



Geochemical sources of vanadium in soils: Evidences in a southern Italy area



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ABSTRACT

Identifying differences of vanadium concentrations in soils is essential to individuate pollution sources and potential risks to humans and the environment. Marked differences in the geochemical composition of the rocks, which form the parent materials of soils, and variations in the intensity of soil-forming processes can result in wide ranges of concentrations of vanadium in soils, even in those unaffected by contamination. Conversely, the anthropogenic input can give rise to contamination in urban soil. The main aim of this study was to analyse the concentrations of vanadium in a southern Italy area, in both rural and urban soils, in order to determine different geochemical sources. In the study area, 149 topsoil samples were collected (0.10 m) and analysed for vanadium and other elements by ICP-MS. Statistical and geostatistical methods were used to identify the main factors influencing the different sources of vanadium in urban and peri-urban soils and to map the concentrations of vanadium. The concentrations of V were higher in the rural soils where were related to the ophiolite-bearing units outcroppings, which influenced importantly the distribution of vanadium, rather than in the urban soil, where were lowly affected by anthropogenic pollution due, predominantly, to circulating vehicle fuels. In urban area the mean concentration of vanadium amounted below the critical threshold value imposed by Italian Decree 152/2006.

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1. Introduction

Geochemical surveys of urban and peri-urban soils are increasing worldwide for the growing environmental awareness and human health risks (Buttafuoco et al., 2016; Cicchella et al., 2015, 2016; Cozza et al., 2015; Jarva et al., 2014; Tarvainen and Jarva, 2011; Tarvainen et al., 2009; Zuzolo et al., 2016). Especially with respect to so-called diffuse input of potential toxic elements, it is of greatest importance to have accurate knowledge of the prevailing range of natural element concentrations in the various surficial compartments (Cicchella et al., 2005; van der Veer, 2006).

Because of its environmental significance, studies to determine risk caused by toxic elements levels in soil on human health have attracted attention around the world allowing to realize some researches such as in Bangladesh (Saha et al., 2016), Bulgaria (Astel et al., 2011), China (Lee et al., 2006), European Union (Tóth et al., 2016), India (Krishna and Govil, 2007; Srinivasa Gowd et al., 2010), Iran (Saeedi et al., 2009), Nigeria (Osuji and Adesiyun, 2005).

Among these elements, vanadium (V) has represented a controversial problem in soil from being a rare and uninterested metal to becoming a major risk to the global environment in facing silent epidemic acute poisoning (Gummow, 2011; Nriagu, 1998; Pacyna, 1998). Its toxicological effects in humans, animals and plants, the different sources of pollution and the consequent potentially significant environmental impact, have increased interest in vanadium concern within the twenty-first century as reported in Baken et al. (2012), Cappuyns and Slabbinck (2012), Hernandez and Rodriguez (2012), Jayawardana et al. (2015), Reijonen et al. (2016), and Teng et al. (2006, 2011). Long-term exposure to V may exert toxic effects on respiratory and digestive organs, kidneys, liver, skin and immune system of human beings (Jayawardana et al., 2015) as well as on the cardiovascular system (Gruzewska et al., 2014). Moreover, vanadium compounds exhibit carcinogenic properties (Korbecki et al., 2012).

Vanadium is widely distributed in the lithosphere, and it is used in modern society. It has been estimated that around 65,000 t of vanadium enter annually into the environment from natural sources (crustal weathering and volcanic emissions) and around 200,000 t because of man's activities (Galloway et al., 1980).

Regarding its geogenic source, vanadium is present in the lithosphere due to various sources and its average concentration in the earth's crust is 97 mg kg⁻¹ (Rudnick and Gao, 2005). The World

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Health Organization (1988) reported that approximately 92% of all V can be found in basic rocks, i.e., basalt, gabbro, amphibolites, and eclogites and 7% in acid and neutral rocks. <1% of the total amount of V is found in ultrabasic alkaline rocks. Breit and Wanty (1991) mentioned that when large amounts of V are found in carbonaceous rocks, relative to average shale, this is principally due to enrichment processes, i.e., syngenetic, diagenetic, and epigenetic, processes.

