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Evaluation of tourism impact on soil metal accumulation through single and integrated indices

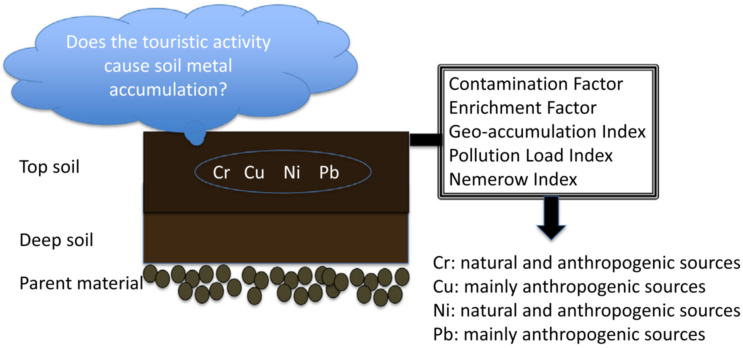
Valeria Memoli [a], Francesco Esposito [a], Speranza Claudia Panico [a], Anna De Marco [a], Rossella Barile [b], Giulia Maisto [a],*

[a] *Dipartimento di Biologia, Università degli Studi di Napoli Federico II, Via Cinthia, 80126 Napoli, Italy*
[b] *Parco Nazionale del Vesuvio, Via Palazzo del Principe c/o Castello Mediceo, 80044 Ottaviano, NA, Italy*

HIGHLIGHTS

- Soils of remote areas exceed the baseline level of metals resulting contaminated.
- Assessing the main activity responsible of soil metal accumulation is essential.
- Single and integrated indices are useful to assess soil accumulation degree.
- Cr and Ni had both natural and anthropogenic origins, Cu and Pb anthropogenic.
- Soils showed high phytotoxicity, but low ecological risk due to metals.

GRAPHICAL ABSTRACT



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ABSTRACT

Recently, surface soils of remote or protected areas, that receive pollutants from the surroundings or in situ activities through dry and wet deposition, exceed the baseline content of heavy metals. In the last decades, the use of single and integrated indices is a powerful tool to process, analyze and convey information about metal accumulation degree for decision makers to better manage protected areas. Single indices provide information about only one metal, whereas the integrated ones give a holistic evaluation. The aim of the research was to assess the temporal trends of three single (Contamination Factor, Enrichment Factor and Geo-accumulation Index) and two integrated (Pollution Load Index, Nemerow index) indices in order to evaluate if the touristic impact caused soil metal (Cr, Cu, Ni and Pb) accumulation. In autumn 2016 and in spring 2016 and 2017, the surface soils (0–10 cm) were collected at eight sites inside the Vesuvius National Park (Southern Italy), characterized by intense tourism from spring to autumn. The metal concentrations were measured in the soils and used to calculate the indices. In addition, the Ecological Risk Factor was calculated and the phytotoxicological assays were performed. The findings showed that the surface soils of the Vesuvius National Park were polluted by Cr, Cu, Ni and Pb, according to both single and integrated indices. The touristic impact would seem to be the main cause of soil metal accumulation, as the highest values of the calculated indices were detected for samples collected at the end of the touristic season and the lowest at the beginning of the touristic season. Anyway, Cu and Pb would seem also to derive by ex situ anthropogenic sources, whereas Cr and Ni also by natural sources, such as spontaneous fires and substrate weathering. Finally, the soils showed phytotoxic effects and low ecological risks.

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* Corresponding author.
E-mail address: g.maisto@unina.it (G. Maisto).

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1. Introduction

Soil heavy metal pollution is a severe problem in many parts of the Earth. In fact, heavy metals, due to their bioaccumulation, toxicity and persistence (Saha and Panwar, 2014; Abdelhafez et al., 2015) negatively affect the welfare of organisms (Fernández et al., 2018).

Heavy metal pollution is more evident in soils of industrial and urban areas that are directly and intensively exposed to these pollutants. Anyway, recently, also surface soils of remote or protected areas exceed the baseline content of heavy metals deriving by the parent material weathering processes (Alloway, 1995; Martínez Cortizas et al., 2003; dos Santos et al., 2017). In fact, these soils are exerted by in situ activities, such as overexploitation of the environment or excessive tourism, and also receive pollutants in gaseous or aerosol forms (Gray et al., 2003; Staszewski et al., 2012; Pan and Wang, 2015; Shen et al., 2016) deriving by anthropic activities of the surrounding areas resulting to be slightly or strongly contaminated (Mazurek et al., 2017; Memoli et al., 2019). In this concern, the distinguishing of heavy metal geochemical background from anthropogenic inputs is essential to assess the contamination degree of soils inside protected areas (Rivera et al., 2015).

