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Spatial distribution of arsenic, uranium and vanadium in the volcanic-sedimentary aquifers of the Vicano–Cimino Volcanic District (Central Italy)

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ABSTRACT

Arsenic concentrations were analysed for 328 water samples collected in the Vicano–Cimino Volcanic District (VCVD), an area where severe contamination of groundwater has become a serious problem following the recent application of the EU Directive on the maximum allowable concentration level for As in drinking waters. In addition, uranium and vanadium concentrations were also analysed in light of the enhanced interest on their environmental toxicity. Waters were collected from springs and wells fed by cold and shallow volcanic-sedimentary aquifers, which locally represent the main drinking water source. Thermal springs (≤ 63 °C) related to an active hydrothermal reservoir and waters associated with a CO₂-rich gas phase of deep provenance were also analysed. The collected data showed that the As concentrations in the shallow aquifers varied in a wide range (0.05–300 µg/L) and were primarily controlled by water–rock interaction processes. High As concentrations (up to 300 µg/L) were measured in springs and wells discharging from the volcanic products, and about 66% exceeded the limit of 10 µg/L for drinking waters, whereas waters circulating within the sedimentary formations displayed much lower values (0.05–13 µg/L; ~4% exceeding the threshold limit). Thermal waters showed the highest As concentrations (up to 610 µg/L) as the result of the enhanced solubility of As-rich volcanic rocks during water–rock interaction processes at high temperatures. Where the local structural setting favoured the rise of fluids from the deep hydrothermal reservoir and their interaction with the shallow volcanic aquifer, relatively higher concentrations were found. Moreover, well overexploitation likely caused the lateral inflow of As-rich waters towards not contaminated areas.

Uranium and vanadium concentrations of waters circulating in the volcanic rocks ranged from 0.01 to 85 µg/L and 0.05 to 62 µg/L, respectively. Less than 2% of analysed samples exceeded the World Health Organization's provisional guidelines for U (30 µg/L), while none of them was above the Italian limit value of V in drinking water (120 µg/L). Lower U (0.07–22 µg/L and 0.02–13 µg/L, respectively) and V concentrations (0.05–24 µg/L and 0.18–17 µg/L, respectively) were measured in the water samples from the sedimentary aquifer and thermal waters. Local lithology appeared as the main factor affecting the U and V contents in the shallow aquifers, due to the high concentrations of these two elements in the volcanic formations when compared to the sedimentary units. In addition, high U concentrations were found in correspondence with U mineralization occurring within the VCVD, from which U is released in solution mainly through supergene oxidative alteration. Redox conditions seem to play a major role in controlling the concentrations of U and V in waters. Oxidizing conditions characterizing the cold waters favour the formation of soluble U- and V-species, whereas thermal waters under anoxic conditions are dominated by relatively insoluble species. Geostatistical techniques were used to draw contour maps by using variogram models and kriging estimation aimed to define the areas of potential health risk characterized by As, U and V-rich waters, thus providing a useful tool for water management in a naturally contaminated area to local Authorities.

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1. Introduction

The peri-Tyrrhenian sector of central and southern Italy is a region of preferential release of naturally occurring toxic trace elements from Plio-Quaternary volcanic rocks into groundwater (Aiuppa et al., 2006;

