



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



Joëlle Duplay^{a,*}, Khadija Semhi^{b,c}, Morgane Mey^{a,d}, Antonia Messina^d, Gaetana Quaranta^a, Fabienne Huber^a, Amélie Aubert^a

^a Laboratoire d'Hydrologie et de Géochimie de Strasbourg, UMR 7517, 1 rue Blessig, 67084 Strasbourg Cedex, France

^b 4, rue de Marlenheim, 67000 Strasbourg, France

^c SQU, College of Science, Oman

^d Università degli Studi di Messina, Dipartimento di Fisica e di Scienze della Terra Viale F. Stagno d'Alcontres 31, 98100 Messina, Italy

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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.

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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, SO₂, 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).

* Corresponding author at: EOST, LHYGES, 1, rue Blessig, 67084 Strasbourg Cedex, France. Tel.: +33 3 68 85 04 24; fax: +33 3 68 85 04 02.
E-mail address: jduplay@unistra.fr (J. Duplay).

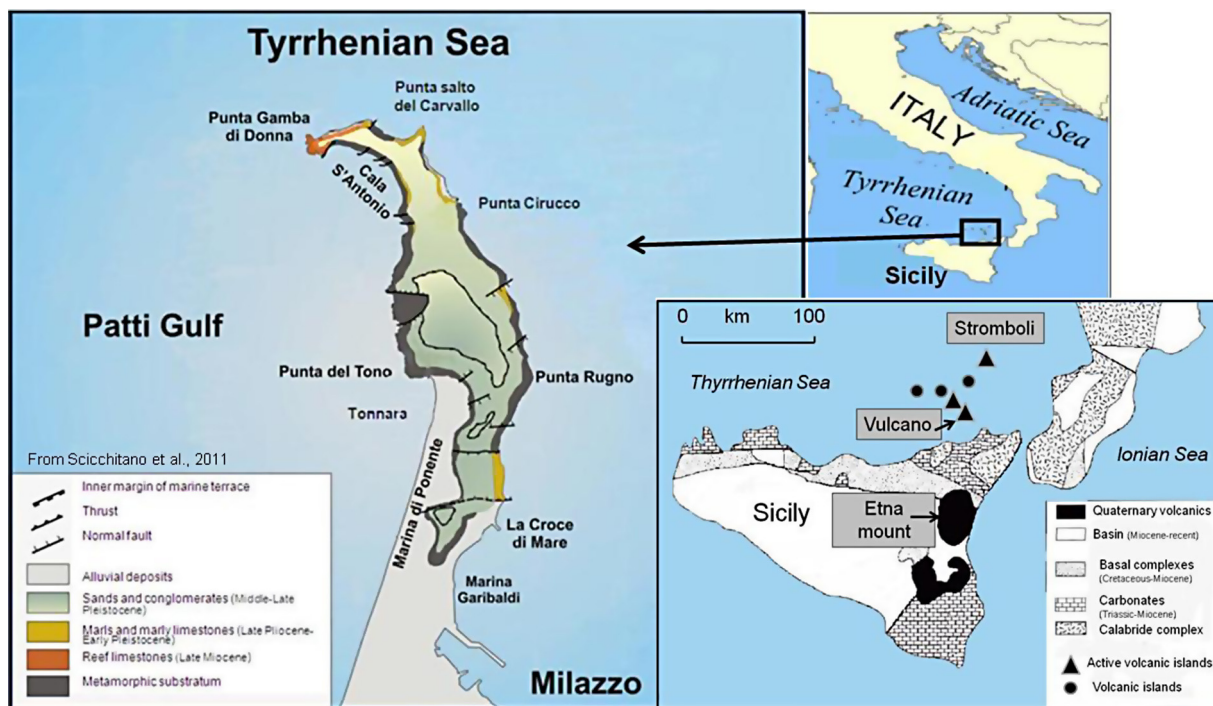


Fig. 1. Milazzo Peninsula (Sicily) and Aeolian volcanic islands situation.

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 volcanic 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

locally covered by Late Miocene deposits consisting of gray-whitish limestones containing corals, algae and mollusks, and by quaternary deposits (Carbone et al., 2011; ISPRA, 2011; Macaione et al., 2012; Messina et al., 2013) (Fig. 1).

A breccia calcareous level is locally sandwiched between the basement and the early quaternary deposit. A marine quaternary terrace fossilized by coarse clastics with molluscan fauna, is followed by fine dark brown volcanoclastic deposits. The last deposit is made up of yellowish calcareous sands, and rests unconformably on both metamorphics and Late Miocene bioherms. The marine terraces of highest order (85–50 m a.s.l.) include shallow water sands and conglomerates (Tonnara to Cala Sant'Antonio; Punta Salto del Cavallo to Punta Ciruccio zones) (Fois, 1990). A second order of marine terraces is located between 45 and 28 m a.s. (Carbone et al., 2011; ISPRA, 2011). The Holocene alluvial deposits characterizing the Barcellona-Milazzo Plain, which includes the south of Milazzo City and the refinery, are mainly made up of crystalline clastic elements of the Aspromonte Unit Variscan augen gneisses and Mela Unit Variscan fine-grained two mica marbles.

3. Potential anthropogenic and natural atmospheric emission sources

3.1. Etna, Vulcano and Stromboli volcanic plumes' spreading

The spreading distance of volcanic plumes may be of tens or thousands of kilometers depending on the wind speed and direction, eruption strength, and volcanic out gassing. Strong volcanic plumes rise into the atmosphere as sub-vertical columns and spread laterally, forming an umbrella region (Sparks et al., 1997). Most particles are concentrated in the umbrella region, and sedimentation occurs mainly from this region. Weak plumes are distorted by the wind, developing bent-over trajectories in the downward wind direction and particles are assumed to be homogenized before settlement (Bonadonna and Houghton, 2005). Dispersal models can describe sedimentation processes of weak long-lasting plumes as was the case for tephra fallout during the 2001 eruption of Mt. Etna (Scollo et al., 2007). During the 2001 eruption event, the deposition distance could be estimated at more than 20 km from the source. Knowing that winds in this region may be either NW to SE or the reverse during the periods of Sirocco winds, it can be assumed that atmospheric particle matter may reach the Milazzo Peninsula, and may settle down in favor of SE to NW winds and rainy events.

During the last Vulcano eruption (from 1886 to 1890, Arrighi et al., 2006), it was reported that ash falls occurred in the surrounding Island Lipari situated a few kms away from Vulcano Island. Knowing that dominant winds are blowing toward Sicily, it is most likely that Vulcano ash falls also occurred at Milazzo Peninsula which is the nearest island relative to the Sicilian coast. Consequently, there is a good chance that atmospheric particulate matter emitted in ancient or recent times by Vulcano or Etna volcanoes could have settled down on Milazzo Peninsula soils and have brought a significant volcanic contribution to their trace element compositions.

Concerning Stromboli volcano, although it is situated around 100 km NNW of Milazzo Peninsula, its atmospheric particles releases may have been transported toward Milazzo Peninsula with the prevailing NW–SE winds. Indeed, Stromboli volcano has been characterized by quasi permanent activity for at least the last 2000 years (Mather et al., 2004; Landi et al., 2006). The intermittent mild explosions take place with continuous gas emissions and most of the aerosol mass is due to smaller particles in the range 0.013–1.2 mm which may have spread at long distances (Allard et al., 2000).

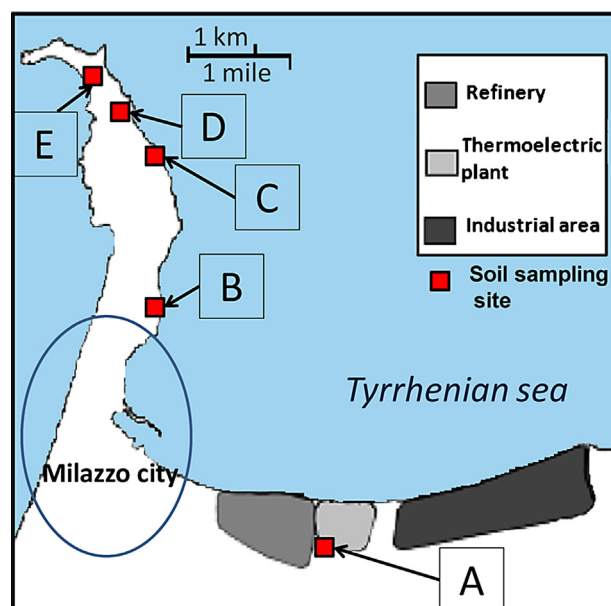


Fig. 2. Situation of soil sampling sites and Milazzo anthropogenic activities.

3.2. Anthropogenic atmospheric emissions

The Milazzo industrial activities such as the refinery and the electric plant (Fig. 2) are known to emit a large variety of pollutants to the air, and to the water (Agenda 21 Milazzo, 2009). Data are available for emissions to these compartments for the year 2007–2011 (European Environment Agency, 2011). The refining process needs several operations, among them combustion and fluidized-bed catalytic cracking (FCC). The FCC operations typically use zeolite catalysts enriched in rare earth elements (REEs), a portion of which escapes to atmosphere with other trace elements in fine particles (PM₁₀, PM_{2.5}) (Mizohata, 1986; Dzubay et al., 1988; Olmez et al., 1988). Sánchez de la Campa et al. (2011) analyzed the metalliferous particulate matter (PM) present within FCC chimney stacks from the San Roque petroleum refinery complex, in the South of Spain. They measured high concentrations of La (>200 μg m⁻³ in PM 0.67–1.3), Cr and Ni in coarse-sized PM (0.7–14 μm). The Milazzo electric plant which uses fuel produced by the refinery also emits fine particles enriched in trace elements. Table 1 gives

Table 1

Emissions to the air of the Milazzo refinery and thermoelectric plant recorded in 2010 (European Environment Agency, 2011), and of illegal waste combustion and road traffic (estimations for year 2010, from Mey, 2013).

