Faculty of Mathematical, Physical, and Natural Sciences
Department of Earth Sciences

PhD project in Earth Sciences (40th Cycle)

Natural geochemical background levels and biogeochemical processes in groundwater of large-scale contaminated sites: insights from the Basin of the Sacco River

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A.Y. 2024-2025

1. State of the Art

Groundwater is an essential resource, not just for meeting human needs, but also for maintaining the balance of natural ecosystems. Unfortunately, it faces constant threats from human activities, climate change, natural events, and geological factors. In the EU, groundwater quality is carefully monitored to ensure it meets safety standards. This is done by checking for various substances against the concentration limits established by the Water Framework Directive (2000/60/EC) and the Groundwater Directive (2006/118/EC). In some cases, the Natural Background Levels (NBL) are also taken into account, adding an extra layer of precision to the process. From an operational perspective, NBL serve as reference values that guide the management of environmental matrices affected by anthropogenic impact. According to Article 2 of GWD, the NBL is defined as "*the concentration of a substance or the value of an indicator in a groundwater body that corresponds to the absence of anthropogenic alterations, or to extremely limited alterations, compared to unaltered conditions*."

The Basin of the Sacco River, located in southern Latium (Italy), includes a large area where safety measures and remediation actions have been requested under Part IV Title V of Legislative Decree 152/2006. In this basin, the first sign of the impact of soil and water pollution was found in 2005 afterwards the detection of beta-hexachlorocyclohexane (β-HCH, a chemical substance found in lindane, a currently banned pesticide) in a milk sample coming from a dairy farm located in Gavignano (Rome). Other environmental issues in this area are chlorinated solvents in groundwater, as well as heavy metals and metalloids in both soil and groundwater, eventually bringing to the definition of a Site of National Interest (S.I.N., Italian acronym) for a large portion of the territory surrounding the Sacco River (72,35 Km^2, Fig. 1). The definition of a S.I.N. is based on the characteristics of the site, the volume and toxicity of the pollutants and the significance of the impact on the surrounding environment, particularly in terms of health and ecological risks. For these sites, the Ministry of the Environment and Energy Security (MASE) holds the administrative responsibility for overseeing remediation processes (https://www.isprambiente.gov.it/en/activities/soil-and-territory/contaminated-sites/contaminated-sites-of-national-interest-sin?set_language=en). The geological and geochemical characteristics of the land within the S.I.N. "Basin of the Sacco River", by their very nature (volcanic rocks, fluvio-marsh alluviums rich in peat and travertines), facilitates the presence in groundwater of several potentially toxic inorganic elements, including arsenic (As), iron (Fe), and manganese (Mn). By comparing the concentrations found in the environmental matrices with the legal limits defined in Italy as Threshold Concentration of Contamination (the Italian "CSC", hereafter "TCC"), exceedances have been observed in groundwater. Their origin can locally be attributed to anthropogenic pollution, but it is also likely that they are of geogenic origin, and the solution to this issue necessitates de definition of appropriate NBLs. Specifically, the toxicity of As is well-documented. Among the potential effects associated with chronic exposure to arsenic through drinking water, carcinogenic effects have received the most attention. Based on the recommendations of the World Health Organization (Guidelines for Drinking Water Quality), a parametric value for As in drinking water of 10 µg/L was established in EU Directive 2020/2184. The same value is commonly applied as environmental threshold in groundwater, unless NBL is stated to be higher. Water-rock interaction under favorable biogeochemical conditions is considered the most important mechanism for the presence of As in groundwater (Mukherjee et al., 2014). The presence of this element, characterized by extremely high levels of toxicity, has been found in various parts of the world, particularly in Asia, America, and Europe. In Italian volcanic systems, arsenic concentrations in groundwater range from 0.1 to 7000 µg/L, with the highest values observed in fracture zones that allow the ascent of hydrothermal fluids (Aiuppa et al., 2003). Additionally, the release of As is attributed to the dissolution of Fe-oxides in reducing environments (Guo et al., 2012), due to the anoxic conditions associated both with the presence of peat in alluvial or lacustrine sediments (Glodowska et al., 2021a; Postma et al., 2007; Postma et al., 2012; Rotiroti et al., 2021) or with anthropogenic pollution, including landfill leachate or landfill gas (Kerfoot, 1994; Kerfoot et al., 2004; Whitlock & Kelly, 2010).