The V total content in soil is the sum of the its concentration derived from minerals in the geological parent material on which the soil has developed (lithogenic source) during weathering and inputs from a wide range of possible anthropogenic (contamination) sources (Alloway, 2012; Guagliardi et al., 2016a). Environmental fate and behaviour of V in natural soil are dynamic: its average content ranges from 10 to 220 mg kg⁻¹ (Jayawardana et al., 2015). In European topsoils, the average aqua regia-soluble vanadium concentration is 38 mg kg⁻¹ (Larsson et al., 2013; Salminen et al., 2005). The Italian agricultural (Ap) and grazing (Gr) soils are characterized by a median V concentration (aqua regia extracted fraction) respectively of 34 mg kg⁻¹ and 35 mg kg⁻¹, that exceed those of European soils stated by Reimann et al. (2014), 25 and 26 mg kg⁻¹ respectively. Also total V (XRF data sets) concentrations in Ap and Gr are well above those of European soils (68 mg kg⁻¹), with median values of 94 mg kg⁻¹ and 100 mg kg⁻¹, respectively (Cicchella et al., 2015). Soil derived from limestone contains higher values of V although peaty soils have the least concentrations. Agricultural and contaminated urban soils also show relatively higher averages: about 200 mg kg⁻¹ and 161 mg kg⁻¹ respectively (Hernandez and Rodriguez, 2012). Median vanadium concentrations from surveys in different countries and regions and average V values in world soils are illustrated in Table 1. The highest median concentrations of V are in the soil of northern California and reflect the rock types (lithogenic source) of this region, which range from ultramafic to acid igneous (Alloway, 2012).

Vanadium is not found in soil in metallic form and can be present in several oxidation states as vanadates of Cu, Zn, Pb, Fe, Mn and Ca (API 1985; Venkataraman and Sudha, 2005). Generally, vanadium naturally present in soil has a low mobility and its solubility is strongly determined by its oxidation state and soil properties. Vanadium sorbs to Fe- and Mn-oxides, clay and organic matter. Iron oxides in soil can hold a substantial fraction of it and can be released to plants gradually

(Agnieszka and Barbara, 2012; Norrish, 1975). It is mainly iron and aluminium (hydr)oxides that determine vanadium mobility in soils (Naem et al., 2007; Peacock and Sherman, 2004; Wallstedt et al., 2010) and there are indications that vanadate binds somewhat more strongly to iron (hydr)oxides than phosphate (Blackmore et al., 1996). The presence of uranium and phosphate can lead to the formation of highly insoluble V⁺⁵ complexes. Vanadium (+3) is relatively abundant in soil, it is less soluble and less mobile than V (+4) and (+5). Vanadyl cation (VO₂) is an important form of V in many soils that tends to mobilize as complexes with humic acid (Bloomfield, 1981; Novotny et al., 2006; Wright et al., 2014).

Soil properties clearly affect the fate of vanadium in soil (Larsson et al., 2013) and it has been reported that V is highly mobile in slightly acidic or alkaline conditions (Brooks, 1972; Wright et al., 2014). The maximum vanadium adsorption was observed at approximately pH 4 in Finnish soils (Mikkonen and Tummavuori, 1994).

Furthermore, vanadyl can form strong complexes with organic matter, and in the presence of organic substances vanadium (V) may be reduced to vanadium (IV), especially at low pH (Lu et al., 1998). Clay and organic matter content were positively correlated to vanadium sorption strength of German soils (Gäbler et al., 2009).

The most important anthropogenic sources of vanadium are associated with metallurgical works followed by the burning of crude or residual oil and coal, and its main field of application is in the steel industry, in alloys (Larsson et al., 2013). The world production of vanadium was about 35,000 t in 1981 (Mineral commodity summaries, 1983), the major producing countries were Chile, Finland, Namibia, Norway, South Africa, USSR and the United States. Most of the vanadium is used in ferrovanadium of which majority is used in high-speed and other alloy steel (usually combined with chromium, nickel, manganese, boron and tungsten). In addition, vanadium is also widely used in chemical and aerospace industries because of many superior performances (Teng et al., 2011).

Geostatistical methods (Matheron, 1971) provide us a valuable tool to study spatial structure of V concentration and mapping its spatial distribution. They take into account spatial autocorrelation of data to create mathematical models of spatial correlation structures commonly expressed by variograms. The interpolation technique of the variable at unsampled locations, known as kriging, provides the 'best', unbiased, linear estimate of a regionalized variable in an unsampled location, where 'best' is defined in a least-square sense (Chilès and Delfiner, 2012; Webster and Oliver, 2007).

