

The groundwater monitoring system in Tuscany according to the EU Directive 2000/60 and the groundwater As contamination in the Versilia coastal plain

Il sistema di monitoraggio delle acque sotterranee in Toscana in accordo con la Direttiva EU 2000/60 e la contaminazione delle acque sotterranee da As nella pianura costiera della Versilia

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Riassunto: La direttiva quadro sulle acque dell'UE 2000/60/CE impegna gli stati membri dell'Unione europea a raggiungere un buono stato qualitativo e quantitativo per tutti i corpi idrici identificati e classificati. La sua applicazione richiede da parte degli stati membri il monitoraggio periodico dei corpi idrici. In particolare, per quanto riguarda le acque sotterranee, la Regione Toscana ha identificato diversi pozzi dove effettuare campionamenti periodici e analisi chimiche.

I risultati di queste analisi sono valutati in modo da permettere il raggiungimento degli obiettivi di qualità fissati dalla direttiva. In alcuni casi, questo monitoraggio delle acque sotterranee può evidenziare situazioni di inquinamento idrico, attivando quindi indagini più dettagliate. In questo contributo, presentiamo il caso di alte concentrazioni di arsenico nelle acque sotterranee, che raggiungono circa 1000 µg/L, da pozzi domestici in un'area della Versilia meridionale (Toscana, Italia), intorno al torrente Baccatoio, corso d'acqua che riceve i drenaggi acidi di un sito minerario ubicato nella parte alta del suo bacino. Inizialmente, l'arsenico rinvenuto nei pozzi della piana, è stato correlato alla contaminazione indotta dalle acque acide di miniera che lisciviano pirite ricche di As dalle miniere della Valle del Baccatoio.

Keywords: arsenic, Baccatoio stream, mine areas, reducing environments.

Parole chiave: arsenico, Torrente Baccatoio, aree minerarie, ambienti riducenti.

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Si supponeva che la pirite fosse la fonte primaria di As nelle acque sotterranee nonostante l'acqua del torrente Baccatoio ne fosse priva. Sebbene la valutazione dell'effettiva presenza di pirite nei sedimenti necessiti di ulteriori indagini, sono state formulate ipotesi alternative. Nei pozzi campionati la concentrazione più alta di As è spesso associata a quantità elevate di ioni ferro e ammonio che nelle acque sotterranee riflettono la presenza di ambienti riducenti. Ciò suggerisce che la presenza As nelle acque sotterranee possa derivare dalla dissoluzione riduttiva di ossidi ed idrossidi di ferro accoppiata alla degradazione della sostanza organica, contenuta negli strati di torba presenti nel sottosuolo, attraverso processi di adsorbimento/desorbimento in ambiente riducente. Lo scopo di questo lavoro è quello di illustrare questa valutazione preliminare sull'origine della contaminazione da As nelle acque sotterranee della pianura versiliese prossima al corso del torrente Baccatoio.

Abstract: : *The EU Water Framework Directive 2000/60/EC commits European Union Member States to achieve good qualitative and quantitative status for all water bodies. Its application requires periodic monitoring of selected water bodies. Concerning groundwater bodies, the Tuscany Region selected monitoring wells for periodic sampling and performing chemical analyses. Results of these analyses are used to assess the qualitative status according to the EU Directive. In some cases, this groundwater monitoring can highlight some water pollution, hence activating more detailed investigations.*

In this work, we present the case of high arsenic concentrations in groundwater, reaching about 1000 µg/L, from domestic wells located in southern Versilia (Tuscany, Italy), close by the Baccatoio stream which receives acidic waters from a former mining site. Initially, the arsenic has been related to acid mine drainage from the nearby sites in the Baccatoio Valley. As-rich pyrite weathering was supposed to be the primary source for As in groundwater despite the Baccatoio stream is As-free. Although the evaluation of the amount of pyrite in sediments needs further investigations, alternative hypothesis were formulated. The highest As concentration is often accompanied by high amounts of iron and ammonium ions reflecting reducing environments. This suggests the occurrence of secondary As-sources such as ferric oxyhydroxide and organic matter, likely in peat layers, undergoing reductive dissolution. The aim of this work is to carry out a preliminary assessment of the origin of the As contamination in groundwater of the Versilia coastal plain.

