Seawater intrusion and heavy metal contamination in the alluvial plain of Quirra and Flumini Pisale rivers, South-Eastern Sardinia

M. Sodde, G. Barrocu

Abstract The alluvial plain of the Quirra and Flumini Pisale rivers is located along the south-eastern coast of Sardinia (Sarrabus) north of the village of Villaputzu. Water supply for the agricultural and animal raising activities carried out in the plain is provided by numerous dug wells that tap the unconfined groundwater hosted in the alluvial sediments.

Groundwater chemistry is significantly affected by seawater intrusion and the widespread presence of tailings in the alluvial sediments. These tailings were produced by the arsenopyrite and galena mines that once operated on the banks of the Baccu Locii river, right tributary of the Quirra river.

As, Pb, Se, Mn, Fe, Al and Cl concentrations exceeding the regulatory limits have been detected in several wells. The presence of two contamination sources, combined with the complexity of ongoing processes in the coastal aquifers, necessitated a detailed hydrogeologic and hydrochemical characterization of the study area.

Geological and stratigraphical data alone did not provide a clear understanding of the hydrogeological setting. The use of geophysical surveys, carried out with electrical tomography, enabled to identify a locally multilayered aquifer hosted in the alluvial terraces of Holocene age that stratigraphically overlie a second layer of well cemented terrace alluvium, with low permeability, resting on the metamorphic basement.

In order to define the areal extent of seawater intrusion and determine groundwater geochemistry and flow properties, different monitoring and sampling campaigns were carried out in the plain from 2004 to 2006. Piezometric level and the physical parameters (T, pH, EC) have been measured at 70 water points, covering an area of roughly 100 km².

Preliminary evaluation of the fresh saltwater interface position, determined by geophysical surveys, is consistent with the Cl and EC concentration distribution throughout the plain.

The chemical data of groundwater samples collected were processed using multivariate statistical methods (factor analysis). Evidence was produced of heavy metals release from sediments affected by saltwater intrusion, and Se and Sb resulted to be the heavy metals most sensitive to salinity changes.

Index Terms Seawater intrusion, heavy metals pollution, electrical tomography, multivariate statistics, factor analysis.

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I. INTRODUCTION

Regulators of highly contaminated sites generally focus their attention on identifying direct contamination sources and mitigating those impacts posing acute threats to the public, ignoring the potential impacts from the gradual accumulation of hazardous materials in soils and sediments over the long term. Different studies over the last decades have proved that changes in environmental conditions can lead to a sudden mobilization of these materials that, released in soluble form in the aquatic environment, become immediately available for biological uptake. Among these potential contaminants, heavy metals in particular are cause for alarm, owing to their persistence in the environment.

The balance between storage and mobilization of heavy metals is controlled by complex factors related to the amount and chemical forms of the metals, conditions of soils and sediments receiving them, land-use policies and practices, human activities and climate conditions. Management and regulation of potential contaminated sites have to control heavy metals input to the environment and consider activities influencing retoxification factors as well.

Groundwater in coastal aquifers represents one of the most vulnerable natural resources as regards the so called “retoxification processes”. Alluvial sediments, in fact, act as long-term “skins” for large amounts of heavy metals, but through reverse chemical processes, such as desorption and dissolution, they can revert into large sources of heavy metals in bioavailable form [1].

Heavy metals can be retained in sediments by sorption and ion exchange processes, inorganic or organic complexation, and precipitation. In estuarine waters it has been demonstrated that they are released into water as free ions or as complexes with dissolved organic matter (DOM) and suspended organic matter (SOM) [2, 3].

The capacity of soils and sediments to store and accumulate heavy metals depends mainly on their cation exchange capacity (CEC) and adsorption capacity (which vary in turn with clay content, type of clay minerals, organic matter and oxide/hydroxide content) [4]. Storage capacity of soils also depends on the chemical speciation of heavy metals, according to pH/Eh changes, and microbial transformations i.e., methylation, ethylation, etc) produced by sediment
dissolved microbes. Redox conditions influence the mobility of metals changing the chemical state (valence) of certain metals (e.g. Fe, Mn and As), indirectly affecting the mobility of metals occurring in one valence state (e.g. Cd and Zn), or acting on the elements they are associated with.