	Refinery ^a	Electric plant ^a	Road traffic	Waste combustion
	(kg/year of substance)			
Arsenic	25	30	nd	–
Cadmium	140	12	<1	–
Chromium	468	190	1	–
Cobalt	200	536	–	–
Copper	64	402	43	13
Iron	1004	1429	–	205
Lead	3098	63	426	1
Manganese	nd	168	–	–
Mercury	10	16	–	–
Molybdenum	100	116	–	–
Nickel	1275	504	2	99
Selenium	4	42	<1	–
Vanadium	3551	15,310	25	272
Zinc	341	194	–	–

^a Substances were measured following the BS EN 14,385:2004 European Standard for the determination of the mass concentration of specific elements in exhaust gases from stationary source emissions.

the mass of substances released to atmosphere during the whole year 2010 (from the [European Environment Agency, 2011](#)). It can be seen that high amounts of V, Fe, and Ni, are released by both activities, in addition to Pb in the refinery and Co and Cu for the electric plant. Other activities such as road traffic or illegal waste combustion may also release toxic substances. [Mey \(2013\)](#) estimated the mass of substances released to atmosphere, and compared them to those of the refinery and the electric plant ([Table 1](#)). Although the released masses estimated for the road traffic and waste combustion are lower than for the refinery and electric plant, there is a concern for Pb, and V, and to a lesser extent for Fe and Ni.

These different kinds of releases to the air may be partially deposited to the soil. The fraction of air-emitted pollutants that ends in the soil depends on the direction of the wind and other climatic conditions. The winds' speed in the Milazzo Peninsula region are very low (1 m/s) which is in favor of a short transport distance of particles [Cellura et al., \(2008a,b\)](#). A map established by [ENEA \(2003\)](#) enables to define the deposition area onto soil of air-emitted particulate matter originating from the refinery and the thermoelectric plant of Milazzo. It corresponds approximately to a circular area measuring 36 km in diameter, the refinery and plant being located in the center of that circular area. [Triolo et al. \(2008\)](#) using the so called CMPM98 model (Climatologic Model for Point Multisource) defined the distribution of estimated SO₂ and total suspended particulate matter concentrations over the studied area with the highest values within a 10 km² area surrounding the industrial emission sources, and the lowest beyond 20 km from the sources. This means that the soils under investigation in this study are under influence of trace elements anthropogenic atmospheric releases.

However, the question arises whether anthropogenic and/or geogenic atmospheric particles may have influenced the trace elements contents in the studied soils. A way to solve the problem is to try to identify the geochemical signature of the different possible inputs in the soils.

4. Materials and methods

4.1. Soil sampling

The soils in Milazzo Peninsula are poorly developed, thin and sandy. The sampling with a hand auger was difficult below the depth of 30–40 cm where the horizons are coarse. Two sampling campaigns were conducted which took place during the dry season in March 2010 and 2011. Five locations where surface (0–20 cm) and deeper soils (20–40 cm) were sampled were chosen in order to represent different distances from the Milazzo industrial zone which releases pollutant emissions to the air ([Fig. 2](#)). The geological formations below the sampled soils are given in [Table 2](#)

Table 2
Geological formations and types of rocks and deposits under the studied soil sites from the Geological Map of Italy – Sheet Milazzo-Barcellona PG ([ISPRA, 2011](#)), and Messina (personal data).

Soil site	Geological formation	Type of deposit	Description
A	Transitional and quaternary deposits	Current Alluvial Deposits	Gravel deposits in heterometric clasts of low- to medium metamorphic grade, where biotite augengneisses prevail.
B (Located between two geological formations)	Calabria-peloritani arc Transizional and quaternary deposits	Proterozoic to Paleozoic Metamorphic Complex of the Aspromonte Unit Middle–Upper Pleistocene Terraced Marine Deposits.	Variscan less mobilized amphibolite lenses up to several meters thick showing green color, oriented texture and made up of hornblende and minor plagioclase, quartz and biotite. Yellow-ocher sands and gravels with mostly crystalline heterometric pebbles in a sandy matrix.
C–E	Calabria-Peloritani arc	Proterozoic to Paleozoic metamorphic complex of the aspromonte unit	Variscan metatexites (from Pan–African granulites). Mobilized gray gneisses and greenish gneissic amphibolites in bodies of hectometer-thick showing banded texture and different quantitative ratios of plagioclase, K-feldspar, quartz, biotite, hornblende and garnet. Leucosomes in decimetric layers consisting of plagioclase, K-feldspar, quartz and muscovite. Melanosomes in millimeter to centimeter-thick layers, made up of biotite (>70%) and subordinate plagioclase and quartz.

where the type of deposit and the description are also summarized. The conglomerates are the first levels of rocks under the soils. Then, with depth are following the different geological formations ([Fois, 1990](#)) which are: the Proterozoic to Paleozoic metamorphic complexes of the Aspromonte Unit for sites C–E; quaternary alluvial deposits for site A. Site B is peculiar because it straddles the border of two geological formations: the Proterozoic to Paleozoic metamorphic complex of the Aspromonte Unit, and the Middle–Upper Pleistocene terraced marine deposits. The soils were stored in clean polyethylene bags for transport to the laboratory, then disaggregated by hand to separate cm-sized soil aggregates, air-dried, and passed through a 2-mm mesh-sized sieve. The <2 mm fraction was stored at 4 °C in polyethylene bags until processing ([Mathieu and Pieltain, 2003](#)).

4.2. Analytical methodology

The mineral composition of the bulk soil was determined on random-powdered samples by XRD (Brüker D5000, 3–65° 2θ scanning angle, 1 s–0.02° upward step, Cu anticathode, wave length λ Kα1 = 1.54056 Å, 30 mA current, 40 kV voltage). The physico-chemical characteristics of the <2 mm fractions of soil were determined for pH, by electrometry in a soil–solvent suspension (1:2.5) (NF EN 12176); organic matter content (OM) by pyrolysis at 375 °C during 16 h after pre-drying at 150 °C (NF EN 12875); carbonate content by the volume of emitted gas during dissolution of carbonates by HCl (volumetric calcimetry, NF ISO 10693).

The soil samples were analyzed at the LHyGeS (CNRS, Strasbourg) by ICP-AES (Jobin Yvon JY 124) for major elements and ICP-MS (VG Plasmaquad PQ2+) for trace elements. An acid digestion was applied as follows: 50 mg of soil dried at 105 °C and grinded with an agate mortar was heated in 1 mL HNO₃ – 4 mL HF at 70 °C for 24 h, and then evaporated; 1 mL HNO₃ – 1 mL HClO₄ was added to the residue and heated at 150 °C for 24 h. The residue was dissolved in 1 mL HCl (6N), and then evaporated. The final residue was dissolved in 5 mL HNO₃ for analysis by ICP-MS ([Semhi et al., 2010](#)).

All reagents used in preparation of samples for chemical analyses were of analytical grade. All relevant material was cleaned prior to use with heated aqua regia, then with distilled water, then heated distilled water and HCl, and finally rinsed with ultrapure water. All material was then allowed to dry at room temperature. The equipment and accuracy controls of each ICP are available in [Samuel et al. \(1985\)](#). Repeated analyses of several certified geostandards such as the GI-O glauconite and the BE-N basalt ([Govindaraju and Roelandst, 1993](#)) were carried out during the course of the study on a regular weekly basis providing an analytical precision for the major and trace elements of respectively ±2 and ±5, ±10% 2σ standard deviation of each analyzed element.

5. Results

5.1. Physico-chemical characteristics and mineralogy of soils

Different types of soils are identified according to their physico-chemical, and mineralogical characteristics ([Table 3](#)). All soils are sandy (65–90% sand). The inorganic fraction of soil is mainly composed of quartz, feldspars and phyllosilicates in all samples, whereas calcite is only present in soils of B site and at the surface of soils from sites A and E, which is in agreement with the data of CaCO₃ contents ([Table 3](#)). The biotite is present in all soils except

Table 3
Soil characteristics.

Label	Sampling depth (cm)	Sampling site	Weight%				Weight%	
			Clay	Silt	Sand	% organic matter	pH	% CaCO ₃ content
Asurf	0–20	Near refinery	5.25	9.95	84.80	6.96	7.31	6.16
Adeep	20–4	Near refinery	1.64	7.84	90.52	2.63	7.84	3.20
Bsurf	0–20	“Croche di mare”, near the sea	3.53	10.87	85.60	3.15	8.53	8.85
Bdeep	20–40	“Croche di mare”, near the sea	1.88	8.32	89.80	2.61	8.57	9.58
Csurf	0–20	“Paradisio”, near the sea	4.78	16.52	78.70	6.81	7.33	1.02
Dsurf	0–20	Camping Milazzo	5.19	13.81	81.00	6.37	7.71	0.76
Ddeep	20–40	Camping Milazzo	9.76	25.54	64.70	6.01	7.58	0.66
Esurf	0–20	Cape Milazzo, near the sea	2.19	10.81	87.00	7.87	8.10	3.48

Table 4
Mineralogy of Milazzo Peninsula studied soils.