Introduction

The environmental monitoring of groundwater is considered by Legislative Decree 152/2006 and Legislative Decree 30/2009, based on the Directives 2000/60/CE WFD (Water Framework Directive) and 2006/118/EC GWDD (Ground Water Daughter Directive). The latter Directive establishes a regime which sets groundwater quality standards and introduces measures to prevent or limit inputs of pollutants into groundwater. The Directive establishes quality criteria that take into account local characteristics and allows further improvements to be made based on monitoring data and new scientific knowledge. Member States establish groundwater monitoring networks based on the results of an initial classification analysis. This in order to provide a comprehensive overview of groundwater bodies chemical and quantitative status.

The Tuscany Region, following the regional regulation DGRT 100/2010, classified the groundwater bodies according to the methods indicated in WFD Guidance Documents (2003) and initiated a monitoring program on 67 of them. These were classified at risk of not achieving the objective of a Good Environmental Status.

In the whole region, there are more than 500 measurement stations. In Figure 1 we reported wells in the north-west Tuscany coast. Sampling started in 2002 and was subsequently modified in terms of both sampling frequencies and monitored parameters, depending on the technical-regulatory evolution. Monitoring is performed by ARPAT, the Environmental Protection Regional Agency of Tuscany. Quantitative monitoring is performed through a measuring network acquiring and remotely-transmitting data to the Regional Hydrological Service. Gathered data is accessible on an interactive map at the website www.arpato.toscana.it.



Fig. 1 - Monitoring wells in the Versilia plain. The red line marks the limits of Fig.3.

Fig. 1 - Pozzi di monitoraggio nella piana Apulo-Versiliese. Con la linea rossa è delimitata l'area rappresentata in Fig.3.

It is also possible to consult and download the groundwater chemistry data archived in a database.

In addition to institutional monitoring activities, ARPAT carries out in-depth investigation activities in the case of specific environmental criticalities. These activities aim at defining the emergency safety measures and the methods of activation of administrative and technical procedures, as required by the groundwater regulations. An example of such in-depth investigation is reported here for the Versilia plain, which is affected by groundwater As contamination. The aim of this work is to carry out a preliminary assessment of the origin of the As contamination.

The interest in arsenic contamination of groundwater and surface water greatly increased in the last decades (Rotiroti et al. 2014), due to the awareness of the adverse effects of this contaminant on human health (e.g. Hong et al. 2014). Indeed, the long-term exposure to As through drinking water is responsible for a variety of health concerns, including cancer, cardiovascular disease and neurological effects. The World Health Organization (WHO 1993), the United States Environmental Protection Agency (USEPA 2001) and the Drinking Water Directive (Directive 98/83/EC) in Europe (in Italy transposed by the Legislative Decree 152/2006) recommend a maximum concentration of 10 µg/L for arsenic in drinking water; the same threshold of 10 µg/L is imposed by Italian Regulations for groundwater.

Materials and Methods

Study Area

The study area is located within the Apuan Alps and the Versilia Plain (Fig. 1). This area hosts an alluvial fan aquifer that evolves downstream to a multi-layer aquifer system in the plain. This alluvial aquifer has a remarkable capacity in terms of groundwater storage and it is tapped by many private wells used for irrigation as well as drinking purposes (Fig. 2).

This system is in continuity with the geological horizons of the plain; here a complex multilayer aquifer system including levels of sands and gravels interbedded by fine sediments, mainly clay and silt, and sometimes lens of peat, occur. Hundreds of domestic wells for irrigation use tap the aquifers and aquitards at different depths, mainly ranging from 10 to 40 meters below the surface. Moreover, in the groundwater hosted in the alluvial fan high contents of arsenic have been found in some wells (Fig. 3). From a geological point of view,



Fig. 2 - Sampled well in the Versilia plain.

Fig. 2 - Uno dei pozzi campionati nella piana della Versilia.