The use of pollution indices is a powerful tool to process, analyze and convey information about metal contamination degree for decision makers, managers and technicians in order to better manage protected areas (Kowalaska et al., 2016; Gong et al., 2008). The commonly used pollution indices are divided into single and integrated (Gong et al., 2008); the former provide information about only one metal, whereas the latter about more than one metal giving a holistic evaluation on the contamination degree of the soil.

Other useful instruments are the assessment of the ecological risk and the evaluation of the ecotoxicity. Since the last decades, the environmental risk index proposed by Håkanson (1980) is widespread used for sediments and soils. Instead, among the ecotoxicological assays, the phytotoxicity ones are commonly used for soils, as plants are very sensitive to the properties of the whole soil matrix and soil extracts, providing information about short- and long-term effects (Dudzik et al., 2010; Memoli et al., 2017; Memoli et al., 2018a).

The aim of the research was to evaluate the temporal variations of soil accumulation of Cr, Cu, Ni and Pb. These metals are good markers of vehicular traffic (Esposito et al., 2019) that, in the investigated area, is strictly linked to tourism, as the two roads leading to the volcano crater are very frequently crossed during the touristic season. To reach the aim, single (such as Contamination Factor - CF, Enrichment Factor - EF, Geo-accumulation Index - I_{geo}) and integrated (such as Pollution Load Index - PLI, Nemerow index - NI) indices were calculated.

2. Materials and methods

2.1. Study area and soil sampling

The study was carried out inside the Vesuvius National Park, characterized by Mediterranean climatic conditions with dry summers and rainy autumns and winters (mean annual temperature: 13.2 °C; annual precipitation: 960 mm).

The Vesuvius National Park was established in 1995 (Italian law D.P.R. 5/6/95) and is located at about 12 km SE of Naples. It contains Mt. Somma, the original volcano, and Mt. Vesuvius originated from 79 CE eruption. After the last eruption that occurred in 1944, Mt. Vesuvius is in a quiescent phase. Around the base of the Vesuvius National Park are located thirteen municipalities with wide urban, industrial and agricultural areas that globally host approximately 352,000 people (ISTAT, 2005). In addition, the Vesuvius National Park undergoes an intense tourism; in fact, approximately, 600,000 visitors per year can be counted inside the park during the touristic season occurring from April to October (www.parconazionaledelvesuvio.it).

The investigated soils are classified as Lepti-Vitric Andosols according to the FAO soil classification (Di Gennaro and Terribile, 1999). The soils were collected at eight sites (Table 1) under pine specimens: four collected at low altitude (L1, L2, L3 and L4), and four collected at high altitude (H1, H2, H3 and H4). In Spring 2016 (S_16), Autumn 2016 (A_16) and Spring 2017 (S_17), at each site, six 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 and phytotoxicological analyses. The soils were collected in Spring and Autumn in order to evaluate the impact of tourism on soil metal accumulation, as the touristic season mainly occurs from April to Autumn. In fact, the soil analyses performed on samples collected in Spring 2016 provided information linked to the beginning of the touristic season, those performed on samples collected in Autumn 2016 provided information linked to the end of the touristic season, and, finally, those performed on samples collected in Spring 2017 provided information linked to the end of the period without touristic impact.

2.2. Physico-chemical analyses

In laboratory, the soil samples were sieved (2 mm) in order to measure pH, water and organic matter contents and total of Cr, Cu, Ni and Pb concentrations. pH was measured in a soil:distilled water (1:2.5 = v:v) suspension by electrometric method; the water content (WC) was determined gravimetrically drying fresh soil at 105 °C until constant weight. The soil organic matter content (OM) was calculated multiplying the C_{org} concentrations by 1.724 (Pribyl, 2010). C_{org}, was measured by gas-chromatography (Thermo Finnigan, CNS Analyzer) on dried and grounded (Fritsch Analysette Spartan 3 Pulverisette 0) samples previously treated with HCl (10%).

Total Cr, Cu, Ni and Pb concentrations were measured on dried and grounded samples previously digested with a mixture of HF (50%) and HNO_3 (65%) at a ratio of 1:2 (v:v) in a micro-wave (Milestone mls 1200 - Microwave Laboratory Systems). Their concentrations were measured by atomic absorption spectrometry (SpectrAA 20 - Varian), via graphite furnace. Accuracy was checked by concurrent analysis of standard reference material (BCR CRM 142R - Commission of the European Communities, 1994) and recoveries ranged from 86 to 98%.

All the analyses were carried out in triplicates.

2.3. Contamination assessment methodology

In order to assess the contaminations degree of each investigated metal, the single indices of Contamination Factor (CF), Enrichment Factor (EF), Geo-accumulation Index (I_{geo}) and Ecological Risk (E_R) were calculated, whereas in order to assess the whole contamination degree the integrated indices of Pollution Load Index (PLI) and Nemerow Index (NI) were calculated.