In coastal environments, salinity increase due to seawater intrusion or other salt sources is one of the major contributors to the large variations in factors affecting heavy metal mobility owing to its influence principally on cation exchange equilibrium [5].

To identify existence of retoxification processes and to study how they are affected by salinity requires an understanding of the potential impact of pollutants in coastal groundwater and marine environments. Management and planning of natural resources in coastal environment cannot disregard these processes, especially considering the possible influence of ongoing climate change and increasing exploitation on retoxification factors.

II. STUDY AREA

A. historical overview of the investigation site

The study site is the coastal and flat alluvial plain of the Quirra and Flumini Pisale Rivers (SE coast of Sardinia).

The plain represents a very important resource for the local inhabitants, due to the suitability of its soils for agriculture. Part of the marshy coastal deposits forming the back shore of the Murtas beach, has been involved in a reclamation scheme over the last 30 years [6]. However, the portion of plain nearest to the sea is uncultivated because of salt water intrusion and salt accumulation in both the topsoil and subsoil. The water for agriculture and animal farming activities, developed in the inner part of the plain, is supplied by numerous dug wells. Cultivated fields are divided into small plots, well irrigated by dripping systems, generally assigned to citrus orchards, market gardens and forage plants.

The abandoned mine of Baccu Locci is located on the northern bank of the Baccu Locci creek, at a distance of about 6 km upstream from the plain. A mixed sulphide ore mainly consisting of arsenopyrite and galena was mined there in the past to produce As. The mine developed upwards to a height of 300 m and the tailings were dumped on the banks of the river. About 500,000 tons of ore were produced and processed from the 1930s to 1964, when the mine was closed. The tailings produced by the flotation plant were discharged into the river Baccu Locci and dispersed by recurrent floods downstream in the river bed and delta plain [7].

The geochemistry of the surface and deep waters of the plain is strongly affected by the widespread distribution of these materials, intimately mixed with other alluvial sediments, the main contamination source in the area. They continue to erode from the dumps along the steep sides of the Baccu Locci valley, and it is significant that there are large sterile areas in the plain, especially along the river Quirra.

Currently, use of the river water, grazing and removal of any soil are forbidden along the watercourse to prevent any possible risks to human beings and animals. A rehabilitation plan has been financed by the Sardinian government and remediation measures are in progress.

B. Geology and hydrogeology

The lithological series of the area consists of a Paleozoic metamorphic basement made up of meta-sandstones and granitoids, covered by Middle Ordovician conglomerates, Permo-Triassic and Jurassic dolomites, and Eocene arenaceous-calcareous sediments. In the study area, Quaternary age formations, consisting of Holocene conglomerates and fluvial sands (inland part) and of marshy deposits (in the coastal zone) made up of silts with organic deposits and clays, laterally passing to aeolian and littoral sands, rest directly on the metamorphic basement. Plio-Pleistocene terraced alluvial deposits, made up of well-cemented and oxidized conglomerates, outcrop south of the Flumini Pisale river, and partly north of the Flumini Durci. They form an overburden about 12 m thick overlying the metamorphic basement [8, 9]. Both present and recent alluvium, are estimated to have medium-high permeability and to contain groundwater. The permeability of the old terraced alluvium is instead thought to be very poor, with local variations, so that within these deposits groundwater flow is insignificant. Both formations are characterized by the presence of a significant clay fraction.
maximum (March) and minimum (October) water table during the hydrological year.

B. Geophysical surveys

A geophysical survey was carried out in the part of the plain nearest to the sea, in order to highlight the sea-fresh water interface and to identify the aquifer structure.

The 2D electrical resistivity tomography technique was chosen as this is the most meaningful and widely used geophysical method in coastal environments to locate brackish or saline waters, and it can also provide geological information.

