Mine Water Environ (2017) 36:163–179
DOI 10.1007/s10230-017-0430-z

TECHNICAL ARTICLE

# The Fate of Base Metals in the Environment and Water Quality in the Mellegue Watershed, Northwest Tunisia

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Received: 29 March 2014 / Accepted: 18 January 2017 / Published online: 16 February 2017

**Abstract** The 130 $Mm^3$-capacity Mellègue reservoir has a broad catchment area. Contaminants include sewage from cities, farm fertilizers, and metals released from mine tailings, all of which threaten Tunisia's water supply. Forty surface water samples were collected from watercourses and 18 from the reservoir during the wet and dry seasons. To evaluate groundwater contamination, the Sarrat basin was considered as a case study, and well water was analysed. The total amounts of base metals and nutrients in the watercourses did not exceed international standards. Evaporites in broad Triassic outcrops and in tailings dissolve, and may fix lead as sulphates; however, sulphate and chloride can complex and increase the solubility of some metals. The nutrient and salt content were highest in the Rmel River, which receives sewage from el Kef. An opposing gradient of metals was observed in the reservoir water column: elements such as Zn, Pb, and Al were enriched upwards, while Mn, Fe, and Cr increased towards the sediment–water interface. The same behaviour was observed for $NO_3^-$ and $O_2$, due to metal release under reducing conditions in bottom waters, and dissolution of Fe and Mn colloids. Fertilizers and sewage may be responsible for the potentially hazardous level of nutrients in the groundwater.

**Keywords** Pollution · Nutrients · Surface water · Groundwater

## Introduction

Tunisia is a water-deficient country, with an annual renewable water reserve of ≈500 $m^3$ per capita, compared to the world standard of >1000 $m^3$/year per capita (Food and Agriculture Organization of the United Nations; FAO 2015). The total water reserves include water stored in groundwater aquifers and a national system of dams and reservoirs. Since the early 1960s, Tunisia has managed the country's dams in the north and central parts of the country based on water quality, economy, and safety, by diverting water from the main watercourses, including the Mejerda, Maaden, Tassa, Harka, Meliane, Sejnane, Barbar, and Mellègue Rivers (oueds). The Mellègue hosts one of the most important dams, constructed in 1954.

However, ore deposits and the mines and associated wastes (e.g. acid waters, tailings), which date back to the early colonial period (1910) has adversely affected water quality. The mine-influenced water has increased metal and metalloid concentrations (e.g. Fe, Pb, Zn, Cu, Ag, Hg, As, Sb) in streams and affected the environment and human health (Mlayah et al. 2013). Leaching of metals in soil and mine wastes and erosion and transport of soluble and metal particulates affect the quality of water in reservoirs, surface water, and groundwater, and may endanger the environment and human health. The Mellègue River drains a large catchment area with at least ten moderate to high-grade polymetallic mines (Pb(Ag)–Zn–Ba, Fe–Pb–Zn, P–U–REE, Pb–Zn–Cu(Hg); Slim-Shimi 1992). Erosion of mine spoils and mine tailings in areas with similar mines have been shown to increase metal concentrations in rivers

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**Electronic supplementary material** The online version of this article (doi:10.1007/s10230-017-0430-z) contains supplementary material, which is available to authorized users.

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and contributed to aquatic pollution (Bhattacharya et al. 2012; Candeias et al. 2013; Grande et al. 2013; Macklin et al. 1999; Mlayah et al. 2009; Olias et al. 2006; Navarro et al. 2007).

Mining in northwestern Tunisia occurs throughout the catchment areas of the Mellègue and Mejerda Rivers, which account for 81% of the total water used for agriculture in the Mejerda valley and the potable water supply for the largest cities, including Tunis, the capital. Previous work in the area has focused on soil and sediment, rather than water quality (Guedria et al. 1989). The purpose of this study was to: (1) evaluate the effects of anthropogenic inputs, including mining (ore processing and waste disposal), the use of fertilizers for agriculture, and wastewater discharges, on the quality of surface water and groundwater in the Mellègue watershed and sub-basins; and (2) assess the vertical distribution of metals in the Mellègue Reservoir.

## Description of the Study Area

The study area covers 10,600 $km^2$ (Fig. 1) in northwestern Tunisia that is characterized by a rugged topography and moderate relief, and is subdivided into two adjacent hydrographic basins: the Mellègue and the south Kaala Khasba watershed. The Mellègue basin contains the Mellègue River, which runs SW to NE from near the Algerian border and empties into the E-W trending Mejerda River, which runs for 253 km across Tunisia. The Mellègue dam and reservoir are located west of Nebeur; the reservoir holds 130 $Mm^3$ and drains a catchment area of 10,300 $km^2$. Abandoned mines in the Mellègue watershed include the Sakiet Sidi Youssef, Garn Halfaya, Boujabeur, Zag et Tir, Nebeur, and Touireuf (Pb–Zn) (Fig. 1; Mlayah et al. 2009). The southern Kaala Khasba watershed covers 400 $km^2$ (Figs. 1, 2a). The Sarrat River valley occupies a NW-SE extending graben for 100 km and is fed by small tributaries. The basin hosts a phosphate (K. el Khasba) and an iron (Jerissa) mine (see Fig. 1). The Kalaa Khasba plain hosts permeable and highly erodible Neogene-Quaternary terrains with high densities of anthropogenic contaminant sources (Fig. 2b; Mlayah et al. 2009, 2013).

The Mellègue basin's geology was mapped in the 1960s (Gottis and Sainfeld 1956) and 1980s by the Office National des Mines de Tunisie. The lithostratigraphy (Fig. 2a) is predominantly Triassic gypsum and halite, Cretaceous-Eocene limestones and marls, and Neogene-Quaternary siliciclastics. The mines are hosted in Triassic evaporates; Cretaceous marls with limestone interbeds; Palaeogene marls, lime and dolostones; Neogene siliciclastics; and Quarternary clays, sands and gravels (Chikhaoui et al. 1994; Perthuisot 1978).

The geology of the study area is characterised by salt extrusions (Masrouhi et al. 2013). Local broad outcrops along faults include extruded Triassic evaporates (gypsum, anhydrite, halite), siliciclastics (sands, sandstones, and variegated clays), and locally interstratified dolostone beds (Fig. 2a). The thick Triassic series are heavily fractured and brecciated (Gottis and Sainfeld 1956; Perthuisot 1978). The Upper Cretaceous series includes marls with intercalated limestones, capped by Maastrichtian limestone beds of the Abiod Formation (Burollet 1956). The Paleogene strata are marls and limestone capped with phosphorite beds, Eocene nummulite-bearing limestone, Lutetian to Priabonian clays and marls with thin-bedded limestones, and Rupelian-Burdigalian transgressive beds of sand with quartz pebbles. The Neogene-Quaternary deposits contain clays and sand layers associated with molasse conglomerate and gravel deposits (Fig. 2).

The climate of the region ranges from semi-arid in the south to sub-humid in the northern part of the study area, and is dominated by two major and severely contrasting wet and dry seasons. The wet season lasts from October to April with intense precipitation. Nearly 50% of the annual rainfall occurs during a colder period from November to January. The dry season lasts from May to September.

### Contaminant Sources

Various contaminant sources affect the study area. Farming is the principal occupation in the area, and fertilizers and complex mineral and organic pesticides are carried in surface runoff to the Mellègue River, and stored in the Mellègue Reservoir. In urban areas, sewage is the primary source of pollution (Ben Hamza 1994).

Ore deposits in the Mellègue catchment area may also directly affect water quality. Polymetallic strata-bound, vein, and stockwork Pb(Ag)–Zn–Fe–Ba, and Fe ores are hosted in Aptian/Cenomanian/Turonian shale and limestone. Vein Pb-Zn–Cu–Hg deposits in local Ypresian limestone occur beneath a Lutetian marl hanging wall (Slim-Shimi 1992). Other Palaeogene-Ypresian lime/dolostones and marls also bear phosphorite deposits (Tlig et al. 1987). The opencast mining of phosphorite, Fe ore, and Fe–Pb–Zn gossan, and underground mining of Pb–Zn sulfides, barite, and siderite in the study area started as early as the pre-Roman period and culminated in large-scale mining from the end of the nineteenth century to the 1950s during colonial development.

