

Groundwater chemistry and arsenic occurrence in the phreatic aquifer system of the San Vitale pine forest

Enrico Dinelli¹, **Martina Kralj**¹, Susanne Schwarz², Marco Antonellini¹,
Giovanni Gabbianelli¹ and Kay Hamer²

¹ Interdepartmental Research Centre for Environmental Sciences (CIRSA) in Ravenna,
University of Bologna, Via S. Alberto 163, I-48100 Ravenna, Italy

² Geochemistry & Hydrogeology Department of Geosciences, Universität Bremen, Germany

ABSTRACT

The groundwater of the San Vitale Pine forest in Ravenna (Italy), are severely affected by coastal saline intrusion. Sixteen piezometers were sampled at various depths in order to understand the dynamics of groundwater chemistry occurring close to the freshwater/saline interface. A staddle packer was applied to recover 3 to 4 samples from the upper aquifer in each piezometer, sampling the top, the bottom of the upper aquifer (ca. 10 m) and some sample above and below the saline interface. Major chemical composition and selected trace elements were investigated in this study and were used to characterize the hydrogeochemical features of the phreatic aquifer in the area. Also arsenic was determined, and the results show total arsenic concentrations in the range of 0.6 to 92 µg/l, the average being 26.6 µg/l. About 60% of these wells reached arsenic concentrations which exceeded the current Italian legal maximum contaminant level of 10 µg/l. The maximum amounts of dissolved arsenic in the groundwater are related to the sample above the saline interface. The concentration profile correlates positively to Fe²⁺, and negatively to S²⁻ and Eh, according to the characteristics of a strongly reducing aquifer derived from alluvium. The occurrence of high As contents in the upper aquifer is a new finding that stimulates further research on the subject.

INTRODUCTION

The object of this work is to investigate the groundwater composition of the upper coastal aquifer at the Adriatic coast near Ravenna (northern Italy), (Figure 1). The groundwater of the San Vitale Pine forest in Ravenna (Italy), are already severely affected by seawater intrusion. Chemical response to marine intrusion at the freshwater/saltwater interface was studied. That includes characterizing the spatial distribution of dominant cations and anions in response to marine ingression. The target is then to highlight the processes which have lead to present water composition. Special focus in this study is laid upon the release of Fe and As in the groundwater due to the changes in redox conditions.

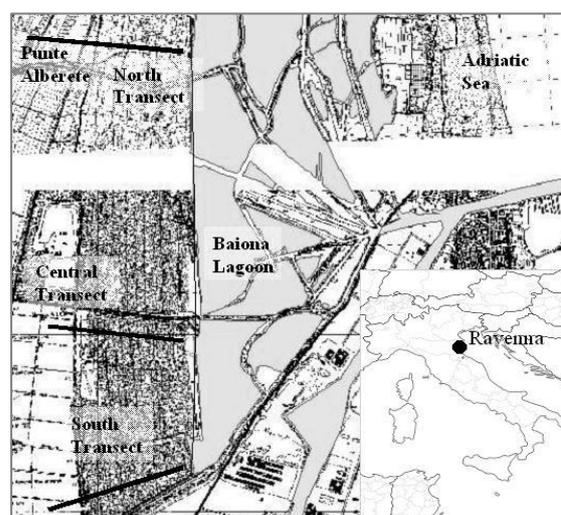


Figure 1: area of study

BACKGROUND

The San Vitale pine forest and the Punte Alberete swamp is situated 3 to 5 km west of the Adriatic Sea on a dune belt system within the Po Plain of northern Italy. Late Quaternary marine as well as continental deposits cover marine sediments of Pliocene to Middle Pleistocene age (Amorosi *et al.*, 1999). The area is particularly affected by rapid subsidence rates due to the natural compaction of sediments, and especially by man's activities in groundwater and natural gas extraction. Considering most parts of the study area lie at or below sea level, the area is already particularly prone to marine intrusion (Carminati & Martinelli, 2002). The studied aquifer includes an unconfined system, primarily based upon beach and dune sandy deposits reaching the depth of 30 meters. At the depth of 15-16 meters there is a layer of silt, dividing the upper and the lower aquifer.

METHODS

Three transects were selected from the Adriatic Sea landward into the San Vitale pine forest and Punte Alberete swamp. Sampling sites, are oriented quite perpendicular to the shore over a distance from 3,500 to 5,800 m from the shoreline.

