Arsenic in the groundwater aquifers of the Venetian Plain: geochemical modelling and occurrence of As-sulfides minerals, a review of data from the medio Brenta domain (Italy)

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Abstract

The Venetian Plain is known for areas with high concentrations of arsenic (As) in groundwater (up to more than 400 μg/L, exceptionally 647 μg/L, in selected areas). A study area was chosen, north of Padua, which exhibits typical residential, industrial, and agricultural characteristics similar to most Western countries and lacks hydrothermal, volcanic, or anthropogenic sources of arsenic. The pilot area was the focus of several studies which are reviewed in this note. The objectives of the studies were to verify the distribution of As concentrations in groundwater and sediments (mineralogical and geochemical analysis of groundwater sediments and of filtered and unfiltered groundwater) and to model the mobility of arsenic arising from water-rock interaction. The grain size of aquifer reservoirs includes gravel, sand, silt, and clay. The amount of organic matter in the aquifer sediments of the study area seems peculiar (higher) compared to other plains in the world; it influences the redox potential and the relative concentration of As in groundwater. Arsenic contamination in groundwater and redox conditions varied greatly in the area. Groundwater under oxidizing and highly reducing conditions had much lower arsenic concentrations compared to groundwater under intermediate reducing conditions. Arsenic minerals (such as realgar-pararealgar) occur in aquifer sediments and they were documented in the studied materials by different analytical techniques for the first time in the context of the Italian plains. The objectives of the studies were to verify the distribution of As concentrations in groundwater and sediments (mineralogical and geochemical analysis of groundwater sediments and of filtered and unfiltered groundwater) and to model the mobility of arsenic arising from water-rock interaction. The grain size of aquifer reservoirs includes gravel, sand, silt, and clay. The amount of organic matter in the aquifer sediments of the study area seems peculiar (higher) compared to other plains in the world; it influences the redox potential and the relative concentration of As in groundwater. Arsenic contamination in groundwater and redox conditions varied greatly in the area. Groundwater under oxidizing and highly reducing conditions had much lower arsenic concentrations compared to groundwater under intermediate reducing conditions. Arsenic minerals (such as realgar-pararealgar) occur in aquifer sediments and they were documented in the studied materials by different analytical techniques for the first time in the context of the Italian plains.
Introduction

Arsenic (As) is a chemical element that belongs to the 15th group of the periodic table, placing it in the same group as nitrogen (N), phosphorus (P), antimony (Sb), and bismuth (Bi). This position indicates, to some extent, a relationship of similarity with these elements, some of which are abundant in living organisms (N and P), while others are scarce (Sb and Bi). Arsenic lies in the middle between N-P (essential elements for life) and Sb-Bi (toxic elements even at low concentration) and this characteristic may be a reason for making arsenic a “special” chemical element worldwide. Three aspects deserve special mention: i) arsenic is present in appreciable quantities in various environmental matrices (water, soil, plant tissues, animal tissues, see for instance Bowel et al., 2014); although not highly concentrated in any of these, its abundances are not negligible, especially when considering As concentrations in relation to specific aspects such as health effects; ii) the element can take on different oxidation states, with the main ones being -3, +3, and +5; for this reason, it can assume different chemical forms and move between matrices; iii) some common chemical forms in nature can be highly toxic even at low concentrations. These three aspects are of a general nature, meaning they are not specific to a geographic area or particular conditions. In fact, issues related to As in water intended for human consumption are well-known worldwide (Nordstrom, 2002), including floodplains where human settlements have concentrated. The Venetian Plain is also located in this context of recently densely populated alluvial plains.

The purpose of this note is to review the knowledge acquired in the last 10 years mainly in a study area in the central part of the Brenta Plain, representative of regional conditions, including geologic, social and economic regime. During this period, the problem of water pollution and climate variability makes the water resource in the Veneto Region a key point of economic and social sustainability.

Material and methods

Limits of Concentration Allowed in Drinking Water

The toxicity of arsenic to the human body has been known for a long time, but acute exposure is associated with very specific conditions (such as industrial processes or deliberate poisonings). In contrast, groundwater contamination represents a typical case of chronic exposure with no immediate effects. However, prolonged exposure to low levels of arsenic over the years poses a serious health risk (Zuzzolo et al., 2020). In this context, water consumed directly or used in food preparation is the most important vector for arsenic because water soluble arsenic is primarily present in an inorganic form, such as arsenite ion (AsIII) and arsenate ion (AsV), which are the most toxic forms (Cubadda et al., 2017).

