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Are conventional statistical techniques exhaustive for defining metal background concentrations in harbour sediments? A case study: The Coastal Area of Bari (Southeast Italy)

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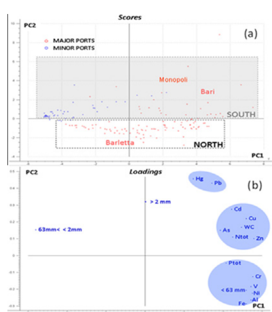
HIGHLIGHTS

- Metal background concentrations in South-East Italy sediments were calculated.
- Three conventional statistical techniques were used and compared to each other.
- The conventional techniques led to the same range of heavy metal background values.
- Mineralogical and multivariate statistical analyses revealed new specific aspects.
- Heterogeneously constituted areas need deeper investigations.

GRAPHICAL ABSTRACT



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ABSTRACT

Sediment contamination by metals poses significant risks to coastal ecosystems and is considered to be problematic for dredging operations. The determination of the background values of metal and metalloid distribution based on site-specific variability is fundamental in assessing pollution levels in harbour sediments. The novelty of the present work consists of addressing the scope and limitation of analysing port sediments through the use of conventional statistical techniques (such as: linear regression analysis, construction of cumulative frequency curves and the iterative 2σ technique), that are commonly employed for assessing Regional Geochemical Background (RGB) values in coastal sediments. This study ascertained that although the *tout court* use of such techniques in determining the RGB values in harbour sediments seems appropriate (the chemical–physical parameters of port sediments fit well with statistical equations), it should nevertheless be avoided because it may be misleading and can mask key aspects of the study area that can only be revealed by further investigations, such as mineralogical and multivariate statistical analyses.

1. Introduction

Port sediments are the largest depositories of potential sources of metallic contamination in the marine environment. This is due

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to the nature of ports, as they are semi-enclosed systems with a limited dispersal of contaminants into the open sea, and are designed to minimize the hydrodynamic energy within them (Dassenakis et al., 2003; Casado-Martínez et al., 2007). An accurate assessment of the quality of port sediments must take into account both natural and anthropogenic factors and requires the precise evaluation of each of them.

Methods for establishing a "threshold value" or a "geochemical background concentration range" for sediments have been widely discussed within the scientific community (Garrett, 1991; Covelli and Fontonlan, 1997; Matschullat et al., 2000; Reimann et al., 2005; Reimann and Garrett, 2005; Galuszka and Migaszewski, 2011; Jiang et al., 2013; Dung et al., 2013). However, a need still exists for globally accepted guidelines that can distinguish polluted from unpolluted sediments.

Generic national threshold levels introduced by national guidelines are currently used for assessing the metal pollution of Italian coastal sediments along the entire Italian coastline.

However, these metal threshold values cannot reflect the complex state of the harbour sediment matrix in each coastal area of Italy, as they do not take into account either the grain-size effect or the wide heterogeneity of Italian coastal zones, particularly from a geochemical perspective (Loring, 1991). Indeed, applying the national Sediment Quality Guidelines (SQGs) for metals is often complex due to the possibility of natural high geochemical background concentrations, as was observed for chromium and nickel in the Ligurian Sea (Mugnai et al., 2010).

Empirical (geochemical), theoretical (statistical) and integrated methods (combining both empirical and theoretical methods) are the main approaches described in the literature for determining Regional Geochemical Background (RGB) concentrations (Reimann and Garrett, 2005; Dung et al., 2013). In geochemical methods, also known as direct methods, a deep core (30 m) sample, or samples collected at a certain distance from anthropogenic pollution sources, is used in order to establish the background levels of metals and metalloids in the sediments or soils of a target area (Matschullat et al., 2000; Desaules, 2012). Although direct methods provide metal and metalloid background concentrations as a single site-specific value. The disadvantages of such techniques are their relatively high costs and the need for a broad knowledge of the study area. Statistical methods determine and eliminate outliers related to anthropogenic sources within the dataset consisting of element concentrations in soils or sediments (Galuszka, 2007) and present a number of advantages, such as a wide range of different statistical tests, graphical methods and readily available computer software for data processing (Varol, 2011; Ho et al., 2012).

