elements (Salminen and Gregorauskiene, 2000; Albanese et al., 2007, 2010), and consequently, distinguish areas that pose potential harm to human beings (Albanese et al., 2013a). Interaction between the environment and human beings are also investigated by environmental geochemists by means of risk assessment studies (Gómez-Gutiérrez et al., 2007; Albanese et al., 2010, 2013b; De Vivo et al., 2013), to evaluate the effect of pollution and remediation (De Vivo and Lima, 2008; Beolcini et al., 2010) as references for governmental management (Long et al., 1995; De Vivo et al., 2008).

Gulfs of Naples and Salerno, which receive both uncontaminated and contaminated inputs from Campania Plain, need to be investigated at larger scale by integrated environmental geochemical approach, as previous studies limit their interest on very specific and limited concerned areas, such as Bagnoli area (Albanese et al., 2010) and Port of Naples (Adamo et al., 2005; Sprovieri et al., 2007). A study focusing on a larger scale area could provide critical information on both background and baseline values highlighting better anthropogenic contribution on PTE distribution in the Gulfs of Naples and Salerno.

However, the interpretation of raw geochemical data is problematic as such data are "closed"; that is, for a composition of D-components, only D-1 components are required (Aitchison, 1982; Filzmoser et al., 2009; Reimann et al., 2011; Buccianti and

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Grunsky, 2014). The most commonly employed approach to cope with dependent variables has been the use of log-ratio transformation (Aitchison, 1999; Aitchison et al., 2000; Martin-Fernandez et al., 2003). Three major methods have been developed: additive log-ratio (alr) transformations (ALT), centered log-ratio (clr) transformations (CLT) and isometric log-ratio (ilr) transformations (ILT). Results of ALT keep consistency of data but are influenced by denominator; CLT is isometric but loses orthogonal references; ILT preserves all metric properties but loses direct relations with element (Egozcue et al., 2003). An ideal solution should be adopted for each situation. In the case of Gulfs of Naples and Salerno, ALT sufficiently addressed the present situation (details discussed in Section 3.3.2).

Currently, Pollution Impact Analysis (PIA) and Ecological Risk Assessment (ERA) are two major approaches used to evaluate the harmfulness of elements and compounds. PIA is based on the comparison between studied samples with respect to the global or regional background concentration (Chapman and Wang, 2001; Lu et al., 2009). Enrichment factor (EF) (Harrison et al., 2003; Santos et al., 2005), Geoaccumulation Index (I_{geo}) and Degree of Contamination (D_c) (Abrahim and Parker, 2008) are the three major parameters taken into account by PIA. ERA outlines the biological adverse effects of pollutants based on the determined "guideline" for each element or compound (Long et al., 1995, 1998; CCME, 2002; Ministero dell'Ambiente, 2010).

The aim of the paper is to make an integrated environmental geochemistry study of Gulfs of Naples and Salerno, taking into account the distribution patterns of elements and the contamination status of PTEs (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn). This study has used samples from three different field activities at both regional and local level, focusing on specific concerned areas (Bagnoli sites and some ports of the Gulf of Naples). For better interpretation of distribution patterns, factor analysis and compositional data analysis are compared with maps generated from raw data. Contamination status is estimated 1) upon baseline values determined by untransformed data; and 2) from potential ecological risk of sediments that is shown by ERA result.

2. Study area

The Gulfs of Naples and Salerno are two marginal seas located along the eastern Tyrrhenian Sea and separated by the Sorrento peninsula (Fig. 1). The Gulf of Naples is semi-enclosed by Ischia and Procida islands in the NW, Campi Flegrei and Campania plain in the NE, and Sorrento peninsula in the SE. The Gulf of Salerno is located in the coastal region of the Sele river plain, on the SE side of the Sorrento Peninsula, relative to the Gulf of Naples. The city of Naples has the second highest population density in Italy with around 3.1 million residents (ISTAT, 2014) living in its metropolitan area; the province of Salerno has a population of 1.1 million inhabitants (ISTAT, 2014).