In particular, six 840 m long 2D electrical resistivity tomographies were performed using the multi-node switching system connected to a SYSCAL-R2 resistivity meter (IRIS-Instruments, Orleans, France). The system consists of 48 electrodes, enabling automatic measurements of apparent resistivity for the shallow subsurface using the linear grid array [10] with an electrode spacing of 10 m. RES2DINV software [11, 12], based on the smoothness-constrained least-squares method, is used and the inversion produces a two-dimensional subsurface model from the apparent resistivity pseudosection.

As shown in Figure 2, the profiles are designed along two different directions, one perpendicular and the other parallel to the shoreline, so as to intercept the drill-holes, dug in 2004 for geological exploration by the Progemma Society.

A large number of studies was carried out using the electrical resistivity methods to determine saltwater intrusion and physical properties of aquifers in many coastal areas.

Van Dam and Meulenkamp (1967) [13] determined salinity of groundwater in the western part of the Netherlands. Their interpretation of resistivity values was closely related with groundwater salinity. They consider 40, 12 and 3 Ω·m as fresh, brackish and saline water, respectively.

In the New England coastal zone, Frohlich et al. (1994) [14] reported that a layer with the resistivity of 230 Ω·m or less is indicative of saltwater intrusion in freshwater lenses.

In the south-eastern region of Virginia and the northern part of North Carolina, Sabet (1975) [15] estimated a range of 20 to several hundred Ω·m for the resistivity of clean sand and gravel (not containing silt or shale) saturated with freshwater. Much lower resistivity values were related to the same sand containing silt, clay or brackish water, so he concluded that horizons with resistivity less than 10 Ω·m cannot contain freshwater and that freshwater-bearing horizons (TDS < 1000 mg/l) show a resistivity varying between 19 and 25 Ω·m.

All these works show that pore water and host rock resistivities are the main factors governing the layer resistivity obtained by inversion processes [16, 17]. Water resistivity may vary from 0.2 to over 1000 Ω·m, depending on its ionic concentration and TDS content. Average seawater has a resistivity of 0.2 Ω·m.

<table>
<thead>
<tr>
<th>Resistivity (Ω·m)</th>
<th>Sediments Interpretation</th>
</tr>
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<tbody>
<tr>
<td>0.5 – 2.0</td>
<td>Very porous sand, or saturated clay Seawater; very saline water; TDS: about 20 000 mg/l</td>
</tr>
<tr>
<td>2.0</td>
<td>Porous sand, or saturated clay Saline water; TDS: about 10 000 mg/l</td>
</tr>
<tr>
<td>4.5</td>
<td>Sandy saturated, or sandy clay Salty Brackish water; TDS: 10 000 1500 mg/l</td>
</tr>
<tr>
<td>10.0</td>
<td>Sandy clay, sandy gravel Brackish water; TDS: 5000 1500 mg/l</td>
</tr>
<tr>
<td>15.0</td>
<td>Sand, gravel, some clay Poor quality fresh water; TDS: 1500 700 mg/l</td>
</tr>
<tr>
<td>30.0</td>
<td>Sand, gravel, minor clay Intermediate quality Fresh water; TDS: 100 mg/l</td>
</tr>
<tr>
<td>70.0</td>
<td>Sand, gravel, no clay Good quality fresh water; TDS small</td>
</tr>
<tr>
<td>More than 100.0</td>
<td>Coarse sand, gravel, no clay Very good quality fresh water; TDS very small</td>
</tr>
</tbody>
</table>

Modified from Zohdy et al. (1993)

To determine the conductivity of rocks containing water and clay, Simandoux, (1963) [18] and Ward (1990) [19] proposed an equation that depends on: rock, pore water and clay fraction resistivity; porosity; water saturation and volume of clay fraction. All these parameters may vary with depth and they are not easily measurable. Thus, a wide range of resistivity is often reported for a particular water saturated material.

Finally, Nowroozi et al. (1999) [20] interpreted resistivity...
data in terms of probable lithology and water quality using the resistivity range in relation to variation as a function of salinity and water quality, proposed by Zohdy et al. (1993) [21] for the Oxnard Plain CA and shown in table I. This classification is used here as a guide for interpreting resistivity cross-sections.