The CF, the ratio between the total concentration of each element in the soil and its background value, was calculated as reported below (Luo et al., 2007):

$$CF = \frac{C}{Bn} \tag{1}$$

Table 1
Localization of the investigated sites.

Site	Geographical coordinates	Altitude (m a.s.l.)
L1	40°49′49.156″N 14°24′0.273″E	600
L2	40°49′49.156″N 14°24′0.273″E	600
L3	40°48′19.04″N 14°26′13.361″E	600
L4	40°48′19.04″N 14°26′13.361″E	600
H1	40°49′51.935″N 14°25′28.606″E	900
H2	40°49′51.935″N 14°25′28.606″E	900
H3	40°48′55.246″N 14°26′18.679″E	900
H4	40°48′55.246″N 14°26′18.679″E	900

where C is the heavy metal content in topsoil, Bn is the background value calculated for the soil sampled according to Cicchella et al. (2005). The CF was distinguished into four classes by Luo et al. (2007): CF < 1, low contamination factor; 1 ≤ CF < 3, moderate contamination factors; 3 ≤ CF < 6, considerable contamination factors; and CF ≥ 6, very high contamination factor.

The EF is the ratio between the metal concentration in the topsoil and background respect to the same concentrations in a reference element. A reference element is an element particularly stable in the soil, which is characterized by absence of vertical mobility and/or degradation phenomena. This index was calculated according to Barbieri et al. (2015) as follow reported:

$$EF = \frac{\left(\frac{C_{element}}{C_{Fe}}\right) topsoil}{\left(\frac{C_{element}}{C_{Fe}}\right) background} \tag{2}$$

where $C_{element}$ is the concentration of the studied and C_{Fe} is the concentration of the reference element (Fe) according to De Nicola et al. (2003). To evaluate the soil quality, the following scale was considered: EF < 2 minimal enrichment, 2 < EF < 5 moderate enrichment, 5 < EF < 20 significant enrichment, 20 < EF < 40 very high enrichment and EF > 40 extremely high enrichment (Barbieri et al., 2015).

The I_{geo} is calculated by the following equation (Müller, 1969):

$$I_{geo} = \log_2 \frac{\mathrm{C}}{1.5\mathrm{Bn}} \tag{3}$$

where C is the heavy metal concentration and Bn the element background concentration according to De Nicola et al. (2003). The constant factor 1.5 was introduced to analyze fluctuations of heavy metals content as a result of natural processes. The I_{geo} was distinguished into seven classes by Müller (1969): $I_{geo} \leq 0$, unpolluted; $0 < I_{geo} \leq 1$, from unpolluted to moderately polluted; $1 < I_{geo} \leq 2$, moderately polluted; $2 < I_{geo} \leq 3$, from moderately to strongly polluted; $3 < I_{geo} \leq 4$, strongly polluted; $4 < I_{geo} \leq 5$, from strongly to extremely polluted; $I_{geo} > 5$, extremely polluted.

The PLI, the geometric mean of the CF for the *n* metals was calculated as reported below (Madrid et al., 2002):

$$PLI = \sqrt[n]{\prod_{i=1}^{n} CF} \tag{4}$$

The PLI was distinguished into two classes: PLI < 1 no pollution and PLI > 1 pollution (Banu et al., 2013).

The NI was calculated taking into account the CFs of the most contaminating metals as proposed by Ogunkunle and Fatoba (2013):

$$NI = \sqrt{\left(\frac{\left(\frac{1}{n}\sum_{i=1}^{n} CF\right)^2 + CF_{max}{}^2}{2}\right)} \tag{5}$$

where CF_{max} is the maximum value of the contamination factors calculated for all the investigated metals and m is the number of the investigated metals. The NI was distinguished into five classes of pollution degree: NI < 0.7, safety domain; 0.7 ≤ NI < 1.0, precaution domain; 1.0 ≤ NI < 2.0, slightly polluted domain; 2.0 ≤ NI < 3.0, moderately polluted domain; and NI > 3.0, seriously polluted domain (Cheng et al., 2007).

The E_r, used to quantitatively express the ecological risk of a given metal, was calculated as suggested by Håkanson (1980):

$$\mathrm{E_r} = \mathrm{T_f} \times \mathrm{CF} \tag{6}$$

where T_f is the toxic response factor that has value of 2 for Cr and of 5 for Cu, Ni and Pb (Håkanson, 1980). The Er was distinguished into five classes: Er < 40, low ecological risk; 40 ≤ Er < 80, moderate ecological risk; 80 ≤ Er < 160, considerable ecological risk; 160 ≤ Er < 320, high ecological risk; Er ≥ 320, very high ecological risk.

