

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)

Arsenico nelle acque sotterranee della Pianura Veneta: modellazione geochimica e presenza di Solfuri di Arsenico, una review dei dati dal settore del Medio – Brenta (Italia)

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Riassunto

La Pianura Veneta è nota per la presenza di aree con alte concentrazioni di arsenico (As) nelle acque sotterranee (fino a oltre 400 µg/L; eccezionalmente 647µg/L, in alcune zone). Un'area di studio è stata individuata a nord di Padova, con caratteristiche residenziali, industriali e agricole tipiche della maggior parte delle pianure nei Paesi occidentali e senza fonti di arsenico idrotermali, vulcaniche o antropiche. L'area pilota è stata oggetto di diversi studi, i cui risultati sono presentati in modo integrato in questa nota. Gli obiettivi di tali studi sono stati quelli di verificare la distribuzione delle concentrazioni di As nelle acque sotterranee e nei sedimenti (analisi mineralogica e geochimica dei sedimenti e delle acque sotterranee, filtrate e non filtrate) e di modellare la mobilità dell'arsenico e l'interazione acqua-roccia. I serbatoi acquiferi comprendono ghiaie, sabbie, limi e argille. La presenza di materia organica presente nei sedimenti acquiferi dell'area di studio appare peculiare (più elevata) rispetto ad altre pianure del mondo; essa influenza il potenziale redox e la relativa concentrazione di As nelle acque sotterranee. La contaminazione da arsenico nelle acque sotterranee e le condizioni redox variano notevolmente nell'area. Le acque sotterranee in condizioni ossidanti e altamente riducenti presentavano concentrazioni di arsenico molto più basse rispetto alle acque sotterranee in condizioni riducenti intermedie. Minerali di arsenico tipo realgar e pararealgar sono presenti nei sedimenti acquiferi e sono stati documentati nei materiali studiati con diverse tecniche analitiche per la prima volta nel contesto della pianura italiana. Poiché questi minerali sono rari nei sedimenti di pianura non interessati da attività vulcanica o idrotermale, la loro presenza costituisce una caratteristica distintiva dell'acquifero della pianura veneta. Nell'area di studio i minerali di arsenico sono stati trovati associati a materia organica. Questo è in linea con i risultati della modellazione geochimica, che richiede condizioni altamente riducenti per la loro precipitazione dalle acque sotterranee. I modelli suggeriscono che in condizioni ossidanti e fino a condizioni leggermente riducenti (da 200 mV a -50 mV), l'arsenico viene adsorbito su fasi solide, ma un'ulteriore diminuzione del potenziale redox porta al desorbimento dell'arsenico dai solidi e alla conseguente contaminazione delle acque sotterranee (da -50 mV a -250mV). Se il potenziale redox diventa ancora più negativo (sotto i -250 mV), le condizioni geochimiche sono favorevoli alla formazione di solfuri di arsenico. La precipitazione delle fasi realgar-pararealgar prevista dal modello geochimico procede estraendo l'arsenico dalle acque sotterranee, e rende conto quantitativamente della minore concentrazione di arsenico misurata nelle acque sotterranee molto riducenti dell'area di studio.

Abstract

The Venetian Plain is known for areas with high concentrations of arsenic (As) in groundwater (up to more than 400 µg/L; exceptionally 647µg/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. Since these minerals are rare throughout the world in plain sediments not affected by volcanic or hydrothermal activity, their occurrence is a distinctive feature of the Venetian Plain aquifer. These arsenic minerals were found in peat sediments of the study area, consistent with geochemical modeling results, which require highly reducing conditions for their precipitation from groundwater. Modeling suggests that under oxidizing and up to slightly reducing conditions (from 200 mV to -50 mV), arsenic is adsorbed on solid phases, but a further decrease in redox potential leads arsenic desorption from solids and consequent groundwater contamination (from -50 mV to -250 mV). If the redox potential becomes even more negative (below -250 mV), geochemical conditions are favorable to the formation of arsenic sulfides. The precipitation of the realgar-pararealgar phases, predicted by the geochemical model, proceeds by extracting arsenic from the groundwater and quantitatively accounts for the lower arsenic concentration measured in the highly reducing groundwater of the study area.

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 time 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 (Zuzolo 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 (As^{III}) and arsenate ion (As^V), 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 165000 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.