C. Spatial variability of physical and hydrochemical parameters in groundwaters

The spatial and temporal variability of hydraulic head, EC and Cl concentration was analyzed by geostatistical methods in order to determine groundwater flow properties and delineate the extent of groundwater salinization.

For mapping purposes, the discrete physical and hydrochemical data collected during the monitoring and sampling campaigns were geo-referenced and regionalized by 2D kriging supported by variogram analysis: in almost all cases, a linear variogram model with a medium rate of anisotropy in the SE direction was used.

D. Multivariate statistics

Factor analysis was applied, in this work, to the chemical data of groundwaters, in order to identify any significant patterns, draw useful information about on-going processes, to identify the governing parameters and how they interrelate with one another.

In factor analysis the number of significant parameters is reduced to a few that are able to explain the processes occurring. Through the behaviour of these governing parameters and their mutual relationships, it is then possible to advance hypotheses about the mechanisms and parameters governing retoxification processes.

The data base used is composed of 26 different parameters, collected at different times: March, May and October 2004, November 2005 and January 2006. First, the different sampling campaigns were considered separately, then a table with all the groundwater data was created and analyzed, and finally factor analysis was applied to a random population chosen from all data.

The hydrochemical parameters used to perform factor analysis contain information about metals (Fe, Mn, As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Se, Sh, V, Zn), cations (Ca, Na, K, Mg), anions (Cl, SO4, HCO3) and other general parameters (pH, EC, Eh).

A first series of factor analyses was performed on all parameters, in order to obtain a preliminary parameter grouping. Then a second series was carried out considering only the metals and the possible governing factors of their mobilization (pH, Eh, Cl/EC), in order to identify any ongoing retoxification processes in the plain.

Some parameters, such as Eh, Cl, Fe, Mn, Al, As, Co, are missing in some sampling campaigns. Therefore, especially in the second step of the factor analysis, the EC was used in place of Cl for the sampling periods where concentration data were missing.

IV. RESULTS AND DISCUSSION

A. Resistivity profiles and hydrogeological explanation

The results of the six 2D electrical resistivity tomographies were joined to form three main resistivity profiles. Here they are schematically explained using the Zohdy classification, on the basis of the corresponding geological cross-sections and groundwater TDS content measured in samples collected from some of the wells covered by geophysical surveys.

Resultant resistivity profiles generally show a vertical and lateral resistivity value variation, probably due to the presence of water with different salinity, different grain size and different porosity of the alluvial formations.

Resistivity Profile 1

The first resistivity cross-section (ABC in Figure 2) has an E-W direction and starts at a distance of about 300 m from the shoreline. Owing to the significant lateral variation of the resistivity, the section may be divided into three different parts. The vertical resistivity ranges, shown for each of them from east to west, can be summarized as follow:

a) 0 450 m from point A
  - from 0 to 10 m depth: very low resistivity values indicate clay and sandy silt saturated with very saline water (0.2-5 Ω·m and a measured TDS content of 110,000 mg/l);
  - from 10 to 30 m depth: a higher resistivity layer (10-20 Ω·m) may be due to the presence of a clayey sand lens, as confirmed by the resistivity profile 2;
  - from 30 to 50-70 m depth: very low resistivity values indicate clay and sandy silt saturated with very saline water (0.2-5 Ω·m);
  - from 50-70 to 80 m depth: resistivity layers with values higher than 30 Ω·m probably pertain to the metamorphic basement.

Thus, this part of the plain, very close to the sea, seems to be composed of Holocene marshy deposits 50-70 m deep, saturated with saline water and resting on the metamorphic basement.

b) 450 700 m from point A
  - from 0 to 20 m depth: very low resistivity values indicate clay and sandy silt saturated with very saline groundwater (0.2-5 Ω·m);
  - from 20 to 80 m depth: resistivity values ranging from 5 to 20 Ω·m are probably due to some beds of sandy sediments and groundwater with different salinity.

