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Hydrological conceptual model characterisation of an abandoned mine site in semiarid climate. The Sierra de Cartagena-La Unión (SE Spain)

VIRGINIA MARÍA ROBLES-ARENAS [1] and **LUCILA CANDELA** [2]

[1] **Instituto del Agua, Granada University**
Ramón y Cajal 4, Granada 18071, Spain E-mail: roblesarenas@ugr.es

[2] **Department of Geotechnical Engineering and Geosciences, Technical University of Catalonia (UPC)**
Jordi Girona 1-3, Barcelona 08034, Spain

─┤ A B S T R A C T ├─

A comprehensive study at Sierra de Cartagena-La Unión (SE Spain) abandoned mine site was carried out to characterise the regime and water quality of the groundwater system after the mine closure. The system consists of five geologic fractured blocks belonging to the Alpujarride and Nevado-Filabride complexes. The aquifer units are composed of limestone and dolostone materials. Recharge is mainly controlled by the N-130 fault system, man-made induced fractures, open-pits and underground workings. Discharge is indicated from open pit lakes by the proximal dome-shaped groundwater level contours. Aquifer natural recharge, assessed by fracture density maps and chloride mass balance, provided consistent results. The water hydrochemical facies show a marked sulphate concentration and acidic pH (average pH of 2.53-6.30). A maximum concentration of 4,100 mg/L of Zn and 40,000 mg/L of sulphate was observed in open-pit lakes. Springs present the lowest residence time and are low mineralised with an average pH of 7.6. Geochemical modelling based on the PHREEQCI code indicates water undersaturation with respect to almost all related mineral species and anoxic conditions prevail in the system. Although an adequate understanding of the regional system is provided, a further detailed hydrochemical study is necessary to assess the undergoing geochemical changes.

KEYWORDS | Fractured aquifer. Open-pit and underground mining. Sierra de Cartagena-La Unión. Acid mine drainage. Semi-arid zone hydrology.

INTRODUCTION

Abandoned mines constitute a worldwide environmental problem. The adverse effects of mining activities and mine closure on the environment have been addressed by many authors in many parts of the world (May et al., 2001; Stamatis et al., 2001; Younger et al., 2002; Lee, 2003; Smolders et al., 2003; Ashley et al., 2004; Razo et al., 2004; Rodríguez and Candela, 2004; Sánchez-España et al., 2005; Gomes and Favas, 2006; Moreno et al., 2007). Long-term deterioration of water quality is among a number of environmental problems produced in derelict mines (Iribar et al., 2000; Lee et al., 2001; Heikkinen et al., 2002; Aykol et al., 2003; Olias et al., 2004; Cidu, 2007;

Pérez-López et al., 2007). Also, water quality deterioration affects water resources and aquatic ecosystems. The chemical reactions caused by mining begin when the mine is still active. Upon closure dewatering ceases and groundwater levels rise, flooding the mine void which dissolves the rock bearing minerals and releases constituents to the water (Appelo and Postma, 2006). Polymetallic sulphide mining ore bodies contain complex sulphide and sulphate mineral assemblages that weather in response to oxidising conditions, leading to one of the major problems related to sulphide mines, acid mine drainage generation (AMD) widely studied in literature (e.g., Younger et al., 2002). If the rebounding groundwater reaches the surface it may appear via old adits (horizontal tunnels), shafts, springs, seepages or even riverbeds. An exhaustive description on the rebound effects from mining is beyond the aim of this paper.

Land-use changes by mining activities have received little attention though may completely modify the previous hydrologic system processes (DeFries and Eshleman, 2004), including changes in water demand, recharge and runoff, as shown by Negley and Eshleman (2006). In some cases, lakes formed by the reorganisation of surface-groundwater drainage, and fed by surface flow or by shallow groundwater, may form as a result of modification of original relief. Also open conduits in the geological structure are generated. Although the discharges from shafts and adits (generally as seepages) are the most visible mine-water sources, surface activities such as mineral processing, tailings and water disposal are also a significant source of pollution.

