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Effects of redox conditions on the control of arsenic mobility in shallow alluvial aquifers on the Venetian Plain (Italy)

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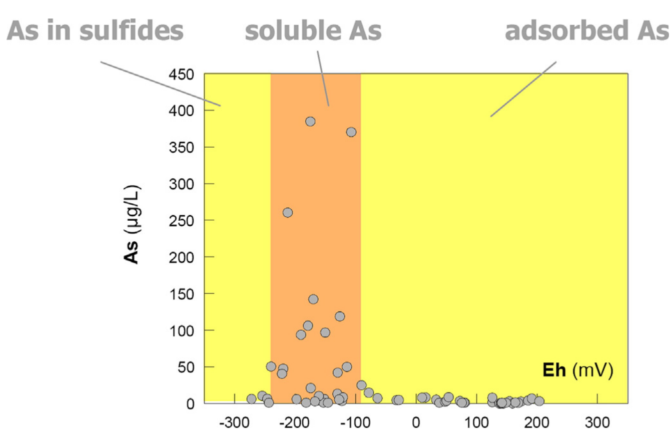
HIGHLIGHTS

- Mildly reducing groundwater on the Venetian Plain is contaminated by arsenic.
- Arsenic contamination decreases in strongly reducing groundwater.
- Peat sediments have very high arsenic concentrations.
- Arsenic sulfide minerals are detectable at the micron- to nano-scale.
- Arsenic mobility is modeled as hydroxide desorption and As-sulfide precipitation.

GRAPHICAL ABSTRACT



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ABSTRACT

The Venetian Plain is known for the occurrence of areas with high concentrations of arsenic in groundwater (greater than 400 μg/L). The study area represents the typical residential, industrial and agricultural features of most Western countries and is devoid of hydrothermal, volcanic or anthropogenic sources of arsenic. The aim of the study is to model the arsenic mobilization and the water–rock interaction by a complete hydrogeochemical investigation (analyses of filtered and unfiltered groundwater sediment mineralogy and geochemistry). The groundwater arsenic contamination and redox conditions are highly variable. Groundwaters with oxidizing and strongly reducing potentials have much lower arsenic concentrations than do mildly reducing waters. The grain size of the aquifer sediments includes gravels, sands and silty-clays. A continuous range of organic material concentrations is observed (from zero to 40%). The amount of sedimentary organic matter is highly correlated with the arsenic content of the sediments (up to 300 mg/kg), whereas no relationships are detectable between arsenic and other chemical parameters.

The occurrence of arsenic minerals was observed as a peculiar feature under the scanning electron microscope. Arsenic and sulfur are the sole constituents of small tufts or thin crystals concentrated in small masses. These arsenic minerals were clearly observed in the peat sediments, in agreement with the geochemical modeling that requires very reducing conditions for their precipitation from the groundwater. The modeling suggests that, under oxidizing conditions, arsenic is adsorbed; moreover, a continuous decrease in the redox potential causes increasing desorption of arsenic. If the reducing conditions become more intense, the formation of As-S minerals would explain the lower concentration of arsenic measured in the strongly reducing groundwater. Even if As-sulfides are rare under low-temperature conditions, the

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anomalous abundance of reductants (organic matter) can locally stabilize As-S minerals, which can scavenge large quantities of groundwater arsenic.

1. Introduction

The occurrence of arsenic in groundwater has been a well known and worldwide problem for many years (Nordstrom, 2002; Smedley and Kinniburgh, 2002), and the areas of environmental concern continue to increase in number and size (Smedley and Kinniburgh, 2013). Regardless of whether the first evidence of health problems involved West Bengal and Bangladesh (Smedley and Kinniburgh, 2013), many countries are now affected, including Western nations (Ravenscroft et al., 2009), where the population remains unaware of their exposure (Zeng and Ayotte, 2015). The health effects of acute poisoning and low chronic exposures have garnered substantial attention (EFSA, 2014; EPA, 2014; WHO, 2001).

A large number of books and scientific papers focus on the chemical composition of groundwater and sediments (Ahuja, 2008; Appelo, 2006; Bhattacharya et al., 2007; Bundschuh et al., 2005; Henke, 2009; Ravenscroft et al., 2009; Welch and Stollenwerk, 2003). In alluvial plains (which are the most populated areas in the world), the reductive dissolution of Fe-oxides and Fe-hydroxides in the aquifers has been identified as the primary mechanism of As mobility and contamination of groundwater (see the extensive review by Smedley, 2006). The As anomalies in groundwater quite often have large spatial variability (Fendorf et al., 2010; Reimann et al., 2009; "hot spot" in Charlet et al., 2007) and limited vertical expression (maximum values occur between approximately 10 to 80 m below ground level; many data are compiled in Fendorf et al., 2010; see also the tabulated data in Anawar et al., 2003; Dowling et al., 2002; BGS and DPHE, 2001; Guo et al., 2008; Kirk et al., 2004; McArthur et al., 2004; Nath et al., 2009; Swartz et al., 2004). Most research efforts have focused on the mechanisms behind the highest values of As contamination, whereas the mechanisms that control the attenuation of contamination have received less attention. The study of natural attenuation of As anomalies in water can yield effective contributions for the assessment of environmental quality and for the decontamination of drinking waters.

