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Baseline

Levels of pollution of rare earth elements in the surface sediments from the Gulf of Pozzuoli (Campania, Italy)

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ABSTRACT

The Gulf of Pozzuoli includes the former second largest Italian steelworks of Bagnoli. The REE, Y, Th and Sc pollution in sediments of the Gulf of Pozzuoli was determined. Ce, La, Nd and Pr had the highest percentage distribution of rare earth elements normalized respect to chondrite with 31.19, 28.35, 19.51 and 8.41% individually. It was observed a marked enrichment of these elements, from west to the east from 26.39 to 111.04 mg/kg and from onshore to offshore from 31.67 to 217.74 mg/kg. The output of the principal component analysis revealed that the REE were mainly of anthropic origin being clearly linked to that of PAHs, metals and organic matter. This, together with their distribution patterns, highlighted the role of the former Bagnoli metallurgical plant in the pollution of the gulf.

Rare earth elements (REE) have become a highly valuable commodity due to their increased use in emerging technology applications (Lambert and Ledrich, 2014). They encompass the 14 lanthanides plus scandium and yttrium. Traditionally, they have been separated into two groups: the light rare earth elements (LREE) lanthanum through europium (Z = 57 through 63) and the heavy rare earth elements (HREE) gadolinium through lutetium (Z = 64 through71) (El-Taher, 2010). Five REE have been identified as economically critical for energy production (Dy, Tb, Eu, Nd and Y) and two additional ones as nearly critical (Ce and La) (US DOE, 2011). They have been used widely in numerous industrial processes such as in the production of superconductors, supermagnets, catalysts, pigments in glasses, plastics, additives, medicines and cosmetics as well as fertilizers (Guo et al., 2014). In recent years, the environmental behaviour of REE has attracted conspicuous attention, especially the study of their geochemistry (Aksentov and Sattarova, 2016; Armand et al., 2015; Silva et al., 2014; Zhang et al., 2014), along with an increased interest in their ecotoxicity (Herrmann et al., 2016; González et al., 2014).

In marine sediments, REE have been intensively studied as natural tracers of biogeochemical processes (Oliveri et al., 2010) and of water mass circulation (Alibo and Nozaki, 1999, 2000) and they are widely used to investigate weathering processes (Leybourne et al., 2006). The REE distribution in sediments is largely controlled by scavenging processes, in particular by Fe–Mn–oxides (Elderfield and Greaves, 1982; Whitfield and Turner, 1987; Elderfield, 1988; Haley et al., 2004), by redox conditions of the overlying water column (Liu et al., 1988), by composition of the terrigenous source (Chaudhuri and Cullers, 1979; Taylor and McLennan, 1985) and by potential anthropogenic inputs (Olmez et al., 1991). Marine sediments represent one of the major sinks (and potential secondary source) for REE, especially those with low solubility (Watts et al., 2017). Insoluble forms of REE have shown low toxicity, whereas high toxicity was reported for soluble ones (Lambert and Ledrich, 2014). In addition, they accumulate in aquatic organisms and have the potential to enter the food chain. Unlike many elements, e.g. As, Cd and Pb, REE are not considered to be priority environmental contaminants.

The Gulf of Pozzuoli, hereafter termed GoP, is placed in the northern part of the Gulf of Naples. In its south-eastern sector there is an industrially contaminated site, ILVA of Bagnoli, formerly the second largest integrated steelworks in Italy, now closed and subject to a government remediation project. The remediation project, funded by the Italian government, started in 1996 and was extended to the coastal area sea sediments facing the brownfield site in 2001. Studies carried out in marine sediments sampled just offshore the Bagnoli area through the morphological criterion have highlighted that the coastal area is strongly contaminated by metals, PAHs and PCBs (De Vivo and Lima,

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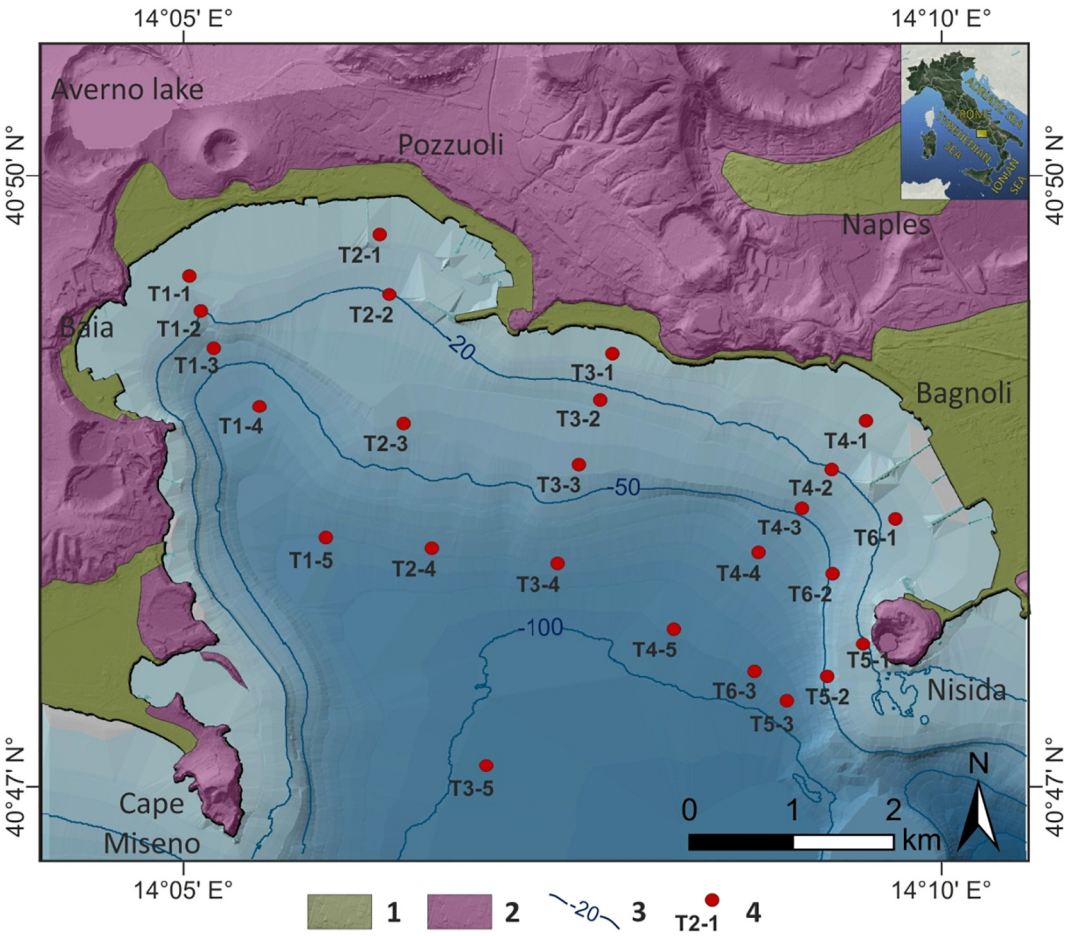