c) 700 m from point A point C
  - from 0 to 10 m depth: relatively high resistivity values from 10 to 20 Ω·m are shown. The stratigraphic information may be due to sand and less gravelly deposits that are saturated with brackish water (~2000-3000 mg/l TDS). A cover consisting of a discontinuous layer of clay and silt is probably present. Some very high resistivity values may be explained as errors due to high contact resistivity;
  - from 10 to 25-30 m depth: resistivity values from 20 to 60 Ω·m are shown. On the basis of the stratigraphy
they may be attributed to a layer of gravel deposits with a silty matrix saturated with poor quality fresh water;
- from 25-30 to 60-70 m depth: resistivity values vary from 10 to 20 $\Omega\cdot$m in the initial part and decrease to 5 $\Omega\cdot$m towards point C. This is probably due to silt and gravel deposits saturated with brackish water, which becomes salty toward point C, may be for a lateral recharge from the river Flumini Pisale;
- from 60-70 to 80 m depth: a resistivity increase from 20 to 70 $\Omega\cdot$m, probably indicates the presence of the metamorphic basement.

Resistivity Profile 2 - EBF (North-South direction)

The second resistivity cross-section (EBF in Figure 2), directed N-S, was placed at about 500 m from the shoreline.

The resistivity ranges measured in profile 2 can be summarized as follows:
- from 0 to 10 m depth: very low resistivity values are indicative of clay and sandy silt saturated with very saline water (0.2-5 $\Omega\cdot$m and a measured TDS content of 110,000 mg/l);
- from 10 to 30 m depth: a higher resistivity layer (10-20 $\Omega\cdot$m) may be due to a lens of clayey sand, as confirmed by the resistivity profile.

This cross-section probably represents a 70 m thick bank of Holocene marshy deposits saturated with saline water overlaying the metamorphic basement.

Resistivity Profile 3

The third resistivity cross-section (DC in Figure 2), oriented N-S, lies at a distance of about 1650 m from the shoreline.

Also in this case, the section can be divided into a northern, central and eastern part, considering the significant lateral variation of resistivity. The different vertical resistivity ranges can be summarized as follows:
- from 0 to 10 m depth: resistivity values hardly vary from north (100 $\Omega\cdot$m) to south (about 30 $\Omega\cdot$m) along the plain. Considering the stratigraphy, they suggest the presence of sand and gravel deposits saturated with fresh water which becomes brackish towards the river Flumini Pisale. The overburden seems to consist of a discontinuous layer of clay and silt. Some very high resistivity values can be explained by errors due to the high contact resistivity;
- from 10 to 35-40 m depth: resistivity values vary from 10 to 80 $\Omega\cdot$m. They probably indicate a prevalently gravel deposit laterally passing to sand and silt, and saltwater. In the north and central part of the plain sediments are likely composed of loose sandy or coarse gravel saturated with poor quality fresh water which in the northern part could be derived from river recharge. A possible increase of the silty matrix and cementation degree, and the presence of good quality fresh water may explain the higher resistivity values in the other part of the plain;
- from 35-40 to 80 m depth: high resistivity values are shown in the North part of the plain with a maximum of about 130 $\Omega\cdot$m in the central part. Southward, the resistivity decreases to 20 $\Omega\cdot$m. As there are few boreholes, different hypotheses can be put forward to explain the hydrogeological setting at this depth.

The chargeability section obtained with the Induced Polarization method in the same profile suggests that the whole formation is composed of sand and gravel with a clay matrix, its water content increasing from north to south along the plain. The lowest resistivity values (20 $\Omega\cdot$m) shown in the southern part may be due to the increase of groundwater salt content. It is possibly due to inland intrusion of salty tidal water or the leaching of saline sediments deposited during different transgressions. In this case, the metamorphic basement could be at a depth of 80 m from the surface, probably decreasing to 50 m in the central part of the plain. However, this is inconsistent with the findings of previous studies, which indicate alluvial deposits 35-40 m thick [22]. Therefore, according to a second hypothesis based on the exam of the tomographic profile, the resistivity values found at a depth of 35-40 m would indicate the presence of a metamorphic basement, probably fractured, bearing water with different salt contents. Concerning the lithologies outcropping in the area, the formation, showing resistivity ranging from 70 to 130 $\Omega\cdot$m, could be composed of marble and calcareous schist, and the 30 $\Omega\cdot$m resistivity layer could be related to a sandstone formation. In accordance with this second hypothesis, some sharp resistivity changes may be interpreted as faults and joints controlling groundwater flow.