There are examples of geostatistical applications in soil concentration of heavy metals and the other hazardous elements studies (Atteia et al., 1994; Brus et al., 2002; Buttafuoco et al., 2010; Goovaerts, 1997; Goovaerts and Webster, 1994; Guagliardi et al., 2012, 2013, 2015; Juang et al., 2001; Lin et al., 2002; McGrath et al., 2004; Queiroz et al., 2008; Reis et al., 2007; Webster et al., 1994).

The study was carried out inside a larger research, which was undertaken to investigate the geochemistry of soils in the Cosenza and Rende municipalities (Calabria region, southern Italy). Its main objective was to determine the origin of vanadium in order identifying its possible sources in urban and peri-urban soil where mainly influences of anthropic activities and cattle ranching respectively occur. The peculiar assemblage of geological, geomorphological, pedological and climatic features of Cosenza and Rende municipalities, make the study area representative of larger areas in the central Mediterranean and in the peri-Mediterranean belt.

2. Materials and methods

2.1. Geological and urban background of the study area

Cosenza and Rende municipalities are located in Calabria region (southern Italy) in the graben of Crati Basin (Fig. 1) which represents a Pliocene to Holocene intermountain basin in the northern sector of

Table 1

Median and maximum total vanadium concentration in topsoil in various countries and mean value for China, Japan and world soils. Alloway (2012) modified.

Country	Vanadium concentration (mg kg ⁻¹)	Data sources
Europe (AR extraction)	25 (188) Ap soils	Reimann et al. (2014)
Europe (XRF)	68 (323) Ap soils	Reimann et al. (2014)
Europe (AR extraction)	26 (552) Gr soils	Reimann et al. (2014)
Europe (XRF)	68 (706) Gr soils	Reimann et al. (2014)
Europe	33 (<281)	Salminen et al. (2005)
Italy (AR extraction)	34 (187) Ap soils	Cicchella et al. (2015)
Italy (XRF)	94 (245) Ap soils	Cicchella et al. (2015)
Italy (AR extraction)	35 (169) Gr soils	Cicchella et al. (2015)
Italy (XRF)	100 (276) Gr soils	Cicchella et al. (2015)
Baltic States	18 (<203)	Reimann et al. (2003)
Ireland	52.2 (<240)	Zhang et al. (2008)
Netherlands	27.7 (<168)	Brus et al. (2009)
N. California	135 (<490)	Goldhaber et al. (2009)
USA	36 (150)	Govindaraju (1994)
China	82	Chen et al. (1991)
Japan	94 (Gleysols)	Takeda et al. (2004)
Japan	250 (Andosols)	Takeda et al. (2004)
World	60	Kabata-Pendias (2001)

AR extraction: Aqua Regia extraction; Ap soils: agricultural soil on regularly ploughed land; Gr soils: grazing land soil (under permanent grass cover).

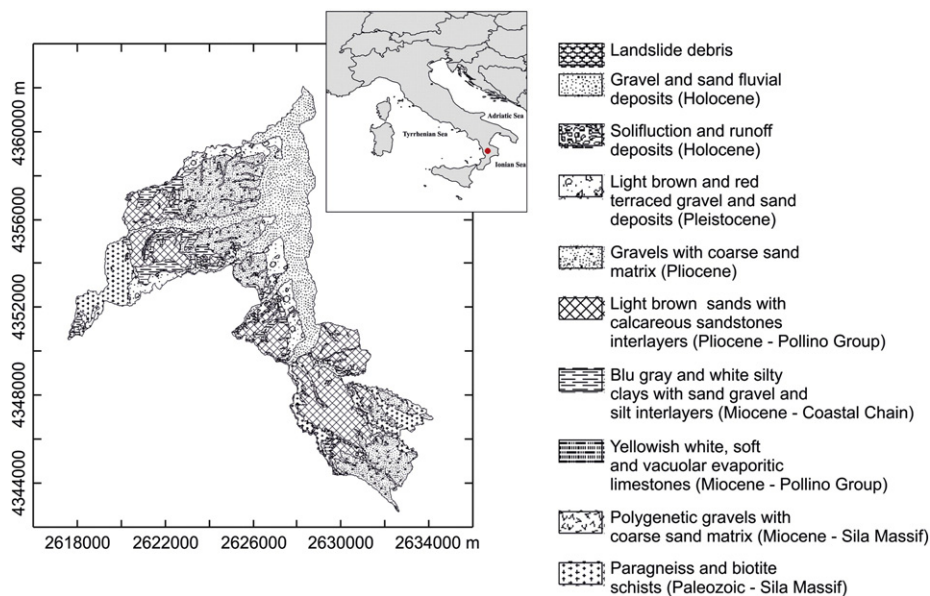


Fig. 1. Study area location and lithologic sketch map.