The study of ecosystems in groundwater is gaining increasing importance, to the point that there is interest in modifying current groundwater regulations to allow greater considerations of the microbial communities present in aquifers. These ecosystems offer vast and complex habitats for various microbial communities. Variations in underground habitats can be attributed to different hydrogeochemical conditions, hydrological and hydrogeological events such as precipitation, floods, natural or anthropogenic temperature fluctuations, and especially to the introduction of contaminants from human activities. All these changes can affect the stability of the aquatic microbial communities and eventually affect the distribution of redox zones in shallow aquifers (Vroblesky & Chapelle, 1994). In many cases, organic pollutants introduced into oligotrophic aquifers modify or increase the local microbial diversity (Cho & Kim, 2000; Baker et al., 2001; Röling et al., 2001; Feris et al., 2004b; Johnson et al., 2004). The contribution of microbial activity to the creation of anoxic (or reducing) environments should not be underestimated. This, of course, results in changes to groundwater chemistry, influencing the mobility of some naturally occurring metals (or those introduced by human activity) in aquifers. Correlations between Fe, As, and methane (CH_4) have been recorded in the Bay of Bengal (Dowling et al., 2002), due to anaerobic respiration of bacterial communities, including methanogens, using organic carbon as electron donor. Preziosi et al. (2024) found similar correlations in lacustrine sediments of Latium (Italy) nearby a landfill site. Glodowska et al. (2020) explored the process of anaerobic CH_4 oxidation driven by Fe and uncovered an intriguing link between dissolved As and CH_4 levels in natural groundwater. Their findings suggest that As could be released in environments where CH_4 and arsenic-bearing Fe(III) minerals coexist, pointing to a potential mechanism that could influence groundwater chemistry in various natural settings. Finally, bacteria can control As mobility directly by changing the redox state of arsenic via As(V) reduction and As(III) oxidation (Borch et al., 2009).

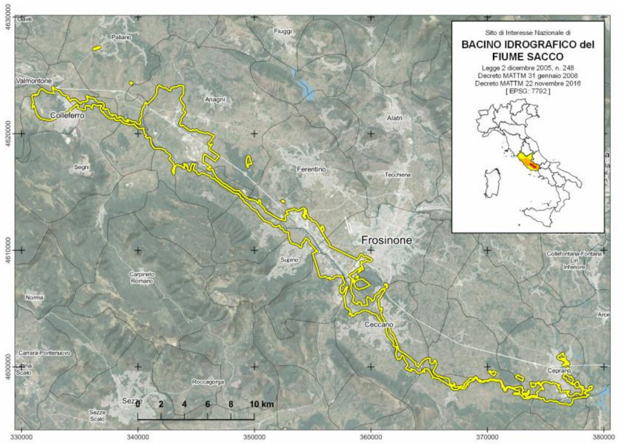


Fig. 1 - Satellite image sourced from the Ministry of the Environment and Energy Security's website, showing the National Interest Site (S.I.N.) "Basin of the Sacco River" (in yellow).

2. Research Goals

2.1. General Objective

Define biogeochemical processes responsible for releasing inorganic contaminants into groundwater under diverse geochemical settings, focusing on reductive dissolution in anoxic conditions.

2.2. Specific Objectives

- Hydrogeological, geochemical, and isotopic assessments to determine natural geochemical background levels of groundwater in large-scale contaminated sites (e.g. Basin of the Sacco River).
- Biogeochemical maps of the case studies to explore the relationships between the geochemical facies of groundwater and the aquatic microbial communities.
- Occurrence of target inorganic contaminants (e.g. As, Fe, Mn, Ni, Cr) due to reductive dissolution processes to understand the relation with organic matter properties, metal speciation, and the structural/functional features of microbial communities.

3. Implications and applications

- Implementing a common language between Hydrochemists and Microbiologists for a more comprehensive characterization of groundwater environment.
- Investigating the links between geochemistry and microbial communities in pristine and impacted areas.
- Defining Natural Background Levels in groundwater thanks to biogeochemical and isotope analysis, in order to manage anthropogenic pollution in the Basin of the Sacco River and in similar sites.

4. Work plan

This PhD project will be inserted in the framework of the “VFN Valle del Sacco” project, (collaboration between CNR-IRSA, ARPA Lazio and Regione Lazio). The research activity for this PhD program involves continuous bibliographic research of the geology and hydrogeology of the investigated areas, with in-depth analysis of geochemical and microbiological studies regarding the natural (or anthropogenic) processes that mobilize metals in groundwater. This study will extend beyond the Basin of the Sacco River to include other contaminated or potentially contaminated sites with similar geological characteristics, allowing for a broader evaluation of the interaction between geological settings and microbiological/geochemical processes involved in the release of As, Fe, and Mn.
Groundwater Sampling will be conducted following ISO (International Standards Organization) guidelines, on a network of water points (wells and springs) still to be identified. In-field measurements include water levels, physicochemical parameters with probes, and redox-sensitive analytes using a portable UV-VIS spectrophotometer. Different aliquots of groundwater will be analyzed at IRSA laboratories (Monterotondo and Bari) or other external facilities including ARPA Lazio for organics.
From a purely geochemical perspective, the analytes considered will include major ions, metals, and trace/minor elements, along with physicochemical parameters, which will serve as excellent indicators to distinguish different hydrochemical facies, with a particular focus on the presence of As, Fe, and Mn, whose origins will be further investigated. Laboratory analysis of inorganic compounds will be carried out using IC, ICP-OES, and ICP-MS. Organic compounds such as Dissolved Organic Carbon (DOC) and Volatile Organic Compounds (VOC) will be analyzed. Finally, the isotope fingerprint of some elements, such as ^{2}H, ^{18}O, ^{13}C, and ^{87}Sr, will be useful to investigate the evolutionary processes of the waters, including the recharge sources of the aquifers, the nature of the lithologies which waters have interacted with, and to distinguish the origin of inorganic carbon. Further, isotope investigations will be used as an innovative method for the definition of natural geochemical background levels.
This project also includes the study of the native microbial community in groundwater, in parallel with hydrochemistry and in collaboration with environmental microbiologists from CNR-IRSA. This research activity will include techniques to study the variation patterns of microbial communities, such as flow cytometry for microbial cell counting, DNA sequencing (e.g., 16S rRNA gene) for assessing phylogenetic community composition, and metabolic profiling (e.g. *Biolog-Ecoplates*).