2.4. Phytotoxicological assays

Phytotoxicological assays were performed, in triplicate, according to EPA (1996) using a monocotyledon (*Sorghum saccharatum* L.) and a dicotyledon (*Lepidium sativum* L.). The phytotoxicity tests were carried out on fresh and sieved (2 mm) samples. Ten seeds for each species were placed in Petri dishes containing an amount of fresh soil equivalent to 10 g of oven-dried soil, subsequently saturated with water. Standard soil (OECD, 1984) and $K_2Cr_2O_7$ were used as negative and positive controls, respectively. After incubation in darkness (72 h, at 25 °C), the number of germinated seeds (*n*) and the total root length (L) were measured and the germination index (GI) was calculated as reported below (Maisto et al., 2011; Manzo et al., 2008) as reported below:

$$\mathrm{GI} = \mathrm{L} \times n \tag{7}$$

The results were expressed as effect percentage (E%) of germination index compared to a standard soil (OECD, 1984):

$$GI\ (\%) = \frac{(GI_{standard\ soil}) - (GI_{sample})}{(GI_{standard\ soil})} \times 100 \tag{8}$$

2.5. Statistical analyses

The normality of the data distribution was assessed by the Shapiro-Wilk test.

The one-way analysis of variance (ANOVA) was performed in order to evaluate the significance of the differences of the single and integrated indices or phytotoxicological assays among the seasons. The ANOVA tests were followed by the post hoc tests of Holm-Sidak.

The …correlation tests were performed in order to evaluate the relation among the heavy metal contents and the phytotoxicological assays.

The statistical assays, performed by Systat_SigmaPlot_12.2 software (Jandel Scientific, USA), were considered statistically significant at least for P < 0.05.

3. Results

3.1. Physico-chemical and phytotoxicological analyses

The mean values of pH, WC and OM contents, total concentration of Cr, Cu, Ni and Pb and the percentage of effect of *Lepidium sativum* L. and *Sorghum saccharatum* L. for each soils sampled in the Vesuvius National are reported in Supplementary material 1. The soil pH was slightly acid in S_16 (6.53) and neutral in A_16 and S_17 (7.11 and 6.97, respectively), although no statistically significant differences were observed among different sampling times (Table 2). The WC content showed statistically higher mean values in soils collected in S_16 and A_16 as compared to soils collected in S_17 (Table 2). The OM content varied from to and did not statistically differ among the sampling times (Table 2).

The investigated metals showed the same temporal trends with the highest values in A_16 and the lowest in S_16 and S_17 (Table 2). In more details, the statistically higher values were observed in A_16, with statistically significant differences for Cr, Ni and Pb, and with statistically significant differences for Ni and S_17 and for Pb in S_16 (Table 2).

Table 2
Mean values of pH, water (WC) and organic matter (OM) contents (expressed as % d.w.), total concentration of Cr, Cu, Ni and Pb (expressed as μg g^{-1} d.w.) and percentage of effect of *L. sativum* L. and *S. saccharatum* L. of the soils sampled inside the Vesuvius National Park in spring 2016 (S_16), autumn 2016 (A_16) and spring 2017 (S_17). Letters indicate statistically significant differences (at least $P < 0.05$).

	S_16	A_16	S_17
pH	6.53^{a}	7.11^{a}	6.97^{a}
WC	28.3^{a}	49.2^{a}	11.3^{b}
OM	11.1^{a}	19.6^{a}	9.17^{a}
Cr	18.5^{b}	31.2^{a}	19.4^{b}
Cu	92.3^{a}	180^{a}	117^{a}
Ni	15.0^{ab}	26.7^{a}	5.13^{b}
Pb	67.0^{b}	140^{a}	80.1^{ab}
L. sativum L.	-37.7^{a}	−43.2^{a}	−19.2^{a}
S. saccharatum L.	24.2^{b}	54.9^{a}	17.2^{b}

The phytotoxicological assays showed biostimulating effects for *L. sativum* L. and inhibiting effects for *S. saccharatum* L. with statistically higher values in A_16 only for *S. saccharatum* L. (Table 2).

3.2. Single and integrated indices

The Contamination Factor (CF) ranged from 0.55 to 5.50 for Cr, from 0.38 to 4.57 for Cu, from 0.29 to 4.75 for Ni and from 0.56 to 4.08 for Pb (Table 3). The Enrichment Factor (EF) ranged from 0.38 to 14.1 for Cr, from 4.90 to 58.5 for Cu, from 0.38 to 6.20 for Ni and from 4.49 to 32.8 for Pb (Table 3). The Geo-accumulation Index (I_{geo}) of all the investigated elements ranged from −1.39 to 1.93 for Cr, from −1.75 to 1.83 for Cu, from −2.36 to 1.66 for Ni and from −0.95 to 1.92 for Pb (Table 3).