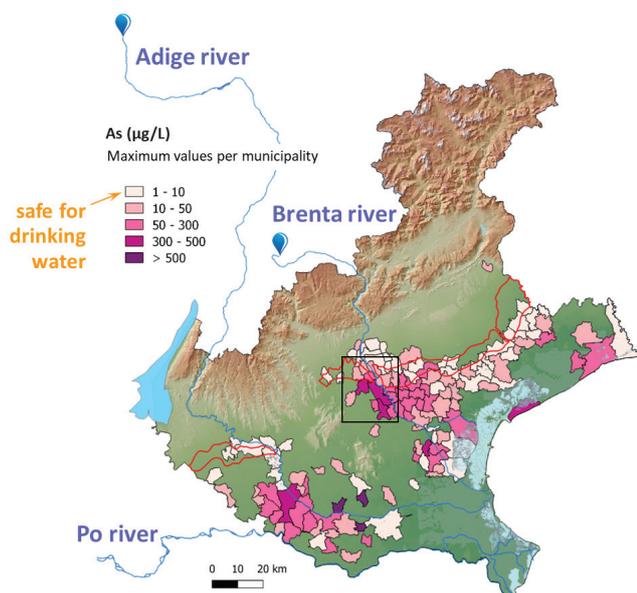


Fig. 1 - Location of the pilot area (black rectangle) and indication of the highest As values in groundwater for the municipalities analyzed by Baldantoni and Ferronato, 1995; ARPAV, 2009; 2019. The resurgence zone is highlighted in red (source: <http://idt2-geoserver.regione.veneto.it>).

Fig. 1 - Localizzazione dell'area pilota (rettangolo nero) e indicazione dei valori di As più alti nelle acque sotterranee per i comuni considerati da Baldantoni e Ferronato, 1995; ARPAV, 2009; 2019. In rosso è evidenziata la zona delle risorgive (fonte: <http://idt2-geoserver.regione.veneto.it>).

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 (Mastrantonio 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 approximately 200 m below ground level (b.g.l.), in addition to the shallow unconfined aquifer (Carraro et al., 2013).
- 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 slightly 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 19.9 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

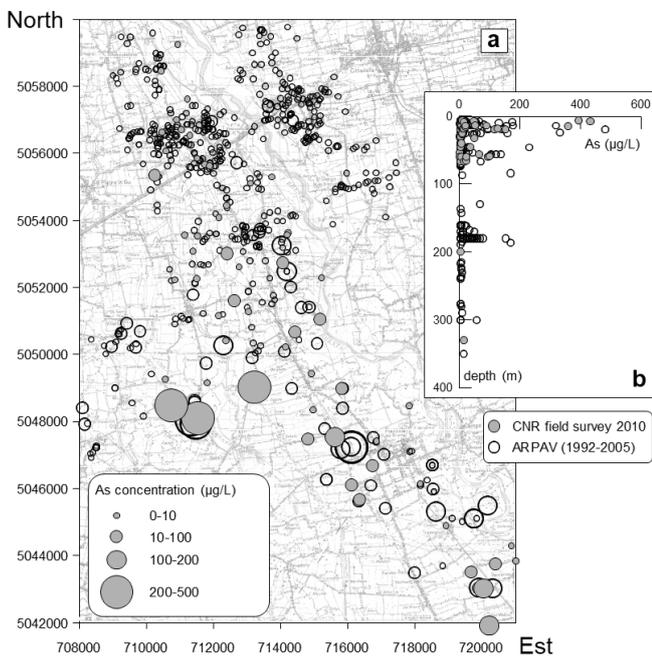


Fig. 2 - Concentrations of As in groundwater from the shallowest aquifers (6-87 meters from the ground surface); the vertical distribution of As in all samples is also shown (modified from Carraro et al., 2015).

Fig. 2 - Concentrazioni di As nelle acque sotterranee degli acquiferi più superficiali (6-87 metri dalla superficie del suolo); viene mostrata anche la distribuzione verticale di As in tutti i campioni (modificata da Carraro et al., 2015).

(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).

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 respect to the redox potential (Fig. 5).