4.1. Milestones

- Geochemical maps showing the distribution of principal elements in groundwater and describing the main idrochemical facies (1st year).
- Definition of the natural geochemical background levels in the groundwaters of Basin of the Sacco River and of the final hydrogeological conceptual model (2nd year).
- Spatial distribution of major taxa of the aquatic microbial community (3rd year).
- Processes for As, Fe, and Mn dissolution and their correlation with microbial communities (3rd year).

4.2. Dissemination plan

During the three years of PhD, I will participate in national and international seminaries, workshops and conferences (e.g., EGU[1] 2025, Flowpath 2025, WRI[2] 2025, Eurokarst 2026)

This project aims to the publication of scientific papers focused on:

- Relationships among As, Fe, and Mn with CH_4 in groundwater and microbial communities.
- Importance and application of isotopic analysis in hydrogeochemical monitoring.
- $^{87}Sr/^{86}Sr$ as a method for the definition of natural geochemical background levels in the Basin of the Sacco River and in similar sites.

[1] European Geosciences Union.
[2] Water Rock Interaction.

4.3. Training activities

I will develop and improve my knowledge in:

- Laboratory activity and equipment (e.g., ICP-OES, ICP-MS, IC, Spectrophotometry UV-VIS) at CNR-IRSA.
- Field activity (e.g., groundwater sampling, sample treatment, and preservation).
- Enhancement of software skills for geostatistical analysis and graphic reconstruction.

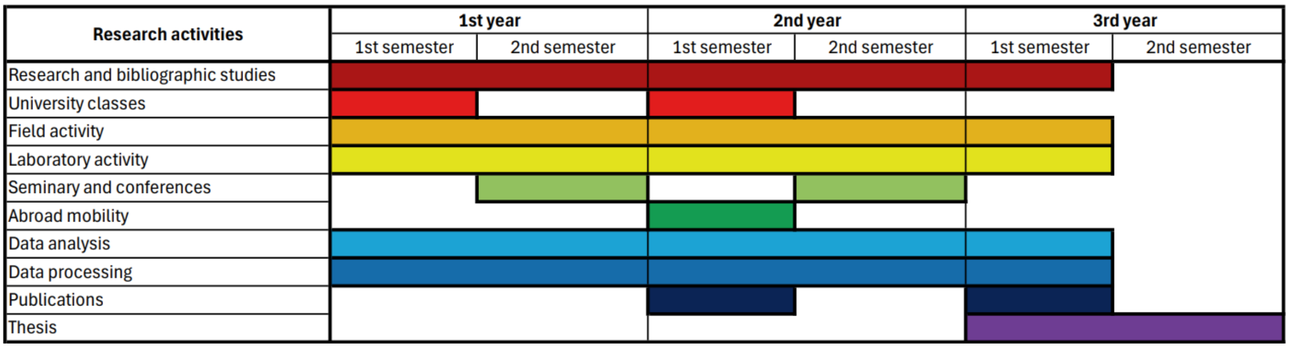
I intend to attend classes provided by the Earth Sciences PhD course of "La Sapienza" University of Rome during my 1st year:

- "GIS Applications" (12 hours).
- "Climate risk" (20 hours).
- "Tips on how to write a scientific paper, prepare a presentation, and draft a research proposal" (10 hours).
- "Some principles about Natural Disasters" (8 hours).
- "Laboratories and research facilities of Department of Earth Sciences" (8 hours)
- "Multiparametric monitoring in natural sperimental fields: principles and technologies" (8 hours)

4.4. Abroad mobility

A training period abroad is planned (from 3 to 6 months) most likely in Switzerland, at Unine (Université de Neuchâtel), under Professor Philippe Renard's supervision to improve my knowledge about recent geostatistical techniques. I am also considering GEUS (Geological Survey of Denmark and Greenland) in Denmark to further explore aspects related to geochemical background levels in collaboration with Doctor Klaus Hinsby.

5. Gantt Chart



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