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Geogenic versus anthropogenic geochemical influence on trace elements contents in soils from the Milazzo Peninsula

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ABSTRACT

Milazzo Peninsula soils and substrates are extremely variable, composed of acidic, mafic and ultramafic metamorphic rocks, carbonatic sedimentary rocks, and sometimes volcanic rocks, thus contributing to a mixed influence on their chemical composition. Moreover, the region is highly polluted due to atmospheric releases from anthropogenic activities, such as refinery industry. In addition, emissions of airborne particles from volcanic eruptions are also likely to fall to the ground and provide trace elements to the soils. The purpose of this study is to distinguish between anthropogenic and geogenic sources contributing to the concentrations of metals in soils by studying their distribution in major and trace elements in relation to substrates. As regards geogenic sources, the major elements composition of soils comes firstly from metamorphic rocks, secondly from carbonates, and to a minor extent from volcanic rocks. Enrichment factors calculations relative to substrate rocks, and using Th as reference element, show that the soils are enriched in As, Pb, Zn, and Ni. Rare earth elements (REEs) patterns normalized to substrate rocks exhibit enrichment in light REEs and a positive anomaly in Gd, indicating anthropogenic contributions in the soil composition. REE ratios and trace elements were plotted to investigate the relationships between anthropogenic sources and substrates in soils compositions. The graphs of La/Ni vs La/Gd and La/Ce vs La/Nd show that soils plot on a line toward substrate rocks on one side, and toward an end member which is represented by a spent catalyst and atmospheric particles emitted by refinery activities. Plots of La vs Cr, and V vs La show similar trends, whereas plots of Zn vs Ni and Pb vs V suggest that another end member, which is unidentified, contributes to soil enrichment in Zn and Pb. A binary mixing model applied to the most Zn enriched soil suggests that anthropogenic inputs from refinery emissions may have contributed to 16% of the anomalies in La/Gd. These results suggest that the trace element composition of Milazzo's peninsula soils partly bears the signature of atmospheric emissions of the refinery.

1. Introduction

Milazzo's Peninsula in the NE of Sicily island (southern Italy) (Fig. 1) is a much polluted area since many studies in recent decades have shown an increasing number of cancers and lung infections in this region (Fano et al., 2008). Indeed, major industries are established in the area of Milazzo, such as a thermo-electric plant and a refinery that produces diesel with low sulfur and unleaded gasoline (Bevilacqua and Braglia, 2002). The air emissions data are available for these activities that demonstrate the presence of significant amounts of V, Fe and Ni in airborne fallouts (European Environment Agency, 2011). There are as well, sewage treatment plants, boating activities, the municipal waste incineration and a high traffic density which also release potentially toxic contaminants for which no quantitative data on emissions is available. However, a recent study on global scale impact assessment of industrial activities from the Milazzo Peninsula showed that emissions to the air (NO_x, SO_2, particulate matter) are by far the most important releases (Mey, 2013). The particulate matter contains trace elements such as Ni, Se, V, Cu and Cd, released by these industries which contribute significantly to damages on the soil ecosystems (Mey, 2013).

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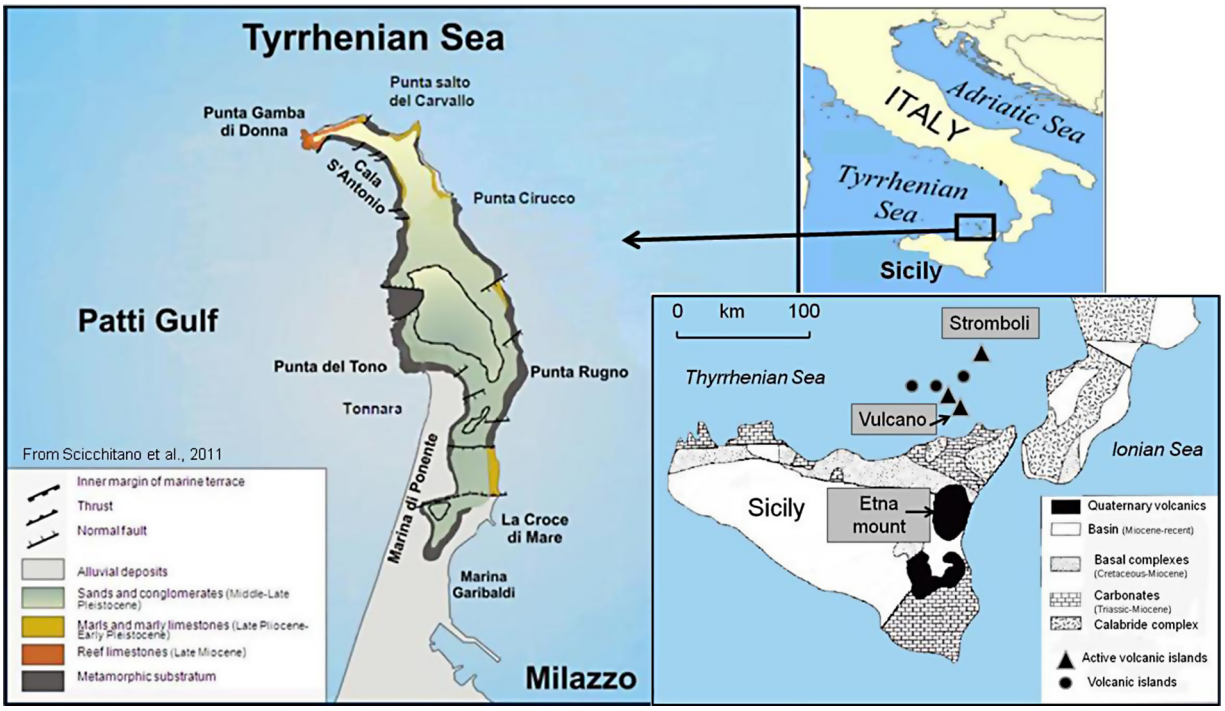