Thus, the interpretation of the electrical resistivity tomography profiles suggests that the plain hosts a main alluvial multilayer aquifer consisting of deep Holocene marshy deposits (organic rich silt and clay) 50-70 m thick, closedi to the sea, and of inhomogeneous Holocene fluvid deposits (clay on the surface, and more or less cemented sand and gravel at depth, sometimes containing silty matrix) probably 35-40 m thick. These alluvial deposits overlay the metamorphic basement and are saturated with very saline water up to 1 km from the shoreline. The salt content of the groundwater decreases inland towards the plain, but at about 1500 m from of the shoreline it is still possible to find poor quality water with high salt content, especially in the deepest layers near the river Flumini Pisale.

B. Areal distribution of groundwater level

The trend of the water table in March 2004 (Figure 3a) is generally regular in the inner part of the plain (N-W), whereas it shows some anomalies in the coastal part, probably related to withdrawals for irrigation purposes. Two main withdrawal zones are evident: the first is in the central part, where there are numerous citrus plantations; the other in the southern part near the river Flumini Pisale, where groundwaters are used for animal farming. This trend differs from that for 2006 where the influence of withdrawals is greater in the central part of the coastal zone but insignificant in the southern part. In October 2004 (Figure 3b), when irrigation water demand is
higher, the influence of withdrawals on the trend of the water table is more evident, especially in the inner part of the plain (N-W) and in the central and north-eastern parts of the coastal area. This trend confirms that for 2005 except for a point of high head in the north-eastern part of the plain near the river Quirra, probably due to lateral recharge coming from the fractured formations close by (Sa Lilla complex).

Additional water level data for the rivers for these periods, suggest that in winter the aquifer recharges the river Flumini Pisale. The relationship between the river Quirra and the aquifer is not so clear, although input from the river to the groundwater can be assumed.

Figure 3  2D distribution of hydraulic head (m a.s.l.) in March (a) and October (b) 2004.

However, by comparing the data of hydraulic head of 2004 with those collected in 2005-2006, it is possible to see that the water level is generally higher in 2005-2006 than in 2004. Even so, the contour line related to null hydraulic head in 2004 was closer to the shoreline than in 2005-2006. This likely shows a possible advance of seawater intrusion during the last years.

C. Groundwater hydrogeochemical characterization

The Hydrochemical Facies (HYF) of groundwaters for March and October 2004, defined according to the classification proposed by Gimenez et al. (1995) [23], as modified by Stuyfzand (1986) [24], are shown in Figure 4a. In March 2004, saline (Cl > 5000 mg/l) and brackish waters (Cl between 1000 and 5000 mg/l) with HYF typical of active seawater intrusion (NaCl(-) and CaCl(-)) appear in the coastal zone and locally in the central area, while, from NW toward the middle of the plain, HYF are typical of groundwater refreshing (CaHCO3, Ca/NaMixB and NaHCO3). In October 2004, saline HYFs disappear and groundwaters show overall dilution, with only a few exceptions.

Figure 4 (a) Classification of groundwaters sampled in two periods; (b) variation of Ca, Na+K, sulphates excess and deficit and bicarbonates concentration for the two periods, ordered according to Na increase.

In fact, groundwater salinization in the plain, apart from local solution of calcium sulphate, indicated by excess of sulphates with respect to pure mixing between freshwater and present-day seawater (horizontal line in Figure 4b), seems mainly caused by seawater intrusion. In March Na deficit is high near the coast: it is accompanied by Ca excess, sulphate reduction and bicarbonate increase (Figure 4b). In October sulphate reduction appears inland, near the recharge front, while the effects of seawater intrusion near the coast decrease.
In both periods the distribution of cation excess and deficit highlights the presence of ion-exchange processes triggered by seawater intrusion [25], which is significantly lower in October than in March.