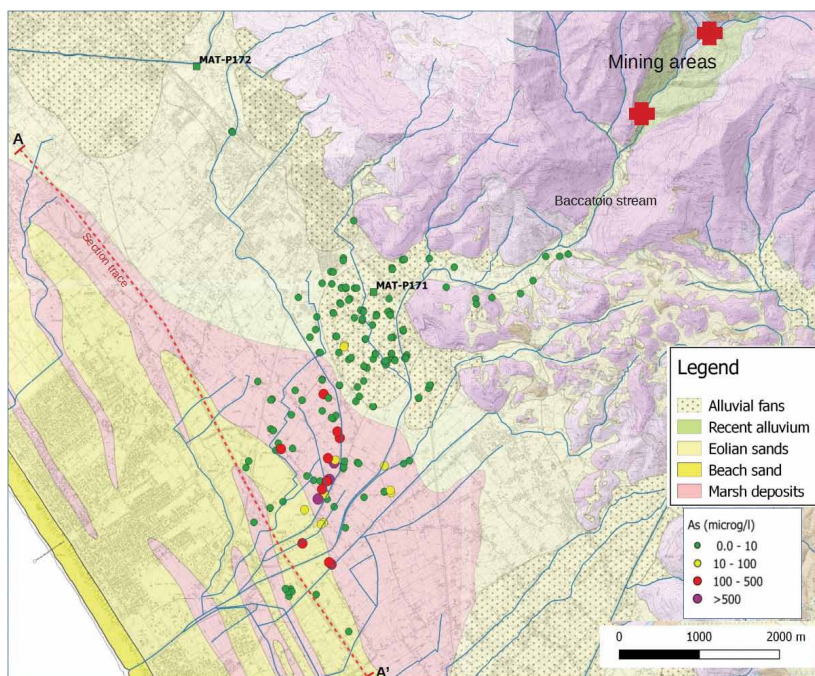


Fig. 3 - As concentration in groundwater of 93 sampled wells in the Versilia plain downstream of Baccatoio alluvial fan.

Fig. 3 - Concentrazione di As nei 93 pozzi campionati sulla pianura costiera del torrente Baccatoio.

the exposed rocks in the upstream part of the catchment include phyllite, quartzite and metarhyolite rocks belonging to the metamorphic complex of the Paleozoic basement, and carbonatic rocks of the Apuan Alps Unit. These lithologies are unconformably covered by the non-metamorphic unit of the Tuscan Nappe, mainly constituted, in this area, by limestones and cataclastic breccias (Molli and Meccheri 2012).

The mountainous area upstream of the alluvial fan aquifer hosts a former mining site where extraction and processing activities of metal sulfide ores had been active for many centuries. Pyrite±baryte±iron oxide±(Pb-Zn-Ag) orebodies form lenses and/or small bodies generally associated with the basement rocks, usually close to the contact with the metadolostones. In particular, the fine-grained pyrite is characterized by high levels of potentially toxic elements, including arsenic, that reaches about 1,000 mg/kg (D’Orazio et al. 2017).

Mining activity ceased around the end of the 20th century, without any intervention to make the site environmentally safe; nowadays, significant quantities of acid drainages

including high concentration of toxic and potentially toxic elements outflow from the abandoned tunnels feeding the stream waters (Perotti et al. 2017).

Surface Water and Groundwater Monitoring

Figure 1 shows the distribution of regional monitoring stations in and around the study area. Because within the investigated area there were only two monitoring stations, not sufficient to perform in-depth investigations, specific monitoring activities were done on surface water and groundwater.

Concerning surface waters, the Baccatoio stream was monitored along its course since 2010 due to the detection of a contamination by heavy metals of mining origin. Concerning groundwater, the additional monitoring involved 96 wells (Figs. 3 and 4) tapping the alluvial fan and the plain multi-layer aquifers.