The combination of statistical and geochemical methods is referred to as an "integrated method" (Galuszka and Migaszewski, 2011). In this method, the analytical results gathered from several deep core samples or from samples collected in pristine and pre-polluted areas are subjected to statistical calculations (Qi et al., 2010; Bini et al., 2011). While this method has the advantages of both empirical and theoretical techniques, it is expensive and cannot always be applied due to the lack of in-depth information about the study area.

Nevertheless, in the absence of other data, several authors (Zahra et al., 2014) still use the global average concentrations reported for shale by Turekian and Wedepohl (1961) as background values for metals and metalloids.

It should be emphasized that the most reliable approach for estimating metal and metalloid RGB values is still the direct method, which is based on the analysis of samples collected from geological areas where the sediment quality has not been altered by anthropogenic activities. Unfortunately, in the case of port areas it is not possible to identify pristine sites, thus other approaches should be applied in the assessment of site-specific background levels.

Within this framework, to gain insight into the most suitable method to be used in assessing metal and metalloid RGB concentrations in harbour sediments (sediments subjected to additional phenomena compared to simple coastal sediments), a specific area (110 km in length) of the southeast Italian coastline known as the Coastal Area of Bari (CAB) was chosen as a case study for the application of three different conventional statistical methods: (i) linear regression analysis (Covelli and Fontonlan, 1997) following geochemical normalization (Redon et al., 2013); (ii) data processing with the construction of a cumulative frequency distribution (Reimann et al., 2005; Jiang et al., 2013); and (iii) the 2σ analysis technique (Lepeltier, 1969; Bouer and Bor, 1995; Matschullat et al., 2000). The dataset consisted of 158 sediment samples collected at different depths (up to 3.50 m) from nearly uncontaminated areas in 3 major ports, 4 minor ports and 6 marine transects from the nearshore area (200 m and 500 m from the coast) covering the entire 110 km of the CAB coastline. This coastal area was chosen for its specific features: the Apulian coast is punctuated by numerous bays and inlets that have served as ports for the traffic of goods and commodities since ancient times.

All three conventional techniques produced the same results, and the chemical–physical parameters of the port sediments were well suited to the statistical equations, initially suggesting a homogeneous nature of the study area. However, additional investigations, such as mineralogical and multivariate statistical analyses, contradicted these preliminary results and highlighted the need for dividing the entire coastline into separate sub-areas prior to assessing the RGB values.

2. Materials and methods

2.1. Study area

The CAB, as defined by the Regional Coastal Plan (RCP) of the Apulia Region, forms part of a regional basin. The coastline is 110 km in length from south of the Ofanto River estuary to the Port of Monopoli, with the Port of Bari at its centre. Although only seven ports were chosen for this study, many natural bays and other minor ports are also present in the CAB area. From a morphological point of view, the coastal ecosystem constitutes two natural physiographic units (NPU), a northern NPU extending from the Ofanto estuary up to the coast of the metropolitan city of Bari and a southern NPU heading southward to Monopoli Beach (Fig. 1a).

Among the cities present along the CAB, Bari and Barletta are the most highly developed, although no heavy industrial activity currently affects the area. In addition to the pollution caused by water washout from the intensively cultivated areas along the coastline and transferred to the sea through the local hydrographic network, two other significant events have affected the area: a heavy bombing campaign during the Second World War and the development of a petrol refinery built in the north of Bari in the late 1930s, which was active until 1974. The area has only recently been the subject of reclamation work to eliminate residual hydrocarbons affecting the quality of the ground water.

2.2. Sampling

The dataset consisted of the chemical–physical parameters of 152 sediment samples collected between 2010–2011 at different depths from nearly uncontaminated areas in 3 major ports [Barletta (BT), Bari (BA) and Monopoli (MP)] and 4 minor ports, which are considered to be natural bays [Santo Spirito (SS),