In previously mined areas, mine-influenced waters, waste slurries, tailings piles, and weathering of ore-minerals have substantially affected water quality in the catchment area (Mlayah et al. 2007a, b, 2009, 2013). Detailed studies of mineral paragenesis in ore bodies from the region indicate labile polymetallic species dominated by: (1) siderite, limonite, hematite, and ankerite in the Jerissa, Slata, and Hameima iron ores; (2) galena, sphalerite, cerussite,

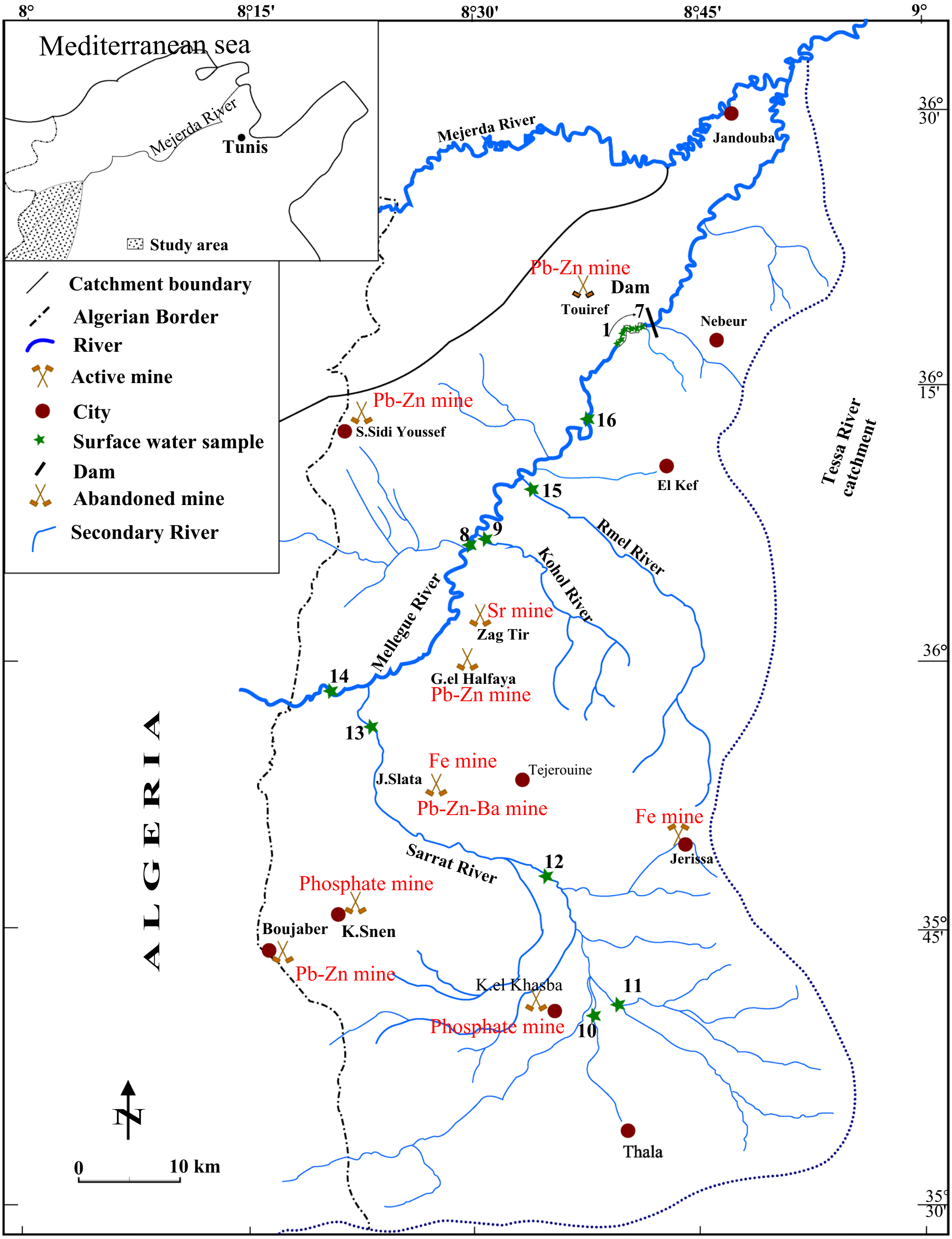

**Fig. 1** Map showing the study area mines, and surface water sampling locations

As-pyrite, and barite in Pb–Zn–Fe–Ba occurrences at e.g. Garn Halfaia, Nebeur, Zag et Tir, and Boujabeur; and (3) chalcopyrite, chalchosite, malachite, and azurite in local copper-bearing ore bodies (Hatira et al. 1990; Mlayah et al. 2009). While Ba-Sr sulphates and celestite ($SrSO_4$) resist dissolution to some extent, halite and gypsum in the country rocks, ore-gangues, and tailings dissolve rapidly and release chloride and sulphate ions, which can complex dissolved metals. Under ambient conditions, base-metal sulphide oxidation generates acidity, increases $SO_4$ and Fe

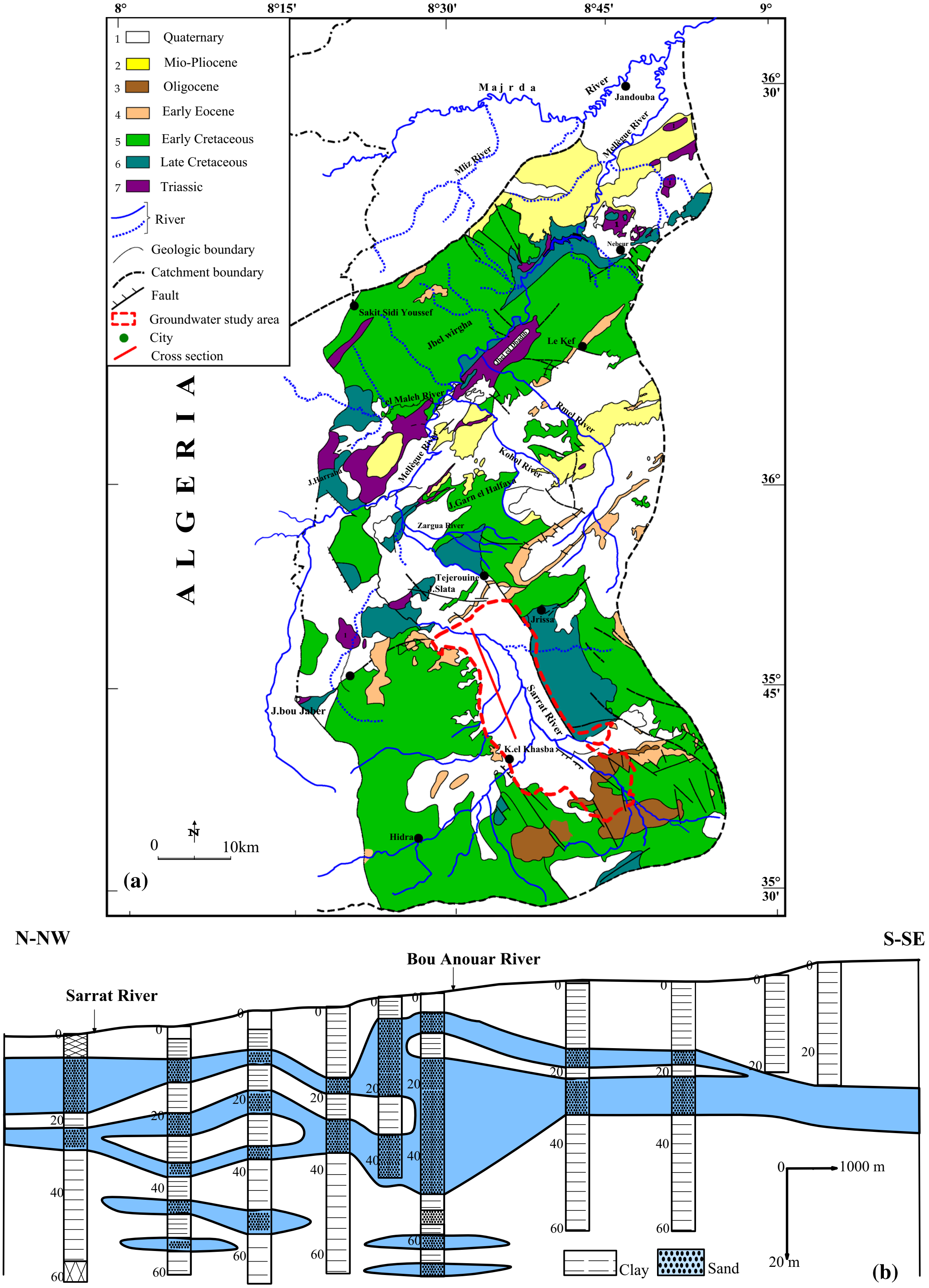

**Fig. 2** **a** Geologic map of the study area (modified from Ben Haj Ali et al. 1985), and **b** NW-SE geologic cross section of Neogene-Quaternary deposits. Key for geologic units in **a**: *1* quaternary: alluvium and silt, *2* Mio-Pliocene: clays, sand, silt, and conglomerates, *3* oligocene: sand, sandstone, and marls, *4* early Eocene: carbonates and marls, *5* early Cretaceous: marls, carbonate, and sandstone, *6* Late Cretaceous: marls, carbonate, and sandstone, *7* Triassic: gypsum, dolomite, sand and clays

concentrations, and releases other related trace metals. For example, areas that surround the large Jérissa Fe mine and other abandoned mines, including former phosphate (Kalaa Khasba and Kalaa Snen), iron (Slata), Pb(Ag)–Zn–Ba (Sidi Amor Ben Salem), and Pb-Zn–Ba–Sr (Sakiet Sidi Youssef, Garn el Halfaya, Boujabeur, and Zag et Tir) mines (Fig. 1) have improperly stored tailings and wastes that continue to release contaminants. In addition, the Sarrat, Rmel, and Kohol rivers receive acidic mine waters, seepage from tailings, and sewage from cities such as El Kef (Fig. 1).

## Sampling and Analytical Methods

### Sampling and Sample Preparation

#### *Tailings Samples*

Representative tailing samples were collected from the mines in the study area (Fig. 1) in September 2004. A total of 37 composite tailings samples were collected from the following locations: Slata Fer (five samples), Jerissa (two samples), Boujabeur (ten samples), Sidi Amor (five samples), Sakiet Sidi Youssef (four samples), Garn el Halfaya (four samples), Zag et Tir (one sample), Kalaa el Khasba (five samples), and Kalaa el Snen (one sample). A composite sample consisted of a mixture of sub-samples taken from depths of 0–10 cm in a 5 m × 5 m area. The samples were collected in plastic bags that were sealed and labeled. Protecting these samples from oxidation was unnecessary because the tailings at all sampling sites were dry and already oxidized on the surface.