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Dall'Aglio et al., 2001; Dinelli et al., 2010; Giammanco et al., 1996; Tamasi and Cini, 2004; Vivona et al., 2007), a process enhanced by extensive thermalism (Cataldi et al., 1995) and the presence of reactive gas species (e.g. CO₂, H₂S) (Chiodini et al., 1999; Minissale, 2004). Since the last decade, understanding the geochemical processes that favour the occurrence of high As contents in large groundwater reservoir of central-Italy used for drinkable waters represents one of the main targets for the Italian scientific community (e.g. Angelone et al., 2009; Baiocchi et al., 2013) and policy-makers, as the maximum allowable concentration in water intended for human consumption was lowered from 50 to 10 µg/L (EC Directive, 1998). Episodes of severe As contamination of drinking waters were reported in several countries (e.g. India, Argentina, Chile, Mexico, etc.) from naturally affected areas (e.g. Katsoyiannis et al., 2007; Rahman et al., 2005; Romero et al., 2003; Smedley and Kinniburgh, 2002; Smedley et al., 2005) together with its effects on human health, which include cardiovascular, renal, haematological and respiratory disorders and also skin and internal (bladder, lung, prostate) cancers (IARC, 2004). Arsenic is sensitive to mobilization at the pH values typically found in ground waters (6.5–8.5) and under both oxidizing and reducing conditions (Smedley and Kinniburgh, 2002). Arsenic is mostly occurring in solution in inorganic form as oxyanions of trivalent arsenite As(III) or pentavalent arsenate As(V) (e.g. Smedley and Kinniburgh, 2002). As-rich waters are commonly associated with 1) the presence of active geothermal systems (e.g. Aiuppa et al., 2006; Ballantyne and Moore, 1988; Webster and Nordstrom, 2003) and 2) enhanced water–rock interaction processes in different stratigraphic and hydrogeochemical settings (e.g. Smedley and Kinniburgh, 2002, and references therein). Anthropogenic processes responsible for As contamination of water are mainly related to mining activities, combustion of fossil fuels and use of arsenical pesticides and herbicides (Smedley and Kinniburgh, 2002).

Uranium was recognized as a toxic contaminant of groundwater since 1998. In 2011, a provisional health-based U guideline concentration of 30 µg/L was promulgated by the World Health Organization (WHO, 2011) for drinking waters, since they represent the primary source of U intake for humans. Although the naturally occurring U is radioactive, the overall risks arising from the biochemical toxicity of U as a heavy metal are considered to be about six orders of magnitude higher than those derived from its radioactivity (Milvy and Cothorn, 1990). Effects of U intake in humans include kidneys disease (nephritis), increased risk related to fertility problems and reproductive cancers (EFSA, 2009). High U concentrations in groundwater were reported in many areas worldwide (e.g. Cicchella et al., 2010; Frengstad et al., 2000; Nriagu et al., 2012; Smedley et al., 2006; Wu et al., 2014), especially in the presence of U-rich granitic terrains and U-mineralized areas. Nevertheless, significant enrichments were also recorded in waters interacting with iron oxides, phosphates, clays and organic matter (Smedley et al., 2006 and references therein). Uranium is a redox-sensitive heavy metal that occurs in oxic waters, mostly as hexavalent U(VI), where uranyl ion (UO₂²⁺) is the dominant form at low pH (<5), whereas at higher pHs carbonate complexes predominate (Smedley et al., 2006; Wu et al., 2014). Under anoxic conditions, U is reduced to its tetravalent form U(IV) and its concentration in water is relatively low as a result of stabilization of the sparingly soluble mineral uraninite (UO₂). Anthropogenic sources include mining activities, nuclear industry and fertilizer manufacture (Smedley et al., 2006).

Increasing interest on the toxicological effects of the ingestion of V from drinking water has grown in the last years. A number of studies have warned on the possible harmful effects of V when present at high concentrations (e.g. Gerke et al., 2010; Wright et al., 2014), leading the U.S. Environmental Protection Agency to list V in the Contaminant Candidate List 3 (USEPA, 2009). However, the toxicological studies are not fully exhaustive and the daily intake of V via drinking water is generally low. Consequently, V has not been yet considered by WHO as a contaminant. As far as contaminant regulation in Italy is concerned, the limit value of V in drinking water was increased from 50 to

120 µg/L, and a new parametric value of 140 µg/L was recently proposed (Crebelli and Leopardi, 2012). Potential natural sources of V in ground-water are related to rock weathering and sediment leaching, while anthropogenic sources include waste streams from industrial processes and iron pipe corrosion by-products (Dinelli et al., 2012; Gerke et al., 2010; Giammanco et al., 1996; Pourret et al., 2012). The behaviour of V in the aquatic environment is mainly regulated by redox and pH of the aqueous system (Wright et al., 2014). Under oxic conditions V is present as pentavalent V(V) and occurs in the oxyanionic form at pH values typically found in ground waters, whereas under reducing conditions the less soluble trivalent V(III) and tetravalent V(IV) species dominate.