The CF, EF and I_{geo} showed wide variability over the time (Fig. 1; Table 3) and the same temporal trends with the highest values detected in A_16, with statistically significant differences for Cr and Ni (Fig. 1).

The Pollution Load Index (PLI) and the Nemerow index (NI) respectively ranged from 0.63 to 3.03 and from 1.22 and 4.25 (Table 4). The PLI and NI showed the same trends with the statistically highest values in A_16 and the lowest values in S_16 and S_17 (Fig. 2).

3.3. Ecological Risk Factor

The Ecological Risk Factor (E_r) ranged from 1.10 to 11.0 for Cr, from 1.91 to 22.9 for Cu, from 1.46 to 23.7 for Ni and from 2.79 to 20.4 for Pb (Table 5). The E_r showed comparable temporal trends with the highest values detected in A_16 and the lowest in S_16 and S_17 (Fig. 3), and widely varied over the time (Fig. 3). The E_r calculated for Cr showed the statistically highest values in A_16 (Fig. 3), whereas those for Ni were observed in S_16 and A_16 (Fig. 3). Statistically significant differences for Cu and Pb were not observed (Fig. 3).

4. Discussion

The wide variability of the element concentrations in the soils collected inside the Vesuvius National Park showed high heterogeneity attributable to different site characteristics such as weathering processes, vicinity of downtown, traffic flow and topography (Memoli et al., 2018b; Mazurek et al., 2017; Peijnenburg et al., 2007).

The investigated volcanic soils appeared to be contaminated by Cr, Cu, Ni and Pb as compared to the soils of the Campania region, Southern Italy (Cicchella et al., 2005), where the Vesuvius National Park is located. In fact, the calculated CFs suggest a moderate or considerable contamination degree (Luo et al., 2007) that highlighted a progressive increase until A_16 and then a decrease, likely due to the intense touristic activity occurring from spring to summer. Although similar temporal trends of

Table 3
Mean values of the Contamination Factor (CF), Enrichment Factor (EF) and Geo-accumulation Index (I_{geo}) calculated for the soils sampled inside the Vesuvius National Park (L1, L2, L3, L4, H1, H2, H3 and H4) in spring 2016 (S_16), autumn 2016 (A_16) and spring 2017 (S_17). In bold are reported the minimum and the maximum values.

	Cr			Cu			Ni			Pb		
	S_16	A_16	S_17	S_16	A_16	S_17	S_16	A_16	S_17	S_16	A_16	S_17
CF												
L1	1.48	2.82	1.49	1.14	2.78	1.13	1.00	2.62	0.41	1.68	**4.08**	0.89
L2	1.22	1.45	**1.21**	2.01	**4.57**	1.70	0.92	1.83	**0.30**	1.80	3.51	1.31
L3	2.68	3.67	2.51	1.04	1.04	0.89	1.55	1.90	0.59	1.21	2.67	1.89
L4	1.79	4.04	2.03	**0.82**	0.96	0.89	1.40	2.36	0.42	1.18	2.80	1.08
H1	2.65	4.98	1.26	0.98	1.83	1.85	1.75	**4.75**	0.33	0.80	1.67	3.20
H2	3.16	**5.50**	4.21	0.85	1.74	1.06	1.90	3.06	0.74	0.83	1.64	0.80
H3	2.21	4.10	3.37	1.13	1.01	1.14	1.73	2.62	0.77	**0.63**	0.98	0.64
H4	2.65	3.55	2.59	0.88	0.93	1.02	1.85	2.42	0.57	0.65	0.98	0.70
EF												
L1	1.61	3.09	1.63	14.6	35.5	14.4	1.30	3.42	0.53	13.6	**32.8**	7.19
L2	**1.33**	1.58	1.34	25.7	**58.5**	21.7	1.20	2.39	**0.39**	14.4	28.3	10.6
L3	2.94	4.02	2.74	13.3	13.3	11.3	2.02	2.49	0.78	9.69	21.4	15.17
L4	1.96	4.42	2.22	**10.4**	12.2	11.4	1.83	3.08	0.55	9.52	22.5	8.71
H1	2.90	5.45	1.38	12.6	23.4	23.6	2.28	**6.20**	0.43	6.42	13.4	25.7
H2	3.46	**6.02**	4.60	10.8	22.2	13.5	2.48	4.00	0.97	6.71	13.2	6.41
H3	2.42	4.49	3.68	14.4	12.9	14.6	2.26	3.41	1.01	**5.03**	7.89	5.12
H4	2.89	3.88	2.84	11.3	11.9	13.0	2.41	3.16	0.75	5.23	7.90	5.65
I_{geo}												
L1	0.03	0.97	0.05	−0.17	1.11	−0.19	−0.59	0.80	−1.88	0.64	**1.92**	−0.27
L2	**−0.25**	0.00	−0.26	0.64	**1.83**	0.40	−0.71	0.28	**−2.32**	0.73	1.70	0.28
L3	0.89	1.35	0.79	−0.31	−0.30	−0.54	0.04	0.34	−1.34	0.16	1.30	0.80
L4	0.31	1.49	0.49	**−0.65**	−0.42	−0.53	−0.10	0.65	−1.84	0.13	1.37	0.00
H1	0.88	1.79	−0.19	−0.39	0.51	0.52	0.22	**1.66**	−2.18	−0.44	0.63	1.56
H2	1.13	**1.93**	1.54	−0.60	0.43	−0.28	0.34	1.03	−1.01	−0.37	0.60	−0.44
H3	0.61	1.51	1.22	−0.19	−0.35	−0.17	0.20	0.80	−0.96	**−0.79**	−0.14	−0.76
H4	0.87	1.30	0.84	−0.54	−0.46	−0.34	0.30	0.69	−1.39	−0.73	−0.14	−0.62

