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Total and fraction content of elements in volcanic soil: Natural or anthropogenic derivation

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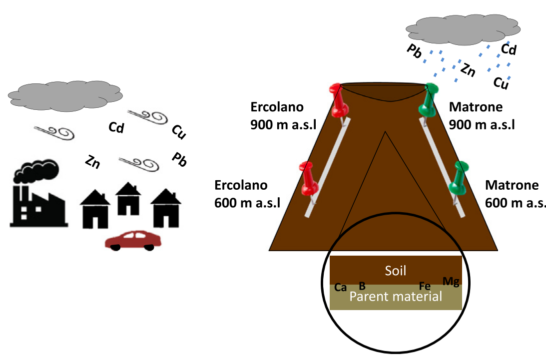
HIGHLIGHTS

- The main derivation of elements in andosols was investigated.
- Soil element fractions and site specific characteristics were related.
- Sequential extractions of elements and multivariate statistics were performed.
- Only Cd, Cu, Pb and Zn out of twentytwo elements have also anthropogenic derivation.
- Acidic-soluble fraction were linked to lava age and reducible or oxidasable to plant cover.

GRAPHICAL ABSTRACT



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ABSTRACT

Soil element composition derives from parent material disaggregation during pedogenesis and weathering processes but also by anthropogenic inputs. Elements are present in soils in different chemical forms that affect their availability and mobility. The aim of the study was to evaluate the main derivation, natural or anthropogenic, of elements in the soils of the Vesuvius National Park (a natural environment strongly affected by human impacts). Besides, the effects of age of the lava from which soils derive, different vegetation covers, traffic fluxes along the two roads connecting the Vesuvius crater and altitudes of the sites on the pseudo-total element concentrations and on their contents in different fraction of soil were investigated. To reach the aims, BCR (Bureau Commun de Référence) sequential extraction was performed in order to determine the distribution of elements into: acid-soluble, reducible, oxidizable and residual fractions. The relationship between the main environmental media and distribution of elements was discussed using non-metric multidimensional scaling (NMDS). The findings showed that, with the exception of Cd, Cu, Pb and Zn that would seem to derive also from human activities, the other investigated elements (Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, La, Mg, Mn, Na, Ni, P, Pb, Si, Ti, V, W and Zn) mainly had a natural derivation. Among the investigated elements, only Cd could represent a potential high risk for the studied andosols. The highest element accumulations in the soils at low altitude could be attributable to an integrated effect of plant cover, vicinity of downtowns and traffic flux. The acid-soluble fraction of elements appeared more linked to lava age; the reducible and oxidizable ones to plant cover; the residual one to the chemical composition of the parent material that gave origin to the soils.

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1. Introduction

Soil element composition derives from the integration of local conditions such as geology, climate and hydrology, and it strongly depends on parent material disaggregation during pedogenesis and weathering processes (De Nicola et al., 2003; Martínez Cortizas et al., 2003). Nevertheless, also external factors, such as anthropogenic activities, directly affect the element composition of soil surface layer (Buccianti et al., 2015). In fact, during the last years, human activities (*i.e.* tourism, agriculture, urbanization and industrialization) have caused an increase of major and trace elements in soils (Wiseman et al., 2013). In addition, human activities are confirmed as primary sources of elements in the air gaseous phase or particulates that can reach the surface soils through dry or wet depositions (De Nicola et al., 2003; Werkenthin et al., 2014). For instance, As, Se, Sb and Hg, showing high affinity for the volatile phase, can be aerial transported and are often associated to long distance contamination (Buccianti et al., 2015). As a result, the human activities can determine a significant modification of the elemental status of the soils. Therefore, the identification of the main derivation of a single soil element by geogenic or anthropogenic sources could be difficult especially originate from both (Buccianti et al., 2015; Cicchella et al., 2005).

Elements are mainly present in soils as acid-soluble, carbonate-associated, Fe-Mn oxide-associated and organic-associated forms (Fernández-Ondoño et al., 2017). Besides, some elements can be strongly bound to silicates, representing the residue form, and cannot be available from organisms (Denaix et al., 1999; Tanneberg et al., 2001). Recently, in order to evaluate element fate in soil system, element mobility along the soil profile and the potential element bioavailability or toxicity, the identification of the element amount in different soil geochemical phases and not only the total content is required (Adamo et al., 2007). Soil element fractionation, distribution and mobility depend not only on chemical composition of the parental material (Maeda et al., 2003), but also on various chemical and physical characteristics of soil, such as pH, cationic exchangeable capacity, water and organic matter contents (Degryse et al., 2009; Peijnenburg et al., 2007). By now, studies dealing with associations of elements in the various fractions in andosols are poorly present in the scientific literature (Hernandez-Moreno et al., 2007).