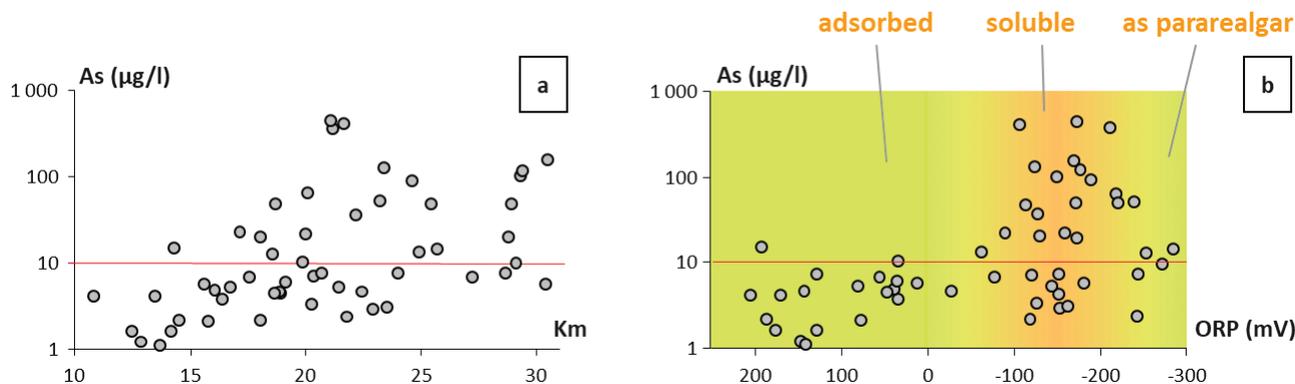


Fig. 3 - Concentrations of As in predominantly collected groundwater from the water table in the study area as a function of a) well locations along the NNO-SSE direction: in the northernmost part (10-18 km), almost all samples are below the 10 µg/L limit, while in the southernmost part, most are either 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).

Fig. 3 - Concentrazioni di As nelle acque sotterranee dell'area di studio prevalentemente raccolte dalla falda freatica in funzione di a) localizzazione dei pozzi lungo la direzione NNO-SSE: nella parte più settentrionale (10-18 km), quasi tutti i campioni sono al di sotto della limite di 10 µg/L, mentre nella parte più meridionale la maggior parte dei valori è sopra o vicino al limite; b) potenziale redox; è schematicamente indicata anche la speciazione dell'As presente nell'acquifero (dati da Carraro et al., 2015).

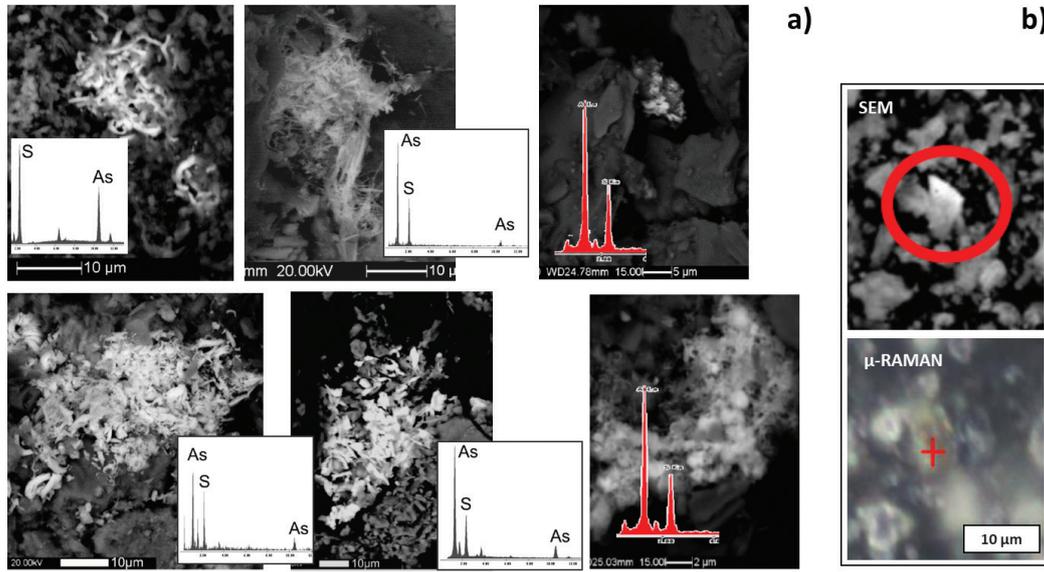


Fig. 4 - Images of As-S crystals under the SEM; the images are associated with the EDS of the bright crystals, showing only As and S as chemical components (a; from Carraro et al., 2015, modified); b) another bright crystal composed by As and S is shown in the SEM picture (upper, sample 17.5, core PM1) and the same crystal is also captured by the optical microscope of the μ-Raman instrument used for point analysis (red cross); the crystal has a greenish colour (data from Artioli et al., 2019).