Hydrometeorological parameters are important factors affecting weathering, secondary minerals formation (e.g. efflorescent sulphate salts) and mineral release in mining areas. Precipitation patterns have a dominant influence on mine planning during the working life by affecting dewatering methods and affect mine hydrology for the long-term after mine closure. Studies on the adverse effect mining have been almost exclusively conducted in temperate areas and only limited information on derelict mining sites in semiarid climates has been reported to date (Rösner, 1998; Wray, 1998; Navarro et al.; 2004, Razo et al., 2004; Moreno et al., 2007). Also, extensive research on geoenvironmental models of mineral deposits in different climatic areas, including effects of mining has been carried out in the US (Plumlee and Nash, 1995; Seal and Foley, 2002). Transient or episodic mass transfer processes are particularly significant in this climatic zone which is prone to flash-floods originating from sporadic storms (Fennemore et al., 1998). Wind is also a frequent meteorological phenomenon causing dust storms, which lead to an enrichment of dissolved solids in rainfall, and an enhancement of open water evaporation from pit-lakes. The latter represents an important loss of groundwater increasing the concentration of solutes. Knowledge of the hydrogeochemical processes that control groundwater characteristics which may also provide evidence of flow, is essential in order to evaluate potential groundwater uses, especially in regions with scarce resources and growing demands (Eshleman et al., 1994; O'Brien et al., 1994; Tang et al., 2001; Chen et al., 2004; Zhang et al., 2007).

At present, the Sierra de Cartagena-La Unión is a derelict mining site located in a semi arid climate, where exploitation of Ag, Pb, Zn, Cu, Fe and Mn in sulphide ore bodies lasted more than three thousands years. Mineral production was the only objective of mining activities, being the hydrogeological understanding of the system disregarded, and the conceptual model still remains unknown. The objective of the present study is to analyse mining delayed effects on the abandoned mine site hydrology by characterising the hydrogeologic units, the groundwater flow system and the hydrochemical characteristics of sampled water. For the assessment of groundwater hydrology, a significant number of groundwater level measurements were collected, and a large set of major and heavy metal components was determined from water samples.

Study site description

The Sierra de Cartagena-La Unión site is an E-W trending coastal mountain range, located at the South-eastern part of the Iberian Peninsula extending over 100 km^2 along the Mediterranean coast (Fig. 1). The climate is semi-arid Mediterranean, characterised by mild winters and hot summers with a minimum of 10ºC (January) and a maximum of 40ºC (August); the mean annual temperature and precipitation are 17ºC and 300 mm, respectively (1975-1998 period). Rainfall usually takes place in spring and early autumn. The most important aspect of the precipitation pattern is its concentration in a few unevenly distributed events that are highly variable through space and time. Convective rain generation can produce heavy storms; a maximum rainfall event of 113.8 mm taking place in a 24 h period was recorded during 1920-1991 (Instituto Geológico y Minero de España-Ministerio de Obras Públicas, Transporte y Medio Ambiente (IGME-MOPTMA), 1996). For the 2003-2004 hydrologic period, annual precipitation was 440 mm, Thornthwaite evapotranspiration was 900 mm/y (García, 2004), whilst estimation from Penman-Monteith method was 1200 mm/y (Sistema de Información Agraria de Murcia (SIAM), 2006). The Easterly humid wind is almost constant in the area.

Perennial streams do not exist, and surface water consists of ten ungaged ephemeral streams with a maximum length of 8 km and a catchment area between 3 and 37 km^2. Watercourses are only operational during heavy rain-

fall events that produce important flood episodes. Runoff accounts for an estimated 15% of the precipitation (Confederación Hidrográfica del Segura (CHS), 2005). Despite the ephemeral character of the streams, as the rainfall intensity may be more important than the total amount of water, flow intensity after some storms may show great variability. Stream flow is flashy and a significant amount of sediment is transported after long-lasting rainfall. Surface water drains either to the Mediterranean Sea or to the Mar Menor, a hyposaline coastal lagoon of approximately 170 km^2 identified as being of international importance in the RAMSAR convention list. Groundwater discharge is produced from four perennial springs and several seepage areas with flow rate between 0.1 and 2 L/s; no flow variation is observed throughout the year. Three perennial open-pit lakes, originating from precipitation, surface runoff or shallow groundwater inflow, have developed in the former abandoned open-pits. The depth of Brunita lake is greater than 30 m and the total amount of stored water is approximately 620,000 m^3 (García, 2004).

The geology of the Sierra de Cartagena-La Unión is the consequence of the Alpine ranges of the southernmost part of the Iberian Peninsula which constitutes de Betic Range. From a geologic standpoint this region belongs to the Internal Zones of the Betic Range (Sanz de Galdeano, 1990; Azañón al., 2002) and three tectonic complex units

