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

Ilaria Guagliardi^{a,c,*}, Domenico Cicchella^b, Rosanna De Rosa^c, Nicola Ricca^a, Gabriele Buttafuoco^a^a National Research Council of Italy, Institute for Agricultural and Forest Systems in the Mediterranean (ISAFOM), Via Cavour 4/6, 87036 Rende, CS, Italy^b Department of Science and Technology, University of Sannio, Via dei Mulini 59/A, 82100 Benevento, Italy^c Department of Biology, Ecology and Earth Sciences, University of Calabria, Ponte Bucci, 87036 Rende, CS, Italy

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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 (Saedi 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 unconcerned 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 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

* Corresponding author at: National Research Council of Italy, Institute for Agricultural and Forest Systems in the Mediterranean (ISAFOM), Via Cavour 4/6, 87036 Rende, CS, Italy.
E-mail address: ilaria.guagliardi@isafom.cnr.it (I. Guagliardi).

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

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).

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