the Calabrian-Peloritan Arc (Amodio-Morelli et al., 1976; Critelli et al., 1993).

The basement of Cosenza and Rende area is covered by the plutonic and high-grade metamorphic rocks, by sedimentary and crystalline rocks and by carbonate and siliciclastic sedimentary rocks (Fig. 1), comprising of the three main lithotectonic units known as Sila Massif, Coastal Chain and Pollino group respectively (Guagliardi et al., 2016b).

Paragneiss, biotite schists, and grey phyllitic schists (with dominant quartz, chlorite and muscovite) are the dominant rocks, overlapped by a thick succession of sediments of Pliocene age made up of light brown and red sands and gravels, blue grey silty clays with silt interlayers, Pleistocene to Holocene alluvial sands and gravels and very small outcrops of Miocene carbonate rocks (Fabbriatore et al., 2014; Guagliardi et al., 2012).

The crystalline rocks are underwent to an intense physical-chemical weathering, which determined most of their morphological evolution. Climate is continental, characterized by large temperatures variations, both daily and annually (Buttafuoco and Caloiero, 2014; Ricca and Guagliardi, 2015).

The Cosenza-Rende area has approximately 106,000 inhabitants and is characterized by typical urban land use, such as housing, intense automobile traffic, a limited presence of industry, commercial activities, and parks and gardens (Guagliardi et al., 2015). Forest, non-agricultural and grazing are the main land uses of peri-urban area.

2.2. Soil samples collection and chemical analysis

A systematic soil sampling strategy was adopted in the study area, dividing the territory into $1 \text{ km} \times 1 \text{ km}$ cells in peri-urban areas and $0.5 \text{ km} \times 0.5 \text{ km}$ cells in urban areas (Fig. 2). Composite topsoil samples (5 subsamples at 0–10 cm depth) were collected at 149 locations including gardens, flowerbeds, parks, cropped areas and forests. Duplicate samples were collected at 10% of sites to enable an estimation of sampling and analytical precision.

All soil samples were dried at 50°C , disaggregated and sieved. Multi-element analysis of fine earth fraction ($<2 \text{ mm}$) was carried out by inductively coupled plasma mass spectrometry (ICP-MS), following digestion in concentrated HClO_4 , HF and HNO_3 (6:5:3), but only the vanadium concentrations and elements related to it are discussed in this paper.

A complete sampling and analytical control scheme was implemented with sampling and analytical duplicates, reference materials and reagent blanks. Quality control results are reported in Table 2.

The laboratory accuracy error was determined using the formula:

$$\text{Accuracy error} = \left(\frac{|X - TV|}{TV} \right) * 100 \quad (1)$$

where X = laboratory's analysis result for the performance sample (standard); TV = true value of the performance sample (standard). Precision was calculated as relative percentage difference (%RPD) using the formula:

$$\%RPD = \left[\frac{|SV - DV|}{\frac{SV + DV}{2}} \right] * 100 \quad (2)$$

where SV = the original sample value, DV = the duplicate sample value (Zuzolo et al., 2016).

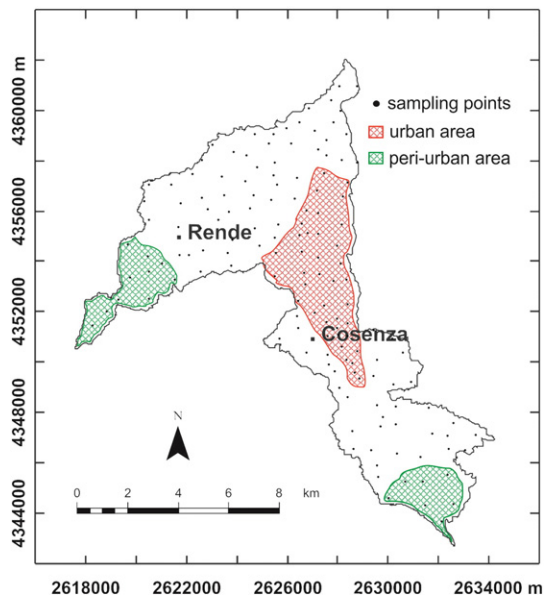


Fig. 2. Sampling sites map.

