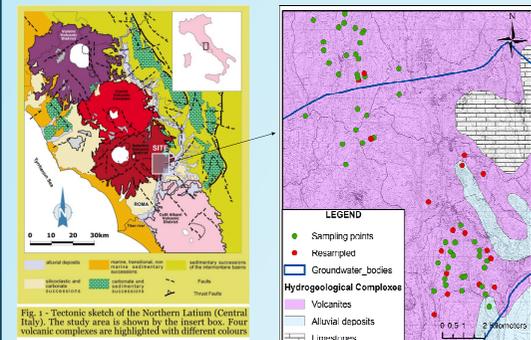


1 Introduction

Several processes can affect the concentration of dissolved substances in groundwater: water-rock interaction, geothermal upwelling fluids, biological activity, residence time, human activities, etc. The first two processes are often considered the main cause of the arsenic presence in volcanic or volcanic-sedimentary aquifers in Central Italy. During three campaigns (from 2012 to 2015) we collected groundwater samples from 69 private wells and springs in a water table aquifer located North of Rome. In addition, 22 rock samples have been collected, to identify the possible mineralogical source of As. Solid and aqueous matrices have been studied, in order to evaluate any significant connections between chemical and mineralogical patterns. Pleistocene volcanites (mainly tuffs) have been sampled and analyzed, so as to determine the total content of As and other metals. Selective Sequential Extraction allowed us to discriminate the different solid fractions containing As and to better understand processes governing As mobility. A Leaching test also provided an estimate of the release rates of arsenic and other elements under extreme conditions. The study of the distribution of some elements in different geochemical spheres and the analysis of water-rock interaction processes, provided a comprehensive framework on the origin and evolution of geogenic contaminants in groundwater.

Study area and monitoring network of groundwater



The study area lies in the eastern sector of the Sabatini Volcanic District. Pleistocene pyroclastic products, usually characterized by medium permeability, overlap in angular unconformity the Plio-Pleistocene sedimentary deposits, whose clays and silts constitute the basic level of the groundwater body.

SAMPLING POINT LOCATION

The sampling points are 69, 17 of which have been resampled 3 times (2012, 2014, 2015) to analyze the time variation of the groundwater chemistry.

2 Methods

Groundwater sampling:
 GPS localization, well depth, water table level, Eh, T, pH, alkalinity, DO, EC



Rock chemical analysis

(powders):
 - Selective Sequential Extraction (SSE)
 - Microwaves acid digestion
 - Leaching test

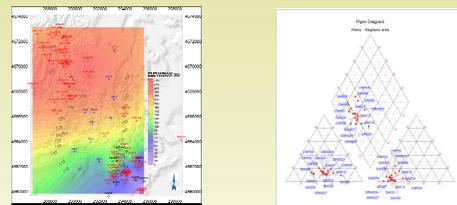


Rock mineralogical analysis

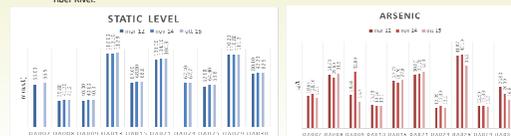
(powders and thin sections):
 - X-Ray Powder Diffraction
 - Scanning Electron Microscopy (SEM)

3 Results (groundwater geochemistry)

Investigated groundwaters ranges from alkaline-bicarbonate types (interaction with K-rich volcanites) to Ca-HCO₃ type downstream (interaction with the sedimentary layers) and show variable levels of natural contaminants such as As, F, V and U. Some parameters (PO₄³⁻, V and Al) show a decreasing trend from North to South, while others (As and F) showed an uneven distribution with no trend and localized peaks. Chemical data confirm that geochemistry is very stable even with different hydrological conditions: the variation of most chemicals from March 2012 to October 2015 is comprised within the laboratory error, even with an increase of groundwater levels up to 2.4 m. In the Riano area As ranges from 12.1 to 43.1 µg/L, always exceeding the drinking water standard (10.0 µg/L).



Piezometric map. Heads decrease according to a main flow direction NNW-SSE, towards the Tiber River.



Trend of the static level and As values during the monitoring period (Riano area).

4 Results (rock chemistry and mineralogy)

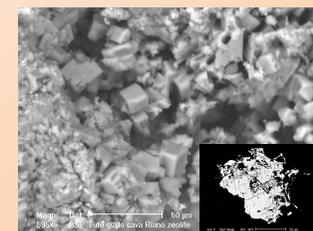
XRPD highlighted the constant and important presence of zeolites (Chabazite/Herschelite) in particular for the Via Tiberina Yellow Tuff, accordingly with the literature (Lombardi & Meucci, 2006). SEM observations on thin sections, allowed to identify pyroxene, magnetite, apatite, titanite, rutile, pyrite, leucite and rare earth oxides. Arsenic in crystalline form was not identified, suggesting its possible presence in a dispersed form.



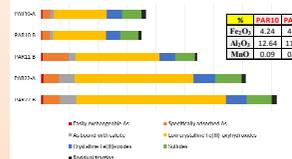
Rock sampling points.