Since the duration of exposure is an important factor in determining health problems, it is difficult to identify a threshold concentration value that indicates the water is drinkable. A better option is to consider the amount of arsenic to which the population is exposed over the entire duration of the permanence in the area (on the order of years or decades). Many health data used to define the drinking water limit refer to studies conducted in Asia, where the problem has manifested itself in a widespread and severe form before elsewhere (see for instance Andrews et al., 2022; Nordstrom, 2002). This regional aspect of epidemiological data has led to a discussion about the generalizability of the results obtained, but in recent times, a detailed study on the health effects of arsenic in water has also been conducted in Italy. The study focused on more than 165,000 inhabitants of the Viterbo area (D’Ippoliti et al., 2015), where the public water supply draws from groundwater relatively rich in arsenic, originating from magmatic and pyroclastic rocks (Armiento et al., 2015). Among the most significant findings of the epidemiological study is the confirmation that exceeding the current legal limit (10 µg/L, Council Directive 98/83/EC, 1998) is associated with the onset of various health conditions. However, even at concentrations lower than 10 µg/L, high mortality rates are observed. Other research conducted in Italy has also critically reviewed the current limit (Bustaffa & Bianchi, 2014). In summary, it is reasonable to consider that the 10 µg/L limit may need to be revised, raising serious issues regarding the supply and treatment of water intended for human consumption.

Study area

Anomalies of arsenic in groundwater have been reported in the Po Valley (Zavatti et al., 1995) and in the Venetian Plain, especially in the middle part of the Brenta River (Baldantoni & Ferronato, 1995), with values far exceeding the legal limits (in the 1990s, set at 50 µg/L, Council Directive 80/778/EEC). Additionally, anomalies were observed in the lower part of the Venetian Plain several years later (ARPAV, 2019) and studied in detail (Dalla Libera et al., 2020; Dalla Libera et al., 2018). To investigate the causes of these anomalies, a pilot area in the province of Padua was selected for detailed studies initiated in 2011, thanks to specific funding from the Veneto Region, ATO Brenta, and the Municipality of Carmignano di Brenta (province of Padua). The overall objective of these activities was to construct a hydrogeological model and to develop the modelling of geochemical data. The experimental data encompassed groundwater and sediment samples from the aquifer, which were investigated with particular attention to provide a complete view of the aquifer system.

The pilot area was centered around the most significant arsenic anomalies previously reported in the region (Fig. 1), spanning the municipalities of Gazzo (province of Padua) and Piazzola sul Brenta (province of Padua) (Baldantoni & Ferronato, 1995; ARPAV, 2009). The study area was chosen, north of Padua, which exhibits typical residential, industrial, and agricultural characteristics of plain zones in most Western countries and lacks hydrothermal, volcanic, or anthropogenic sources of arsenic.
A further aspect of interest in the pilot area is the presence of an important well field for drinking use (Camazzole). In the last ten years the use of Camazzole groundwater passed from a local level to a strategic one for the Veneto Region, because many other water resources have been found polluted by PFAS (perfluoroalkyl substances), triggering serious health alerts in the area (Mastrandotonio et al., 2017; WHO, 2017). The PFAS contamination involves the provinces of Vicenza, Verona, Padova and Rovigo (WHO, 2017; ARPAV, 2023), so the administrative authorities redesigned the water supply of the Region, selecting the upper part of the pilot area under study as the alternative source of clean water (for instance DGR 1352, 18 September 2018). Today, the Camazzole site is the most important well field of the Veneto region, with a maximum planned extraction up to 950 L/sec (www.viveracqua.it/acqua-pedemontana-per-600-000-residenti-veneti-grazie-al-savec). Within the pilot area selected for our works, various types of studies were conducted, which can be summarized as follows:

- **Reconstruction of the hydrostratigraphic framework:** Three confined aquifers were identified in the area up to approximatively 200 m below ground level (b.g.l.), in addition to the shallow unconfined aquifer (Carraro et al., 2015).

- **Chemical characterization of water:** this involved geostatistical analysis using ordinary kriging to map the distribution of arsenic and indicator kriging to define the probability distribution of exceeding the drinking water limit (10 µg/L), identifying anomalous zones (Carraro et al., 2013).

- **Development of geochemical modelling:** (using Visual MINTEQ; Gustafsson, 2013), accounting for the arsenic mobility mainly in response to changes of redox conditions observed in the field, considering all available data, such as water chemistry, the mineralogy and geochemistry of aquifer sediment, sorption reactions on labile Fe-hydroxides (Carraro et al., 2015).

