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FIRST RESULTS ON THE PRESENCE OF METALLIC CONTAMINANTS IN WATERS AFTER THE ABANDONMENT OF A SULPHIDE MINING DISTRICT (LINARES, SPAIN)

M. C. Hidalgo Estévez [1], J. Benavente Herrera [2] and J. Rey Arrans [1]

[1] Departamento de Geología, E. U. P. Linares. Universidad de Jaén
Linares, Jaén, Spain
[2] Instituto del Agua. Universidad de Granada
Tierno Galván s/n
18006, Granada, Spain
e-mail: jbenaven@goliat.ugr.es

ABSTRACT

In the mining district of Linares (Jaén, Spain) an important underground mining activity has taken place for centuries, based on the exploitation of metal sulphides related to a framework of dikes within a granite batholith. Lead and silver were the main elements obtained from the ores. Since the mid 80's, the mining and metallurgic works have been abandoned, leaving as a result an important number of voids (shafts and galleries) in the granitic body as well as a number of old tailings -from both mineral extraction and smelting industry- which are frequently located in the vicinity of the main streams.

Ore extraction works required the implementation of different draining schemes, mainly pumps, most of which did not raise the water to ground level but instead connected it by means of a general drainage gallery (12 km) running at a lower altitude in the direction of the Guadalimar river, one of the main tributaries of the Guadalquivir river in its headwater basin.

After the closure of the mines, as a consequence of the drainage pumping operations stopping, the potentiometric levels have risen and the majority of the artificial voids are currently flooded. This means that a relatively important volume of groundwater is stored, associated with a marked anisotropy within a hydrogeological setting of very low hydraulic conductivity. In this context, the old general drainage gallery now operates as the main groundwater discharge of the batholith. As the demand for water is ever increasing for irrigation purposes (olive trees), farmers are currently beginning to satisfy this demand by pumping water from the old mining shafts. As a result, an environmental risk must be considered, associated with the possibility of heavy metal mobilisation through groundwater use.

Another environmental concern stems from the fact that -especially after the anomalous rainy periods of 1996 and 1997- leaching from the old tailings may deteriorate the quality of the streams, apart from the possibility of some of the leachates accumulating in closed depressions and becoming temporary lakes.

A water quality monitoring network has been designed in order to characterise the above-mentioned human influences on the quality of the water resources of the area. Previous results indicate that the stream waters

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present a relatively high Mn-Zn content (up to nearly 1 mg/l) and, in addition, an important suspended load related to the erosion of fine-grained tailings.

The poorest groundwater quality (with highest contents of Fe, Mn, Pb and Zn, as well as several hundred sulphates) is found in the most intensively pumped shafts. This suggests a pyrite oxidation process which mobilises the metallic elements, accompanied by a neutralisation reaction -induced by the carbonate minerals present in the dikes- which is responsible for the non-acidic character of the aqueous solution (pH around 7,5). However, the maximum levels of dissolved metallic species (of some mg/l) are found in a number of small ponds that collect the leachates from smelter wastes. The water storage in these ponds is closely related to the climatic conditions: they usually dry up in summer periods, but after heavy rains they can spread and join up with other hydrological environments.

At present, the fate of the metallic contaminants originating from the mining works is not well understood, both after their contact with agricultural soils following irrigation and as regards their behaviour in response to abnormally wet conditions affecting the polluted ponds, given that they could easily reach the superficial drainage network or infiltrate in nearby phreatic alluvial aquifers which are also pumped for different purposes.

INTRODUCTION

Coal and sulphide exploitations generally pose a serious risk to water quality, often linked to heavy metal contamination. These problems usually occur because acid water forms as a result of the oxidation of the mineralisations of these elements (basically S_2Fe). In spite of the fact that reactivity of galena and sphalerite is much lower than pyrite, acid water also forms in exploitations of Pb and Zn, as this pyritic gangue generally is found to be present along with them.