Sample	Site	Quartz	Plagioclase	K-feldspar	Biotite	Hornblende	Calcite	Chlorite
Asurf	Near refinery	x	x	x			x	
Adeep	Near refinery	x		x			x	
Bsurf	“Croche di mare”, near the sea	x	x	x	x	x	x	x
Bdeep	“Croche di mare”, near the sea	x	x	x	x	x	x	x
Csurf	“Paradisio”, near the sea	x	x	x	x	x		x
Dsurf	Camping Milazzo	x	x	x	x			
Ddeep	Camping Milazzo	x	x	x	x			
Esurf	Cape Milazzo, near the sea	x	x	x	x	x	x	

in those of site A. Other minerals such as hornblende and chlorite were identified in soils of sites B and C (Table 4). Although garnet is common in the area, it was not identified. Accessory minerals are apatite, zircon, and magnetite.

The organic matter content ranges between 2.6% (B soils and A deeper horizons of soil) and 7.9% (E site, surface soils), which is rather high and corresponds to contents in organic soils. Organic matter may come from the household waste amendment. Rather high values (6–7%) are also recorded in A surface soils and C and D soils. The carbonate content (CaCO₃%) ranges from 0.7% (Soil D) to 9.6% (Soil B). The soil pHs are moderately alkaline with values ranging from 7.3 to 8.6.

The analyzed soils have a silicates dominant composition, and are overall Al- and Fe-rich, and Ca-rich for site B (Table 5). The concentrations of trace elements vary in the following ranges (in µg/g): V (69.7–162.2), Ni (27.9–73.1), Cr (45.7–152.2), As (4–9.6), Cd (0.12–0.43), and Pb (19.9–59.2). Surface samples compared with deep samples in cores B and D show higher abundances for V, Ni, Cr and Th, but not of As and Pb. Moreover the Ni, Cr, As and Pb concentrations are overall significantly higher than those reported by Triolo et al. (2008) for soils around industrial sites of Milazzo city. The elements can be sorted in 3 groups according to their correlations (Table 6). Ni, Cr and Zn to a lesser extent, form a group which is also associated with Mg, Ca and K. This group characterizes soils of site B. Another group characterizes soils of site C, and consists of Zn, Co, V, Cu, As, Th associated with Fe, Al and Mg. The element Pb characterizes surface soils of site D, and Cd characterizes surface soils of site E; these two elements are not correlated with any other element considered.

5.2. Milazzo Peninsula soil substrates

Chemical data of Milazzo peninsula substrate rocks were taken from the literature. As mentioned above (Section 4.1) there are different types of metamorphic and sedimentary rocks beneath the soils in Milazzo Peninsula, which have been previously described by Fois (1990), Carbone et al. (2011), and Messina et al. (2013). As for the rest of the North-Eastern region of Sicily, these metamorphic rocks consist also of metamafigs and metultramafics enriched in Cr and Zn (Dinelli et al., 2011). Representative compositions of substrates are given in Table 5 which includes chemical compositions

of rocks belonging to the Milazzo Peninsula (amphibolites, gneiss, leucosome – from Macaione et al., 2012; Messina et al., in preparation) and surrounding areas of the medium-lower continental crust segment characterizing the Aspromonte Unit of the Peloritani Chain (metaperidotite and metahornblendites – from Macaione et al., 2010). Average chemical compositions are also given for Peloritani metamorphic rocks (Variscan two mica marbles of the Mela Unit – from Messina et al., 2004a,b), and sedimentary rocks (limestones – from Messina et al., 2004a,b). Moreover, mean representative compositions of Etna and Eolian lavas were taken from Calabrese et al. (2011), Del Moro et al. (1998) and Landi et al. (2006).

Principal component analysis (PCA) was conducted to describe the variation in the set of multivariate data (Rouaud, 2012) using ADDINSOFT software (XLSTAT-Pro, v. 2011–2). The purpose was to determine the chemical similarities of soils with the potential natural sources of elements i.e. substrates. The matrix includes major elements contents in the soil samples and in associated substrates. The PCA results showed that the two principal components F1 and F2 accounted for 83.49% of the total variance in the data: the first factor explained 59.98% of total variance, and the second 23.51% of the remaining explained variance. Fig. 3 shows the distribution of the investigated variables and observations on a biplot representation. Along the first principal component axis (F1), Ca exhibited a high and positive loading (0.95), and Al, Fe, K, Mn, Na, and Ti, exhibited a high but negative loading (–0.72 to –0.94) (Fig. 3), whereas Mg exhibited a high and positive loading (0.77) along F2 axis. Moreover, Fe and Ti also showed a low but positive loading along F1, and Na and K a negative loading along F1. Most soils are well represented in F1–F2 plan, within the quadrants corresponding to the F1 negative axis, and thus are positively correlated with Al, K, Na, Mn, Fe and Ti, but in opposition with Ca and the limestones which plot along F1 positive axis. The soils from site B are represented in intermediate position near the center of the biplot indicating a mixed influence of the different variables. Moreover, deeper soils of site A are in the same quadrant as the gneiss substrate, while soils of sites C–E soils and A surface soils are closer to amphibolitic and volcanic (Etna) substrates.

Thus, soils may be grouped depending on their correlations with variables (major elements) and their position relative to substrate rocks. The soils of site B show a mixed influence of the limestones and AsU rocks, whereas A, C–E soils show a major influence of AsU

Table 5
Major elements and trace elements abundances in the Milazzo peninsula soils and substrates (rocks from the Aspromonte unit (AsU), volcanic lava, limestones), refinery FCC spent catalyst and stack particles.

	Weight% of element								
	Al	Mg	Ca	Fe	Mn	Ti	Na	K	P
Asurf1	38.7	5.02	9.78	24.8	0.55	2.67	8.97	9.15	0.37
Asurf2	39.6	5.81	10.7	23.1	0.69	2.12	7.84	9.67	0.39
Adeep1	42.4	5.12	6.08	22.0	0.51	2.36	10.4	10.8	0.36
Adeep2	43.4	4.29	5.85	18.1	0.48	1.69	14.2	11.8	0.31
Bsurf1	32.9	7.57	20.8	19.6	0.42	2.03	7.00	9.04	0.69
Bsurf2	30.4	7.49	23.8	20.1	0.40	1.91	6.55	8.51	0.88
Bdeep1	31.3	8.96	21.4	18.9	0.36	1.85	6.95	9.84	0.45
Csurf1	37.8	7.98	9.17	26.0	0.48	2.54	6.45	9.20	0.34
Csurf2	37.5	8.16	10.1	25.6	0.48	2.37	7.13	8.37	0.32
Dsurf1	35.7	6.82	13.2	24.6	0.50	1.95	8.12	8.77	0.37
Dsurf2	36.0	7.26	13.4	23.9	0.51	2.07	7.47	8.87	0.44
Ddeep1	36.9	7.03	12.2	24.8	0.50	2.02	7.74	8.57	0.35
Ddeep2	35.9	7.20	12.5	24.5	0.50	2.10	7.62	9.29	0.38
Esurf1	36.8	7.82	15.7	21.2	0.46	1.95	7.75	7.78	0.49
Esurf2	35.8	7.45	12.1	24.1	0.48	2.58	7.86	9.00	0.61
Etna lava ^a	29.0	9.32	22.4	23.2	0.41	2.97	8.49	4.25	nd
Vulcano lava ^b	31.1	7.35	16.2	19.2	0.40	1.31	9.98	14.0	0.49
Stromboli lava ^c	29.2	11.7	24.9	19.7	0.39	1.72	6.13	5.59	0.65
Upper continental crust ^d	36.6	6.05	13.6	15.9	0.27	1.36	13.1	12.7	0.32
Lower continental crust ^d	28.6	12.8	20.4	27.7	0.57	2.02	6.99	0.94	nd
Metahornblendite (AsU) ^e	16.2	16.5	33.5	25.7	0.32	3.82	2.51	1.25	0.19
Amphibolite (AsU) ^e	24.2	12.0	24.3	28.5	0.54	4.22	3.19	2.18	0.79
Amphibolitic (AsU) ^e	30.4	9.82	14.8	26.5	0.46	3.09	5.56	8.98	0.41
Gneiss (AsU) ^e	39.6	7.25	11.2	16.7	0.25	1.68	12.8	10.2	0.34
Leucosome (AsU) ^e	45.5	4.43	12.3	12.3	0.17	1.14	17.4	6.48	0.33
Metaperidotite (AsU) ^e	8.20	50.9	10.3	27.4	0.39	1.53	0.45	0.72	0.13
Reddish limestone ^f	0.70	1.00	96.9	0.67	0.13	0.04	0.16	0.34	0.11
Pale-pink limestone	3.10	1.88	90.5	2.40	0.13	0.17	0.44	1.34	0.12
Grayish limestone ^g	0.61	28.9	67.5	2.32	0.21	0.07	0.17	0.22	0.01
Marble ^f	0.50	0.51	98.5	0.22	0.07	0.02	0.09	0.08	0.02
	µg/g								
	V	Ni	Cr	As	Cd	Pb	Zn	Th	
Asurf1	98.3	38.7	60.2	8.32	0.14	52.5	113	8.15	
Asurf2	94.9	39.5	76.2	5.54	0.15	26.9	134	9.72	
Adeep1	84.4	32.5	50.7	6.01	0.31	26.6	78.3	8.21	
Adeep2	69.7	28.4	45.7	4.73	0.15	20.0	61.1	6.17	
Bsurf1	100	49.0	84.0	6.2	0.14	35.6	80.4	9.08	
Bsurf2	121	52.9	90.2	5.29	0.12	29.1	80.4	7.55	
Bdeep1	103	73.1	122	4.41	0.14	31.2	140	13.1	
Csurf1	150	62.9	152	9.61	0.2	30	523	15.8	
Csurf2	144	59.1	135	7.23	0.16	28.8	358	15.5	
Dsurf1	155	30.9	66.4	7.32	0.23	59.2	92.7	13.6	
Dsurf2	126	28.0	69.3	5.92	0.18	46.8	198	14.7	
Ddeep1	158	31.8	62.6	7.32	0.28	39.9	95.3	14.7	
Ddeep2	162	33.1	73.0	7.46	0.23	37.8	88.1	18.2	
Esurf1	103	32.1	61.2	4	0.17	40.0	108	7.89	
Esurf2	144	37.7	75.8	4.56	0.43	44.9	115	10.1	
Etna lava ^a	277	29.8	35.6	nd	0.2	8.09	117	9.8	
Vulcano lava ^b	nd	32.2	75.3	nd	nd	nd	nd	25.91	
Stromboli lava ^c	284	41.0	62.4	nd	nd	19.7	69.8	15.71	
Upper continental crust ^d	60.0	20.0	35.0	1.50	98.0	20.0	71.0	10.7	
Lower continental crust ^d	285	135	235	0.80	98.0	4.00	83.0	1.06	
Metahornblendite (AsU) ^e	406	35.2	390	0.55	0.40	27.7	96.5	0.95	
Amphibolite (AsU) ^e	292	56.2	88.0	5.00	5.00	19.0	149	4.41	
Amphibolitic (AsU) ^e	232	37.5	93.0	2.40	5.00	13.3	114	8.52	
Gneiss (AsU) ^e	83.6	35.8	78.2	4.74	5.00	17.6	79.3	27.9	
Leucosome (AsU) ^e	51	19.7	50.3	5.00	5.00	21.3	40.3	7.99	
Metaperidotite (AsU) ^e	126	1090	2219	0.83	0.17	32.4	nd	1.07	
Reddish limestone ^f	11.0	3.45	13.7	1.70	0.45	28.0	8.50	0.55	
Pale-pink limestone ^f	19.0	5.15	13.7	1.75	0.50	55.0	14.5	1.45	
Grayish limestone ^g	9.5	2.65	13.7	0.6	23	97	281	0.35	
Marble ^f	5.00	17.0	13.7	5.00	5.00	6.00	nd	0.55	
FCC spent catalyst ^g	445	1094	133	6.31	<0.5	nd	153	nd	
FCC stack ^h	145	819	962	1.63	2.92	6.41	98.7	2.14	