The northern transect is situated in the Punte Alberete wetland and the northern part of San Vitale pine forest, the second transect is situated in the central part and the third in the southern part of San Vitale the pine forest.

Groundwater sampling along all three transects, was performed on a network of pre-installed piezometers, during a field-campaign spanning from May to September 2009. The piezometers, sampled in the northern transect, are cased in steel, they are screened only in the last meter, and penetrate the aquifer to a depth of 6 m. The piezometers located in the central and southern part, on the other hand, are cased by polyvinylchloride (PVC) and screened from 0.5 m down to 15 m, penetrating most of the upper aquifer. Three Piezometers are cased in PVC and screened from 13.7 m until a depth of 27m, in a way to extract groundwater only from the lower aquifer.

Before groundwater collection the entire chemical analysis testing equipment was decontaminated by deionised water. A depth profile of the temperature, electronic conductivity (EC), and salinity from the water table to the piezometer's bottom was measured on-site (CTD-probe AquaTROLL[®]200). On the base of the EC results the sampling depths were selected close to the water table, at depths where abrupt changes in EC would occur, because this might indicate the interface of fresh and saltwater, and finally at the bottom of the piezometer.

Operating a staddle field packer system, with a resolution of 20 cm, the piezometers were flushed at the specific sampling window until achieving constant values of EC and salinity or three times the total volume. Non-filtered samples provided readings of pH, redox potential (Eh) and temperature utilizing a HANNA[®] HI 9026 pH meter. In order to prevent extended aerial exposure and the consequent risk of precipitation and flocculation, the measurements of sulphide, ferrous iron and total iron concentrations were conducted on-site by applying a HACH[®] DR/2010 Spectrophotometer. Subsamples of groundwater were filtered through a 0.45 µm mesh and filled into 250 ml polyethylene (PE) bottles acidified with nitric acid (HNO₃) down to a pH < 2 for cation and trace element analysis or were left non-acidified for major anion

detection respectively. Total alkalinity was determined in the laboratory by the titration method with 0.02 HCl at pH of 4.5. Major nutrient (nitrate, nitrite, ammonia, phosphate) determination was performed on filtered non-acidified groundwater samples employing a HACH® DR/2010 Spectrophotometer. These analyses were implemented within 24 h after sampling to avoid biogeochemical alterations. For cation determination an AAAnalyst 100 Atomic Absorption Spectrometer was operated, and detection limits are listed as 0.01 mg/l. Previously filtered samples for major anion (SO_4^{2-} , NO_3^- , F^- , Br^- , Cl^-) were analysed with ion-chromatography (IC) analysis (DIONEX®DS5 Detection Stabilizer, detection limits: 0.01 mg/l). Trace element analyses (As, Ni, Cu, Mn, Fe, Si, B) were performed with the inductively coupled plasma (ICP) method using an ICP 6000 Series ICP atomic emission Spectrometer.

RESULTS AND DISCUSSION

By comparing the data of the three transects it is clear that the salinisation increase with depth and approaching the coast and that the thickness of the freshwater lens is related to the topographic level. The electrical conductivity range between 1.5-64.2 mS, with maximum at the bottom of the piezometer adjacent to the lagoon, that divide the pine forest from the sea, and the lower value in the surface of the most landward located piezometer, both in the central transect.

A first analysis of the data was made using a Piper diagram. The data of the northern transect indicate a conservative mixing for most of the samples. In the most seaward piezometer there is an replacement of Na^+ ion with Ca^{2+} on the exchanger(X) during ion exchange, that indicate salt water intrusion of that part of the aquifer according to Appelo & Postma (2005):



The upper samples of the most landward piezometer and the central one, shows a replacement of Ca^{2+} and Mg^{2+} in solution by Na^+ , that denote freshening, according to Appelo & Postma (2005):



Particular interest was given to the central transect, according to the major range of salinity, the homogeneity of the distribution of the piezometers. The data plotted on the Piper diagram distribute on the mixing line between seawater and freshwater. Only the upper sample of the landward piezometer shows a freshening process according to equation (2). In the most seaward position, adjacent to the lagoon, Na^+ and Cl^- fairly exceed seawater values

The southern transect seems to be the one most affected by seawater intrusion, in the Piper diagram all the sample lies on the mixing line of the sea/fresh water, suggesting a salinisation of the aquifer, equation(1).