This paper focuses on the qualitative analysis of the water resources in the region of Linares, where an important mining district used to exist. Basically dike mineralisations of Pb-Ag antimony-sulphide and Cu-Fe sulphide were exploited, mainly associated to granites. Although the exploitations have been known to exist for centuries, the maximum activity took place between the end of the 19th and beginning of the 20th century, and the region even became the most important in the world for its lead production. The large subterranean voids which were gradually abandoned as the exploitation advanced, were filled in many cases with mine waste rocks, in which pyrite existed. The oxidation of these sulphides could have generated acid water rich in heavy metals.

The mining works made it necessary to pump out considerable amounts of water, which in many cases influenced their design. After the progressive abandonment of the various exploitations and the cease in pumping, the piezometric levels slowly began to spontaneously recover, flooding a considerable part of the mining area. Currently these old mine shafts are being used to install pumps to extract water for agricultural and industrial use.

Furthermore, the mining past of this region is reflected in the landscape by the profusion of tailing embankments and remains of old mining concessions, among which flow some tributaries of the Guadalquivir river.

The basic objectives of this study were to establish the effect of the mining activities on the physical-chemical quality of the ground and surface water, paying special attention to those related to the old mining tailings.

GEOLOGICAL CONTEXT

The study area is situated on the Tabular Cover of the Meseta (*sensu* Azéma *et al.*, 1979). Among the earlier papers on the region's geology, it is worth referring to the works of Azcárate and Argüelles (1971), Perconig (1971), Azcárate (1977) and Fontboté (1982). These distinguish two great geological units: the Palaeozoic substratum and the Tabular Cover of the Meseta. The former is made up of a potent series of grey beds in which some quartzite levels are interspersed ("a" in Figure 1). These materials, which were intensely deformed in the hercynian orogeny, make up the basement to the Mesozoic sedimentary cover. A granitic batholith ("b" in Figure 1) exists, which intrudes on the philites mentioned above and affects them with a metamorphism of contact. It is precisely in this granite where the dikes of Pb-Ag antimony-sulphide and Cu-Fe sulphides of are embedded, which were the target of the mining exploitation in the district of Linares.

The posthercynian subhorizontal cover appears in discordance, over the hercynian basement, and fossilising these mineralisations. This sector is exclusively made up of Triassic, Miocene and Quaternary materials. The Triassic materials were deposited on a Palaeozoic palaeorelief, filling in irregularities. This unit is 80-120 m thick. Its reddish colouring is characteristic, leading to it also being known as "Red Detritic Facies" on the edge of the Meseta. The series begins with a group of conglomerate or sandstone levels interspersed in clays with a thickness of 10-20 m ("c" in Figure 1). The conglomerates contain rounded pebbles and have diameters ranging between 2 and 5 cm. A thick sedimentary group is developed over these base levels, fundamentally made up of wine-red lutites, in which sandstones are also interspersed ("d" in Figure 1).

Directly over the Triassic, materials from the upper Miocene appear (upper-Messinian Tortonian, "e" in Figure 1), from which a stratigraphic discontinuity can be deduced. At the base a discontinuous level of calcareous and sandy conglomerates exists, over which a potent series of grey and blue marls is developing.

The presence of quaternary materials is limited to the alluvial infillings ("f" in Figure 1), where they appear in layers around 10-20 m thick. They are basically made up of silts, among which layers of conglomerates and clays are interspersed.

HYDROGEOLOGICAL BEHAVIOR OF THE MATERIALS

As can be seen in Figure 1, the dominant lithology of the study area corresponds to Palaeozoic basement and granitic intrusion, which are basically impervious materials with an aquiclude-aquifuge behaviour. In spite of this, locally, the granitic batholith is sometimes very fractured, generating secondary permeable areas which permit a preferential circulation of groundwater. The pumps extract up to 4 l/s from these fracture zones (3, 4 and 5 in Figure 1), (Hidalgo et al., 1996). Additionally, the upper part of the granite, where it joins the sedimentary cover, is usually partially weathered. This secondary porosity explains the small catchments, only a few meters deep, which exploit this unit.