can be identified from bottom to top as (Ovejero et al., 1976; Manteca and Ovejero, 1992): Nevado-Filábride, Alpujárride and Maláguide complex. Only a small outcrop of the Maláguide (less than 1% of the surface area) exists (Fig. 1). The Nevado-Filábride unit consists of graphite micaschists, greyish quartzites, quartzitic schists, micaschists, white quartzites, marbles and "green rocks" (ortho-amphibolites with chloritic schists). The Alpujárride complex is composed of epimetamorphic rocks, quartzites and phyllites, and carbonate series with some diabases and dolerite intrusive bodies of pre-orogenic volcanism overlying the Nevado-Filábride. The three units are locally covered by pelitic rocks, including sandy and conglomeratic levels of Miocene and Quaternary age, and subvolcanic (rhyolite-dacite and andesite) and volcanic events (alkaline basalt). Two important fault systems, N-70 and N-130, developed during the Eocene and Middle Miocene period, an important tectonic phase (Manteca and Ovejero, 1992). After the Middle Miocene tectonic reactivation of the fracture set formed the present horst and graben geologic features of Sierra de Cartagena-La Unión bedrock (Gagny and Marconnet, 1994).

The main orebody (mantos) is hosted by two stratabound polymetallic sulphide deposits (pyrite, sphalerite, marcasite, galena and locally pyrrhotite, chalcopyrite, arsenopyrite, tetrahedrite, stannite and greenalite), inter-
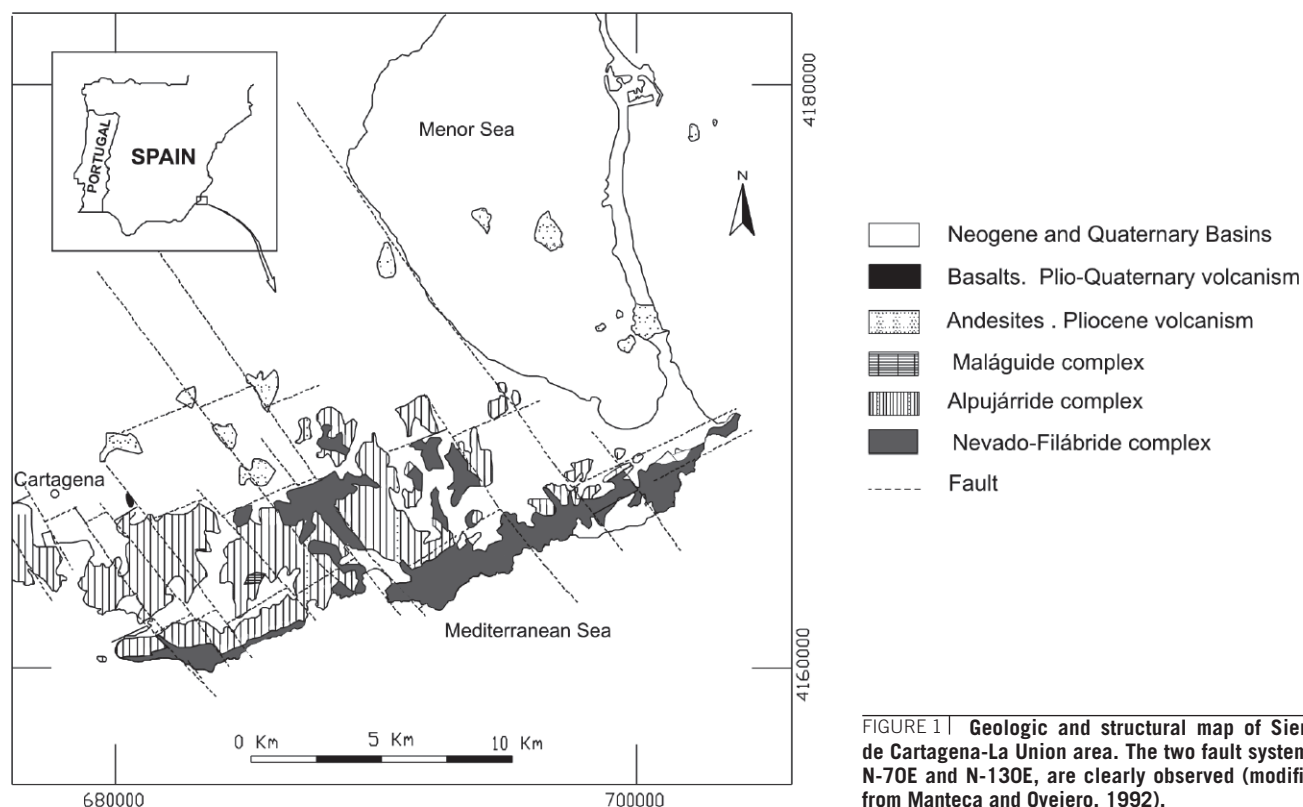

FIGURE 1 | **Geologic and structural map of Sierra de Cartagena-La Union area. The two fault systems, N-70E and N-130E, are clearly observed (modified from Manteca and Ovejero, 1992).**

layered in carbonate sequences of the Nevado-Filábride and Alpujárride complex. The mineralisation is also disseminated in Miocene materials (pyrite, marcasite, galena, and pyrrhotine and chalcopyrite as secondary minerals), oxides and hydroxides in gossans (goethite, hematite, magnetite, and manganese oxides), stockworks and veins. The orebody was exploited by underground mining (shafts and adits) and surface mining in open-pits.