^a From Calabrese et al. (2011).

^b From Del Moro et al. (1998).

^c From Landi et al. (2006).

^d From Taylor and McLennan (1985) and McLennan (2001).

^e From Messina (unpublished).

^f From Messina et al. (2004).

^g From Kulkarni et al. (2006).

^h From Sánchez de la Campa et al. (2011).

Table 6
Pearson correlation matrix of major and trace elements contents in Milazzo Peninsula soils.

Elements	Al	Mg	Ca	Fe	Mn	Ti	Na	K	Sr	Ba	V	Ni	Co	Cr	Zn	Cu	Pb	As	Cd	Th
Al	1.00	0.28	-0.26	0.69	0.55	0.56	0.30	0.57	-0.02	0.56	0.50	0.31	0.65	0.52	0.58	0.90	-0.27	0.63	0.15	0.54
Mg	0.28	1.00	0.72	0.62	0.05	0.54	-0.48	0.39	0.60	0.59	0.59	0.74	0.75	0.78	0.43	0.35	0.02	0.10	-0.08	0.57
Ca	-0.26	0.72	1.00	0.11	-0.24	0.09	-0.40	0.28	0.66	0.28	0.15	0.54	0.25	0.34	-0.16	-0.24	0.04	-0.26	-0.34	0.03
Fe	0.69	0.62	0.11	1.00	0.63	0.82	-0.35	0.24	0.45	0.65	0.91	0.35	0.97	0.62	0.60	0.87	0.28	0.71	0.22	0.79
Mn	0.55	0.05	-0.24	0.63	1.00	0.42	-0.20	0.06	0.06	0.21	0.50	-0.02	0.53	0.21	0.32	0.63	0.10	0.57	0.09	0.47
Ti	0.56	0.54	0.09	0.82	0.42	1.00	-0.37	0.25	0.12	0.31	0.61	0.54	0.80	0.69	0.64	0.70	0.14	0.63	0.27	0.48
Na	0.30	-0.48	-0.40	-0.35	-0.20	-0.37	1.00	0.42	-0.32	0.10	-0.34	-0.29	-0.39	-0.37	-0.31	0.02	-0.32	-0.12	0.06	-0.30
K	0.57	0.39	0.28	0.24	0.06	0.25	0.42	1.00	0.09	0.47	0.09	0.56	0.24	0.45	0.15	0.32	-0.44	0.14	-0.07	0.25
Sr	-0.02	0.60	0.66	0.45	0.06	0.12	-0.32	0.09	1.00	0.75	0.68	0.00	0.49	0.07	-0.16	0.17	0.45	0.09	0.08	0.45
Ba	0.56	0.59	0.28	0.65	0.21	0.31	0.10	0.47	0.75	1.00	0.78	0.10	0.65	0.29	0.19	0.62	0.19	0.36	0.21	0.69
V	0.50	0.59	0.15	0.91	0.50	0.61	-0.34	0.09	0.68	0.78	1.00	0.07	0.88	0.37	0.37	0.73	0.44	0.51	0.39	0.81
Ni	0.31	0.74	0.54	0.35	-0.02	0.54	-0.29	0.56	0.00	0.10	0.07	1.00	0.45	0.89	0.54	0.22	-0.35	0.12	-0.36	0.20
Co	0.65	0.75	0.25	0.97	0.53	0.80	-0.39	0.24	0.49	0.65	0.88	0.45	1.00	0.70	0.61	0.82	0.16	0.55	0.17	0.75
Cr	0.52	0.78	0.34	0.62	0.21	0.69	-0.37	0.45	0.07	0.29	0.37	0.89	0.70	1.00	0.83	0.53	-0.26	0.35	-0.24	0.50
Zn	0.58	0.43	-0.16	0.60	0.32	0.64	-0.31	0.15	-0.16	0.19	0.37	0.54	0.61	0.83	1.00	0.67	-0.17	0.56	-0.10	0.51
Cu	0.90	0.35	-0.24	0.87	0.63	0.70	0.02	0.32	0.17	0.62	0.73	0.22	0.82	0.53	0.67	1.00	0.05	0.80	0.18	0.72
Pb	-0.27	0.02	0.04	0.28	0.10	0.14	-0.32	-0.44	0.45	0.19	0.44	-0.35	0.16	-0.26	-0.17	0.05	1.00	0.25	0.26	0.22
As	0.63	0.10	-0.26	0.71	0.57	0.63	-0.12	0.14	0.09	0.36	0.51	0.12	0.55	0.35	0.56	0.80	0.25	1.00	-0.02	0.55
Cd	0.15	-0.08	-0.34	0.22	0.09	0.27	0.06	-0.07	0.08	0.21	0.39	-0.36	0.17	-0.24	-0.10	0.18	0.26	-0.02	1.00	0.15
Th	0.54	0.57	0.03	0.79	0.47	0.48	-0.30	0.25	0.45	0.69	0.81	0.20	0.75	0.50	0.51	0.72	0.22	0.55	0.15	1.00

In bold: statistical significance of each variable with 95% degree of confidence.

rocks with a more or less important contribution of the different rock types (gneiss, leucosome, amphibolitic, amphibolite).

5.3. Rare earth elements (REEs) distribution in soils and substrates

The REEs are useful geochemical markers because they inherit the REE composition of their source. They can be used to determine the possible mantle sources in the magmatism (e.g. Schiano et al., 2004), to follow the typology of sediments (Plank and Langmuir, 1998), to help determining the source rocks of sediments or soils (e.g. Hossain Bhuiyan et al., 2011; Armstrong-Altrin et al., 2012). The REEs are also useful to distinguish the contributions of anthropogenic sources and geogenic sources (e.g. Kulkarni et al., 2006; Moreno et al., 2008, 2012). Thus, REEs distribution patterns relative to a reference, and ratios between elements, are used in this study to trace the possible natural and anthropogenic geochemical sources of the elements in Milazzo soils.

As mentioned above there are different substrates in Milazzo Peninsula (AsU metamorphic and sedimentary rocks, Etna and Eolian volcanic rocks) and also anthropogenic atmospheric inputs.

To illustrate the contribution of these different sources, the REE concentrations in soils and substrate rocks are displayed in a PCA diagram.