Table 2
Basic statistics of vanadium concentration (mg kg^{-1}) in peri-urban and urban soils.

	Whole data set	Peri-urban soils	Urban soils
Minimum	54	184	54
Maximum	239	239	133
Mean	107.36	200.17	91.2
Median	102	197	89
Lower quartile	87	188	78.75
Upper quartile	123	198.5	100.5
Standard deviation	30.8	20.1	19.84
Skewness (–)	1.27	1.87	0.27
Kurtosis (–)	5.34	4.01	-0.43
Detection limit	0.05	0.05	0.05
Precision (RPD)	2.9	3.5	3.2
Accuracy (%)	5	5.7	5.1

2.3. Data processing

In order to assess vanadium pollution in soil, the contamination factor (C_f) (Rapant et al., 1999) was determined as:

$$C_f = \frac{\text{vanadium soil concentration}}{\text{upper permissible vanadium threshold (normative value)}} - 1 \quad (3)$$

The upper permissible limit of vanadium in soil, based on Italian Environmental Decree (D.L. 152, 2006), is 90 mg kg^{-1} .

Vanadium concentration data were further subjected to the statistical and geostatistical analysis in order to individuate the different sources of contamination.

Pearson's correlation coefficient was used for determining the linear correlation between variables. Pearson's correlation can range from -1 to 1 . A correlation coefficient of -1 indicates a perfect negative linear relationship between variables, a correlation coefficient of 0 indicates no linear relationship between variables, and a correlation coefficient of 1 indicates a perfect positive linear relationship between variables.

2.4. Geostatistical approach

To analyse and map the spatial variation of V concentration data was used a geostatistical approach whereby the set of unknown values of V concentration is regarded as a set of spatially dependent random variables $Z(\mathbf{x})$ and each measurement $z(\mathbf{x}_\alpha)$ at different locations \mathbf{x}_α (\mathbf{x} is the location coordinates vector and α the sampling points = $1, \dots, N$) is interpreted as a particular realization of a random variable $Z(\mathbf{x}_\alpha)$. For a detailed presentation of the theory of random functions, interested readers should refer to textbooks such as Chilès and Delfiner (2012), Goovaerts (1997), Isaaks and Srivastava (1989), Journel and Huijbregts (1978), Wackernagel (2003), Webster and Oliver (2007), among others.

The quantitative measure of spatial correlation of the regionalized variable $z(\mathbf{x}_\alpha)$ is the experimental variogram, $\gamma(\mathbf{h})$, which is a function of the distance vector (\mathbf{h}) and direction of data pairs values. Subsequently, to estimate the variogram value analytically for any distance \mathbf{h} , a theoretical function is fitted to the experimental variogram.

The fitted variogram model has the objective of building a permissible model that captures the major spatial features of the attribute under study (V concentration in this study). Experimental variograms can be modelled using only functions that are conditionally negative definite, in order to ensure the non-negativity of the variance of the prediction error. The variogram model generally requires two parameters: (i) range, which is the distance over which pairs of soil V concentration are spatially correlated; and (ii) sill, which is the variogram value corresponding to the range.

The optimal model fitting will be chosen based on cross-validation, which checks the compatibility between the data and the structural model considering each data point in turn, removing it temporarily from the data set and using its neighbouring information to predict

the value of the variable at its location. The goodness of fit was evaluated by the Mean Error (ME) and the Mean Squared Deviation Ratio (MSDR). The ME, which is the difference between the measured and estimated values, proves the unbiasedness of estimate if its value is close to 0 , while the MSDR is the ratio between the squared errors and the kriging variance (Webster and Oliver, 2007). If the model for the variogram is accurate, the mean squared error should equal the kriging variance and the MSDR value should be 1 .

The fitted variogram was used to estimate V concentrations at unsampled locations using multiGaussian kriging (Verly, 1983) at the nodes of a $25 \text{ m} \times 25 \text{ m}$ interpolation grid.