Additionally, there exists an enormous volume of voids in the granite, which are currently flooded, corresponding to the hundreds of kilometres developed by the old mining galleries. This important volume of voids confers a greater hydrogeological potentiality to the granitic batholith, meaning that its exploitation provides flows in the order of 30-50 l/s (points 10, 17, 20, 21, 23, 25, 26, 29, 31 and 32 in Figure 1). There is a collecting gallery (1 in Figure 1) which currently evacuates the water from

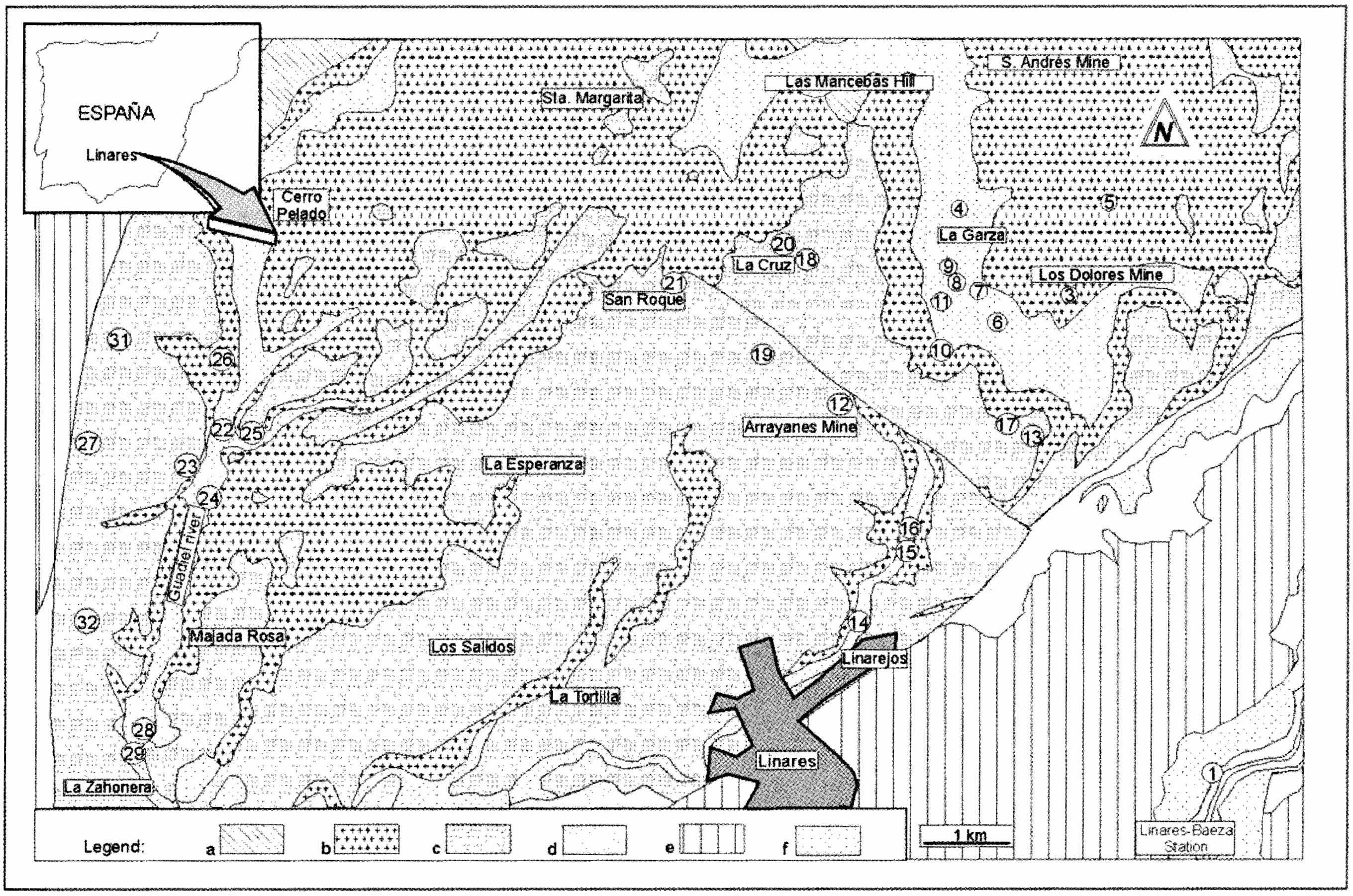


Figure 1.- Geological map of the studied area (modified from Azcárate, 1977) and location of the sampling points. Legend: a.- phyllites and quarzites (Palaeozoic). b.- granite. c.- conglomerates, sands and clays (Triassic, lower part). d.- clays and red sandstones (Triassic, upper part). e.- marls, sandstones and calcarenites (Upper Miocene). f.- conglomerates, sands and silts (Quaternary).

the system by gravity into the river Guadalén (tributary of the Guadalquivir) and constitutes the main discharge point from the granitic system (Hidalgo et al., 1998a).

On the other hand, it is worth noting the layers of sandstones and conglomerates at the base of the Trias in the sedimentary cover. These constitute a multi-layered aquifer which generally provides flows in the order of 1-4 l/s in the region. However, in the sector considered in this study, the Triassic materials have practically eroded away, with the exception of a thin base layer which crowns the topographically highest points.

Miocene materials proliferate to the East and South-east of Linares. These are of scarce hydrogeological interest, except for the brecciated base level.