#### *Water Samples*

The coordinates of all samples were recorded using a GARMIN handheld GPS device. The water samples were stored in polytetrafluoroethylene (PTFE) bottles that were pre-washed using an alkaline solution and rinsed with deionised water (Mlayah et al. 2011). Field temperature (T), electric conductivity (EC), and pH were measured using portable field instruments: a Cond 97i conductivity meter, a WTW Measurement Systems device, and a Metrohm 704 pH meter. The water samples were stored at 4 °C prior to filtering using 0.45 µm Millipore membranes. A sample fraction for determining major cations and metals was acidified to pH 2 with $HNO_3$.

#### *Stream Samples*

Surface water samples were collected at 16 sampling sites that considered the location of wastes and tailings, lithologies, physiographical features, and drainage conditions (Fig. 1). The potential for these factors to constrain pollutant transport was also considered (Mlayah et al. 2013). Water samples from the Mellègue River and its major tributaries (Sarrat, Rmel, and Kohol) were collected in the dry season (September 2004) and wet season (March 2005) to assess seasonal variability in element concentrations. Only one sample was collected from each location. Stream water samples were generally collected near the mouths of tributaries and upstream of tributary inputs in the Mellègue River to better understand the pathways of metals released into the watercourses. Sample sites were selected under low stream sedimentation and moderate flow-rate conditions.

#### *Mellègue Reservoir Samples*

The distribution of metals and nutrients in the Mellègue Reservoir water column was also monitored. Seventy-two water samples were collected in a Niskin bottle immersed at different depth intervals (0–4 m, and then at each meter down to the water–sediment interface).

#### *Groundwater Samples*

Groundwater samples were collected from wells in the Sarrat River catchment area (Figs. 1, 2a, b). Fifty groundwater samples from depths of 7–70 m were collected during March 2005 for piezometric interpretation. Only 47 samples were analysed for water quality. Prior to sampling, the wells were purged by continuous pumping for 20–30 min until T, EC, and pH stabilized.

### Analytical Techniques

#### *Tailing Samples*

Analytical work was performed at the ACME Analytical Laboratories in Vancouver, Canada, where the fine-grained (<63 µm) fraction was subjected to a modified aqua-regia digestion, ICP-MS analysis, and Hg analysis by flameless atomic absorption spectrometry (AAS; Perkin Elmer, AAnalyst 200). The modified aqua regia digestion of the sample extracts only a fraction of the major elements (pseudo-total analysis) because some phases are not completely dissolved. This digestion method is suitable for the dissolution of metals bound as water-soluble salts, in cation-exchange sites, statically bound to clay particles, in organic chelates in amorphous oxides and hydroxides of Mn and Fe in carbonates, sulphides, and some sulphates. It also partially dissolves metals in silicates (generally, the darker ferromagnesian-rich silicates) and some crystalline oxides of Fe, Ti, and Cr. Refractory Ta, Hf, Zr, and Nb minerals (zircon and some oxides) and Ba sulphate are most resistant to attack (Cicchella et al. 2005). Owing to this limitation, results are total to near-total for trace and base metals and possibly partial for rock-forming elements such as Na, Mg, Al, K, Ca, Mn, and Fe. However, environmentally relevant components like base metals or potentially toxic elements (Alloway 1995) that are not incorporated in silicates are efficiently dissolved (Ure 1995) and can be used to assess potential toxicity. The precision of the analytical methods is based on routine replicate sampling (20 samples). The quality of all analytical procedures was checked by incorporating random duplicate samples and quality control standards in each analytical set (provided by the ACME Analytical Laboratory).

X-ray diffraction (XRD) techniques (Philips PW1130/90 and X'Pert PW3040/60; CuKα; 2θ) were applied to tailings samples after grinding of representative sub-samples. The instrument conditions used were 40 kV voltage, 30 mA current, and a 0.5 nm slit. Scans were run between 2° and 60° (2θ). Mineralogical determinations followed the criteria proposed by Thorez (1976).

### *Water Samples*

Major anions (Cl, $NO_3$, $SO_4$, and $PO_4$) were determined by ion chromatography (Metrohm). Major cations (Ca and Mg) were determined by flame AAS using standard solutions, while K and Na were determined by atomic emission spectrometry (AES). Alkalinity was analysed by titration using $H_2SO_4$ (N/50). The total concentrations of Ag, As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, P, Pb, S, Sr, and Zn were determined by ICP–MS at the ACME Analytical Laboratories in Vancouver, Canada, while Hg was determined by flameless AAS. Water from the 30 wells in the upper basin were analysed by the same methods and used to assess the impact of urban and farming factors to the environment.

## Results and Discussion

### Mineralogy and Geochemistry of Mine Waste Deposits

Metals in tailings and other wastes can present a threat to the environment at and around mine sites. Inclusions of polymetallic minerals such as sulphosalts (bournonite, jordanite, geochronite, seligmannite, tennantite-tetrahedrite series, cinnabar, metacinnabar, and polhemusite) that are abundant in the study area (Slim-Shimi et al. 1996) contribute to the release of various toxic elements. The concentrations of Ag, As, Ba, Ca, Cd, Cr, Cu, Fe, Hg, Mn, Mo, P, Pb, S, Sr, and Zn in tailings from the different mines were published by Mlayah et al. (2009).

The samples from the Slata Fer and Jerissa Fe mines showed high concentrations of Fe and Mn (Supplemental Table 1). The Jerissa tailings contained the main ore mineral siderite, with accessory hematite and ankerite, and limonite, pyrolusite, and goethite in the gossans. Minor amounts of galena, cerussite, sphalerite, chalcopyrite, arsenopyrite, malachite, and azurite were also identified. The Slata Fer samples presented higher concentrations of Pb, Ag, and Ba than the Jerissa samples. At Boujabeur, the tailings samples containing calcite and quartz displayed high concentrations of Pb, Zn, Hg, and Ba (Supplemental Table 1).

At the Sidi Amor Mine (Pb(Ag)–Zn–Ba), the mine waste samples were enriched in Pb, Zn, and Ba, but presented low average Hg concentrations. Sr concentrations were also elevated (Supplemental Table 1). The tailings contained primary calcite over quartz, minor strontianite, and, in a few samples, gypsum.

At the Sakiet Sidi Youssef Mine, Pb–Zn sulphides in the tailings generated elevated concentrations of Pb, Zn, and Cd (Supplemental Table 1). These tailings consist of gangue-derived calcite, gypsum, and quartz, and accessory galena, sphalerite, siderite, pyrrhotite, gypsum, anhydrite, dolomite, and clays.

At the Garn Halfaya Mine (Pb–Zn–Ba), high concentrations of Pb, Zn, Sr, and Hg were detected in the tailings (Supplemental Table 1). The mineral occurrences are similar to those in the Sakiet Sidi Youssef samples, and both included common minerals present in the parent ores (Mlayah et al. 2009).

Tailings at the Kalaa Khasba and Kalaa Snen mines contained P, Sr, and apatite. Cr, Zn, and Cd were also detected. Tunisian phosphorites contain U, Zn, Cd, Cr, Sr, Zn, and rare earth elements (da Silva et al. 2010; Tlig et al. 1987). Phosphorite mine waste samples contained calcite and lesser amounts of clays, quartz, and dolomite (Mlayah et al. 2009; da Silva et al. 2010).

## River Water Quality Results

### *Field Parameters*

The results for the filtered river and reservoir samples are shown in Table 1. Surface water temperatures ranged from 16 to 23 °C in winter to 20–29 °C in summer. The somewhat alkaline pH was influenced by carbonates and alkalinity linked to the dissolution of limestone, halite, and gypsum as well as ion exchange by marls after a dry season (Table 1). It is likely that acid mine waters released in the rainier winter season undergo dilution and pH buffering by carbonate minerals (Olias et al. 2006), thus leading to a higher pH. In contrast, due to intense evapotranspiration and photosynthetic activity in the summer, along with scarce river flows, the pH values in the reservoir are less alkaline during the dry season, with a simultaneous increase in EC.

The EC data clearly show a seasonal decrease during the winter (Table 1). ECs were not measured in the Mellègue River southwest to the El Maleh River confluence near the Algerian border (Fig. 1).

### Major Cations

Na, Ca, Cl, and $SO_4$ dominated the surface water ionic composition (Table 1), due to dissolution of the Triassic evaporites that outcrop in the area. These salts are responsible for the higher EC values in summer when evaporation is favoured and salinities increase. The Cl and $SO_4$ concentrations increase from south to north in the main watercourses. For example, in the Sarrat River in the summer, Cl and $SO_4$ concentrations increased from 290 to 731 mg $L^{-1}$, in sample 10 (head waters) to 519 and 1039 mg $L^{-1}$ in sample 13 (near the mouth; Fig. 1). To the west in the Mellègue basin, surface waters are predominantly Na–Cl-type waters (Baccar 1988; Mlayah 2010). The EC values correspond to high dissolved chloride concentrations and leaching of Ca, Mg, and Na from the salt outcrops.

