



Hydrogeochemical overview and natural arsenic occurrence in groundwater from alpine springs (upper Valtellina, Northern Italy)



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SUMMARY

High arsenic (As) concentrations (up to 230 $\mu\text{g/L}$) have been historically observed (since 1999) in the upper Valtellina valley groundwater (UVV, central Italian Alps), and measured in samples collected during four campaigns of one full hydrological year (summer 2012–summer 2013). During these campaigns, water has been collected from both cold springs and thermal springs. The hydrogeochemistry of aquifers and superficial waters through the hydrologic year, and the long-term regional As distribution and time variability were analyzed.

Although the studied springs belong to different catchments with different hydrochemical and lithological conditions, they present some typical characteristics: (1) the water types are dominated by Ca–Mg and $\text{SO}_4\text{--HCO}_3$ main ions, with seasonal variations for the second end members; (2) the Cl concentration is always very low, and poorly correlated with other ions; (3) the circulation time obtained from isotopic data ranges between 5 and 10 years for thermal springs and it is lower than 2 years for cold springs; (4) dominant oxidizing conditions have been observed for most of the cold and for the thermal springs; (5) anthropogenic contamination is absent, while natural contamination of arsenic affects most of the springs, with a natural background level for the entire UVV of 33 $\mu\text{g/L}$; (6) both As (V) and As (III) are present in all the springs analyzed, with a marked prevalence of As (V) among the cold ones. These conditions suggest that the latter belong to recent hydrochemical immature aquifers, where the presence of arsenic is mostly related to alkali desorption and sulfide oxidation, while the thermal springs derive from the rapid uprising of deep-circulation water, with a high concentration of geothermal arsenic.

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1. Introduction

Natural arsenic is found in groundwater, usually with concentrations lower than 10 $\mu\text{g/L}$, even though concentrations up to 350 $\mu\text{g/L}$ have been measured around the world, mainly in Bangladesh, China, Nepal, Argentina and Mexico (Mukherjee et al., 2014). Since 1993, the WHO (World Health Organization) established a maximum As concentration level in water for human consumption of 10 $\mu\text{g/L}$. Water consumption with concentrations over 50 $\mu\text{g/L}$ for more than one year can be at the origin of skin problems and chronic lung diseases and even cancer for 1 out of 100 exposed persons (Smith et al., 2000).

Natural arsenic was found also in the European Alps in different locations. In Switzerland, anomalous natural As concentrations were found in the Graubünden, Ticino and Wallis cantons (Pfeifer et al., 2002, 2004, 2007, 2012) and along the Insubric fault in different ecosystems (Beatrizotti and Pfeifer, 2004). In Austria, anomalous As concentrations were found in stream sediments of the eastern Carinthia (Göd and Zemann, 2000), and in groundwaters from eastern Croatia in the Drava and Sava depressions (Ujevic et al., 2010). In France, natural As was found in metamorphic rocks along the Tinée river valley (Barats et al., 2014). Tisserand et al. (2014) studied the distribution of geogenic arsenic in the aquifers of the External Crystalline Massifs (ECM) in the Western Alps (France and Switzerland) observing high As variability, probably due to differences in local source geology, hydrogeochemical transport conditions and depth of groundwater circulation. High As concentrations are found in water samples from Alpine sediments of the Po plain (Castelli et al., 2005; Magnani et al., 2005; Rotiroti, 2013). Initial studies dealing with As treatment methodologies in the Lombardy region were carried out by Berbenni and Bernini (1997).

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Arsenic presents two main inorganic species in groundwater, As (III) arsenite and As (V) arsenate, which are controlled mainly by pH and redox potential, being As (III) fifty times more toxic for human health than As (V) (Smedley and Kinniburgh, 2002). Analytical As speciation, allows to determine the dominant species in the sampled waters, and to confirm the redox conditions measured in the field, which is useful for hydrochemical characterization and, indirectly, for the development of appropriate treatment methodologies (Vance, 1995).

Four main mechanisms for arsenic mobilization are known (Smedley and Kinniburgh, 2002; Bhattacharya et al., 2007; Ravenscroft et al., 2009): (1) alkali desorption (AD), that produces alkali-oxic waters and causes the desorption of As from Fe, Mn, and Al oxides at high pH levels; (2) sulfide oxidation (SO), that produces acid-sulfate waters and mobilizes As through the oxidation of As-bearing sulfides such as arsenopyrite, pyrite and pyrrhotite; (3) reductive dissolution (RD), that produces near-neutral reducing waters, and causes the mobilization of As(III) from unstable sorbent such as Fe, Mn, and Al oxides; (4) geothermal Arsenic (GA), which is formed by high-temperature leaching of silicate rocks in aquifers with rapid and deep circulation. These processes are controlled by pH and redox potential, and can possibly co-exist in the same aquifer (Ravenscroft et al., 2009), and can occur in different geologic settings (Mukherjee et al., 2014).