MultiGaussian approach allows spatial prediction at unsampled locations regardless of the shape of the sample histogram (Goovaerts, 1997; Verly, 1983; Wackernagel, 2003). MultiGaussian approach is based on a multiGaussian model and requires a prior Gaussian transformation of the initial attribute $\{Z(\mathbf{x}), \mathbf{x} \in R^2\}$ into a Gaussian-shaped variable $\{Y(\mathbf{x}), \mathbf{x} \in R^2\}$ with zero mean and unit variance. Such a procedure is known as Gaussian anamorphosis (Chilès and Delfiner, 2012; Wackernagel, 2003). The kriging results must be back-transformed to the raw distribution afterwards.

All statistical and geostatistical analyses were performed by using the software package ISATIS®, release 2016 (www.geovariances.com).

3. Results and discussion

Basic statistics for vanadium concentration are reported in Table 2. Vanadium concentration values range between 54 and $239 \text{ (mg kg}^{-1}\text{)}$ for whole data set, whereas between 184 and $239 \text{ (mg kg}^{-1}\text{)}$ in peri-urban soils and between 54 and $133 \text{ (mg kg}^{-1}\text{)}$ in urban soils. Data from whole data set depart significantly from normality with a skewness equal to 1.27 .

The results of contamination factor (C_f), calculated using Eq. (3) for each sampled soils, were classified as follow:

- $C_f < 0$ = no contamination;
- $0 < C_f < 0.5$ = low contamination degree;
- $0.5 < C_f < 1$ = moderate contamination degree;
- $> 1 C_f$ = high contamination degree.

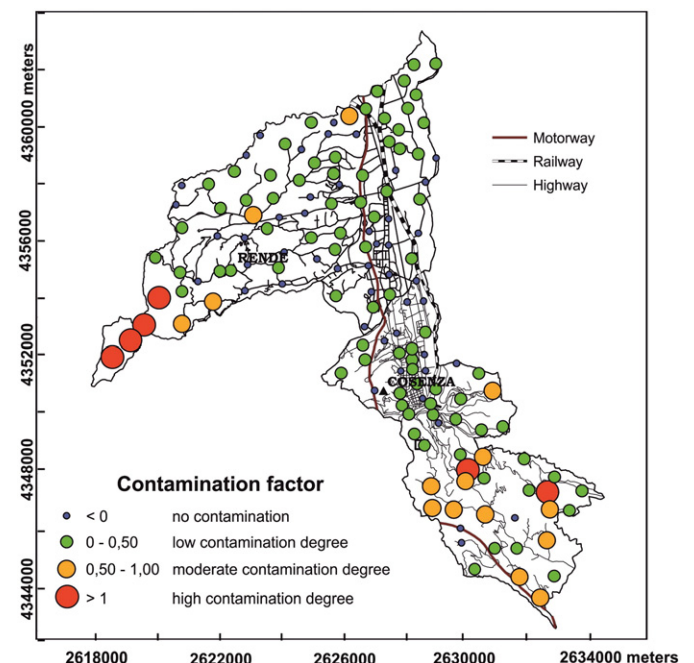


Fig. 3. Distribution map of contamination factors.

The dot map of contamination factor (Fig. 3) indicates a contamination occurring in the whole study area and, particularly, discriminating the different input of vanadium from urban and peri-urban areas, the results of C_f vary widely attesting higher contamination status in the rural area than in the urban centre.

For subsequently analysis, V data were transformed to a normal distribution using the above mentioned Gaussian anamorphosis.

V data were analysed before drawing a variogram map (not shown) which revealed no relevant difference as a function of direction (anisotropy) and the experimental variogram looked upper bounded. Then, a bounded isotropic variogram model was fitted and included a nugget effect (0.49) and a spherical model with a range equal to 8500 m and a sill of 0.50. The nugget effect implies a positive intercept of the variogram. It arises from errors of measurement and spatial variation within the shortest sampling interval (Webster and Oliver, 2007). The results of cross-validation were satisfactory because the statistics used, i.e. the mean of the estimation error was close to 0 and the variance of the mean squared deviation ratio close to 1.

The above variogram model was used with the multiGaussian kriging to produce the maps of the predicted V concentrations at the node of the interpolation grid and their kriging standard deviation.

From a visual inspection of the map of soil vanadium concentrations (Fig. 4, left) it is clear that the high values are located in peri-urban soils whereas low values in urban soils.