- **Analysis of aquifer sediments:** sediment samples were collected from 5 boreholes distributed across the entire area (including two continuous core drilling samples up to -30 m), analyzing both chemical components and mineralogical properties (Carraro et al., 2015). The mineralogical studies first involved X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM), and later also µ-Raman techniques, leading to the identification of realgar-pararealgar phases, i.e. sulfide minerals which are unusual in non-hydrothermal environments and are documented for the first time in the aquifer sediments of Northern Italy (Artioli et al., 2019).

**Results and discussion**

The hydrostratigraphic arrangement of the study area (Carraro et al., 2013) effectively represents the configuration of the Venetian Plain, featuring a large unconfined aquifer extending for 15-20 km south of the southern edge of the Prealps. The unconfined aquifer has a thickness of 200-300 m and is extensively utilized for water supply. It transitions into a confined or semi-confined multilayered system to the south of the resurgence belt, where the water table emerges, giving rise to classic plain springs. The unconfined aquifer is substantially under oxidizing conditions and is unaffected by arsenic contamination, despite occasional occurrences of values slight exceeding the normative threshold value of 10 µg/L.

The multilayered system constitutes the majority of the study area. Examination of numerous stratigraphic data and two continuous core drillings has confirmed the presence of heterogeneous sediments (comprising sands, silts, and clays) in the multilayered system, as well as sediments rich in organic matter, concentrated in dark peaty intervals, but also dispersed in sediments of all grain sizes (Carraro et al., 2015). Some peaty materials extracted from boreholes in Piazzola sul Brenta (PD) were dated using the $^{14}$C system, providing ages ranging from 199 Ka cal BP to 27.3 Ka cal BP for sediments located approximately -9 m to -28.5 m from the ground surface (Rossato et al., 2018). It should be noted that the widespread presence of diffused and concentrated organic matter (from undetectable, up to 21.9% organic carbon) is peculiar of the Venetian Plain and played a crucial role in modeling the mobility of As.

The distribution of As in groundwater during the latest survey (Carraro et al., 2013; 2015) exhibits general trends recognizable over distances of several kilometers, as well as abrupt local variations, resulting in significant fluctuations in As concentrations even within 500 m. The highest value measured in water samples filtered at 0.45 µm is 385 µg/L.
(431 µg/L in the unfiltered sample), approximately 40 times higher than the drinking water limit of 10 µg/L. Overall, about 30% of the sampled wells yielded water with As levels exceeding 10 µg/L. A general trend of groundwater As concentration was identified (Fig. 2, Fig. 3a), in which As values increased from NNO to SSE, corresponding to the direction of groundwater flow in the Venetian Plain, at least on a regional scale. Along the same direction a general progressive reduction in redox potential (ORP) was also observed (Fig. 3b).

Fig. 2 - Concentrations of As in groundwater from the shallowest aquifers (6-87 meters from the ground surface); the vertical distribution of As in all samples is also shown (modified from Carraro et al., 2015).

Fig. 3 - Concentrations of As in predominantly collected groundwater from the water table in the study area as a function of a) well locations along the NNO-SSE direction: in the northernmost part (10-18 km), almost all samples are below the 10 µg/L limit, while in the southernmost part, most are either above or close to the limit; b) redox potential: the speciation of As present in the aquifer is also schematically indicated (data from Carraro et al., 2015).

Qualitatively, the reduction in ORP is consistent with the higher presence of organic matter in the sediments. Based on these considerations, a geochemical model was developed to predict the movement of groundwater into progressively reducing conditions, as actually observed in the field samples. Two other useful pieces of information for refining the model pertain to the solid components of aquifer reservoirs, specifically the presence of: i) iron hydroxides dispersed in the water, and ii) small crystals and aggregates composed only by As and S (no oxygen) in sediment rich in organic matter, identified by SEM with energy dispersive spectroscopy system (EDS) and modeled as As-sulfides. Iron hydroxides are often observed in sand filters as precipitates at well outlets, and analyzed for their mineralogical and chemical features. Their presence is also evident from the differing iron concentrations between filtered and unfiltered water samples (0.45 µm). The arsenic content sorbed on iron hydroxides can be very high, reaching thousands of ppm of arsenic in examined cases, which is approximately 100 times higher than in the bulk sediment (Carraro et al., 2015). Hydroxides are stable under oxidizing conditions in the aquifer, so they retain adsorbed As, but tend to dissolve in reducing environments. In contrast to hydroxides, arsenic sulfides are stable in reducing environments. Indeed, the arsenic sulfides in the examined samples were found in muddy sediments or near organic remains (such as vegetal fragments). These materials occurred as aggregates of very small crystals, often nanometric in size, sometimes irregular in shape, and at other times needle-like.