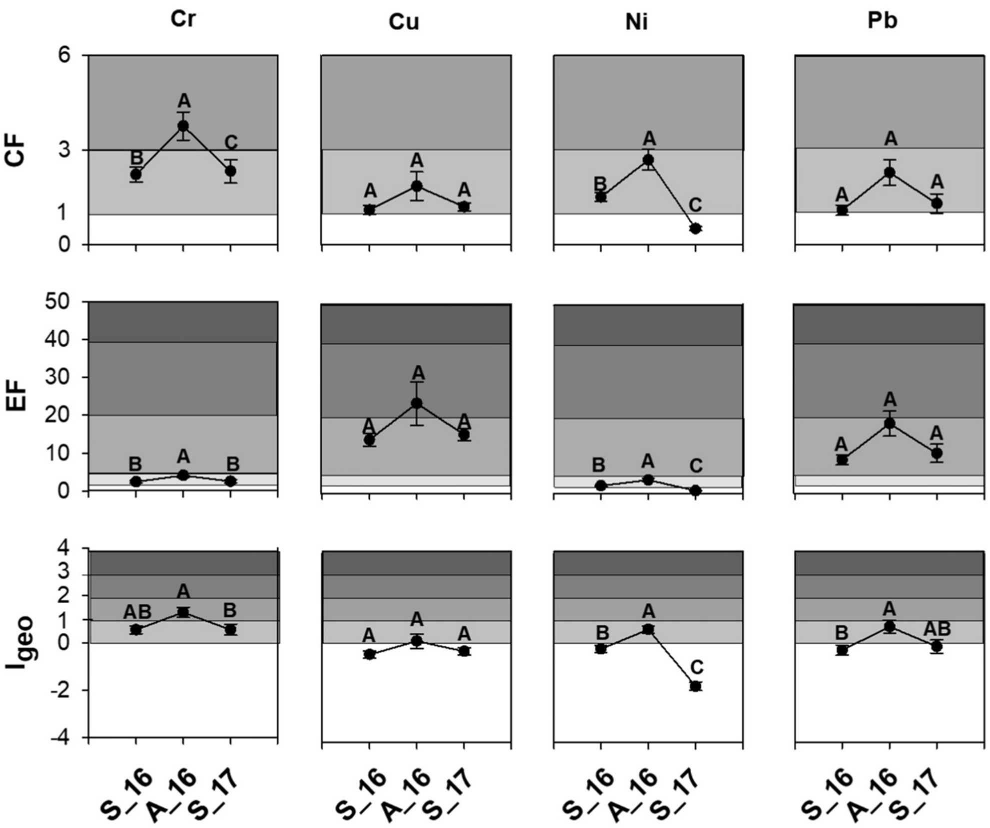

Fig. 1. Mean values (±s.e.) of the Contamination Factor (CF), Enrichment Factor (EF) and Geo-accumulation Index (Igeo) for the investigated soils at different sampling times (S_16, A_16 and S_17). The backplanes show different toxicity classes: from slightly contaminated (light grey) to strongly contaminated (dark grey). Different letters indicate statistically significant differences ($P < 0.05$) among the seasons (one-way analysis of variance with Holm–Sidak post hoc test).