Conversely, a gradual decrease in bicarbonate concentrations occurs from south to north because carbonates are uncommon in the abundant Triassic salt outcrops in the area. All ion concentrations, including Ca, Na, Mg, and K, were higher in the summer due to evaporation.

### Major Anions

The Sarrat River water (sites 10 and 12; Figs. 1, 2; Table 1) was dominated by bicarbonate and sulphate, which progressively decreased northward (Mlayah et al. 2009). The high sulphate concentrations in all water samples (Table 1) were related to acidic waters associated with the sulphide ores (Pb–Zn–Ba) and tailings from the Slata, Boujabeur, Sakiet Sidi Youssef, and Garn Halfaya mines and from sporadic Triassic gypsum deposits bordering the Mellègue valley.

Overall nitrate concentrations ranged from 3 to 65 mg $L^{-1}$, with the highest value in the Rmel River during the summer (Table 1). This is likely due to the release of poorly treated sewage from the municipal facilities near El Kef. In contrast, the Kohol River contained less $NO_3$. The Mellègue River waters had $NO_3$ concentrations 5 to 20 times higher than average background literature values (2.5–4 mg $L^{-1}$; Song and Müller 1999). With the exception of the Rmel River, nitrate values were two to three times higher in winter than in summer, which may reflect fertilizer input. Indeed, farming is the major source of $NO_3$; other sources may include mineralization of organic detritus, manure applications (Trabelsi et al. 2007), and livestock operations (Krapac et al. 2002).

Phosphate concentrations in stream waters ranged from 0.014 to 7.2 mg $L^{-1}$, with the higher values observed in the Rmel River tributary. The variability is attributed to daily and seasonal fluctuations in the $PO_4$ content of the El Kef sewage. Other rivers had lower phosphate levels (Table 1). The widespread use of fertilizers by farmers may help explain the $PO_4$ concentrations in streams.

### Metals

Magnesium and other elements, such as Fe and Mn, and even Sr (Table 1), are associated with carbonates and Triassic salts. Cd, Pb, Cu, Zn concentrations were not elevated in the Mellègue or Sarrat Rivers (Table 1). Metal concentrations vary depending on the distance from the pollution source and the nature and behaviour of the elements released from mine wastes and tailings (Mlayah et al. 2005). During winter, some rivers (Rmel and Kohol for Cd, and Sarrat for Pb) had concentrations below the detection limit. The concentrations met the World Health Organization standards (WHO 2011) for drinking water (Cd, 3 μg $L^{-1}$; Pb, 10 μg $L^{-1}$; Cu, 13 μg $L^{-1}$; Hg, 1.6 μg $L^{-1}$), possibly due to dilution from unpolluted tributaries. During the winter season, pH increased somewhat due to the input of waters made alkaline by limestone dissolution and most metal concentrations decreased due to dilution. Average base metal concentrations in the Mellègue waters were less than world averages of trace metals concentrations (Klavins et al. 2000; Olias et al. 2004).

Samples with low summer pH values were associated with higher dissolved concentrations of major elements and base metals (Table 1). Coefficients of determination ($r^2$) for element pairs were calculated using the metal concentrations in the Mellègue Reservoir samples from all depths during summer and winter. During the summer months, Fe, Zn, and Cu concentrations were positively correlated with sulphate and formation of abundant sulphate salts. Base metals may precipitate or be adsorbed onto hydrated metal-sulphate precipitates downstream (Navarro et al. 2007).

Cadmium concentrations in water samples were generally low and lower during the wet winter period. Cd and Zn may be fixed onto colloids or be complexed, dissolved, and transported by chlorides and sulphides (de Livera et al. 2011; Peng et al. 2013).

Lead concentrations were low in the Sarrat and Mellègue rivers, but higher in the Rmel and Kohol rivers and the Mellègue Reservoir (Table 1). Pb may precipitate as insoluble anglesite (Olias et al. 2006). Pb concentrations were high in the winter but negatively correlated with sulphate ($R^2 = 0.61$). Hydrated sulphate minerals and particularly gypsum are favourable sinks for Pb (Buckby et al. 2003;

**Table 1** Average concentration and range of chemical components in filtered river and reservoir water samples in summer (S) and winter (W)

| | Sarrat River | | Mellègue River | | Oued Rmel | | Oued Kohol | | Mellègue Res. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | S | W | S | W | S | W | S | W | S | W |
| pH (SU) | | | | | | | | | | |
| Avg. | 8.2 | 8.43 | 8 | 8.1 | 8 | 8.2 | 8 | 8.1 | 7.52 | 8.25 |
| Range | 8.08–8.34 | 8.29–8.51 | 7.7–8.35 | 8–8.35 | – | – | – | – | 7.3–7.62 | 8.2–8.3 |
| EC (mS cm$^{-1}$) | | | | | | | | | | |
| Avg. | 2.23 | 1.48 | 9.89 | 8.2 | 2.55 | 2.71 | 5.1 | 4.85 | 5.2 | 3.21 |
| Range | 1.1–3.4 | 1.4–2.57 | 7.7–13.7 | 2.7–8.1 | – | – | – | – | 4.4–6.8 | 3.06–3.9 |
| Ca (mg L$^{-1}$) | | | | | | | | | | |
| Avg. | 170 | 130 | 387 | 181 | 650 | 367 | 436 | 257 | 279 | 262 |
| Range | 80–220 | 79–230 | 317–436 | 165–210 | 650 | 367 | 436 | – | 252–300 | 242–307 |
| K (mg L$^{-1}$) | | | | | | | | | | |
| Avg. | 4.7 | 4.3 | 11.7 | 5.3 | 21.9 | 7.6 | 11 | 3.5 | 7.53 | 6.85 |
| Range | 2.6–7.3 | 1.8–7.6 | 9–15 | 4.6–5.8 | – | – | – | – | 5.8–8.6 | 5.5–8 |
| Mg (mg L$^{-1}$) | | | | | | | | | | |
| Avg. | 81.7 | 55.4 | 136 | 106 | 54.8 | 32.1 | 150 | 96.8 | 175 | 60.4 |
| Range | 57–108 | 21–97 | 129–148 | 86–119 | – | – | – | – | 124–211 | 55–66 |
| Na (mg L$^{-1}$) | | | | | | | | | | |
| Avg. | 268 | 249.6 | 1904 | 775 | 258 | 881 | 773 | 624 | 841 | 442 |
| Range | 101–490 | 72–673 | 1340–2600 | 700–912 | – | – | – | – | 740–1090 | 415–564 |
| SO$_4$ (mg L$^{-1}$) | | | | | | | | | | |
| Avg. | 651 | 391 | 1360 | 748 | 666 | 493 | 914 | 647 | 1370 | 903 |
| Range | 253–924 | 213–668 | 2230–1520 | 693–850 | – | – | – | – | 1020–1590 | 719–1010 |
| HCO$_3^-$ (mg L$^{-1}$) | | | | | | | | | | |
| Avg. | 310 | 115 | 340 | 154 | 850 | 520 | 390 | 200 | 240 | 126 |
| Range | 220–360 | 80–0.40 | 270–420 | 100–200 | – | – | – | – | 140–440 | 104–140 |
| Cl (mg L$^{-1}$) | | | | | | | | | | |
| Avg. | 295 | 132 | 2680 | 883 | 425 | 288 | 2440 | 765 | 1020 | 591 |
| Range | 117–519 | 90–200 | 1410–4430 | 717–1130 | – | – | – | – | 752–1360 | 510–843 |
| NO$_3$ (m gL$^{-1}$) | | | | | | | | | | |
| Avg. | 10.3 | 24.7 | 10.5 | 34.4 | 49 | 43.3 | 3.6 | 15.4 | 7.2 | 23 |
| Range | 2.6–29 | 19–36.5 | 2.1–27 | 27–39.6 | 33.5–64.5 | 38.2–48.2 | – | – | 7–9.1 | 16.5–25.9 |
| NO$_2$ (mg L$^{-1}$) | | | | | | | | | | |
| Avg. | 0.13 | 0.32 | 0.17 | 0.69 | 8 | 2.26 | 0.11 | 0.08 | 0.3 | 0.44 |
| Range | 0.04–0.24 | 0.23–0.4 | 0.03–0.45 | 0.56–0.9 | – | – | – | – | 0.18–0.2 | 0.32–0.8 |
| PO$_4$ (mg L$^{-1}$) | | | | | | | | | | |
| Avg. | 0.11 | 0.09 | 0.08 | 0.1 | 3.5 | 5.71 | 0.08 | 0.05 | 0.11 | 0.12 |
| Range | 0.04–03 | 0.05–0.4 | 0.014–0.2 | 0.06–0.2 | – | – | – | – | 0.05–0.27 | 0.05–0.29 |
| Ag (μg L$^{-1}$) | | | | | | | | | | |
| Avg. | 0.08 | BD[a] | 0.46 | BD | BD | BD | 1.4 | BD | 0.8 | BD |
| Range | BD–0.12 | – | 0.05–0.8 | – | – | – | – | – | 0.05–4 | – |
| As (μg L$^{-1}$) | | | | | | | | | | |
| Avg. | 1.9 | 0.7 | 4.5 | 0.8 | 3.7 | BD | 5 | BD | 2.8 | BD |
| Range | 1–3.2 | 0.5–1.1 | 2.8–9.8 | 0.5–1.2 | – | BD | – | – | 1.9–4.5 | – |
| Ba (μg L$^{-1}$) | | | | | | | | | | |
| Avg. | 38.4 | 28 | 75 | 25 | 53 | 50 | 39 | 28 | 47 | 38 |
| Range | 33–42 | 25.7–29 | 63–100 | 21–27 | – | – | – | BD | 40–57 | 35–54 |
| Cd (μg L$^{-1}$) | | | | | | | | | | |
| Avg. | 0.13 | 0.1 | 0.14 | 0.08 | 0.6 | BD | 0.05 | BD | 0.3 | BD |
| Range | 0.05–0.4 | 0–0.2 | 0.05–0.14 | 0–0.25 | 0.6 | – | 0.05 | – | 0.05–1 | – |