Lastly, the presence of quaternary alluvial materials is of note. They constitute aquifers of intergranular porosity, although they have a low productivity due to their scarce thickness (Hidalgo et al., 1996). Thus, the flows in the open wells in the area (6, 7, 8, 14, 15 and 16) are generally below 1 l/s. In spite of this, as the water draining from the numerous tailings embankments is connected to the fluvial watercourses, their study is of particular interest.

PHYSICAL-CHEMICAL CHARACTERIZATION OF THE WATER

Methodology

In June of 1996, a hydrochemical sampling campaign was carried out in which 32 water points were included, selected with the aim of characterising the different hydrogeological mining environments developed in this area, as shown in the diagram in Figure 2. As can be seen, the samples obtained correspond to both the ground water – coming from the old mine shafts (A and B in Figure 2) and from pumps exploiting the quaternary deposits and the areas of granite fractures (E and F, respectively, in Figure 2) – and the surface water (C in Figure 2). For the purpose of this study, two small permanent lakes are included in the group referred to as "surface water" (points 9 and 11 in Figure 1), whose origin is linked to the flooding of the mining galleries. An analysis of the leachates generated over the tailings of an old smelter was also made (D in Figure 2). These effluents accumulate, forming small pools in the topographically depressed surrounding areas and may occasionally be carried by the runoff through the quaternary materials (Hidalgo et al., 1998b).

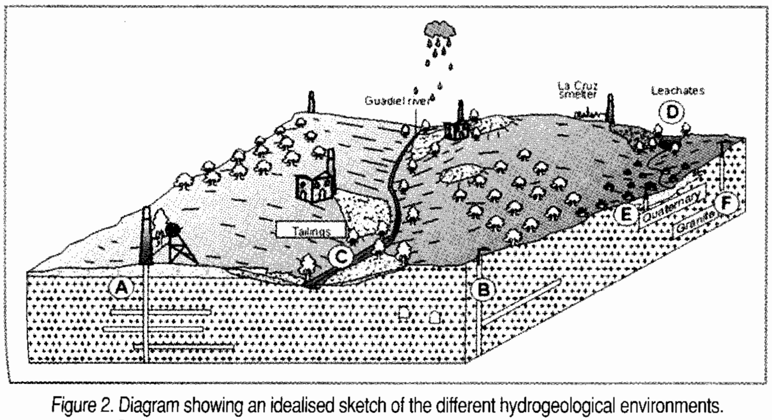


Figure 2. Diagram showing an idealised sketch of the different hydrogeological environments. A and B: ground water related to old mine shafts, C surface water (Guadalén river), D: leachates (smelter of La Cruz), E: wells exploiting the Quaternary aquifer, F: boreholes in granite.