Figure 4 shows different morphologic types of As-S crystals and aggregates found in the cores PM1 and RB1 (Carraro et al., 2015). Based on the geochemical model, it is due to the formation of these arsenic minerals that As concentrations in groundwater can return near or within the potable condition, interrupting the increase of As from NNO to SSE. A comparison between observed and modelled concentration of As and Fe in groundwater is reported (Fig. 5).

Fig. 4 shows different morphologic types of As-S crystals and aggregates found in the cores PM1 and RB1 (Carraro et al., 2015). Based on the geochemical model, it is due to the formation of these arsenic minerals that As concentrations in groundwater can return near or within the potable condition, interrupting the increase of As from NNO to SSE. A comparison between observed and modelled concentration of As and Fe in groundwater is reported (Fig. 5).
Despite the chemical composition of these As-S minerals seem easy to identify and very homogeneous according to SEM-EDS results, their mineralogical identification is not, as many different phases are composed by As and S with different stoichiometric ratios and crystallographic features. To access this issue, μ-Raman analyses were conducted on crystals and aggregates already identified as composed only by As and S by SEM-EDS. The spectra collected resembled pararealgar and realgar references of the RRUFF database (Lafuente et al., 2015), but the database is not completely devoid of ambiguities and the equipment used to acquire original data differs respect to the ones of the RUFF collection. In order to avoid any methodological bias, Artioli et al. (2015) collected large crystals of realgar (AsS) and used them as a reference. The comparison with μ-Raman spectra from the Venetian Plain was rather good, but not perfect, so, to obtain also a reference for pararealgar, they altered the realgar powders by UV radiation for different times, from 120 up to 330 minutes. The result of the alteration experiment was checked by XRPD, showing the formation of arsenolite (As2O3) and pararealgar (AsS), with quantities increasing with the alteration time. The μ-Raman spectroscopy of realgar and pararealgar give similar results, but materials progressively enriched in pararealgar show a progressive broadening of the Raman bands and the decrease of the band at 273 cm⁻¹ (Fig. 6). These features confirm the occurrence of pararealgar in the aquifer sediments of the Venetian Plain, even though realgar, pararealgar and other possible polymorphs of As-S do not show marked differences in their Raman spectra. A notable point is that pararealgar (and realgar) are rare outside hydrothermal environments (O’Day, 2006) and irregular morphologies and very small crystals are often linked to the activity of microorganisms (Dove et al., 2003). The role of microorganism in As sulfides precipitation under sedimentary
conditions is emerging in recent literature (Drahota et al., 2017; Falteisek et al., 2019) and the Venetian Plain can be a well constrained study area.

A final remark deals with the stability of pararealgar in the aquifer sediments. If in the case studied pararealgar formation improves water quality by significantly lowering arsenic concentrations, in the same plain exchanges with the atmosphere can rapidly induce oxygenation of the shallow aquifer (0-9 meters b.g.l.), changing arsenic solubility (Dalla libera et al., 2020). Pararealgar emerges as the switch that regulates arsenic contamination in waters of the Venetian Plain; its stability with respect to thermodynamic conditions in the aquifer, global change and possible links with the microbiological community make it a key player in groundwater quality.

Fig. 6 - Representative μ-Raman spectra of As-S crystals and aggregates from the aquifer sediments of the Venetian Plain (upper); μ-Raman spectra of reference material: realgar powder by single crystals (98% purity, by XRPD), realgar powder irradiated by UV for 2h (5% pararealgar formed, by XRPD), realgar powder irradiated by UV for 5.5h (10% pararealgar formed, by XRPD); the effects of UV radiation on the spectra is indicated: broadening of several bands and intensity decrease of a single band (data from Artioli et al., 2019).

Fig. 6 - Spettri µ-Raman rappresentativi di cristalli e aggregati di As-S provenienti dai sedimenti acqueferi della pianura veneta (in alto); spettri µ-Raman del materiale di riferimento: polvere di realgar da cristalli singoli (purezza del 98%, mediante XRPD), polvere di realgar irradiata da sorgente UV per 2h (5% di pararealgar formato, mediante XRPD), polvere di realgar irradiata da sorgente UV per 5.5h (10% pararealgar formato, mediante XRPD); sono indicati gli effetti della radiazione UV sugli spettri: allargamento di più bande e diminuzione di intensità di una singola banda (dati da Artioli et al., 2019).


Gustafsson, J.P., 2013. Visual MINTEQ. ver. 3.0 Available 2013 at:. http://www2.lwr.kth.se/English/Oursoftware/vminteq/


Acque Sotterranee - Italian Journal of Groundwater 2024-