the CFs were observed for all the elements, more similarity was observed between Cu and Pb as well as between Cr and Ni suggesting different sources of contamination for the two couples of metals. The Cr and Ni contamination would seem to derive from intense and brief emission sources strictly occurring during summer 2016. In that period, in addition to touristic activities, also numerous fires, responsible of metal emissions in the environment (Abraham et al., 2017), occurred in the investigated area. These metals show lower volatilization rates as compared to Cu and Pb (Wang et al., 2017a, 2017b). The rapid decreases of CFs observed for Cr and Ni after A_16 could be due to the climatic conditions that favour re-suspension of soil-derived dusts (Bilos et al., 2001; Soltani et al., 2015). Instead, Cu and Pb are well-known vehicular traffic markers (De Silva et al., 2016; Wang et al., 2017a, 2017b; Santorufo et al., 2014; Maisto et al., 2011) and their accumulation in the soils of the National Park could be mainly derived by emissions of vehicular exhausts due to tourism occurring in summer time inside the park and by the deposition of air particulate coming from the high-density populated surroundings during the other periods (Liu et al., 2018), as Cu and Pb present high volatilization rates (Wang et al., 2017a, 2017b). In fact, the CFs of Cu and Pb did not statistically vary among the time samplings. As suggested by the EFs, calculated as ratio between the metal concentration in the topsoil and background respect to the same concentrations of Fe (considered a stable metal), the collected soils were affected by minimal to moderate enrichment of Cr and Ni and by significant to very high enrichment of Cu and Pb (Barbieri et al., 2015; Memoli et al., 2018b). Thus suggests that Cr and Ni were more stable and less affected by vertical mobility (Buccianti et al., 2015). Besides, EFs would corroborate the hypothesis, already deriving by the trend of the CFs, that Cu and Pb would seem to depend on air deposition factors more than on substrate weathering or natural sources that instead would seem to affect Cr and Ni (Bilos et al., 2001; Soltani et al., 2015).

Different origins of the investigated metals can be supposed according to the I_{geo}. Cr likely could derive from a double sources (natural and anthropogenic) as I_{geo} identified the soils as slightly to moderately polluted during the whole investigated period. Then, the probable source emissions of Cr could be substrate weathering or other natural sources as well as vehicular emissions. Instead, anthropogenic sources of Cu, Ni and Pb were evident especially in summer 2016 as the I_{geo} in A_16 were higher than 0 (Müller, 1969).

According to the single indices also the integrated ones highlighted that the soils of the Vesuvius National Park were contaminated, as PLI

Table 4
Mean values of the Pollution Load Index (PLI) and Nemerow Index (NI) calculated for the soils sampled inside the Vesuvius National Park (L1, L2, L3, L4, H1, H2, H3 and H4) in spring 2016 (S_16), autumn 2016 (A_16) and spring 2017 (S_17). In bold are reported the minimum and the maximum values.

	PLI			NI		
	S_16	A_16	S_17	S_16	A_16	S_17
L1	1.30	**3.03**	**0.88**	2.01	4.08	**1.90**
L2	1.42	2.55	0.95	2.12	3.90	1.98
L3	1.51	2.10	1.26	2.21	3.54	2.19
L4	1.25	2.25	0.95	1.99	3.69	1.97
H1	1.38	2.91	1.26	2.16	**4.25**	2.32
H2	1.44	2.63	1.27	2.26	4.01	2.35
H3	1.28	1.80	1.17	2.07	3.45	2.20
H4	1.30	1.68	1.02	2.13	3.32	2.03

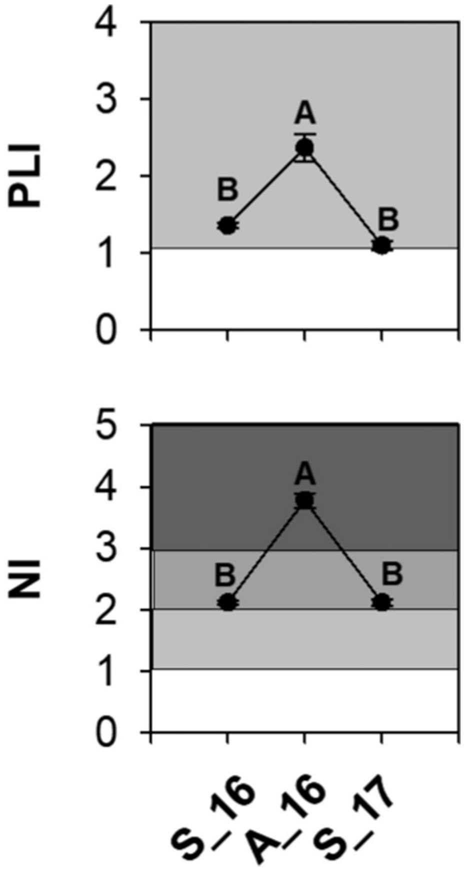

Fig. 2. Mean values (±s.e.) of the Pollution Load Index (PLI) and the Nemerow Index (NI) for the investigated soils at different sampling times (S_16, A_16 and S_17). The backplanes show different toxicity classes: from slightly contaminated (light grey) to strongly contaminated (dark grey). Different letters indicate statistically significant differences ($P < 0.05$) among the seasons (one-way analysis of variance with Holm–Sidak post hoc test).

was higher than 1 and NI identified the soils as slightly to seriously polluted. This was particularly true in the sampling carried out in A_16 when both the single and integrated indices were the highest likely due to the end of intense touristic activity (from April to October) occurred inside the park.