In 1990 and as part of the mining operations, a mixture of sludge and seawater was deposited in the Tomasa open-pit mine (Fig. 2). Disposal of approximately one million of cubic meters of seawater took place over a period of six months. Shortly after, an increase in chloride was observed in some shafts, and several springs emerged in the surrounding area of the open-pit (Confederación Hidrográfica del Segura (CHS), 1991). Since the 1991 closure programme, the area has remained abandoned. In 2003 a post-mining evaluation of the site took place and

catalogued 12 open-pits and 2,351 mine waste dumps and flotation tailing dams were deposited over 9 km^2 (García, 2004; Robles-Arenas et al., 2006; Robles-Arenas, 2007). In addition, approximately 25 million cubic meters of waste were discharged into the sea in the inner part of Portman Bay and offshore over a 30 years time span. The geologic subsurface has been highly modified by thousands of km of underground workings, more than 3,000 open mine shafts and an unknown number of adits.

An intensive literature search for existing published or unpublished local hydrologic and hydrogeologic information was carried out with little success. The few existing works are of local interest, focussing on partial hydrogeological aspects or only carried out in some sectors of the Sierra de Cartagena (Carulla, 1977; García et al., 1978 and Confederación Hidrográfica del Segura (CHS), 1991; Instituto Geológico y Minero de España-Ministerio de Obras Públicas, Transporte y Medio Ambiente (IGME-
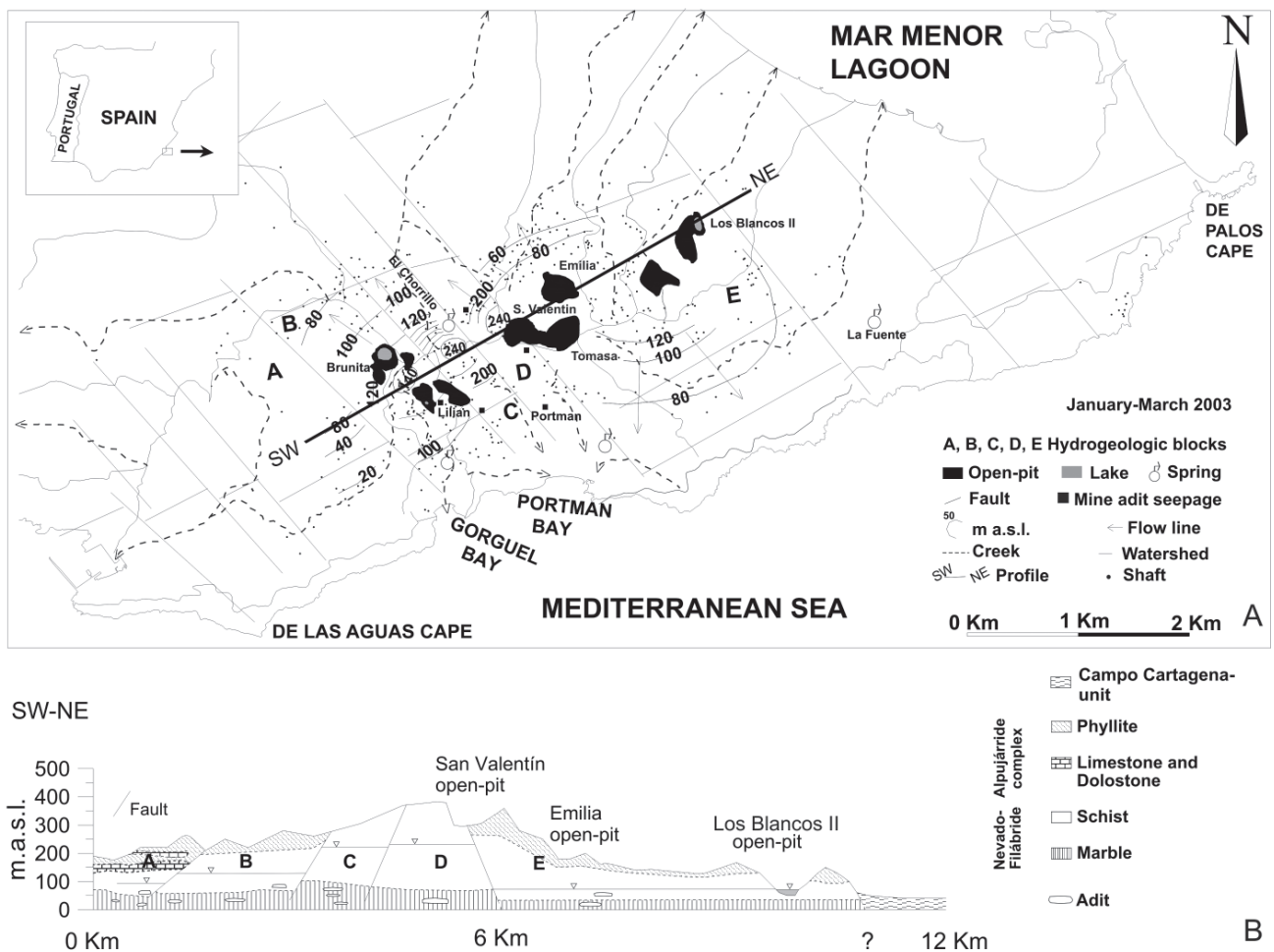