The results are illustrated in the F1–F2 factorial plan (Fig. 4) which accounted for 95.46% of the total variance in the data. The heavy REEs (HREEs) characterize the quadrant formed by the F1 and F2 positive axes, whereas light REEs (LREEs) characterize the quarter of the F1 positive and the F2 negative axes. The PCA analysis enables to distinguish groups of soils according to their position in the biplot. One group gathers the surface soils of site C, and deeper soils of sites B and, in the same quadrant with Etna and Stromboli substrate rocks represented by the LREEs. Another group consists of A site deeper soils and B, D and E surface soils, with the limestone in the quadrants at the opposite of the REEs. A soil of site A, apart from other soils is characterized by HREEs and a major influence of the metahornblendite substrate rock. Moreover, the total content of REEs in soils from C sites is particularly significant (about 203–213 $\mu\text{g/g}$) compared to the other soils. Thus, REEs' distribution in soil allows distinguishing surface soils of sites A and C enriched in REEs, with the rest of the soils, less enriched in REEs and characterized by a mixed influence of limestone and AsU rocks.

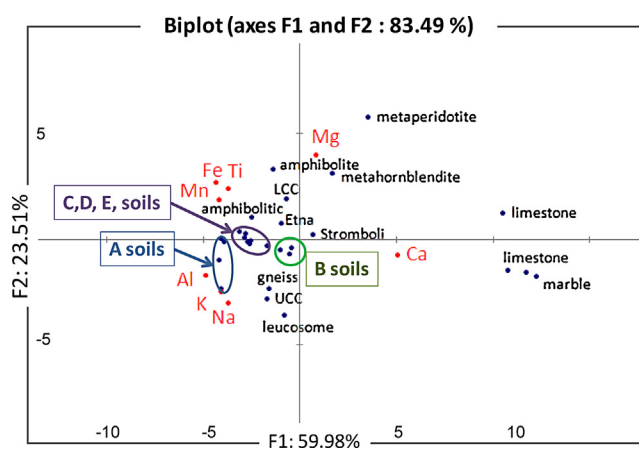


Fig. 3. PCA graphic representation of studied soils in the biplot factorial plan of F1 and F2 principal components. Axis 1 represents carbonates on the positive side, Na and K compositions (in relation to feldspar and mica contents), and oxides and Fe silicates on the negative side. Axis 2 represents Mg-rich minerals on the positive side.

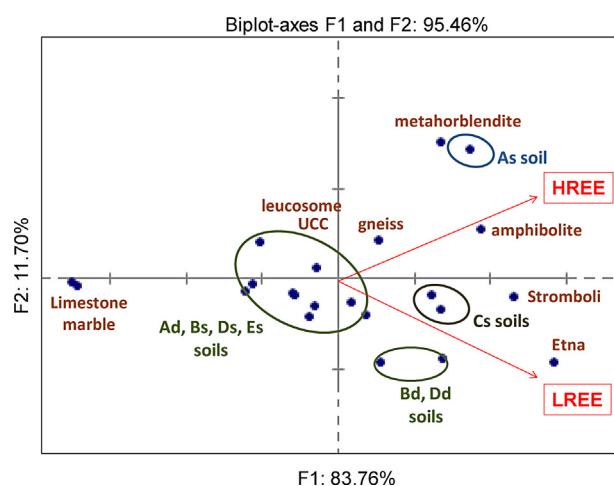


Fig. 4. PCA graphic representation of studied soils, substrate rocks and UCC, in the biplot factorial plan illustrating correlations between observations and REE variables (LREE: light REEs; HREE: heavy REEs).

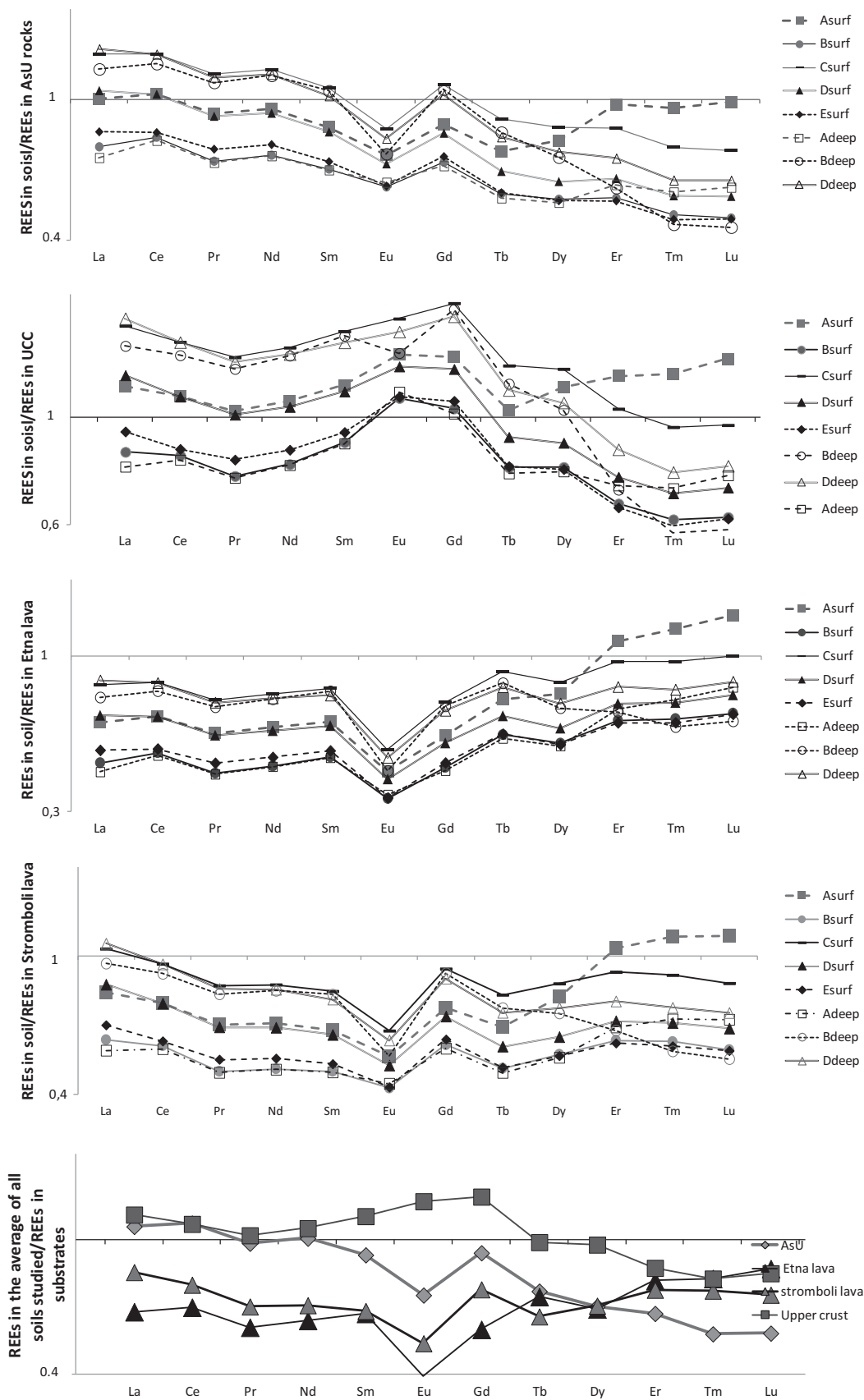


Fig. 5. REE patterns of Milazzo Peninsula individual soil samples, and average of all soils studied, normalized to Aspromonte Unit (AsU) Peloritani rocks, Upper Continental Crust (UCC), Etna and Stromboli lava.

Table 7

Rare earth elements abundances in the Milazzo peninsula soils and substrates (rocks from the Aspromonte unit (ASU), volcanic lava, limestones), refinery FCC spent catalyst and stack particles, and atmospheric particles.