**D. Aerial distribution of Cl and EC concentration**

Cl (mg/l) and EC (μS/cm) areal distributions were reconstructed to delineate the extent of groundwater salinization in March and October 2004.

![Cl (mg/l) distribution in March 2004](image)

![Cl (mg/l) distribution in October 2004](image)

![EC (μS/cm) distribution in March 2004](image)

![EC (μS/cm) distribution in October 2004](image)

Chloride (Figure 5) and EC distributions (Figure 6) show the same trend in the two periods. Maximum values are always found to the East close to the coast; groundwaters show the lowest values inland to the NW. Chlorides and EC in October show average values lower than in March, as emerged from the hydrochemical study. March and October are respectively the periods of maximum and minimum groundwater levels: however, chemical data indicate that the hydraulic head increase in March does not result in groundwater dilution, but corresponds to an unusual increase in groundwater salinity. This occurrence could be explained by the contribution of recharge water rich in Cl, which can be the result of both leaching of salts deposited on soils due to evaporation during the previous dry season or of airborne dry deposition.

**E. Factor analysis**

Factor analysis aims mainly at reducing data and creating hypotheses about any significant patterns. By analyzing the relationships within the set of hydro-geochemical parameters examined a small number of hypothetical parameters are created, which are able to summarize the essential information in the set of observed data. Obviously, the aim is to obtain results that are representative of the ongoing processes and that provide evidence of the retoxification process. Therefore, in light of the knowledge about the hydro-geochemical parameters variability in the site and the most important reactions governing a heavy metal contaminated site, it is possible to give a first interpretation of the results obtained.

As result of the factor analysis performed considering all the parameters for the groundwater data measured in March the following factors were extracted:
- Factor 1: Cl, Na, K, Mg, Sb, Se, SO4, EC, Ca, Co, Fe, HCO3, Eh (-), Mn;
- Factor 2: Cd, Zn, Ni, Co, pH (-), Cu;
- Factor 3: Pb, Al, Cu, V;
- Factor 4: Cr, Ni;
- Factor 5: As (-).

Whereas, using the October data the following result was achieved:
- Factor 1: Se, Na, Cl, K, EC, V, Mg;
- Factor 2: Co, Ni, Al, Pb, Cu, Zn, Cr, Fe, Cd, Sb;
- Factor 3:Mn, HCO3;
- Factor 4: As (-), Eh (-), Sb (-);
- Factor 5: SO4, Ca.

Also using the May data another parameter grouping was obtained, as follows:
- Factor 1: Ca, Mg, SO4, Hg, Cr, K, Na, EC, Fe, HCO3, Mn;
- Factor 2: Eh (-), pH, As (-);
- Factor 3: Pb, Zn.

Within the factors the variables are represented by decreasing load.

The first factor in both analyses clearly represents the parameters involved in ion exchange processes associated with groundwater salinization. Besides the main anions and cations, responsible for EC, the factor includes some metals, such as Sb, Se, Co, Fe, Mn, V, Hg and Cr, which are also involved in cation exchange reactions. Therefore, processes of
retoxification due to salinity increase can be assumed for these metals. Even so, some of them, such as Fe, Mn, V and Cr show a sensitivity to mobilization also due to changes in Eh and/or pH conditions. The predominance of one parameter over the others probably depends on local hydrochemical conditions. Moreover, in winter the high salinity measured in groundwater are associated with Eh according to an inverse relationship. This probably means that during winter the salinization processes are partly due to seawater intrusion and partly to evaporites and hypersaline brines dissolution that occur under reducing conditions.

The second factor, extracted from the March data, is instead clearly representative of the different heavy metals, such as Cd, Zn, Ni, Co, and Cu, that are sensitive to mobilization under acidic conditions. Thus, retoxification processes due to a decrease in pH are assumed for them.

The third factor includes Pb, Al, Cu and V, that evidently behave in a similar way in groundwater and that probably undergo solubilization under reducing conditions.