**Table 1** (continued)

| | Sarrat River | | Mellègue River | | Oued Rmel | | Oued Kohol | | Mellègue Res. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | S | W | S | W | S | W | S | W | S | W |
| Cr (μg L$^{-1}$) | | | | | | | | | | |
| Avg. | 2.4 | 1.13 | 3.3 | BD | 1.2 | 2.1 | 0.5 | BD | 2.44 | 1.05 |
| Range | 0.7–2.5 | 0.5–2.4 | 2.3–3.4 | – | – | – | 0.5 | – | 0.5–4.3 | 0.5–1.8 |
| Cu (μg L$^{-1}$) | | | | | | | | | | |
| Avg. | 4 | 3 | 12.7 | 7.4 | 2.7 | 1.9 | 14.5 | 5.6 | 8.9 | 6.2 |
| Range | 2.3–4.8 | 2–4 | 6.9–16.6 | 5.3–8.7 | 2.7 | 1.9 | 14.5 | 5.6 | 6.4–12 | 3.7–10.4 |
| Fe (μg L$^{-1}$) | | | | | | | | | | |
| Avg. | 1450 | 57 | 3330 | 160 | 1160 | 520 | 1660 | 125 | 2040 | 139 |
| Range | 698–1920 | 10–175 | 2920–3710 | 100–249 | – | – | – | 125 | 1530–2600 | 100–285 |
| Hg (μg L$^{-1}$) | | | | | | | | | | |
| Avg. | 0.2 | BD | 1.6 | BD | 0.4 | 0.3 | 1.4 | BD | 0.25 | BD |
| Range | 0.1–0.4 | – | 1.4–1.8 | – | – | – | – | – | 0.1–0.9 | – |
| Mn (μg L$^{-1}$) | | | | | | | | | | |
| Avg. | 9 | 7 | 75 | 25 | 15 | 8 | 14 | 9.5 | 20.6 | 7.3 |
| Range | 2.8–18 | 1.2–16 | 61–100 | 21–27 | – | – | – | – | 6.3–51 | 0.5–33 |
| Pb (μg L$^{-1}$) | | | | | | | | | | |
| Avg. | 0.4 | BD | 1.4 | 0.5 | 13.6 | 4 | 39 | 3 | 17 | 8 |
| Range | 0.2–0.5 | – | 1.2–1.7 | 0.2–0.7 | – | – | – | – | 12–22.4 | 5–12 |
| Sr (mg L$^{-1}$) | | | | | | | | | | |
| Avg. | 5 | 3.8 | 10.2 | 5 | 6.8 | 4.1 | 7.3 | 5.2 | 7.1 | 6.7 |
| Range | 1.8–7.2 | 2.1–6.7 | 9.6–12 | 4.5–5.7 | – | – | – | – | 5.9–8.2 | 6.5–7.4 |
| Zn (mg L$^{-1}$) | | | | | | | | | | |
| Avg. | 36 | 4.4 | 9.8 | 6.8 | 4.3 | 3.5 | 6 | 2 | 12.4 | 7.8 |
| Range | 6.7–72 | 2.5–8.3 | 7.1–12.5 | 5–8.9 | – | – | – | – | 6.6–25 | 6.9–16.4 |

[a] *BD* below limit of detection

Hudson-Edwards et al. 1999; Nieto et al. 2003; Sahoo et al. 2012). Hence, it may be argued that since sulphide oxidation and gypsum dissolution generate sulphate that stores soluble Pb, if conditions favour Pb-sulphate formation.

Arsenic levels were low in the winter, but in summer, As ranged between 0.5 and 10 μg L$^{-1}$ (Table 1). Arsenic was more highly correlated with Fe ($r^2=0.52$) than Mn ($r^2=0.12$) and may be scavenged by Fe precipitates, thus minimizing migration of As in watercourses. A positive correlation between As/Fe and As/$SO_4$ suggests that As could be associated with Fe or sulphate solids.

Zn concentrations were elevated in the tailings (Table 1; Mlayah et al. 2007a, b). In stream waters, Zn was very weakly positively correlated with Mn and Fe in summer when metal levels were generally higher (Table 1). Free and complexed species of Zn, Cu, and Cd can be fixed by Fe-Mn and other solids, depending on salinity and pH.

With the exception of the Rmel River, Hg concentrations in surface waters collected in winter were below the detection limit of 0.05 μg L$^{-1}$ (Table 1). Samples collected in summer had higher concentrations, sometimes exceeding the WHO and EU standard for potable water (1 μg L$^{-1}$). The Hg concentrations in the Mellègue River exceeded those measured in many other rivers (Zhang et al. 2014), with higher values in summer in the Mellègue River (1.4–1.8 μg L$^{-1}$) and its Kohol tributary (1.4 μg L$^{-1}$); this could be due to complexing of Hg by Cl and $SO_4$ as well as an association with Fe–Mn and other colloids. The order of metal concentrations (μg L$^{-1}$) detected in the Mellègue River in summer was Cu > Zn > As > Cr > Hg > Pb > Cd, which differs from Cheung et al. (2003), and could be indicative of anthropogenic effects, notably from mining.

The dissolution of Triassic salts in outcrops or tailings can release Cl, $SO_4$, and Ca. Under certain conditions (e.g. high evaporation), NaCl, $MgCl_2$, $CaCO_3$, $MgSO_4{\cdot}2H_2O$, $CaSO_4{\cdot}2H_2O$, and $CaCl_2$ salts may precipitate and fix base metals dissolved from the mine wastes. Fe, Mn, and Al precipitates can also adsorb metals (Huelin et al. 2004; Mlayah et al. 2009), though the tendency of base metals to complex with chloride, sulphate, and bicarbonate/carbonate anions can also enhance their dissolution.

High amounts of carbonates that influence the alkalinity and pH of soils in and around mine areas can cause metals to precipitate as carbonates (Mlayah et al. 2007a, b;

Navarro et al. 2007; Olias et al. 2004; Segura et al. 2006). The pH values ranged from 7.3 to 8.5, with a noticeable increase in winter, at least in the Mellègue Reservoir, which could be due to dissolution of carbonate from the limey soils.

## Groundwater Level and Quality Results

To evaluate anthropogenic impacts to groundwater, we selected the catchment area of the Sarrat River, which is affected by mine waste, agricultural runoff, and sewage from towns (including Tajreouine, Jrissa, Thala, and Kalaa Khasba). The multi-layer unconfined aquifer is a Neogene-Quaternary molasse with heterometric sand layers (Fig. 2b). The recharge derives from rainfall and infiltration from the hydrographic network. The groundwater flow directions in the aquifer are approximated by surface drainage (Supplemental Fig. 1). The piezometric surface ranges from 750 to 550 m, and the static water depth ranges from 10 to 13 m, thus implying a relatively thick unsaturated zone that could mitigate the impacts from base metals and their transport through the unsaturated zone (Supplemental Fig. 1).

### *Field Parameters*

Physicochemical data for 46 groundwater samples from the Sarrat River alluvial aquifer are summarized in Supplemental Table 2. The pH values were neutral to slightly alkaline. Approximately, 5% of the samples had pH values greater than 8, possible due to sewage from nearby towns. EC values vary broadly from 950 to 4.650 µS $cm^{-1}$ in the wells and generally increase down-gradient along the Sarrat River. Generally, the highest EC values were measured downstream where the Sarrat River changes direction from east to west (Supplemental Fig. 2) and where the river drains the groundwater system. The highest EC value (sample 34; see Fig. 2b), south of Kaala Khasba, is attributed to intense irrigation near there.

### *Major Cations*

Na, Ca, and Mg were the dominant cations (Fig. 2a; Supplemental Table 2). Calcium and Mg derive predominantly from lime- and dolostones and gypsum, and K derives from dissolution of evaporate rocks or cation exchange from clays, notably smectites. The leaching of these elements from limestones and dolostones is enhanced by low pH. High Na and Ca concentrations in groundwater, relative to Mg and K, are influenced by high dissolution rates of country rocks including halite, gypsum, calcite, and dolomite (Hamed and Dhahri 2013). In addition, manures and fertilizers deliver K and Na. The transport of these elements is hampered by highly sorbent soil components, notably organic matter and clays (Brigatti et al. 2000; Mlayah et al. 2005, 2011).

Further reactions help soften waters by releasing Na and adsorbing Ca and Mg as the water moves through clay-rich deposits. Divalent ions are more strongly adsorbed and tend to replace monovalent ions, unless high activities of monovalent ions are present (Appelo and Postma 1999; Mlayah et al. 2011). The high Ca and Mg concentrations in wells located in the southern, southeastern, and western portions of the aquifer may have dissolved from outcropping lime- and dolostones. The piezometric measurements point to groundwater flowing from ESE to WNW (Supplemental Fig. 2). Sodium values increase along the flow path, possibly due in part to Ca and Mg adsorption and Na release from clays in the central portion of the aquifer.