During the sampling campaign, in situ measurements were taken of temperature, pH and electrical conductivity. The conservation conditions of the samples depended on the parameters to be determined in each case. Thus, the fraction destined to be analysed for metallic elements was acidified with HNO_3 at 0,3%, whilst for the majority constituents, preservatives were not used. The metals analysed were Al, Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb. The analytical determinations were made in the laboratory of the Water Research Institute of the University of Granada (Spain).

Results and discussion

Table 1 sums up the analytical results corresponding to the various water groups considered in this study. As can be seen, the range of pH values is very similar in every case, revealing waters with a slightly alkaline character, with average values of around 7.8. In the case of the leachates, this alkaline character is considerably accentuated, the pH recorded being almost 9. The high conductivity of these waters is also of note (around 10,000 µS/cm), presumably associated with re-concentration processes by evaporation in the pools where they accumulate.

The conductivity levels recorded in the rivers Guadalén and Guadiel (730 µS/cm on average) are consistent with the sampling sequence, the degree of mineralisation of the water increasing as the water progresses downstream. The maximum value (1116 µS/cm, point 29 in Figure 1) is located downstream from the granitic batholith. The saline content of the water from the quaternary aquifer is only a little higher than that of the surface water, with average values of around 800 µS/cm (Table 1). This value increases significantly in water originating from the mine shafts, characterised by a mean conductivity of 1128 µS/cm.

As regards the major constituents in the ground water, it is worth noting that the highest contents are found in the waters proceeding from the old shafts and mining galleries (263 mg/l of SO_4^{2-}, 243 mg/l of HCO_3^- and 117 mg/l of Ca^{2+}, as average values). However, in the waters linked to the areas of fractured granite, which are hardly affected by the mining works, the content in SO_4^{2-} ion is the lowest in the sector (between 10-40 mg/l). If the waters from the quaternary aquifer and the fractured granite are considered together, the distribution range of the major constituents is found to be very similar to that of the surface water (Table 1). Hydrochemical facies of Ca-HCO_3-SO_4 type predominate, whilst the water from the mine shafts is characterised by a SO_4-HCO_3 to sulphate hydrofacies.

The leachates generated from the smelting tailings are worth a separate mention, with hydrochemical facies of Na-SO_4 type and very high contents in SO_4^{2-}, HCO_3^- and Na^+ (3800 mg/l,

					(mg/l)						(µg/l)			
		T° (°C)	Cond.	pH	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	HCO_3^-	Cl^-	Al	Fe	Mn	Pb
Quaternary aquifer and granite	Min	19.5	570	7.6	78	16	30	26	108	22	17	34	3	1
	Average	21.343	896	7.8	116	25	47	162	223	50	65	122	16	7
	Mean	**20.4**	**828**	**7.8**	**114**	**20**	**33**	**194**	**226**	**38**	**56**	**68**	**5**	**5**
	Max	23.8	1160	7.9	149	42	114	261	279	94	128	295	61	22
	Samples	7	7	6	7	7	7	7	7	7	6	7	7	6
		T° (°C)	Cond.	pH	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	HCO_3^-	Cl^-	Al	Fe	Mn	Pb
Shafts and mining galleries	Min	18.9	456	7.3	56	12	14	13	120	10	41	20	7	4
	Average	22.4	1041	7.8	131	32	57	291	250	52	79	233	1201	51
	Mean	**22.7**	**1128**	**7.8**	**117**	**34**	**58**	**263**	**243**	**53**	**90**	**109**	**224**	**25**
	Max	26.6	1600	8.2	240	55	136	740	363	85	141	1220	6080	210
	Samples	12	13	12	13	13	13	13	13	13	9	12	13	12
		T° (°C)	Cond.	pH	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	HCO_3^-	Cl^-	Al	Fe	Mn	Pb
Surface waters	Min	23.8	310	7.4	53	8	3	68	103	4	81	7	3	1
	Average	28.6	765	7.8	93	25	38	131	240	43	164	288	455	97
	Mean	**27.7**	**730**	**7.7**	**90**	**26**	**41**	**135**	**216**	**35**	**182**	**260**	**525**	**100**
	Max	37.7	1116	8.3	124	49	75	210	360	82	220	480	700	260
	Samples	7	7	7	7	7	7	7	7	7	6	7	7	7
Leachates	Average	25	10000	9.4	40	25	2500	3800	1400	150	--	1200	2000	200