Fig. 1. Milazzo Peninsula (Sicily) and Aeolian volcanic islands situation.

The Milazzo Peninsula is in a region located between the volcanic activities of the Etna Mount to the South, and the Vulcano and Stromboli Aeolian Islands to the North (Fig. 1). The Etna and Stromboli volcanoes emit pyroclastites of which the ash is sometimes transported over a long distance. An aircraft survey of particulate matter in the plume of Mt. Etna, carried out by Bergametti et al. (1984), showed that particulate sulfur can be identified at a great distance (260 km) from the emission point. These particles may also contain various trace elements, as reported by several studies on the volcanic plumes. Among them, Piccardi et al. (1979) identified the presence of trace elements (Cu, Zn, Cd, Sb, Bi and Pb) in the fumarolic gases of Vulcano Island. Buat-Ménard (1978) also mentioned the enrichment of trace elements (Cu, Zn, Se, Hg, Cd and Pb) in the discharge aerosols from Mount Etna, which are for Cd, Hg, Cu and Zn, comparable to anthropogenic atmospheric releases from the bordering countries of the Mediterranean basin, and predominant for Se, in the Mediterranean atmospheric environment. More recently, Calabrese et al. (2011) characterized Etna's emissions and atmospheric depositions and identified volatile trace elements (As, Bi, Cd, Cs, Cu and Tl) as well as refractory elements (Al, Ba, Co, Fe, Ti, Th, U, and V) scavenged from the plume.

As for atmospheric anthropogenic particulate matter, particles from volcanic activity fall to ground during rainy and windy events and release contaminants in terrestrial and aquatic ecosystems. Calabrese et al. (2011) estimated in case of Etna plumes that more than 90% of volcanogenic trace elements are dispersed further away, and may cause a regional scale impact.

Up to now, only two studies were devoted to the trace elements contamination assessment in soils from Milazzo region. The first study was a multidisciplinary approach on Milazzo region soils performed by Triolo et al. (2008) to evaluate the impact of atmospheric pollutants emitted by the industrial settlement. The authors pointed out a correlation between fluctuations of metabolic profiles of microbial communities in soils and the predicted concentrations of airborne fallouts from the industrial plants. On the basis of their work, the V concentrations in soils were found to exceed the threshold values fixed by the Italian law for public and private green areas. But they also suspected that industrial emissions are not the only pollution sources in this area. As mentioned above, Mey (2013) analyzed, among others, ecotoxicological impacts of anthropogenic activities on terrestrial and aquatic ecosystems, and has identified the trace elements such as As, Ni, Pb, V, and Zn, which can cause toxic damages on terrestrial ecosystems.

If it is clear that anthropogenic activities or that volcanic atmospheric particles release contaminant elements, it is difficult to relate trace element contents in soils to one or the other of those activities. Moreover, uncontaminated soils are the result of the bedrock weathering that also provides trace elements which constitute the natural background. To assess impacts of industrial activities it is therefore essential to be able to distinguish the influence of inputs from these different sources.

The aim of the present paper is an attempt to distinguish the contributions of geogenic and anthropogenic sources in the composition of trace elements in soils. The three steps approach begins by estimating the trace elements enrichments (enrichment factors) in soils relative to the global and local geochemical background. The second step is dedicated to highlight the influence of the substratum in the soil geochemical signature. The third step is to determine whether the volcanic activities (the fumaroles activity, as occurring at Vulcano Island, or the ash deposition as occurring around Mt Etna) or anthropogenic activities may be allochthonous sources of metals in the soil environment of Milazzo Peninsula.

2. Study area

The Milazzo Peninsula belongs to the Alpine Peloritani Chain in the Southern Sector of the Calabrian Peloritani Arc (Messina et al., 2004a,b; Carbone et al., 2011 and reference therein; ISPRA, 2011).

The Peninsula is made up of the Aspromonte Unit (AsU) Variscan high-medium grade basement, which consists of Variscan gneissic bodies including metric amphibolite (s.l.) lenses. Locally, Variscan two mica marbles (Punta Rugno), augen gneissic bodies (north-east slope), and Late-Variscan peraluminous leucomonzogranites (south of Cala Sant'Antonio) are also present. The basement is