	μg/g												
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Lu
Asurf1	28.8	59.5	6.25	24.1	4.57	1.07	4.47	0.57	3.19	0.60	1.86	0.26	0.28
Asurf2	40.8	81.9	8.39	32.1	5.94	1.31	5.67	0.75	4.90	1.10	3.75	0.55	0.57
Adeep1	27.3	60.4	6.07	23.6	4.46	1.06	4.31	0.54	2.92	0.54	1.62	0.22	0.21
Adeep2	20.1	44.1	4.57	17.9	3.49	0.93	3.43	0.44	2.49	0.51	1.70	0.26	0.28
Bsurf1	28.4	58.5	5.94	22.9	4.36	1.03	4.30	0.54	2.93	0.53	1.61	0.21	0.21
Bsurf2	22.5	48.3	4.80	18.7	3.63	0.90	3.63	0.47	2.60	0.48	1.44	0.19	0.19
Bdeep1	42.2	86.1	8.95	34.9	6.65	1.20	6.40	0.75	3.63	0.58	1.63	0.19	0.19
Csurf1	48.0	93.7	9.75	37.1	6.90	1.40	6.64	0.82	4.42	0.80	2.38	0.31	0.30
Csurf2	44.9	89.8	9.18	35.5	6.68	1.42	6.47	0.82	4.41	0.81	2.41	0.32	0.31
Dsurf1	38.6	73.7	7.53	28.6	5.35	1.23	5.03	0.62	3.34	0.62	1.90	0.25	0.25
Dsurf2	34.8	67.6	6.90	26.0	4.83	1.02	4.55	0.55	2.86	0.52	1.57	0.21	0.20
Ddeep1	43.1	79.7	8.00	30.1	5.53	1.22	5.39	0.64	3.43	0.63	1.90	0.25	0.25
Ddeep2	53.2	103	10.5	40.2	7.34	1.43	6.92	0.82	4.09	0.71	2.05	0.26	0.25
Esurf1	23.1	46.4	4.90	18.7	3.55	0.92	3.48	0.43	2.36	0.44	1.33	0.18	0.18
Esurf2	33.0	63.7	6.70	25.8	4.84	1.02	4.74	0.58	3.11	0.56	1.66	0.22	0.21
Etna lava ^a	58.2	113	13.3	48.8	8.74	2.91	9.40	0.93	5.43	nd	2.51	0.33	0.31
Etna plumes ^b	147	415	33.9	117	19.9	8.54	25.5	3.50	17.4	nd	7.95	1.20	1.31
Vulcano lava ^c	53.0	101	nd	nd	7.31	1.86	nd	0.76	nd	nd	nd	nd	nd
Stromboli lava ^d	44.4	96.9	11.5	44.0	8.59	2.32	7.15	1.06	5.31	nd	2.67	0.36	0.37
Upper continental crust ^e	30.0	64.0	7.10	26.0	4.50	0.88	3.80	0.64	3.50	0.80	2.30	0.33	0.32
Lower continental crust ^e	11.0	23.0	2.80	12.7	3.17	1.17	3.13	0.59	3.60	0.77	2.20	0.32	0.29
Refinery catalyst (fresh) ^f	7613	4493	1069	1718	161	9.96	367	7.96	17.3	1.46	8.78	0.28	0.32
Refinery catalyst (spent) ^f	10,019	770	502	716	157	5.7	493	5.70	22.0	nd	6.50	0.40	0.10
FCC stack ^g	865	76.3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Atmospheric particles (PM 10) ^h	2.10	0.85	0.14	0.33	0.05	0.02	0.10	0.01	0.05	0.01	0.03	nd	nd
Atmospheric particles (PM 2.5) ^h	1.48	0.55	0.09	0.22	0.04	0.02	0.09	0.01	0.05	0.01	0.04	nd	nd
Metahornblendite ⁱ	9.63	22.3	3.34	15.5	3.73	1.15	3.50	0.54	3.25	0.57	1.53	0.24	0.19
Amphibolite ⁱ	35.5	70.4	8.20	33.2	7.12	2.50	7.15	1.10	6.08	1.10	2.92	0.40	0.36
Amphibolitic ⁱ	28.7	57.2	6.58	26.2	5.70	1.47	5.91	0.98	5.92	1.15	3.30	0.48	0.49
Gneiss ⁱ	34.4	66.6	7.31	27.2	5.34	1.36	4.89	0.74	4.16	0.79	2.27	0.34	0.36
Leucosome ⁱ	25.0	50.0	5.54	20.5	3.96	1.46	3.56	0.56	3.04	0.56	1.65	0.24	0.26
Reddish limestone ^j	6.15	5.10	1.24	4.10	0.90	0.20	0.68	0.09	0.82	0.14	0.44	0.07	0.06
Pale-pink limestone ^j	8.75	14.6	2.09	6.85	1.34	0.29	1.27	0.18	1.28	0.24	0.7	0.10	0.09
Grayish limestone ^j	1.75	2.05	0.28	1.25	0.24	0.06	0.29	0.05	0.21	0.04	0.15	0.02	0.02
Marble ^j	3.40	3.30	0.69	2.50	0.61	0.14	0.50	0.09	0.47	0.14	0.33	0.06	0.06

^a From Calabrese et al. (2011).

^b From Gauthier and Le Cloarec (1998).

^c From Del Moro et al. (1998).

^d From Landi et al. (2006).

^e From Taylor and McLennan (1985) and McLennan (2001).

^f From Kulkarni et al. (2006).

^g Sánchez de la Campa et al. (2011).

^h From Moreno et al. (2008) (in ng/m³).

ⁱ From Messina (unpublished).

^j From Messina et al. (2004).

In order to have a better insight on the origin of soil REEs, we constructed their distribution patterns relative to several substrate rocks (Fig. 5 and Table 7). Relative to UCC, most of soils are characterized by an enrichment in LREEs and MREEs relative to HREEs, except the soils of site A which show flat patterns. The explanation of the slight enrichment in MREEs in soils B, C, and D can be a precipitation of phosphate complexes in the soils during their formation, or it could be an heritage from parent rocks. There is also a slight positive anomaly in Gd and Eu for all soils except E surface soils. Relative to the REEs in Etna and Stromboli lavas, the soil normalized REE patterns are rather flat (Fig. 5) with a slight negative anomaly in Eu but a positive anomaly in Gd. Such distribution patterns indicate a similar source of REEs in soils and substrates. The soils normalized relative to Aspromonte Unit Peloritani rocks exhibit a similar trend of patterns as for normalization relative to UCC with ratios close to 1 indicating a close relationship of these soils with metamorphic background rock. In addition, patterns show similar trends for all surface soils except for surface soils from site A showing a slight enrichment in HREEs which would indicate a different origin of REEs in these samples. The REEs normalized relative to the limestone (not represented) exhibit very high ratios (>4) and a

decreasing pattern from LREEs to HREEs, which indicates a weak correlation between soils and limestone.

5.4. Trace elements enrichment

The enrichment factors (EF) calculated for trace elements were considered to assess soil pollution. The calculation of EFs is based on normalization of the element concentration in the sample, relative to its concentration in a reference material taken from the literature, or from analyses of local representative sediments or rocks, which allows a more precise estimation of elements enrichment (Duplay et al., 2012). The normalization requires also considering a geochemical marker of the dominant natural mineralogical phase (Szefer et al., 1998).

Furthermore, the variation coefficient of the reference element must be low.

Trace elements enrichment factors in Milazzo soils were calculated according to Eq. (1)

$$EF = \left(\frac{[CX_{\text{sample}}]/[CR_{\text{sample}}]}{[CX_{\text{ref}}]/[CR_{\text{ref}}]} \right) \quad (1)$$

where CX and CR refer respectively, to the concentrations of the element of interest in the sample, and to the concentration of the conservative element in the reference material (Loska et al., 1997; Romero et al., 2013). The contamination is identified for $EF > 2$ (Szefer et al., 1998). The reference conservative element used in this study is Th, because it is commonly used in volcanic aerosol studies (Vié le Sage, 1983; Varekamp et al., 1986; Crowe et al., 1987; Allard et al., 2000; Moune et al., 2006, 2010; Calabrese et al., 2011).

Since statistical studies on major and REE elements showed firstly the main influence of AsU rocks, secondly of limestones, and possibly of Etna lava in the compositions of soils, the enrichment factors were calculated using these three local reference materials for normalization. In addition, a global reference was considered: the upper continental crust (Taylor and McLennan, 1985; McLennan, 2001). The metamorphic reference rock consists in an average chemical composition of the Aspromonte Unit Peloritani Mountain metamorphic rocks (from Macaione et al., 2010, 2012; Messina et al., in preparation). The reference limestone consists in an average composition of local carbonates (from Messina et al., 2004a,b). The local lava reference is a mean composition of Etna rocks given by Calabrese et al. (2011).

The calculations of EF relative to the upper continental crust and the AsU rocks show the same trends with enrichment in As and Pb in most soils ($EF > 2$) especially in soils near Milazzo industrial zone and in surface soils near the coastal road and camping area (Fig. 6). The highest EF values for As are observed in soils around Milazzo industries (A soils), and for Pb in soils near the coastal road (E soils). The calculations relative to Etna lava give higher enrichment factors than for the UCC and AsU rocks, with enrichment in Pb in surface soils, especially in A and E surface soils. The enrichment factor for As could not be calculated due to lack of data. The calculations of EF relative to the limestone show an enrichment lower for As, the highest values being observed in soils A and B. Moreover, the general trend in all calculations was the highest enrichments in Zn in surface soils of site C, and a lower enrichment in Ni in soils of site B. In addition, there is only a slight, or no enrichment in V, and no enrichment in Cd (not represented). Concerning Cr, only calculations relative to Etna lava show enrichment, with the highest EF values observed for B soils.

In summary, all sites are more or less strongly enriched in trace elements. Sites near Milazzo industrial area show the strongest enrichments in As and Pb, and Zn is significantly enriched in soils of site C. These findings indicate a contribution of an anthropogenic source in soils during their evolution.

6. Discussion

Based on geological data, PCA of major elements, and on REE patterns, most of soil's compositions could be firstly related to the AsU magmatic rocks, and secondly to the AsU carbonates forming the substrates of the soils. Distribution patterns also indicated a source of REEs in soils related to volcanic rocks. Moreover, surface soils from sites C and A, exhibit peculiar REE patterns indicating enrichments of LREEs in soils from site C (Fig. 5), and of HREEs in soils near Milazzo industries (site A). In addition, enrichment in Gd relative to UCC, AsU rocks, and Stromboli lava, was observed in all soils. Such enrichment in Gd has already been observed by Zhu (1999) in soils from a site suspected of being polluted, and in a polluted river (Kulaksiz and Bau, 2011). The enrichment factor calculations indicated that there is a contamination in As, Pb in all soils and locally a low enrichment in Ni and Zn. There is also evidence of a very low contamination in Cr and V.