Although the soils appeared contaminated, low ecological risk has been observed in the investigated area, as the values of the E_r were lower than those reported by Håkanson (1980). Notwithstanding, the investigated soils showed high phytotoxicity as biostimulating and inhibitory effects were observed, respectively, for *L. sativum* L. and *S. saccharatum* L. especially for the samplings carried out in A_16 (Czerniawska-Kusza et al., 2006; Memoli et al., 2018b).

5. Conclusions

In conclusion, the surface soils of the Vesuvius National Park appeared to be polluted by Cr, Cu, Ni and Pb, according to both single and integrated indices. The touristic impact would seem to be the main cause of soil metal accumulation as the highest values of the calculated indices were detected for samples collected in Autumn 2016 (at the end of the touristic season), and the lowest for soils collected in Spring 2016 and 2017 (at the beginning of the touristic season). Anyway, further emission sources can be supposed. In fact, Cu and Pb would seem also to derive by ex situ anthropogenic sources, whereas Cr and Ni also by natural sources, such as spontaneous fires and substrate weathering.

Finally, the soils had low ecological risks linked to the investigated metal accumulation although they showed phytotoxic effects.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.05.211.

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Table 5

Mean values of the Ecological Risk Factor (E_r) calculated for the soils sampled inside the Vesuvius National Park (L1, L2, L3, L4, H1, H2, H3 and H4) in spring 2016 (S_16), autumn 2016 (A_16) and spring 2017 (S_17). In bold are reported the minimum and the maximum values.

	E_r											
	Cr			Cu			Ni			Pb		
	S_16	A_16	S_17	S_16	A_16	S_17	S_16	A_16	S_17	S_16	A_16	S_17
L1	2.95	5.65	2.98	5.69	13.9	5.64	5.00	13.1	2.04	8.42	20.4	4.47
L2	2.43	2.89	**2.42**	10.04	**22.9**	8.50	4.61	9.16	**1.51**	8.98	17.6	6.56
L3	5.36	7.34	5.01	5.19	5.21	4.43	7.75	9.52	2.97	6.03	13.3	9.43
L4	3.58	8.09	4.05	**4.08**	4.79	4.45	7.00	11.8	2.09	5.92	14.0	5.42
H1	5.30	9.96	2.53	4.91	9.13	9.24	8.73	**23.7**	1.66	3.99	8.35	15.98
H2	6.33	**11.0**	8.41	4.24	8.68	5.29	9.51	15.3	3.72	4.17	8.19	3.98
H3	4.42	8.20	6.73	5.65	5.03	5.72	8.67	13.1	3.86	**3.13**	4.90	3.18
H4	5.29	7.10	5.19	4.42	4.66	5.09	9.25	12.1	2.87	3.25	4.91	3.52

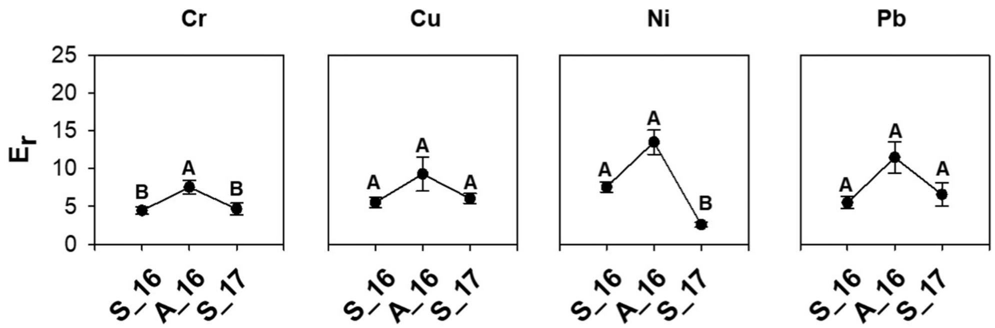

Fig. 3. Mean values (±s.e.) of the Ecological Risk Factor (Er) for the investigated soils at different sampling times (S_16, A_16 and S_17). Different letters indicate statistically significant differences ($P < 0.05$) among the seasons (one-way analysis of variance with Holm–Sidak post hoc test).

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