Table 1. Field measurements and analytical data for the various water groups considered in this study (conductivity expressed in µS/cm).

1400 mg/l and 2500 mg/l, respectively). This peculiar hydrofacies must to a large extent respond to the mineralogy of the tailing (predominantly hematite, accompanied mainly by calcite, magnetite and andalusite) and the nature of the fluxes used in the process (probably sodium carbonates). These lixiviates are also characterised by concentrations in the order of mg/l in Fe and Mn.

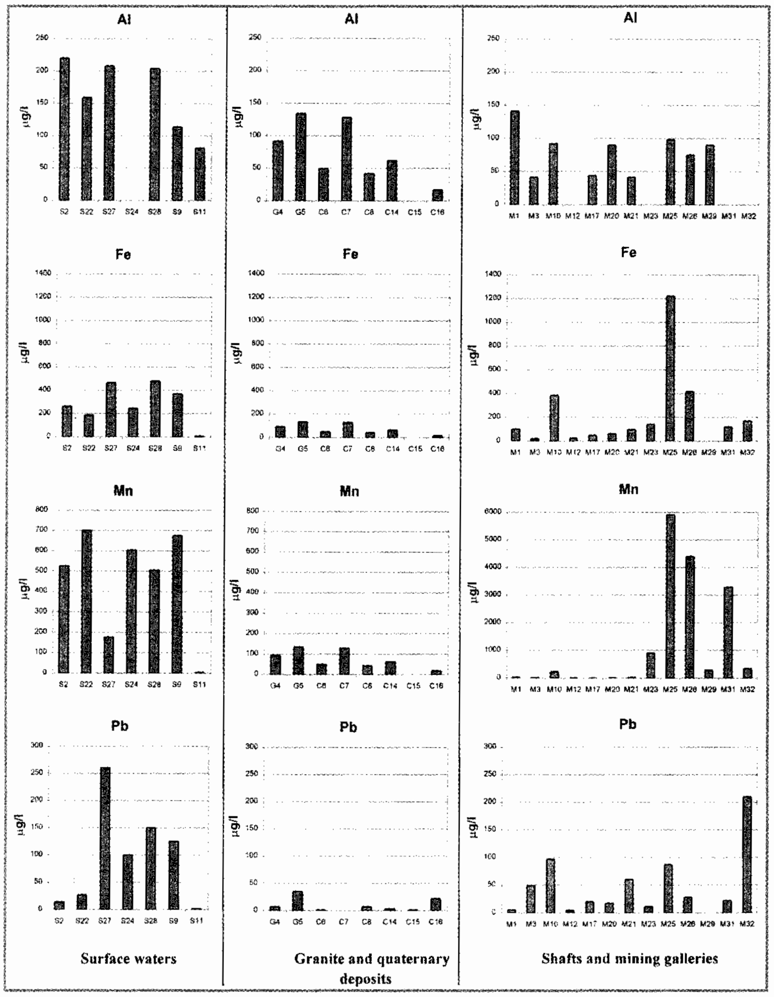
Of the different metallic elements analysed, only Al, Fe, Mn and Pb appear in most of the waters in concentrations over the detection limit of the analytical technique used.