In this study, 328 water samples from springs, private domestic and municipal wells, mostly used for human consumption, were collected from the Vicano–Cimino Volcanic District (VCVD) and analysed for As, U and V concentrations. Thermal and cold waters associated with a CO₂-rich bubbling gas phase, which are relatively common in the peri-Tyrrhenian sector of central Italy (Chiodini et al., 1999; Minissale, 2004), were also analysed. The main aims were to i) investigate the source of As, U and V and the main factors controlling their chemical behaviour in this natural environment and ii) reconstruct the spatial distribution of their concentrations and evaluate the potential health risk for areas affected by anomalous contamination.

2. Geodynamic, hydrogeological and petrological settings

VCVD is located along the peri-Tyrrhenian sector of central Italy, between the Tyrrhenian coast and the Apennine chain (Fig. 1). This sector has undergone a post-collisional Plio-Quaternary extensional phase, that led to a strong crustal thinning (<25 km; Scrocca et al., 2003) and generated heat flow anomalies (locally higher than 200 mW/m²; Barberi et al., 1994; Cataldi et al., 1995) and subduction-related magmatism (Barberi et al., 1994; Peccerillo, 1985). Extensional tectonics formed preferentially NW–SE oriented horst and graben structures with clastic marine sediments filling the structural lows (Barberi et al., 1994).

The Cimino and Vicano volcanic complexes belong to two different magmatic cycles, respectively: 1) the acid cycle, represented by SiO₂-rich magma of the Tuscan Magmatic Province and 2) the undersaturated K-alkaline cycle of the Roman Magmatic Province (Aulinas et al., 2011; Barberi et al., 1994; Perini et al., 2004; Sollevanti, 1983), respectively. The Cimino complex was active from 1.35 to 0.94 Ma (Nicoletti, 1969). It consists of a series of rhyodacitic domes and ignimbrites emplaced along a NW–SE trending fracture zone. At the end of the eruptive activity a central volcano, emitting latitic and olivine-latitic lavas, developed (Cimarelli and De Rita, 2006). The Vicano complex (0.42–0.09 Ma; Laurenzi and Villa, 1987) consists of a strato-volcano developed on a NW–SE elongated graben at the intersection with a NE–SW fracture, with a central caldera depression hosting Lake Vico. Alternating explosive and effusive phases, producing fall deposits, lava and pyroclastic flows, were followed by circum-caldera hydromagmatic and strombolian eruptions. The products of the Vicano complex are mainly leucitites, phono-tephrites and leucite-phonolites (Perini et al., 2004). The volcanic products overlie a sedimentary sequence that made up of, from top to bottom (Fig. 1): 1) a Plio-Pleistocene complex that includes conglomerates, sandstones and mudstones, 2) a Cretaceous–Oligocene(?) Ligurian and Sub-Ligurian units, referred hereinafter to as Ligurian s.l. and 3) Mesozoic carbonates overlying Triassic evaporites (Burano Fm.).

The Vicano–Cimino volcanites constitute a water reservoir limited by the low-permeability Plio-Pleistocene sedimentary complex and the Ligurian s.l., which act as aquicludes (Baiocchi et al., 2006; Capelli et al., 2005). A continuous basal unconfined aquifer and several perched aquifers of limited and discontinuous extent were identified in relation to the complex hydrostratigraphy that includes relatively high-permeability formations (i.e. ignimbrites and lava flows) alternated to

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