The origin of vanadium in soil can be ascribed to the contribution of parent materials, especially in rural areas anthropogenically less active, and/or the human activity added to geochemical baseline through air deposition, agrochemical application, wastes, residual sediments, precipitation, or irrigation (Guagliardi et al., 2013; Kabata-Pendias, 1995).

The exceeding value of vanadium found in peri-urban soils of Cosenza and Rende territory, as well as the high values of Co, Cr, Fe and Mg (Guagliardi et al., 2012, 2016a), can be explained by the occurrence in the study area of the ultrabasic rocks in which these elements are predominant. Highest baseline values of these elements appear to be highly correlated to the igneous-metamorphic complex found below the Pliocene deposits but that outcrops mostly in the NW and SE sectors of the territory. The complex can be ascribed to the pile of tectonic nappes forming the mountain chain of the northern Calabrian Arc, described in Tortorici et al. (2009), which includes an intermediate structural element made up of ophiolite-bearing units that mostly extend along the Tyrrhenian side of the arc to form a westward convex arc-shaped belt

separated from the southern Apennines by the roughly E–W trending left-lateral strike-slip fault zone, the Sangineto line in Amodio-Morelli et al. (1976). This unit is represented by a tectonic mélange constituted by a monotonous sequence of phyllites, quartzites, and calcschists including metric to kilometric lens-shaped blocks of ophiolitic rocks. These rocks are mainly represented by serpentinized ultramafics and by glaucophane-bearing meta-basites with remnants of their sedimentary cover and rare meta-gabbros (Tortorici et al., 2009).

Pearson product moment correlation for the elements in the rural soils was calculated. Strong positive relationships were observed between V and Fe ($r = 0.92$), Ti ($r = 0.84$), Cr ($r = 0.80$) and Ni ($r = 0.77$) concentrations (Table 3). These correlations further confirmed a single provenance for these elements since the ability for the mobilization of these elements during the weathering processes is similar. Significant positive correlations also exist between Fe and Cr ($r = 0.78$), Ti ($r = 0.90$) and Ni ($r = 0.70$) in the peri-urban soils. This additionally concludes that those elements may have been released due to weathering of Fe-Ti oxides bearing mafic rocks (Evans et al., 1978; Nriagu, 1998; Prytulak et al., 2013).

Anthropogenic releases of vanadium to soil are less widespread than natural releases and occur on a smaller scale. Indeed, conversely to peri-urban area, the vanadium content was found low in the urban soils, where the correlation between trace elements was different from that found in the rural soils. Here, vanadium had a highly significant correlation with Ni ($r = 0.89$), Zn ($r = 0.74$), Pb ($r = 0.51$), as shown in Table 4, typical elements occurring in hydrocarbons (Guagliardi et al., 2015), which could be the possible source for V in the urban soils. In fact, the most important anthropogenic sources of vanadium include the combustion of fossil fuels, particularly residual fuel oils, which constitute the single largest overall release of vanadium to the atmosphere.

Other anthropogenic sources include leachates from mining tailings, vanadium-enriched slag heaps, municipal sewage sludge, and certain fertilizers. After all, no representative anthropogenic input of vanadium classically affecting centres, as metallurgical works, steel industries, occurred in the study area such to justify higher vanadium contents.

4. Conclusions

A comprehensive soil survey was conducted to investigate vanadium contents in peri-urban and urban areas of Cosenza and Rende municipality (Calabria, southern Italy).