In June 2018, a preliminary sampling survey was carried out by the Earth Sciences Department of the University of Pisa in some of the wells located in that area. The data on water

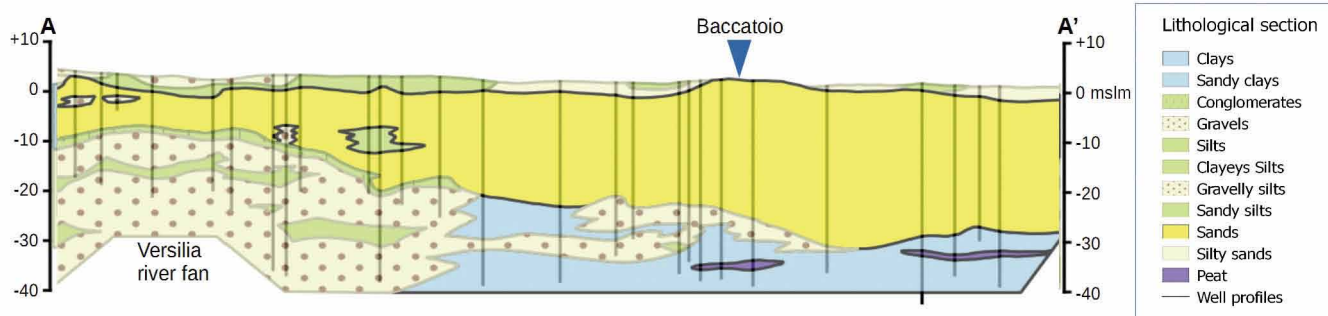


Fig. 4 - Litological section parallel to coastline.
Fig. 4 - Sezione litologica parallela alla linea di costa.

chemistry revealed an exceptional high As concentration (up to about 1,000 µg/L) in some of the wells.

In 2018 the municipality of Pietrasanta (Lucca), in collaboration with ARPAT, started a systematic sampling survey of wells for domestic and irrigation use in some cases detecting very high As values in comparison with the limits set by the Italian regulation (Franchi et al. 2019; Bresciani 2020). This extensive investigation aimed at understanding the causes of the high concentrations of arsenic also. About one hundred wells were sampled and waters analysed for physico-chemical parameters and chemistry,

In the investigation, a reconstruction of the paleogeographic and paleoclimatic evolution of the area was carried out, through the research of literature data. Subsequently, a database was created with all the existing geochemical data concerning stream surface water, groundwater, and sediments.

During sampling, the main chemical-physical parameters of the waters were measured in situ through the use of multiparametric probes (temperature, pH, electrical conductivity, dissolved O₂ and oxygen saturation). Alkalinity was measured by means of acidimetric titration as well as the determination of major ions and trace elements content, respectively by ion chromatography (IC) and ICP-MS (Inductively coupled plasma - mass spectrometry). Thanks to the results obtained from laboratory analyses, it was possible to carry out a chemical-physical characterization of the sampled waters. All the data have been organized and reworked on a GIS project including also the basic area information (geological, hydrogeological and topographical characteristics of the area). The geochemical features were then related to the evolution of the Versilia plain.

Results and Discussion

The contaminated area is currently limited and confined to the flattest and topographically most depressed portion of the plain (Fig. 5), characterized by sediments from both alluvial and lake/marsh environments. High As concentrations in the water wells are associated to relatively high values of ammonium (up to 4.5 mg/L NH₄-N) and Fe (up to 4,000 µg/L) testifying the presence of reducing conditions.

The stratigraphic information of the area shows clayey-silty-peaty horizons at depth ranging from 20 m to 30 m, rich in organic material and approximately compatible with the depth of the most contaminated wells. These sediments are linked to the Holocene Versilian Transgression. These environments are reducing due to the anaerobic decay of the organic substance.

The anaerobic degradation of the organic matter is coupled with different terminal electron accepting processes. Under these processes, As may become mobile, being released from sediments and in particular Fe oxides-hydroxides by desorption/dissolution and humic acids, possibly following the release from pristine geogenic sources related to the As-rich mineralization, which characterize the southern sector of the Apuan Alps.