All these metals (Cd, Zn, Ni, Cu, Al, Co, Cr, Pb) together with the October data are included in the same factors, probably because there is no clear predominance of a decrease in Eh or pH as retoxification factors. The behaviour of Fe and Sb is difficult to interpret. Their mobilization in fact seems to occur under both salinity increasing and Eh decreasing conditions. But also a dependence on pH cannot be excluded, especially for Fe. The inverse relationship between Sb and Eh is confirmed by the fourth factor extracted for the October data.

One of the factors extracted for all the analyses performed is the As, which behaves differently from other metals in groundwater. It is probably mobilized under oxidizing and acidic conditions, as indicated by its direct relationship with Eh and inverse relationship with pH shown by the analyses performed using the October and May data.

Other particular relationships are shown.

The first is between Cr and Ni, that in March evidently behave similarly in groundwater.

Another one is the inverse relationship between Mn and Eh. So, it is not clear whether Mn dissolution occurs only under reducing conditions or also when salinity increases. Both retoxification processes however seem possible.

The other direct relationship is between Pb and Zn that in May seems to behave in the same way in groundwater.

The same interpretation also holds for the results of factor analyses performed considering only the heavy metals and the factors governing their mobility.

Summing up, the most important heavy metals involved in retoxification processes can be grouped as follows according to the related retoxification factors:

- increase in salinity: Sb, Se, Co, Fe, Mn, V, Hg, Cr;
- decrease in pH: Cd, Zn, Ni, Cu, Al, Co, Pb;
- decrease in Eh: Pb, Al, Cu, V and Mn;
- increase in Eh and decrease in pH: As.

As explained above this classification cannot be regarded as rigid owing to the fact that some metals may be sensitive to different retoxification factors and that one factor may prevail over the other depending on local hydrochemical conditions.

V. CONCLUSION

This research work confirms the complexity of studying the variation of heavy metal concentrations in a real world context, such as the coastal aquifer of the alluvial plain of Quirra, which is contaminated by wastes from past mining activities and vulnerable to salinization processes. In a laboratory study the influence of each retoxification factor can be observed separately, whereas in actual fact, all retoxification factors act contemporaneously.

In a coastal aquifer, groundwater chemical characteristics vary mainly in relation to the variation of total salt content, following the seasonal dynamics of seawater intrusion and being on average higher in March than in October. However, as in this case, also salinization due to evaporite dissolution, which occurs under reducing conditions, or salinization due to sea spray or solution of salts deposited on soil by evaporation of irrigation water can potentially cause the release of heavy metals. Variation in groundwater salinity, whatever the source, brings about changes in constituent concentrations and physico-chemical properties such as pH, Eh, and ionic strength, i.e. of those parameters which can act as retoxification factors.

The results of the different factor analyses performed with the hydrochemical data collected, indicate that metals react to one or more retoxification factors, all depending on aquifer salinization dynamics. Thus, in relation to changes in salinity, pH or Eh, most heavy metals are released from sediments where they reside, being adsorbed there or in the exchange complex. In particular, the ion exchange process, whose action during groundwater salinization and refreshing is demonstrated by the occurrence of peculiar hydrochemical facies in the two survey months, can be identified as the most important process: direction of exchange changes depending on pH, Eh and salinity changes, and ultimately govern the mobility of most heavy metals.

Se, Sb, Co, Fe, Mn, V, Cr, Se are the heavy metals most responsive to salinity changes, even if Se is the only metal which seems to be clearly mobilized when salinity changes. Co is able to mobilize from sediments also when pH decreases, whereas Pb, Al, V and Mn are more mobile under reducing conditions. Only As always behaves differently from the other heavy metals, as it is present in solution with high concentrations both under oxidizing and acidic conditions.

The results of the study suggest that, in a coastal aquifer, owing to the risks of groundwater contamination by metals accumulated in soils and sediments, remediation strategies and measures for the site should also consider the effects of any retoxification processes. The site examined is highly significant from a hydrogeological point of view and the results achieved so far may be assumed to be true of many coastal aquifers contaminated by heavy metals.
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REFERENCES