Fig. 4 - Immagini di cristalli di As e S al SEM; le immagini sono associate allo spettro EDS dei cristalli chiari, mostrando solo As e S come componenti chimici (a; da Carraro et al., 2015, modificato); b) un'altro cristallo chiaro composto da As e S è mostrato nell'immagine SEM (in alto, campione 17.5, carota PM1) e lo stesso cristallo è anche fotografato dal microscopio ottico dello strumento μ-Raman utilizzato per l'analisi puntuale (croce rossa); il cristallo ha un colore verdastro (dati da Artioli et al., 2019).

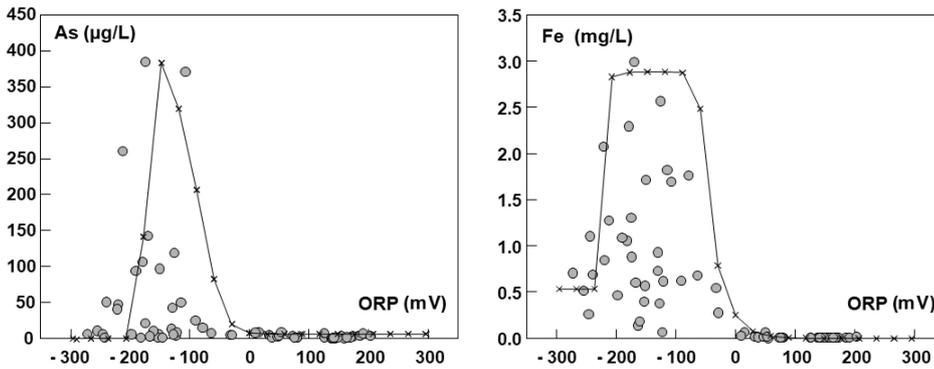


Fig. 5 - Comparison between measured values (gray circles; samples filtered at 0.45 μm) and values calculated by the geochemical model (crosses) for As and Fe in groundwater (modified from Carraro et al., 2015).

Fig. 5 - Confronto tra valori misurati (cerchi grigi; campioni filtrati a 0,45 μm) e valori calcolati dal modello geochimico (croci) per As e Fe nelle acque sotterranee (modificato da Carraro et al., 2015).

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 (As₂S₃) 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.

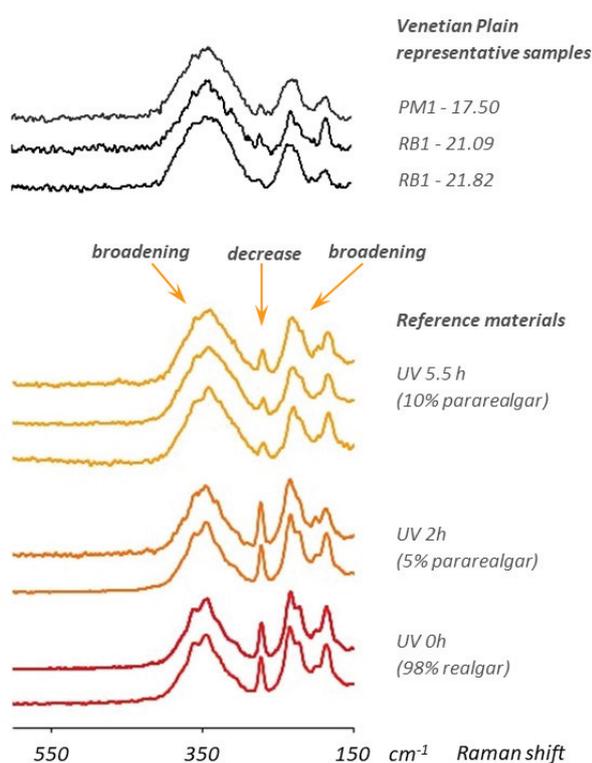


Fig. 6 - Representative μ -Raman spectra of As-S crystals and aggregates from the aquifer sediments of the Venetian Plain (upper); μ -Raman spectra of reference material: realgar powder by single crystals (98% purity, by XRPD), realgar powder irradiated by UV for 2h (5% pararealgar formed, by XRPD), 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 acquiferi 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% di pararealgar formato, da 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).

Competing interest

All authors, declare no competing interests.

Author contributions

Collection of data: FT, PF, MCD, LP; Interpretation of results: FT, PF, MCD, LP; writing-original draft preparation: FT; writing-review and editing: FT, PF, MCD, LP. All authors have read and agreed to the final version of the manuscript.

Additional information

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