Instead, the results obtained seem to exclude an active role of the Baccatoio stream in the dispersion of arsenic through the aquifer, although further information is necessary. Indeed, the stream water, contaminated from the acid drainage only near mining areas, do not carry pollutants towards the coastal plain. This is sustained by the fact that the Baccatoio stream waters flowing through the Versilia plain resulted generally uncontaminated despite the acid mine water inputs at the

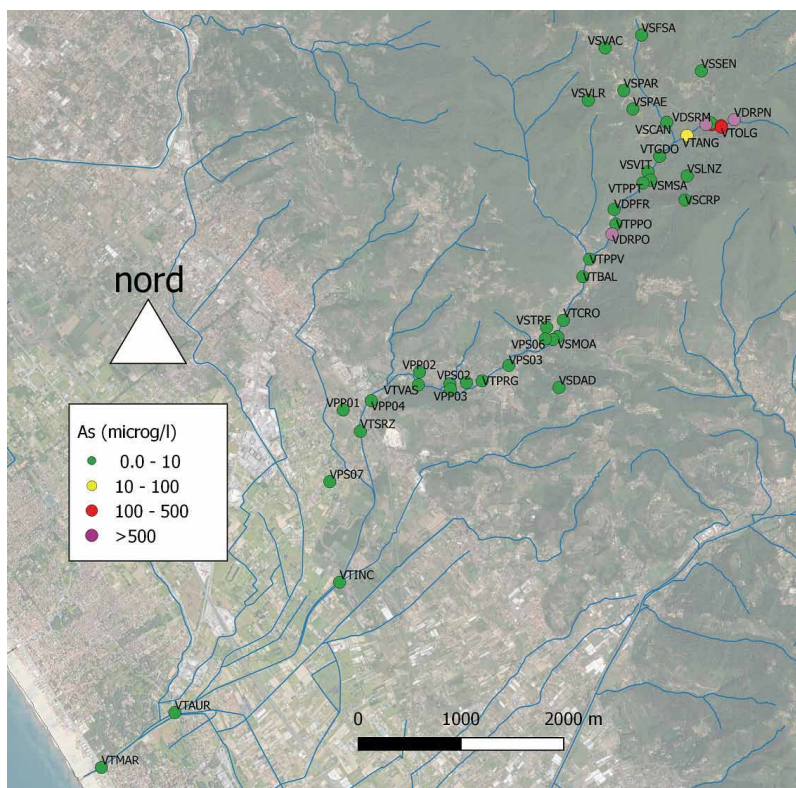


Fig. 5 - As concentration in Baccatoio stream water (from Bresciani, 2020).

Fig. 5 - Concentrazioni di As nelle acque del torrente Baccatoio (da Bresciani 2020).

old mining areas (Fig. 5). These data seem to exclude an active role of the Baccatoio stream in the dispersion of arsenic through the aquifer. Currently, seasonal monitoring of the stream waters is underway to verify this hypothesis.

Another hypothesis is related to the fact, that, mostly due to the extensive hydrous ferric oxides precipitation as pH increases, As and other heavy metals in solution, are early removed from water and accumulates in streambed sediments. However, the oxidation conditions, typical of stream sediment environment, relegates the contaminant into solid matrix preventing its remobilization towards the water matrix. So, also the hypothesis of a remobilization of arsenic from the stream sediments towards the alluvial aquifer should be excluded.

Conclusions

This work evaluated possible sources and mobilization mechanisms of As in the Versilia coastal plain. The contaminated area by As is currently limited and confined to the most flat and topographically most depressed portion of the plain, characterized by sediments from both alluvial and lake/marsh environments. These sediments are characterized by various levels rich in organic matter which, being oxidized, contribute to decreasing redox potentials. Under Fe-oxide reduction, As can be released to groundwater due to the reductive dissolution mechanism. Release of As due to acid drainage from the former mining site located in the higher Baccatoio valley can be likely excluded.

Once the cause of the observed pollution is ascertained, a careful health and environmental risk analysis will have to be carried out, in order to identify acceptable levels of contamination. If the contaminant represents a serious risk for human health and the environment it will be necessary setting up safety and remediation interventions.

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