Code	Formation	XRPD Analysis
PAR01	Subvolcanic (P. tuffi)	Qtz, Cls, Anls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR02	Subvolcanic (P. tuffi)	Qtz, Cls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR03	Subvolcanic (P. tuffi)	Qtz, Anls, Cls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR04	Via Tiberina Yellow Tuff	Tuff (Chabazite/Herschelite), Qtz, Cls, Mnls, Plg
PAR05	Subvolcanic (P. tuffi)	Qtz, Cls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR06	Subvolcanic (P. tuffi)	Qtz, Cls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR07	Via Tiberina Yellow Tuff	Zeol (Chabazite/Herschelite), Qtz, Cls, Kfs, Mnls, Bt, Cls, Plg
PAR08	Subvolcanic (P. tuffi)	Qtz, Cls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR09	Subvolcanic (P. tuffi)	Qtz, Cls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR10	Via Tiberina Yellow Tuff	Zeol (Chabazite/Herschelite), Qtz, Cls, Kfs, Mnls, Bt, Cls, Plg
PAR11	Via Tiberina Yellow Tuff	Zeol (Chabazite/Herschelite), Qtz, Cls, Kfs, Mnls, Bt, Cls, Plg
PAR12	Subvolcanic (P. tuffi)	Qtz, Cls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR13	Subvolcanic (P. tuffi)	Qtz, Cls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR14	Subvolcanic (P. tuffi)	Qtz, Cls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR15	Subvolcanic (P. tuffi)	Qtz, Cls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR16	Subvolcanic (P. tuffi)	Qtz, Cls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR17	Subvolcanic (P. tuffi)	Qtz, Cls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR18	Via Tiberina Yellow Tuff	Zeol (Chabazite/Herschelite), Qtz, Cls, Kfs, Mnls, Bt, Cls, Plg
PAR19	Via Tiberina Yellow Tuff	Zeol (Chabazite/Herschelite), Qtz, Cls, Kfs, Mnls, Bt, Cls, Plg
PAR20	Via Tiberina Yellow Tuff	Zeol (Chabazite/Herschelite), Qtz, Cls, Kfs, Mnls, Bt, Cls, Plg
PAR21	Subvolcanic (P. tuffi)	Qtz, Cls, Plg, Mnls, Kfs, Bt, Kfs, Anls, Cls
PAR22	Via Tiberina Yellow Tuff	Zeol (Chabazite/Herschelite), Qtz, Cls, Kfs, Mnls, Bt, Cls, Plg

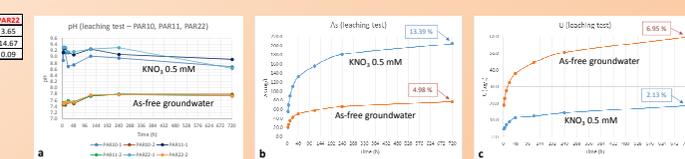
Results of XRPD analysis. In bold the samples selected for the SSE.



SEM images: zeolites and pyrite (right) within the Via Tiberina Yellow Tuff.



Sequential extraction results (7 steps, modified from Wenzel 2001, Costagliola et al. 2013, Torres & Auledda 2013). The table (right) shows the weight percentage of interesting oxides in the rocks.



Leaching test results, using two different solutions (KNO₃ 0.5 mM and As-free groundwater collected near the study area). a – pH monitoring during the test (3 rock samples in two replicates); b – As concentrations measured during the test (sample PAR11); the box shows the % of As released over the total of the rock; c – U concentrations measured during the test (sample PAR11); the box shows the % of U released over the total of the rock.

Arsenic in the sampled rocks is in the range of 17.5 – 40.9 mg/kg. Sequential extraction procedure shows As distribution among different solid fractions. Most of As (63–70%) is linked to Fe oxy-hydroxides, especially low crystalline, which nevertheless constitutes a on average only 4% of the solid matrix. As release during leaching test shows considerable mobility in the initial stages of the experiment, especially in the first 48h, and reached a plateau after 240hr. It was sensibly affected by pH and less by the presence of other exchanging anions as we observed in the case of Uranium. The fast mobilization of As promoted by lower pH let us hypothesize that the presence of As in groundwater is mainly related to As easily exchangeable, specifically adsorbed and related to calcite (first 3 steps in SSE).

5 Highlights

- Groundwaters showed a certain stability of chemical parameters, even with different hydrological conditions; As presents concentrations widely and permanently above the drinking water limits.
- Mineralogical analysis of outcropping rocks in the study area did not provide information about the presence of As in the identified mineral phases. It can suggest a diffuse presence of the element in the tuffs.
- The sequential extraction highlighted how As in the tuffs is particularly associated with low crystalline Fe(III)-oxyhydroxides; Fe₂O₃ is a limited fraction of the whole rock (about 4%), but it can be associated with most of the total As. Arsenic in groundwater could partly result from desorption phenomena, in presence of non specific/exchanger for arsenate (e.g. phosphate).
- The extreme conditions of the leaching test showed a significant As release rate, even under restricted time (48h). The strong pH-dependence suggests a mobilization mainly associated with the first three SSE steps (As easily exchangeable, specifically adsorbed and bound with calcite).

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 Lombardi G., Meucci C. (2006) - *Il Tufo Giallo della Via Tiberina (Roma) utilizzato nei monumenti romani*. Rend. Fis. Acc. Lincei 17, 263-287.
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 Wenzel WW., Kirchbaumer N., Prohaska T., Stingeder G., Lombic E., Adriano D.C. (2001) - *Arsenic fractionation in soils using an improved sequential extraction procedure*. Anal. Chim. Acta 436, 309-323.

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