The aim of the present study is to establish the mechanisms of groundwater As contamination and As removal within an area that includes i) the main regional zone of groundwater supply (the so-called "fontanili belt") and ii) areas with strong, moderate and low As contamination in groundwater that are downgradient with respect to the "fontanili belt". The area is also relatively barely investigated for arsenic mobilization into groundwater and represents the typical residential, industrial and agricultural organization of most Western countries and is devoid of hydrothermal, volcanic or anthropogenic sources of arsenic.

The mechanisms of As mobility are investigated via by a complete hydrogeochemical investigation.

2. Study area

The pre-Alps defines the northern boundary of the hydrogeological domain of the Venetian Plain (Fig. 1). The Venetian Plain can be broadly divided into the "high" (northern) and "low" (southern) plains. The high plain is essentially of fluvial origin but also experienced glacial and fluvioglacial influences near the pre-Alps. During and after the Würm glacial period, the Brenta formed large alluvial fans that overlapped and were laterally penetrated by fans from adjacent rivers. The grain size of the sediments is generally highly variable from north to south according to the hydraulic features of each river. The gravel fans of the various watercourses extend downstream for variable distances. This area is principally composed of gravel; in particular the pebbly subsoil is composed of highly permeable coarse materials. In the high plain, where the water table is at maximum depth, an undifferentiated aquifer is present. To the southeast this aquifer becomes a multi-layered confined or semi-confined aquifer system directly connected to the unconfined one. Where the water table intersects the topographic surface, it outcrops in the most depressed zones creating the typical plain springs known as "fontanili" (Fig. 1; Fabbri and Piccinini, 2013; Fabbri et al., 2011; Vorlicek et al., 2004). This 2 to 10 kilometer wide band of springs is continuous over approximately 500 km in the Po plain (Cucchi et al., 2008; Pilla et al., 2006), and represents the source of many important rivers.

The low plain extends from the gravel layers transition to sand to the Adriatic coast. The low plain features a subsoil composed essentially of silt and clay layers intercalated with sandy layers. In this region the gravels are absent, with certain exceptions at considerable depths (e.g. 300 m below ground level, later on m.b.g.l.).

The main recharging factors of this hydrogeological system are irrigation, river losses, precipitation and groundwater inflow from the fractured aquifers in the pre-Alps. The order of importance of these factors varies from area to area; thus, in the past, the river losses were considered the most important recharge factor. These recharge processes are only effective in the high part of the Venetian Plain, where surface water infiltration can reach the water table of the unconfined aquifer and then the artesian aquifers linked to it.

The study area is located the right bank of the current Brenta River on the Brenta megafan (defined by Fontana et al., 2008) in the central part of the Venetian Plain and straddles the transition from the "high" to "low" plains (Fig. 1). The megafan covers more than 2500 km^2 (including Venice), and contains more than 1,900,000 inhabitants.

The geometry of the Brenta megafan influences the hydrogeologic gradient and the dispersion of sediments. To account for fan geometry, the distance from the apex (i.e., the town of Marostica) was used to locate the position of the boreholes and wells, and is indicated by the parameter DW (measured in meters, Fig. 1).

The soils developed on the Brenta megafan (sampled from the uppermost 1 m) are characterized by high concentration of As (Giandon et al., 2011; Tarvainen et al., 2013; Ungaro et al., 2008), indicative of substantial As accumulation processes in the sedimentary materials. The As concentrations in these soils are often higher than the Italian limit for public, residential, and private uses of soil (Giandon et al., 2011), which has been established as 20 mg/kg (national regulation D.Lgs. 152/2006). The natural-anthropogenic background value (95 percentile) is found at 45 mg/kg in the Brenta subsoil (Giandon et al., 2011), but local values as high as 169 mg/kg have been reported (Ungaro et al., 2008). The origin of the As anomaly over a very wide area has been ascribed to the sulfide mineralization in the uppermost catchment area (Giandon et al., 2011; Mion et al., 2009). However, a compositional study of the plain's sediments below the 1 m soil profile has never been performed prior to this study.

As anomalies in the groundwaters of the Brenta megafan have been reported to occur in various places (Mion et al., 2009). Very high As concentrations were found for the first time by Baldantoni and Ferronato (1995), who measured values as high as 480 μg/L. These results have been confirmed by a recent study (Carraro et al., 2013) that found up to 431 μg/L As in groundwater. The same sampling survey performed by the latter authors is used in the present study, with the addition of filtered waters (<0.45 μm) and sediment compositions.

The environmental concern with regard to As contamination in soils and waters increased after detecting high concentrations of the most hazardous species of As (inorganic As; EFSA, 2014 and references therein) in food materials (wheat grains, D'Amato et al., 2011) from the Venetian Plain (Cubadda et al., 2010).