The Tyrrhenian Sea is the result of Miocene-Quaternary extension contemporaneous to eastward accretion and anticlockwise rotation of the Apenninic fold and thrust belt during the roll-back of the subducting Adria plate (Milia and Torrente, 1999; Bruno et al., 2003; Sacchi et al., 2005; Insinga et al., 2008). The Campanian Plain and the Gulf of Naples, together with the Sele Plain and the Gulf of Salerno are parts of half-graben basins developed along the eastern Tyrrhenian margin (Sacchi et al., 2005).

The sea-floor of the Gulfs of Naples and Salerno is covered by Plio-Quaternary sedimentary and pyroclastic fall deposits (Bruno et al., 2003). Two small coalescent deltas, the Sebeto and Sarno rivers, characterize eastern depositional system of the Gulf of Naples (Insinga et al., 2008). Along Sorrento peninsula, the island of Capri and the Gulf of Salerno, Mesozoic–Cenozoic carbonate Units dominate the composition of surface sediments (Milia and Torrente, 2003).

Volcanic processes during the late Quaternary significantly influenced the morphology and deposits in the Gulf of Naples (Milia and Torrente, 1999, 2003, 2007; De Vivo et al., 2001; Aiello et al., 2005). Several volcanic eruptions occurred in volcanic systems of the Campanian Plain: Campi Flegrei, Mt Somma-Vesuvius, Ischia, and the eruption of several ignimbrites (De Vivo et al., 2001, 2010; Rolandi et al., 2003).

The territories of Naples and Salerno are amongst the most tourist-oriented areas around Mediterranean Sea (Euromonitro, 2007). The port of Naples is one of the most important ports in Europe. Naples has one of the largest transportation networks in south Italy, including railway, highway and various road connections into and around the region (Fig. 1). Agriculture and agro-industries in the Campania region still provides the major economic income and, from an environmental point of view, the stream network system in the Campanian and Sele plains is responsible for carrying fertilizers and related products into the sea (Albanese et al., 2007) (Fig. 1).

The Bagnoli area is one of the largest brownfield sites in Italy. Various heavy-industries were concentrated in the area such as steelworks, asbestos materials manufacturing, cement and fertilizer production factories. All of these industries were dismissed in the early 1990's. Although it has been the subject of a large

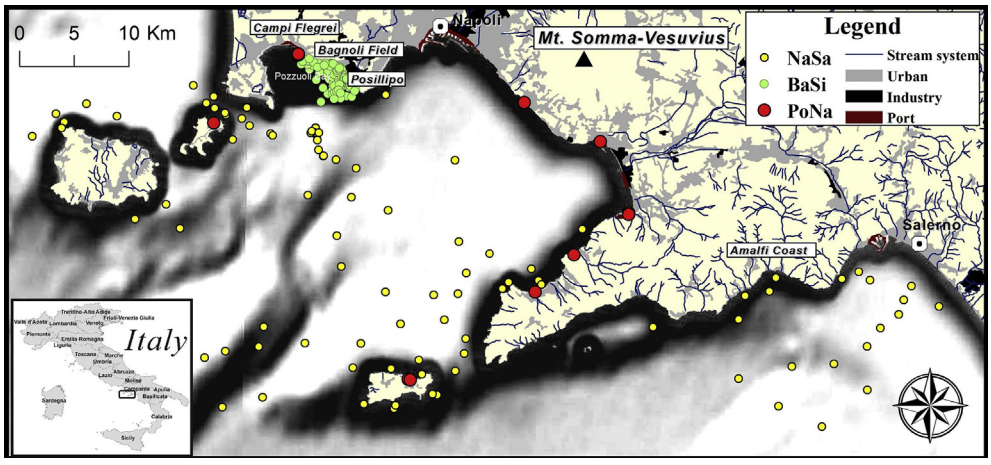

Fig. 1. Study area and sampling site locations.