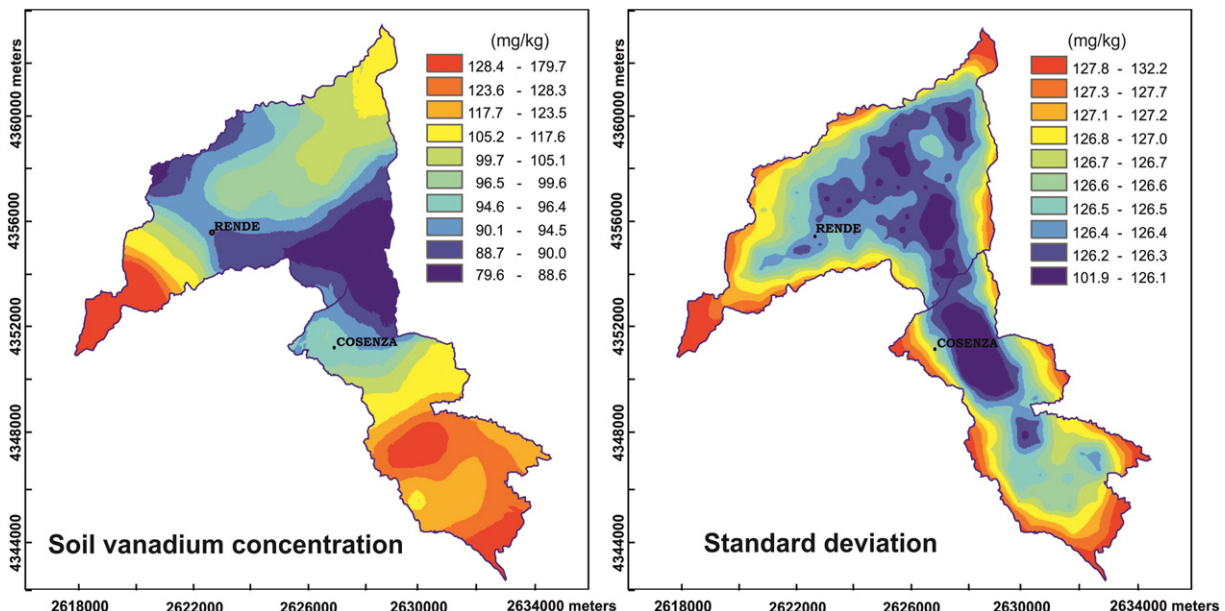


Fig. 4. Interpolated distribution and kriging standard deviation maps of the vanadium concentration.

Table 3

Pearson product moment correlation matrix for the selected elements in peri-urban soils.

	V	Cr	Ni	Pb	Zn	Fe ₂ O ₃	TiO ₂	Al ₂ O ₃
V	1.00	−0.80	0.77	−0.45	0.47	0.92	0.84	0.08
Cr		1.00	0.90	0.28	−0.003	0.78	−0.69	0.08
Ni			1.00	0.31	0.32	0.70	−0.50	0.24
Pb				1.00	0.46	−0.04	−0.11	−0.38
Zn					1.00	0.58	0.32	−0.59
Fe ₂ O ₃						1.00	0.90	0.26
TiO ₂							1.00	−0.47
Al ₂ O ₃								1.00

Table 4

Pearson product moment correlation matrix for the selected elements in urban soils.

	V	Cr	Ni	Pb	Zn	Fe ₂ O ₃	TiO ₂	Al ₂ O ₃
V	1.00	0.26	0.89	0.51	0.74	0.49	0.15	−0.04
Cr		1.00	0.88	−0.07	0.09	−0.08	−0.44	0.14
Ni			1.00	−0.15	−0.03	−0.01	−0.50	−0.01
Pb				1.00	0.82	0.16	0.04	−0.52
Zn					1.00	0.26	0.36	−0.26
Fe ₂ O ₃						1.00	0.38	−0.33
TiO ₂							1.00	0.10
Al ₂ O ₃								1.00

Statistical and geostatistical analysis of the distribution patterns of vanadium in topsoil were used to identify the sources of pollution according to local geology and to anthropogenic activities.

The mean vanadium concentrations in peri-urban soils were higher than urban area and especially enriched at some specific sites. Spatial distribution patterns showed that V was controlled by the parent material in peri-urban areas where, particularly, ophiolite-bearing units outcroppings play an important role in the distribution of the element.

The concentrations of vanadium are high in such a large area that there are sources of potentially harmful vanadium in a large area. The risk to the environment may also be high if there is a pathway from the source to the vulnerable receptors (plants, animals, water sources). The risk may be smaller if vanadium is strongly bound to the Fe-precipitates and there are no reasons for fast weathering of the precipitates. Conversely, no clear evidences of pollution occurred in urban area where the mean concentration of vanadium amounted below the critical threshold value imposed by Italian Decree 152, 2006.

Certainly, in the study area it is not possible to state of pollution because it occurs when a substance is present in soil in greater than natural concentration as a result of human activities and having a net harmful effect upon the environment and its components.

In its natural state contaminants may not be classified as pollutants and consequently it is not possible carry out any type of remediation in interested area.

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