Considering the average content in heavy metals in each group, it was observed that the highest values correspond to the surface waters (Table 1). This circumstance is not unusual if one considers that the banks of these rivers are marked by numerous tailings of varying granulometry, which drain directly into the water courses. In particular, the average concentrations of Fe (260 µg/l), Mn (525 µg/l) and Pb (100 µg/l) in these waters is above the maximum admissible level (MAL) in drinking water established by the European regulations (200, 50 and 50 µg/l, respectively). Moreover, only one of the samples (lake 11) has contents below the MAL for all the elements analysed (Figure 3).

The two groups of groundwater, on the other hand, show marked differences in metallic element content. In the case of water from the fractured granite area and the quaternary materials (G and C in Figure 3), the average values of content in Mn and Pb are very low (5 µg/l in both cases) and the range of concentration of Al and Fe (around 60 and 70 µg/l, respectively) is similar to other waters related to metapelites and granites in areas unaffected by mining activities. It does not therefore seem that there currently exists any kind of modification in the quality of these waters associated with the old mining activities.

The results obtained in the waters pumped from the mining voids are very different. Although the average values of the heavy metal contents only exceeds the MAL in the case of Mn (Table 1), on analysing the distribution of the cases, the situation changes considerably. According to Figure 3, there are a certain number of shafts with high concentrations mainly of Fe and Mn (in the order of mg/l). These concentrations can reach values at some points above those recorded even in the smelting leachates.

The waters with a marked sulphate character are also those which have the highest contents in heavy metals. The origin of the sulphates in this hydrogeological context must be linked to an oxidation process of the metallic sulphides present in the old galleries and, to a lesser extent, in the waste rock fill materials. This process is characterised by the generation of acid waters. However, all the waters analysed in this study have an alkaline character, which could be due to various processes. Firstly, the flooding of the galleries prevented the entry of oxygen into the mines and this must therefore have reduced the formation of acid waters. Additionally, the galleries having been closed for several decades, the circulation of water must have partially leached the abandoned voids. On the other hand, the dikes are characterised by an abundant carbonate fraction, which could possibly neutralise part of the acid waters that may have been generated.



Surface waters **Granite and quaternary deposits** **Shafts and mining galleries**

Figure 3. Al, Fe, Mn and Pb contents in the sampling waters.

The progressive neutralisation of the waters would explain the separation of the aqueous phase of the heavy metals and, therefore, the lower concentration of these in solution. This would not have been possible in the case of elements such as Mn, as the precipitation of the constituent requires very high pH values, generally even over 10.

This evolution to alkaline waters could change in the near future, as currently the old mine shafts are being used to install pumping equipment for agricultural purposes. One consequence of this exploitation could be the fall in water levels, thus allowing the system to come into contact with the air, which could again lead to the formation of acid waters (Figure 3). In this regard, it is significant that the lowest pH values and highest contents in SO_4^{2-} correspond to those points where pumps have been extracting water most intensively in recent years (mainly at points 21, 25, 26 and 31).

CONCLUSIONS

The waters which currently occupy the mining voids of the batholith of Linares has an alkaline character and are characterised firstly by a high concentration in sulphate ion (several hundred milligrams/litre) which distinguish them from other waters associated with the granites in the sector (several tens of milligrams/litre). Secondly, they may present high contents mainly in Al, Fe and Mn. The generation of these sulphate waters is probably related to a process of sulphate oxidation, which would also lead to the increase in metals in the water.

The alkaline character currently found in the waters responds to the combination of various processes, such as the lack of oxygen after the mining voids were flooded, the leaching experienced over the years since the mines were abandoned and the neutralisation of the waters due to the reaction with the carbonate minerals present in the dikes.

The surface waters that drain from this old mining district on average have a higher content in metallic elements than the majority of the ground waters, with contents which often exceed the MAL. However, the maximum concentrations of heavy metals correspond to a specific type of leachates generated in the smelting tailings, characterised by a highly contaminating load.

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