In this framework, the Vesuvius National Park is a good environmental model to provide a contribution to the present knowledge about the evaluation of natural or anthropogenic derivation of some elements in the soils. In fact, the soils of the Vesuvius are mainly andosols or present andic character (Arnalds et al., 2007) and, deriving by pyroclastic materials (Shoji and Ono, 1978), are rich in neoformed amorphous aluminosilicates and organo-mineral compounds that have high capacity to bind elements (Eswaran et al., 1993; Tanneberg et al., 2001). It is been reported that the chemical species composition of the Vesuvius substrates is a function of the age of the lava and pyroclastic materials and of the time and degree of alteration. In fact, Belkin et al. (Belkin et al., 1998) have reported that silicate-melt inclusions showed a decrease of some components such as total alkalis, SO_3, Cl, Li, B and Sr and a decrease of Zr and Y passing from samples of lava of 25,000 yr B.P. to 1631–1944 CE The Vesuvius is located at few kilometres from Naples, one of the most populated cities in Campania (Southern Italy) where various and intensive human activities occur, emitting pollutants in the atmosphere (*i.e.* intensive vehicular traffic, small industries, domestic heating). In addition, itself is a touristic destination of thousands of people per year who reach the crater by any kinds of vehicles.

The aims of the study were to evaluate the main derivation (natural or anthropogenic) of elements in the soils of the Vesuvius National Park and their behaviour in the soils. The identification of the main source of contaminants can be useful to contain their emissions in order to preserve and/or restore the soils quality inside the park. To reach the aims, the element fractions were detected according the BCR (Bureau Commun de Référence) sequential extraction (recommended by the Commission of the European Communities, 1987, and modified by (Ure et al., 1993)) in order to separate the elements into: acid-soluble, reducible (associated to Fe-Mn oxides), oxidizable (associated to organic matter content and sulphides) and residual fractions (associated to primary and secondary well-crystallized minerals). The acid-soluble fractions are considered as bioavailable, the reducible and oxidizable fractions can be potentially bioavailable, whereas the residual fraction is considered not available for organisms (He et al., 2006; Ma and Rao, 1997; Rodríguez et al., 2009). In addition, the element pseudo-total content (calculated as the sum of the content of the four fractions) was also used. Other aim of the research was to investigate the relationships between the element pseudo-total or fraction contents to different: i) age of the lava from which soils derive, ii) vegetation covers, iii) traffic fluxes along the two roads (one accessible over the year long and the other one accessible only for six months a year) connecting the Vesuvius crater, iv) microclimate conditions, considering sites at two altitudes (approximately 600 and 900 m a.s.l.).

2. Materials and methods

2.1. Study area

The Vesuvius National Park was established in 1995 and is located 12 km SE of Naples. It covers an area of 8482 ha and contains Mt. Somma (maximum height: 1132 m a.s.l.), the original volcano, and Mt. Vesuvius (maximum height: 1281 m a.s.l.), originated from 79 CE eruption. The soil of Mt. Vesuvius are classified as Lepti-Vitric Andosols according to the FAO soil classification (Di Gennaro and Terribile, 1999) and the vegetation is constituted by native Mediterranean vegetation based in trees (such as holm oak, maple, alder) and shrubs (such as myrtle, laurel, viburnum, brambles, brooms), but are present some species such as black pine and black locust (De Marco et al., 2013; De Nicola et al., 2003). In addition, especially on soils of recent origin and on emergent rocks inside mature soils, lichens and mosses were also present.

Vesuvius is one of the most studied volcanoes because it has been active for about 25,000 years and for the alternation of explosive and effusive activities. At the present, Vesuvius is in a quiescent phase and the last eruption started in 1913 and finished with the paroxystic phase in 1944 (Rolandi, 2010). Because of the various eruptions, the slopes of the Vesuvius present diversified landscapes as result of different lava flows. In the last decades, Vesuvius is subject to intensive touristic flux. Ercolano road was, for a long time, the unique road to reach the crater, but in 2012 also Matrone road was opened to reach the crater only by old military vehicles and only from April to October.

2.2. Soil sampling

In this concern, the study focused on the soils in proximity of the two roads that lead to the Vesuvius cone: Matrone (M) and Ercolano (E). At high altitude (H), the soils derive from the 1937 and 1891–1893 eruptions, respectively at Matrone and Ercolano roads, whereas at low altitude (L), the soils in proximity of Matrone road derive from the 1906 eruption whereas those in proximity of Ercolano by the 1944 one (Table 1).

In order to highlight probable differences according the traffic flow and microclimatic conditions, on November 2016 a total of eight sites were selected along each road (Fig. 1): four sites were selected at high altitude (approximately, 900 m a.s.l.) and four at low altitude (approximately, 600 m a.s.l.). At each altitude, two sites were selected at each edge of the road and two at approximately 30 m from the previous towards the vegetation (Table 1). At each site, five subsamples of surface soil (0–10 cm) were collected, after litter removal, and mixed to obtain a homogeneous sample, in order to perform the physico-chemical analyses.

2.3. Physico-chemical analyses

All the physico-chemical analyses were carried out on triplicates of sieved (<2 mm) soil samples according to the methods reported by