Fig. 1. Map of GoP lithology and of sampling stations. Legend: 1, marine and alluvial deposits (Holocene); 2, pyroclastics of Phlegrean Fields (Late Pleistocene-Holocene); 3, isobath (m bsl); 4, sampling site. Geographic coordinate system is WGS84.

Table 1
Sampling locations associated to water depths, TOC and grain size of sediments.

Sampling stations	Latitude (N)	Longitude (E)	Depth (m)	TOC[a] %	Gravel %	Sand[b] %	Silt %	Clay %	Class[b]
T1-1	40°49′27.55″	14°05′02.94″	8.0	1.34	4.68	94.9	0.33	0.05	Fine sand
T1-2	40°49′16.89″	14°05′08.74″	24.8	1.51	1.59	97.3	0.96	0.16	Fine sand
T1-3	40°49′06.81″	14°05′15.07″	45.1	3.27	35.3	60.3	4.10	0.29	Medium sand
T1-4	40°48′49.34″	14°05′31.38″	58.6	1.72	33.7	61.7	4.36	0.19	Coarse sand
T1-5	40°48′10.61″	14°05′58.29″	80.0	1.59	0.35	84.3	14.4	0.92	Very fine sand
T2-1	40°49′41.34″	14°06′19.46″	8.0	1.75	0.69	99.3	–	–	Coarse sand
T2-2	40°49′23.95″	14°06′21.93″	25.8	1.84	1.50	97.0	1.4	0.10	Very fine sand
T2-3	40°48′42.91″	14°06′29.06″	34.0	0.98	6.72	91.8	1.32	0.15	Fine sand
T2-4	40°48′06.96″	14°06′39.17″	72.5	1.40	4.18	85.9	9.30	0.61	Very fine sand
T3-1	40°49′05.98″	14°07′50.41″	7.5	0.09	0.67	99.3	–	–	Medium sand
T3-2	40°48′53.02″	14°07′46.26″	23.8	0.64	5.10	94.9	–	–	Fine sand
T3-3	40°48′33.38″	14°07′38.47″	38.0	1.17	2.89	96.1	0.88	0.12	Fine sand
T3-4	40°48′02.54″	14°07′28.73″	75.3	1.66	0.83	89.0	9.71	0.45	Coarse sand
T3-5	40°46′59.22″	14°07′06.01″	100.0	1.65	2.35	83.9	13.3	0.46	Very fine sand
T4-1	40°48′46.43″	14°09′30.87″	7.7	9.20	0.06	99.9	–	–	Fine sand
T4-2	40°48′32.74″N	14°9′17.63″E	21.5	2.6	0.57	98.89	0.47	0.07	Fine sand
T4-3	40°48′20.83″	14°09′05.43″	47.8	10.0	6.89	67.1	25.9	0.13	Very fine sand
T4-4	40°48′06.92″	14°08′49.11″	71.5	4.28	9.42	68.1	21.7	0.75	Very fine sand
T4-5	40°47′33.22″N	14°8′11.91″E	98.0	2.17	1.87	93.54	4.29	0.3	Fine sand
T5-1	40°47′33.96″	14°09′28.91″	22.7	0.34	49.1	50.8	–	–	Very fine gravel
T5-2	40°47′29.99″N	14°9′17.74″E	47.8	0.12	0.29	99.07	0.52	0.12	Fine sand
T5-3	40°47′24.71″	14°09′00.89″	91.2	2.44	0.23	88.0	11.4	0.41	Very fine sand
T6-1	40°48′19.38″	14°09′46.08″	13.4	2.04	1.6	93.2	5.3	–	Fine sand
T6-2	40°48′02.28″	14°09′21.12″	37.1	1.83	7.5	81.3	11.1	–	Fine sand
T6-3	40°47′28.08″	14°09′01.38″	87.5	2.27	–	88.2	11.5	0.2	Very fine sand

[a] TOC: total organic carbon.
[b] Classification of grain size sediment (Folk and Ward, 1957).

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