Several sources, natural or anthropogenic as described above (Section 3), may be at the origin of the trace elements contamination recorded in the soils of Milazzo peninsula. The Mount

Etna volcanic aerosols are known to be enriched in trace elements such as Cu, Zn, Se, Hg, Cd and Pb (Andres et al., 1993). Moreover, the discharge from Mount Etna in the Mediterranean atmospheric environment is comparable for Cd, Hg, Cu and Zn to the anthropogenic release, but insignificant for Pb, and predominant for Se (Buat-Ménard and Arnold, 1978). Concerning the anthropogenic activities (Milazzo refinery and oil-burning electric plant), data on air emissions showed that high amounts of Fe, V, Ni, Cr and Zn are emitted. At Gela (Italy, Sicily) and Terragona (Spain) petrochemical plants, high correlations between emissions of vanadium and nickel, arsenic and selenium, and lead and tin, were linked to refinery processes and fossil combustibles (Bosco et al., 2005; Nadal et al., 2009).

Thus, the enrichments in trace elements recorded in soils may be indicators of the refinery and electric plant activities' atmospheric emissions. According to Kitto et al. (1992) the most reliable indicators of refinery emissions are the enrichments in LREEs and the high La/Sm ratios on fine ambient particles. This is because a common material employed in petroleum refinery and petrochemical manufacturing, is zeolite which is enriched in REEs. Zeolite is used as FCC catalyst and which particles may partly be released to the atmosphere during catalytic cracking (Sánchez de la Campa et al., 2011). Kitto et al. (1992) and Kulkarni et al. (2006) showed that refining and petrochemical catalytic cracking operations can be predominantly responsible in the REE enrichment of ambient fine particles. Moreover, ratios between REEs analyzed in atmospheric fine particles around FCC atmospheric emissions indicated anomalies in La concentrations because this element is released from the fluid catalytic converters (Moreno et al., 2008, 2012). All the fluid cracking catalysts used in United States, Japan and Europe, also exhibit significant contents in Cr, V, Ni, Ce, Gd and Nd. Thus, light REE contaminations in sediments, soils and atmospheric particles may be explained by deliveries of La-based catalysts in petroleum refineries through atmospheric fallouts (Olmez et al., 1988; Kulkarni et al., 2006; Moreno et al., 2008).

Moreover, metals and metalloids are naturally present in crude oils or may be added during refinery processing (Lienemann, 2005; Sánchez et al., 2013). Metals such as V, Ni, and Fe, are all present at high concentrations (Dunning et al., 1960; Caumette et al., 2009). Other elements such as Pb, Ba, Sn, Ag, Co, Cu, Mo, Ti, Zn, Hg and As are also present at lower concentrations (Ali and Abbas, 2006; Duyck et al., 2007). All these elements have the tendency to concentrate in the residual fuel oil fraction during refining (Ball et al., 1960). Thus, elements present in petroleum products and derivatives, such as As, Cd, Co, Cu, Hg, Ni, Pb, S, and V, are recognized to induce environmental pollution. The Milazzo electric plant uses heavy fuel oil from the refinery, for its processes. According to Olmez and Gordon (1985) some catalyst materials may be present in oil produced by refineries because emissions from oil-fired plants also have high La/Sm ratios, typically about 30. Moreover, emissions of Cr and Ni also occur from plants burning heavy fuel oil.

In order to try identifying the sources of trace elements enrichments in Milazzo soils, several diagrams were constructed using the above mentioned trace elements encountered in Etna and Stromboli aerosols, and in emissions to the air of the refinery, and of the electric plant. The selected elements were as follows: La, V, Ni, Pb and Cr. In addition, REE ratios such as La/Sm, La/Ce, La/Gd and La/Nd, were also considered. In these diagrams we plotted values of soils, of local substrate rocks (AsU magmatic rocks and limestones, Etna and Stromboli lava), Upper Continental Crust (UCC), and depending on available data, of spent refinery FCC catalysts (from Kulkarni et al., 2006), of FCC stack particles (from Sánchez de la Campa et al., 2011), and of atmospheric particles around a refinery (from Moreno et al., 2008, 2012).

From the relationship between La and Cr (Fig. 7) and from the ratios La/Gd and La/Ni (Fig. 8) it appears that most soils plot

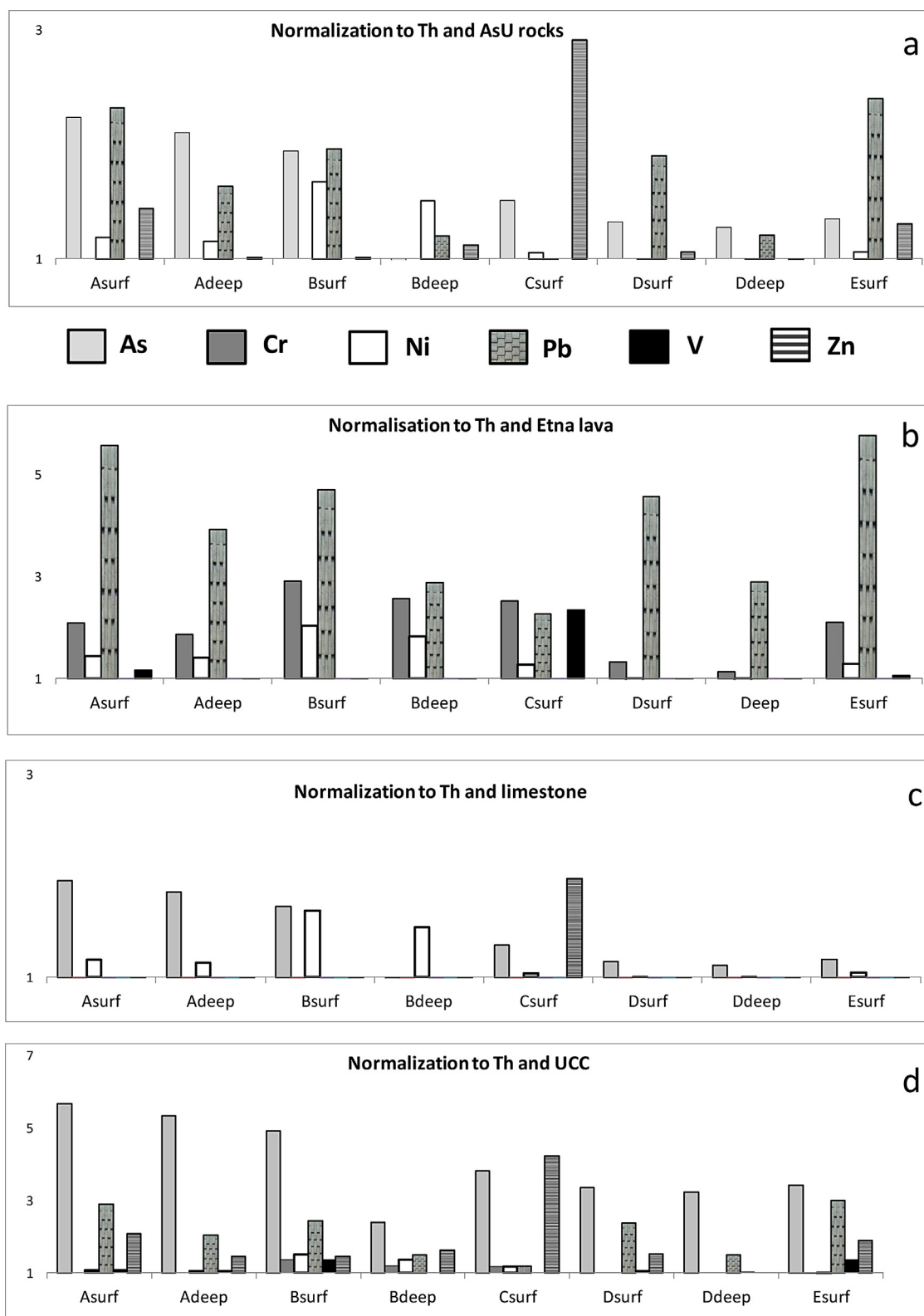


Fig. 6. Enrichment factors of trace elements in Milazzo Peninsula soils, calculated using as reference (a) Aspromonte Unit Peloritani rocks (from Messina, unpublished data); (b) Etna lava (from Calabrese et al., 2011), (c) limestone (from Messina et al., 2004a,b), and (d) the continental upper crust (UCC; Taylor and McLennan, 1985; McLennan, 2001).

around substrate rocks, some of them along a line directed on one side toward AsU rocks and the limestones, and on the other side toward the FCC stack or the spent zeolite catalyst. Moreover, on Figs. 9 and 10, soils are clearly apart from the substrate rocks, along

a line directed toward the spent catalyst and the atmospheric particles, which indicates an influence in the trace elements distribution of the soils samples, greater for the catalyst end member than for the natural substrates. Thus, V, Cr, Ni, although very little enriched

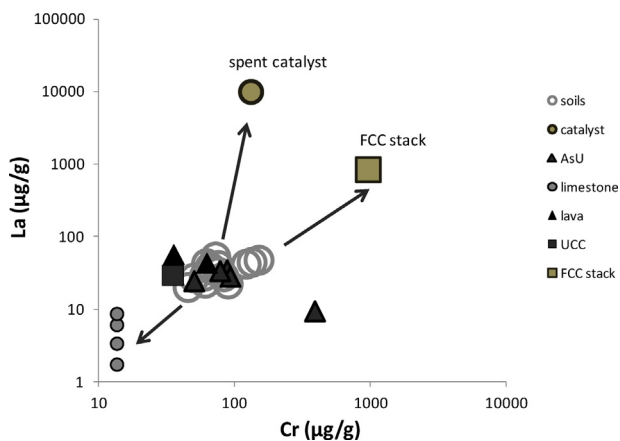


Fig. 7. Milazzo soils, regional background rocks (Peloritani metamorphic rocks and carbonatic sediments, volcanites and volcanoclastites), continental upper crust (UCC), and refinery catalyst (zeolite) and stack, plotted in a La vs Cr diagram showing a mixing between probable REE sources i.e. upper crust, limestone and refinery catalyst.