### *Major Anions*

High concentrations of Cl, $SO_4$, and $NO_3$ can deteriorate groundwater quality and affect its potability. Concentrations of Cl ranged from 85 to 1030 mg $L^{-1}$, consistent with varying ECs, while $SO_4$ and $NO_3$ (Supplemental Table 2) were elevated in some water samples. $HCO_3$ ranged from 220 to 793 mg $L^{-1}$, originating mainly from carbonate dissolution, with the higher values generally found in wells near the aquifer boundaries.

Chloride values reflected the piezometric and EC values. Salinity (data not shown) ranged from 1 to 1.5 g $L^{-1}$, depending on proximity to recharge areas. Along the groundwater flow path, interaction with sands, gravel, pebbles, and clay lenses increased $SO_4$ and Cl concentrations; bicarbonate concentrations decreased down-gradient until salinities approximating 2.5 g $L^{-1}$ were attained. Chloride in groundwater could also have come from farm fertilizers.

Sulphate in aquifers can originate from oxidative weathering of sulphides in shales (Gomo and Vermeulen 2013; Hill 1990), ore deposits, and mine waste. Also, the buffering capacity of groundwater often decreases as it flows through an aquifer, due to mineralization of organic matter and mineral dissolution, which decreases alkalinity.

Phosphate concentrations in the groundwater were low and ranged from 0.01 to 0.07 mg $L^{-1}$ (Supplemental Table 2) in a region known for its high production of crops and phosphate mines. The $PO_4$ ion is strongly adsorbed onto Fe and Al colloids in soils. The $PO_4$ concentrations in groundwater relate to its excess above the amount forming insoluble iron phosphate. Although high P contents were measured in soils, the amount of $PO_4^{3-}$ in associated water samples in the spring were low.

Nitrate concentrations ranged from 5.7 to 157 mg $L^{-1}$; wells 34 and 35 had the highest concentrations. Groundwater samples collected near Kalaa Khasba and Jerissa had higher $NO_3^-$ concentrations relative to overall geochemical background values, which may be less than 2 mg $L^{-1}$ (Mueller and Helsel 1996).

High $NO_3^-$ values occurred in three zones: around Thala, where concentrations exceeded 100 mg $L^{-1}$; and near Jerissa and the villages of Kalaa Khasba. This is partly related to sewage from septic systems (Vizintin et al. 2009), but this potential source appears less important than farming and associated land uses (Peña-Haro et al. 2010). Areas with nitrate concentrations exceeding 10 mg $L^{-1}$ are located upstream in zones of intensive farming, while areas with less $NO_3^-$ coincide with forage crops and pasturing activities.

### *Groundwater Types*

The measured major ion concentrations were converted to milliequivalents and plotted on a Piper diagram (Fig. 3). Only 16 samples from the northern part of the aquifer were enriched in Na. However, all of the water samples were Na–$SO_4$-type waters. Water in the recharge areas (upstream) had nearly equimolar concentrations of Ca and Na, while water in the discharge areas (downstream) were strongly Na-dominant (Fig. 3). The longer the residence time of water in the aquifer, the higher the Na + K percentages and the lower the alkalinity.

### *Metals and Minor or Trace Constituents*

Metal concentrations in groundwater all, with the exception of some B values, met EU drinking water standards (European Union 1998). Concentrations of Ni, Cr, Pb, and Co were less than the detection limits in 100, 75, 50, and 35% of the studied wells, respectively. Aluminium levels ranged from 3 to 165 µg $L^{-1}$ but most (75%) ranged from 57 to 165 µg $L^{-1}$. This Al is likely associated with phyllosilicates and aluminosilicates in the aquifer.

Average As concentrations in groundwater (1.93 µg $L^{-1}$) were below WHO guidelines and EU and USA standards (<0.01 mg $L^{-1}$) for drinking water, and were poorly correlated with Ca and Fe. Arsenic correlated positively but poorly with $SO_4$ in groundwater samples ($r^2 = 0.305$). This may indicate that As is not readily mobilized from oxidized metal sulphides, including As-bearing pyrite (Halim et al. 2009) or that As is preferentially removed. The Jerissa mine tailings contain high amounts of As-bearing pyrite and dissolved As in AMD (Mlayah et al. 2009), and As can be coprecipitated and adsorbed onto Fe–Mn oxyhydroxides

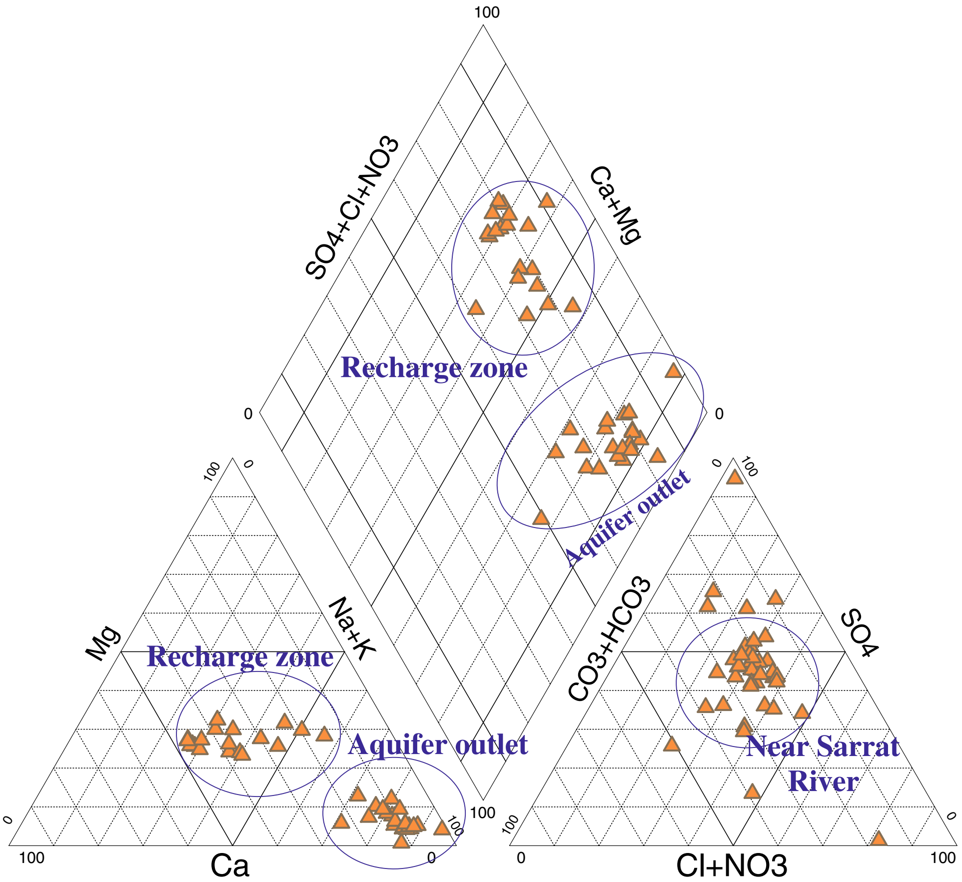

**Fig. 3** Piper diagram illustrating the chemical composition of groundwater samples in the study area

that form with increasing pH (Casiot et al. 2003; Smedley and Kinniburgh 2002).

Boron, which is released by dissolving evaporates and clays, exceeded the EU drinking water standard in 10% of the wells. Boron strongly correlated with Na ($r^2 = 0.7096$). Boron concentrations increased along the groundwater flow path from the aquifer boundaries to the middle of the aquifer (near the Sarrat River, Fig. 1), in a manner similar to Na. Calcium adsorption onto clays can also release Na and B (Mlayah et al. 2011).

Copper values in groundwater ranged from 1.4 to 4.1 µg $L^{-1}$, which is well below the EU drinking water standards. According to Komarek et al. (2009), higher pH decreases Cu concentrations and increases hydrolyzed Cu species. In the study area, pH is near neutral, and most Cu is probably adsorbed onto aquifer material, including clays and organic matter.

Manganese concentrations in the Kalaa Khasba and Jerissa groundwater ranged from 1.21 to 4.48 µg $L^{-1}$, well below the 1998 EU standard (50 µg $L^{-1}$). Water from well 10, which was completed in rocks from the Jerissa Mine (Mlayah et al. 2011), was of poorer quality.

Strontium behaved similarly to Ca, ranging from 1.5 to 12.1 mg $L^{-1}$. Strontium can replace Ca in calcite, aragonite, dolomite, and gypsum, and can be incorporated in swelling clays. The correlation between Sr and $SO_4$ ($r^2 = 0.51$) was stronger than with $HCO_3^-$ (0.23), suggesting that the Sr could have originated from gypsum dissolution.

Zinc ranged from 5.8 to 112 µg $L^{-1}$. Well 10 (individual data not shown) had the highest concentrations and could be due to the Kalaa Khasba Mines.

Base metal concentrations in sediments were at least four times higher than background values, and the highest pollution index was obtained for As (Mlayah et al. 2007a, b, 2011). The order of contamination was As > Pb > Cu > Zn (Mlayah et al. 2007a, b, 2011). The topsoil in this area likely acts as a pollutant barrier (Carlson et al. 2011). The lowest metal concentrations (Zn, Cu, Cd, and Co) were measured in wells 2, 4, 12, and 16, located at the southwestern aquifer boundary. In this area, soils and the unsaturated zone are dominated by limestone, which can limit metal concentrations (Lee et al. 2007).