The trace metal analysis shows how the central and southern transects are affected by a strong Arsenic pollution, with concentrations ranging between 0.6 a 95 ppb. The maximum values of this metalloid correspond to the sample above the freshwater/saltwater interface.

The main characteristics of the aquifer are strongly reducing conditions and pH near neutrality.

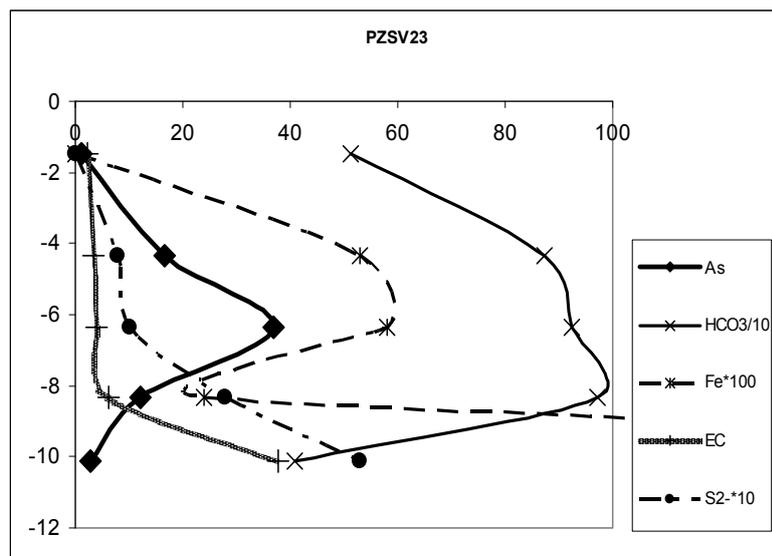


Figure 2: depth profiles of the conductivity and some ions related to As release

Figure 2 illustrates an example of the depth profile of one of the piezometer in the central transect. The maximum values of As correspond to the sample above the freshwater/saltwater interface. At the same depth this value of As is associated with the maximum concentration of Fe²⁺ and increasing concentrations of S²⁻ and alkalinity. The enrichment might be explained by the peat layer accumulated at 6.3 m to 6.5 m. Arsenic shows a strong affinity to bind with organic matter, as it is decomposed, Fe-oxides and hydroxides are reduced to the ferrous state and release As, nitrate depletes at these sampling sites,

meanwhile Fe²⁺ and S²⁻ increases with depth contrary to sulphate which ceases. The behaviour of all these elements is characteristic of reductive dissolution in alluvial aquifers (Ravenscroft, Brammer & Richards, 2009). All the other piezometers of the northern and southern transect except for the most landward in the south are enriched in As at the depths ranging from 5 to 7 meters below the sea level supporting the thesis of the organic matter as guide reaction.

Salt/fresh-water interface fluctuations play a role on a seasonal scale for As mobilization, changing the aerobic conditions of the aquifer.

CONCLUSIONS

Instead of the traditional depth integrated method, where the piezometer is fully flushed before extraction, thus mixing up bottom and top groundwater, sampling with the straddle Packer sampler allow to identify the changes in the groundwater composition with the depth. The data obtained with the planed sampling (water table, under/above saline interface and bottom of the piezometer) are really useful to detect the depth and the type of geochemical processes occurring in the groundwater with a good precision. A specific study of isotopes of water and sulphate of the central transect will be applied to classify the provenance of the water. The behaviour of others environmental relevant species, mobilized by the process of the Fe-oxides and hydroxides reduction, and its relation with the salt/fresh water interface are the objective of the next studies.

REFERENCES

- Amorosi *et al.* 1999. Sedimentary response to Late Quaternary sea-level changes in the Romagna plain (northern Italy). *Journal of Sedimentology*. 46:99-121
- Appelo & Postma 2005. *Geochemistry, groundwater and pollution*. Balkema. 535p
- Carminati & Martinelli. 2002. Subsidence rates in the Po Plain, northern Italy: the relative impact of natural and anthropogenic causation. *Engineering Geology*. 66: 241-255
- Ravenscroft, Brammer, Richards, 2009. *As Pollution: a global synthesis*. Wiley-Blackwell. 616 p