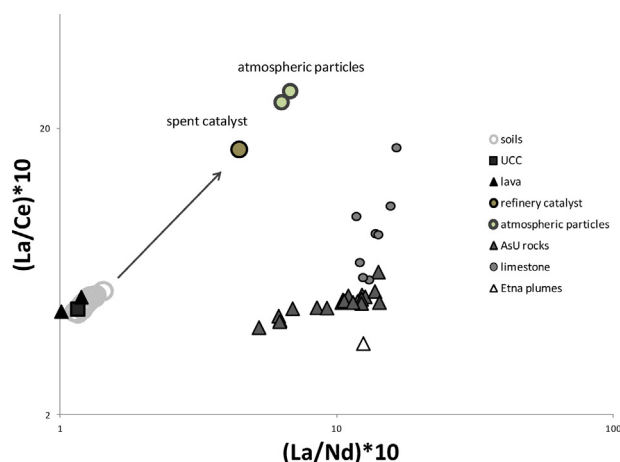


Fig. 10. Milazzo soils, regional background rocks (Peloritani metamorphic rocks and carbonatic sediments, volcanites and volcanoclastites), continental upper crust (UCC), refinery catalyst (zeolite) and atmospheric particles around refinery plotted in a La/Nd vs La/Ce diagram.

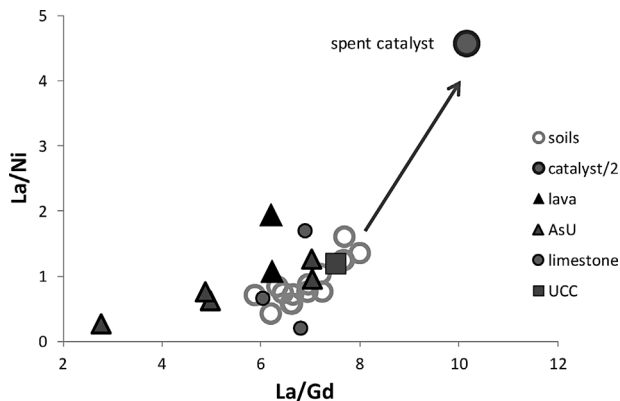


Fig. 8. Milazzo soils, regional background rocks (Peloritani metamorphic rocks and carbonatic sediments, volcanites and volcanoclastites), continental upper crust (UCC), and refinery catalyst (zeolite) plotted in a La/Ni vs La/Gd diagram showing a mixing between probable REE sources i.e. upper crust, chondrite, lava, and refinery catalyst.

in soils, appear to be indicators of anthropogenic emissions in these soils. There may be other sources of contamination of trace elements as suggested by Fig. 11 where soils are placed along a line toward an unknown end-member, clearly far from representative

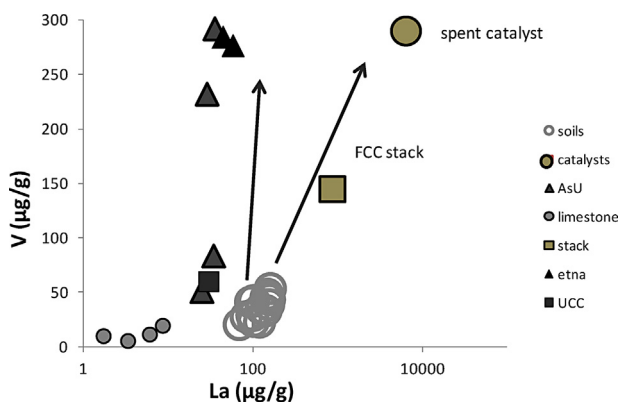


Fig. 9. Milazzo soils, regional background rocks (Peloritani metamorphic rocks and carbonatic sediments, volcanites and volcanoclastites), continental upper crust (UCC), refinery catalyst (zeolite) and stack, plotted in a V vs La diagram.

points of the spent catalyst, or of FCC stack. Therefore, the enrichment in Zn recorded in soils of site C seems to be partly related to an anthropogenic activity different from the refinery or electric plant activities. In the diagram (not represented) of Pb vs V, the soils are again placed apart from the substrate rocks, toward the AsU rocks and lava on one direction, and toward an unknown end member on another direction. The concentrations in Pb were not available for the spent catalyst and for FCC stack, which did not enable to identify the possible catalyst end member. The enrichment factor values showed that soils are enriched in Pb; however, the source of the contamination could not be identified. It is nevertheless highly probable that refinery activities and oil-burning plant contribute to the contamination of Pb in the soils.

On the base of the different correlations highlighted in the diagrams, it is possible to identify potential sources of enrichments in trace elements in Milazzo soils, which are emissions from the refinery and oil-burning plant, volcanic aerosols, and an unidentified activity.

A mixing equation with two end members (FCC and Etna) was used to evaluate the contribution from these two identified anthropogenic sources in soils. Eq. (2) is as follows: $(2)F \times C1 \times R1 + (1 - F) \times C2 \times R2 = Cs \times Rs$ With F : fraction of end-member1 in the soil; $(1 - F)$: fraction of end-member2 in the soil; $C1$, $C2$ and Cs : concentration of elements in end-member 1,

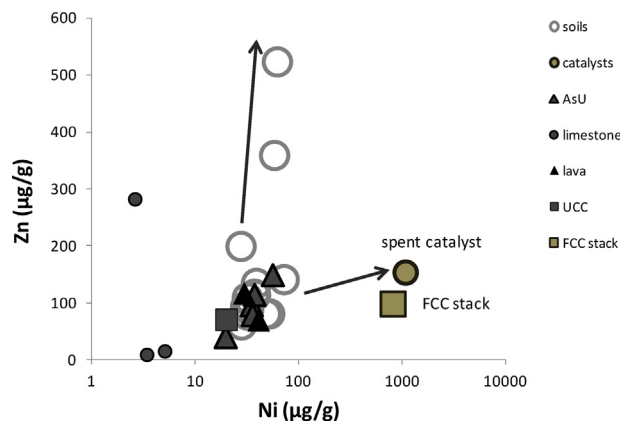


Fig. 11. Milazzo soils, regional background rocks (Peloritani metamorphic rocks and carbonatic sediments, volcanites and volcanoclastites), continental upper crust (UCC), refinery catalyst (zeolite) and stack, plotted in a Zn vs Ni diagram.

2 and soil respectively. The concentrations in soil were corrected from the fraction originating from weathering of the parent rock; R1, R2 and Rs: ratio between REEs in end member 1, 2 and soil respectively.

The selected ratio for the present calculation was La/Nd. The calculation was established for Zn in soil C. The calculation, based on a binary mixing in the anthropogenic fraction of soils, showed that about 16% of Zn concentrations in these soils can be attributed to refinery catalyst inputs, and about 84% to Etna plumes inputs. Other calculations using La/Ce and Ni and Cr showed aberrant values that indicate a contribution of other sources in Ni and Cr. These sources were not identified during this study.

7. Conclusion

Milazzo Peninsula soils formed on diverse metamorphic, sedimentary and volcanic substrates which may have a mixed influence on their chemical composition. The study of trace elements chemistry and particularly distribution patterns of REEs in Milazzo soils showed that a part of trace elements abundances are related firstly to the natural metamorphic rocks rather than sedimentary or volcanic background rocks.

Anthropogenic activities in Milazzo, such as refinery industry, oil-burning electric plant, waste combustion and road traffic, release atmospheric fine particles which may contaminate soils, thus contributing to their trace elements composition. Indeed enrichment factors calculations showed anomalies in As, Pb, Zn, Ni and Cr. Moreover, normalized REE patterns show enrichments in LREEs and anomalies in Gd which suggest contamination by anthropogenic activities. Fluidized-bed catalytic cracking (FCC) operations are a significant source of emissions to the air which take place on a large scale. The most important industrial metal emissions are V, Fe, Ni, and Pb. These metalliferous aerosols are typically extremely fine in size and therefore potentially bioavailable when deposited on the soil. Moreover, these airborne particles are enriched in LREEs especially in the vicinity of petrochemical industries.

Trace element concentrations of soils were plotted in diagrams and compared to those of substrate rocks and REE enriched FCC spent catalysts, FCC stack or atmospheric particles around refinery from the literature. The La/Ni vs La/Gd, and La/Ce vs La/Nd diagrams allow recognition of the FCC source of contamination, characterized by enrichments in La, Ni and Gd. Plots of Zn vs Ni and Pb vs V suggest that another source of contamination, which could not be identified, contributes to soil enrichment in Zn and Pb.

Our results show that the events of air pollution specifically related to emissions from the refinery can be identified in soils by using ratios between REEs such as La/Gd on one hand and trace elements such as Ni on the other hand. Although vanadium is recognized as a major constituent in atmospheric emissions of refineries, our results did not reveal any notable influence in enrichment of Milazzo soils. Thus, V may have a limited usefulness as tracer of refinery. Moreover, multiple sources in airborne particles containing the same trace elements complicate interpretation, as observed for Zn and Pb.

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