## Water Quality in the Mellègue Reservoir

The water quality of the Mellègue Reservoir at the surface and the sediment–water interface is shown in Table 2. Dissolved oxygen (DO) and pH were generally lower and EC values higher near the sediment–water interface (6–10 m deep) than at the reservoir surface. A similar trend was recorded in the neighbouring Sidi Salem Reservoir on the Majerda River (Sternick 1991). In fresh water, particulate organic matter can rapidly consume $O_2$ and deplete it a few millimetres below the sediment–water interface. Watercourses can move substantial amounts of particulates and organic matter from farms and surrounding areas and generate high COD (Sagemann et al. 1994).

The seasonal compositions of waters in the Mellègue Reservoir were less differentiated, with composites of Na/Ca–$SO_4$/Cl, to Na/Ca/Mg–$SO_4$/Cl, to Na/Ca/Mg–Cl/$SO_4$ hydrogeochemical facies. The major ions pairs for the Mellegue Reservoir surface water (Table 3) generally had higher $r^2$ values in winter than in summer. $CaSO_4$, $CaCO_3$, and $MgSO_4$ may locally precipitate during the dry season and dissolve during the rainy period, thus favouring higher concentrations of major elements and higher $r^2$ values for ions in the winter. The correlations for Na/Cl, Ca/$SO_4$, Mg/Cl, Na/$SO_4$, Mg/$SO_4$, and Na/Br were high (Table 3) and could reflect dissolution of salts in the Mellègue catchment area. Moreover, the significant correlations between Ca/Sr, Na/Sr, and Ca/Mg in surface waters point to similar sources and geochemical affinities for these elements. The strong Ca/Sr correlation lends support to their origin in shell and bioclastic fragments in Cretaceous limestones that contain high amounts of these metals.

The Mellègue Reservoir receives solutes from upstream areas in the winter. In contrast, in the summer, the reservoir receives more saline water, as shown in Table 4 by the higher summer concentrations of sulphate and chloride. Furthermore, higher $NO_3$ concentrations occur at higher temperatures and higher temperatures can stimulate bacteria activity and the mineralization of organic matter (Sagemann et al. 1994).

Phosphate concentrations were sometimes higher at depth in the water column of the Mellègue Reservoir. This could be due to active P release by organic matter oxidation, and chemical and biological reduction of Fe and Mn. Ferrous phosphates (e.g. $Fe_3(PO_4)_2.8H_2O$) may be forming due to reducing conditions, and insoluble P minerals may be depositing at the sediment–water interface.

The water in the Mellègue Reservoir stratifies during the summer with a lack of input from upstream. This generates reducing conditions and reduction of $SO_4^{2-}$ to $HS^-$ in the bottom sediments. Hydrogen sulphide can interact with metal ions and form insoluble sulphide precipitates (Song and Müller 1999), whereas mineralized organic matter releases $Mn^{2+}$ and $Fe^{2+}$ in water at the sediment–water interface and dissolution of Fe–Mn oxyhydroxide can release adsorbed metals. In the Mellègue Reservoir, Mn, Fe, Cu, Zn and Pb concentrations were often greater at depth, while Hg concentrations were <0.1 µg $L^{-1}$ (Table 4).

## Toward Model Reactions and Conclusions

Despite the acidic mine waters, mine wastes, and the high concentrations of toxic metals in tailings, the trace element

**Table 2** Ion concentrations in the water column of the Mellègue reservoir (mg $L^{-1}$)

| | SW1 | | SW2 | | SW3 | | SW4 | | SW5 | | SW6 | | SW7 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Sum | Win | Sum | Win | Sum | Win | Sum | Win | Sum | Win | Sum | Win | Sum | Win |
| DO | | | | | | | | | | | | | | |
| Surf. | 9 | 8.1 | 8.5 | 9 | 8.9 | 8.5 | 9 | 8.6 | 8.9 | 8.4 | 8.7 | 8.3 | 8.7 | 8.5 |
| Inter. | – | – | 8.6 | 8.8 | 8.6 | 8.3 | 8.2 | 8.1 | 5.9 | 5.9 | 5.7 | 5.8 | – | – |
| $NO_3$ | | | | | | | | | | | | | | |
| Surf. | 18.5 | 16.1 | 19.9 | 18.5 | 22.8 | 17 | 25.3 | 17.3 | 24.5 | 21.1 | 25.8 | 17 | 26.5 | 25.8 |
| Inter. | – | – | 167.1 | 16.8 | 14.3 | 19.4 | 16.3 | 22.9 | 17.4 | 20.4 | 12 | 16.5 | – | – |
| $NO_2$ | | | | | | | | | | | | | | |
| Surf. | 0.19 | 0.8 | 0.18 | 0.51 | 0.18 | 0.6 | 0.19 | 0.4 | 0.24 | 0.33 | 0.27 | 0.32 | 0.18 | 0.3 |
| Inter. | – | – | 0.18 | 0.61 | 0.16 | 0.4 | 0.18 | 0.3 | 0.18 | 0.28 | 0.18 | 0.27 | – | – |
| $PO_4$ | | | | | | | | | | | | | | |
| Surf. | 0.19 | 0.29 | 0.18 | 0.22 | 0.18 | 0.23 | 0.18 | 0.06 | 0.18 | 0.47 | 0.18 | 0.3 | 0.18 | 0.05 |
| Inter. | – | – | 0.18 | 0.24 | 0.18 | 0.25 | 0.19 | 0.1 | 0.24 | 1.13 | 0.27 | 0.38 | – | – |
| $NH_4$ | | | | | | | | | | | | | | |
| Surf. | 0.04 | 0.02 | 0.048 | 0.03 | 0.058 | 0.041 | 0.056 | 0.045 | 0.058 | 0.04 | 0.045 | 0.033 | 0.04 | 0.03 |
| Inter. | – | – | 0.045 | 0.04 | 0.055 | 0.03 | 0.135 | 0.034 | 0.21 | 0.13 | 0.24 | 0.18 | – | – |
| $SO_4$ | | | | | | | | | | | | | | |
| Surf. | 1790 | 1070 | 1600 | 926 | 1640 | 809 | 1680 | 1030 | 1770 | 1060 | 1210 | 1090 | 1150 | 1140 |
| Inter. | – | – | 1500 | 860 | 1990 | 1010 | 1540 | 1140 | 1280 | 1140 | 1300 | 1130 | – | – |
| Cl | | | | | | | | | | | | | | |
| Surf. | 1360 | 843 | 1050 | 558 | 1050 | 586 | 1020 | 759 | 1080 | 597 | 775 | 608 | 752 | 564 |
| Inter. | – | – | 1150 | 530 | 1370 | 510 | 907 | 553 | 919 | 555 | 925 | 552 | – | – |
| T (°C) | | | | | | | | | | | | | | |
| Surf. | 21.1 | 22.1 | 24.7 | 22.7 | 25 | 22.2 | 26.2 | 23.5 | 25.8 | 23.1 | 26.1 | 23.8 | 26.2 | 24.4 |
| Inter. | – | – | 24.5 | 23 | 25.5 | 23.5 | 28.4 | 18.3 | 25 | 16.7 | 25.2 | 16.5 | – | – |
| pH (SU) | | | | | | | | | | | | | | |
| Surf. | 7.53 | 8.3 | 7.56 | 8.29 | 7.32 | 8.2 | 7.56 | 8.27 | 7.61 | 8.24 | 7.45 | 8.22 | 7.62 | 8.24 |
| Inter. | – | – | 7.40 | 8.35 | 7.32 | 8.35 | 7.36 | 8.32 | 7.37 | 8.05 | 7.30 | 7.99 | – | – |
| EC (mS $cm^{-1}$) | | | | | | | | | | | | | | |
| Surf. | 3.90 | 6.83 | 3.14 | 5.16 | 3.16 | 4.84 | 3.08 | 4.78 | 3.07 | 4.57 | 3.06 | 4.55 | 3.06 | 4.43 |
| Inter. | – | – | 3.15 | 5.58 | 3.19 | 5.62 | 3.16 | 4.90 | 3.18 | 4.91 | 3.18 | 4.86 | – | – |

*Surf* surface, *Inter*. above the sediment–water interface, *sum* summer, *win* winter

**Table 3** Binary correlations between major cation–cation and cation–anion pairs in Mellègue Reservoir surface waters

| | Ca/Cl | Ca/Sr | Ca/Mg | Ca/Na | Na/Cl | Na/SO4 | Na/Sr | Na/Br | Mg/Cl | Mg/Br | Ca/SO4 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Summer | 0.365 | 0.863 | 0.08 | 0.43 | 0.98 | 0.53 | 0.487 | 0.604 | 0.613 | 0.877 | 0.9 |
| Winter | 0.64 | 0.95 | 0.796 | 0.65 | 0.95 | 0.696 | 0.67 | 0.93 | 0.797 | 0.71 | 0.87 |
| | Mg/Sr | Mg/K | K/Cl | K/Br | K/Na | K/Sr | Cl/Br | $SO_4$/Br | $SO_4$/Cl | Sr/$SO_4$ | Mg/SO4 |
| Summer | 0.26 | 0.073 | 0.2 | 0.18 | 0.19 | 0.005 | 0.64 | 0.24 | 0.46 | 0.95 | 0.47 |
| Winter | 0.797 | 0.84 | 0.74 | 0.71 | 0.64 | 0.598 | 0.9 | 0.695 | 0.78 | 0.85 | 0.53 |

concentrations in the Mellègue surface water and reservoir samples were low. This may be attributed to two antagonistic processes operating in the watershed: acid production by oxidation of pyrite and other sulphide minerals, and calcite dissolution, which produces carbonate alkalinity and neutral to slightly alkaline pH values, dominated by carbonate equilibria. Hence, the lithology plays a dominant role in metal fate and transport and water composition. When acid water reacts with limestone, pH increases and Fe–Mn oxyhydroxides form, which in turn can absorb dissolved trace metals.