While most of the previous studies in the Lombardy region have been focused on the As in aquifers of the Po plain (since Castelli et al., 2005), which are also the most exploited source for drinking water in Italy, this paper focuses on the As presence and speciation in a mountain region where hydrochemical conditions are less studied (Kilchmann et al., 2004). Moreover, the hydrogeochemical characterization of a large mountain area poses a challenge due to the high variability of chemical conditions even at local catchment scale (Tisserand et al., 2014). The aim of this research is the characterization of the Alpine upper Valtellina valley (UVV) aquifers by means of hydrogeological, hydrogeochemical, As speciation, isotopic and whole-rock data analyses, in order to understand the processes responsible for As release and mobilization, improving the knowledge in the alpine orogen.

2. Study area

The UVV covers 800 km² in the central Italian Alps, including five municipalities (Valdisotto, Bormio, Valdidentro, Valfurva and Livigno; Sondrio Province), with a total population of about 25,000 people, increasing of about 25% during the summer period. The elevation in the UVV ranges from 1150 to 3500 m asl (Fig. 1).

The study area belongs to the Austroalpine Domain (Froitzheim et al., 2008), located between two important tectonic lines, the Periadriatic lineament to the south, and the Engadine line to the northwest (Fig. 1B). The tectonic structure and metamorphic composition of this area have been well described by Conti (1994) and Froitzheim et al. (1997).

The major regional structures occurring in the area are the Schlinging Line (Froitzheim et al., 1997), the Trupchun Braulio thrust and the Zebrù Line (ZL, Conti et al., 1994, Fig. 1). The ZL separates the Campo Nappe (low/medium metamorphic unit, phyllites and micaschists) to the south from the overlying Ortles sedimentary cover (Triassic carbonate unit, Dolomia Principale) to the north (Conti et al., 1994). Towards the municipalities of Sondalo and Valdisotto, the gabbro of Sondalo, with transitions to diorite of Mesozoic age, crops out (Fig. 1).

The UVV is subdivided into two major drainage basins by the Foscagno pass (Fig. 1): the Inn-Danube basin to the North and the Adda-Po basin to the south (Fig. 2). A complex network of diversion tunnels distributed along the UVV basin and constructed since the

1960s, brings water to the Cancano and San Giacomo di Fraele artificial lakes (Fraele valley, see Fig. 1). An unknown amount of water is therefore used for hydropower energy generation, hampering the calculation of a complete water budget for the study area. The average annual precipitation measured in the Bormio monitoring station in the period 1921–2012 ranges from 790 to 1490 mm/y. Because of the winter solid precipitations, the aquifers recharge is delayed to the cold alpine springs and thermal springs during the spring season.

The geomorphology of the UVV is characteristic of a typical high Alpine valley, dominated by fluvial valleys and large U-shaped valleys. Weathering of mountain rock slopes results in residual soils, further transported and deposited as alluvial materials in the lower valleys. These soils are characterized by fine to coarse materials, hosting rich aquifers exploited only in case of water shortages, especially in the municipalities of Valdidentro and Valdisotto.

Most of the mountain aquifers along the UVV slopes present medium/high hydraulic conductivities controlled by the fracturing developed during the Alpine orogeny, metamorphism and by successive long-term weathering, finally influencing the large number of natural springs emerging in the UVV. These springs were classified into two main groups: the thermal springs (TS) (Bagni Vecchi area, north of Bormio) and the cold alpine springs (CS). The TS are the result of the contact, between sedimentary permeable rocks (Dolostone – *Dolomia principale* Formation), and the underlying metamorphic pseudo-impermeable rocks (Berra, 1994) along the Zebrù line (Fig. 1).

The presence of numerous deep-seated gravitational slope deformations (DSGSD) in the study area is an important structural characteristic that influences the local groundwater flow in the mountain slopes, the spring occurrence and, indirectly, the hydrochemical conditions (Agliardi et al., 2009; Crosta et al., 2013, 2014).

3. Materials and methods

Historical data on water quality from springs, wells, lakes, rivers and public fountains were obtained from the Lombardy Region Health Agency (ASL). The available analyses (3050) from five municipalities (Bormio, Livigno, Valdidentro, Valdisotto and Valfurva) span from 1996 to 2011, and have been organized in a hydrogeochemical database (AquaChem software, Calmbach, 1997). The use of these historical data for hydrogeochemical characterization is biased by the fact that most of them come from public fountains, which in some cases do not collect water from one single spring but rather from multiple springs generally clustered in a specific area. Samples through the 2012–2013 hydrologic year were collected and analyzed across the study area (Fig. 2) during four different campaigns: June 2012, October 2012, May 2013, and September 2013.

During the first campaign, most of the accessible springs in the UVV (59 springs) were sampled for a regional characterization and to identify areas with high As concentrations (Table 5). Specific electrical conductivity (EC, at 20 °C), temperature and pH were measured in the field by a multi-parameter probe (Hanna Instruments, HI 9828). An arithmetic correction was applied to field data measured for the ORP (oxidation/reduction potential), by adding 205 mV to the ORP measured, in order to report the results with respect to the standard hydrogen electrode.

Springs with As concentrations higher than 10 µg/L were grouped in ten selected areas (SA) (Fig. 2), which were sampled again in October 2012, May 2013, and September 2013. The springs were grouped in 10 main clusters because of proximity reasons within each SA and because belonging to the same mountain aquifer, with expected similar hydrogeochemical characteristics. Furthermore, the SA are distributed over the entire study area and they are representative of all the different lithologies (Fig. 2).

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