**Table 4** Metal concentrations in surface waters and waters above the sediment–water interface in the Mellègue Reservoir (μg $L^{-1}$)

| | SW1 | | SW2 | | SW3 | | SW4 | | SW5 | | SW6 | | SW7 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Sum | Win | Sum | Win | Sum | Win | Sum | Win | Sum | Win | Sum | Win | Sum | Win |
| Ag | | | | | | | | | | | | | | |
| Surf. | 0.86 | BD | 0.18 | BD | BD | BD | BD | BD | 4 | BD | 0.41 | BD | 0.1 | BD |
| Inter. | – | – | 0.1 | BD | 0.11 | BD | BD | BD | 0.14 | BD | 0.09 | BD | – | – |
| As | | | | | | | | | | | | | | |
| Surf. | 4.5 | BD | 3.2 | BD | 2.9 | BD | 1.9 | BD | 2.1 | BD | 2.3 | BD | 2.5 | BD |
| Inter. | – | – | 3 | BD | 2.2 | BD | 2.8 | BD | 2.1 | BD | 2.7 | BD | – | – |
| Ba | | | | | | | | | | | | | | |
| Surf. | 55 | 45 | 42 | 44 | 49 | 40 | 44 | 42 | 51 | 51 | 57 | 46 | 50 | 47 |
| Inter. | – | – | 44 | 40.5 | 53 | 43 | 51 | 44.6 | 45 | 47 | 51 | 49 | – | – |
| Ca | | | | | | | | | | | | | | |
| Surf. | 289 | 278 | 237 | 251 | 275 | 253 | 263 | 289 | 307 | 290 | 255 | 292 | 246 | 300 |
| Inter. | – | – | 288 | 255 | 302 | 294 | 285 | 308 | 264 | 298 | 272 | 309 | – | – |
| Cd | | | | | | | | | | | | | | |
| Surf. | 0.25 | BD | 0.12 | BD | 0.5 | BD | 0.05 | BD | 1.08 | BD | 0.27 | BD | 0.6 | BD |
| Inter. | – | BD | 0.18 | BD | 0.5 | BD | 0.06 | BD | 1.08 | BD | 0.16 | BD | – | BD |
| Cr | | | | | | | | | | | | | | |
| Surf. | 1.2 | 0.9 | 0.6 | BD | BD | BD | 2.2 | BD | 4 | BD | 4.2 | BD | 4.3 | BD |
| Inter. | – | – | 0.7 | BD | 1.7 | BD | 2.8 | BD | 4.5 | BD | 3.2 | BD | – | – |
| Cu | | | | | | | | | | | | | | |
| Surf. | 12 | 10 | 8.7 | 5 | 8.3 | 3.7 | 10 | 4.3 | 9.7 | 4.7 | 7.9 | 7.2 | 7.9 | 8.1 |
| Inter. | – | – | 7.4 | 4 | 18 | 8 | 8.6 | 11.6 | 7.8 | 8.9 | 7.8 | 5.2 | – | – |
| Fe | | | | | | | | | | | | | | |
| Surf. | 1910 | 985 | 1750 | 1230 | 1530 | 1120 | 2120 | 1460 | 2070 | 1430 | 2290 | 1600 | 2300 | 1.37 |
| Inter. | – | – | 1650 | 1120 | 1930 | 1290 | 2210 | 1580 | 2290 | 1990 | 2600 | 1760 | – | – |
| Hg | | | | | | | | | | | | | | |
| Surf. | BD | BD | BD | BD | BD | BD | BD | BD | BD | BD | BD | BD | BD | BD |
| Inter. | – | – | BD | BD | BD | BD | BD | BD | BD | BD | BD | BD | – | – |
| K | | | | | | | | | | | | | | |
| Surf. | 8.56 | 8 | 8.1 | 6 | 8 | 5.5 | 7.8 | 6.9 | 8.3 | 6.96 | 5.8 | 7 | 5.8 | 7.1 |
| Inter. | – | – | 7.4 | 5.9 | 9.8 | 7.1 | 7.3 | 7.8 | 6.2 | 7.1 | 6.2 | 7.2 | – | – |
| Mg | | | | | | | | | | | | | | |
| Surf. | 197 | 65.3 | 172 | 55.3 | 193 | 55.9 | 181 | 58.5 | 145 | 60.4 | 124 | 61.3 | 119 | 66 |
| Inter. | – | – | 188 | 55.6 | 234 | 58.7 | 182 | 67 | 211 | 63.5 | 133 | 66 | – | – |
| Mn | | | | | | | | | | | | | | |
| Surf. | 33 | 51 | 9.7 | 6.3 | 2.6 | 7.1 | 2.3 | 9 | 3 | 17 | 4 | 38.7 | 4 | 16 |
| Inter. | – | – | 9.5 | 5.8 | 6.5 | 9.4 | 2.7 | 26 | 5.1 | 53.4 | 5.8 | 130 | – | – |
| Na | | | | | | | | | | | | | | |
| Surf. | 1090 | 564 | 833 | 415 | 7980 | 427 | 767 | 411 | 843 | 423 | 740 | 418 | 711 | 439 |
| Inter. | – | – | 831 | 417 | 1020 | 506 | 751 | 575 | 852 | 450 | 815 | 459 | – | – |
| Pb | | | | | | | | | | | | | | |
| Surf. | 6.2 | 1.5 | 4.2 | 0.5 | 2.1 | 0.5 | 2.5 | 1.5 | 3.1 | 2.3 | 2.1 | 2 | 1.8 | 1.4 |
| Inter. | – | – | 5.2 | 0.6 | 5.8 | 0.3 | 3 | 2 | 4.2 | 1.9 | 3.2 | 1.5 | – | – |
| Sr | | | | | | | | | | | | | | |
| Surf. | 8.4 | 8 | 7.8 | 6.7 | 7.4 | 5.9 | 7.4 | 6.8 | 8.3 | 7 | 6.9 | 7.2 | 7.1 | 7.6 |
| Inter. | – | – | 7 | 6.9 | 8.4 | 7 | 7.6 | 7.6 | 7.4 | 7.4 | 7.4 | 7.7 | – | – |
| Zn | | | | | | | | | | | | | | |
| Surf. | 33 | 16.7 | 28 | 11.2 | 11.3 | 7.5 | 10 | 6.7 | 10.5 | 6.6 | 14 | 13 | 7 | 25 |
| Inter. | – | – | 28.4 | 13.5 | 14 | 10.3 | 11.5 | 11 | 12 | 20.8 | 15.5 | 15.7 | – | – |

*Sum* summer, *Win* winter, *Surf.* surface, *Inter.* above the sediment–water interface, *BD* below limit of detection

Weathered gypsum releases $SO_4$, which can immobilize Pb if concentrations of both are high enough. In addition, metals can be adsorbed or otherwise scavenged by the ubiquitous clays in the country rock and accessory amorphous silica, phosphates, sulphates, and organic flocculates with high absorptive capacities.

Four factors may explain the observed mine-related contaminant concentrations: (a) ore deposits in the watershed contain significant amounts of carbonates and evaporates that limit trace metal release and acid drainage; (b) there is no direct hydrologic connection between the mine sites and the Sarrat and Kohol rivers, and downstream transport of various pollutants could be limited; (c) a large number of tributaries in the Mellègue basin deliver uncontaminated water to the river and dilute contaminants from active mine sites; (d) the natural buffering capacity of the local carbonate and evaporate beds in country rocks raises alkalinity and pH (7.3–8.7) in the river systems; and (e) the lack of sampling of small streams directly downstream of mines and mine wastes. Additional work is needed to resolve the relative importance of these factors.

Active carbonate components in near the mine wastes promote alkaline pH in the soil and play a major role in metal fixation. These interactions can limit metal migration to the particulate form, and metal precipitates can settle out downstream. The dominant groundwater type is Na–$SO_4$, due to dissolution of salt outcrops; solute concentrations change along the groundwater flow path.

Concentrations of most metals met EU and WHO drinking water standards in the study area. Adsorption onto colloids, various detritus in suspended matter, and soils with carbonates, calcium sulphates, Fe–Mn colloids, clays, and organic matter presumably all contribute to the scavenging of metals from the water.

Binary correlations show that the major cations mainly originate from dissolution of country rock. However, imprints from farm fertilizers and urban sewage were also detected, based on water sample compositions relative to generalized background values. The complexity of the Mellègue catchment requires more investigation of pollution sources and contaminant transport to groundwater and streams, including sampling closer to mining sources. Further potential investigation strategies for the separation of pollution sources include isotopic analysis of sources and waters, and sampling of river sediment.

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