FIGURE 2 | A) Groundwater level contour map of the studied Sierra de Cartagena-La Unión area (January-March 2003 period). B) Schematic NW-SE hydrogeological cross-section (aquifer units not at scale).

MOPTMA), 1996). As the principal aim of mining was always ore exploitation and mineral production, the few works undertaken had the sole objective of dewatering to decrease the groundwater level (and even up to depletion). Reports or information on the recovery tests (Instituto Geológico y Minero de España-Ministerio de Obras Públicas, Transporte y Medio Ambiente (IGME-MOPTMA), 1996; Rodríguez-Estrella, 2000) did not allow an insight to the test procedure, aquifer hydraulic assumptions and recorded measurements during the recovery test, impairing data assessment or reinterpretation. The hydrogeological understanding was seldom considered, and available reports or studies were generally of local interest focussed on mining exploitation. When pumping ceased, groundwater levels rebounded and surveys, if any, were always developed disregarding any research attempt on mining delayed effects or groundwater sustainability. Presence of water in shafts and pits was considered the consequence of rainwater storage.

During the late 1950's, tourism and irrigated agriculture development took place in the neighbouring areas leading to important land-use changes. Currently, most of the area is a regional park and still remains unpopulated except for the coastal plains. Drinking water supply for the population is mainly provided by basin external sources of surface water (Canal del Taibilla) while groundwater and the Tajo-Segura water transfer are used for agriculture. Spring water does not meet water quality standards, although it is currently used as drinking water supply. The Water Framework Directive (2000/60/EC) has been incorporated into the Spanish legal framework, and according to the corresponding Royal Decree (Law 62/2003) various control and protection measures are being implemented. However, compliance, problem-oriented groundwater monitoring networks are not yet established by the competent authorities. In recent years, the area is facing important water demand pressures due to an increase in the local population and new tourism resorts development.

METHODS

Data sets

In order to characterise the hydrology and hydrogeology of the area new data were generated from two field campaigns carried out in 2003 and 2004. During January-March 2003, 388 groundwater level measurements were taken and 137 duplicate water samples for physico-chemical determinations were collected. Groundwater was sampled from shafts of varying diameter (<0.5 m to >4 m), different depth (15 to 250 m) and cross-section, and from two springs and two seepages. Water samples were collected from two open pit lakes (water surface), six runoff samples from one rainfall event, and 20 rainfall samples from two

rain-gauges operated by the meteorological survey department. Water samples from rainfall events were collected in permanently open samplers during October 2003-April 2004. All water samples were stored at 4 °C prior to chemical determinations.

In the first set of water samples major ions, hardness, pH, electrical conductivity (EC), total dissolved solids (TDS) and alkalinity (ALK) were determined. The second set of samples was filtered (0.45 μm, Millipore®) and acidified with nitric acid for heavy metal analysis. Major ion content, hardness, pH, EC, TDS and ALK were analysed by a commercial laboratory following standard procedures. Fe and Mn concentrations were obtained by Atomic Absorption Spectroscopy (AAS) and concentrations of Ni, Zn, Cd, Pb and Sr by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Only 7% of the chemical analyses displayed a non acceptable difference in the cation-anion balance. However, the common balance error based on major anions and cations does not adequately assess the reliability of a water analysis when trace metals are present in high concentration, and therefore were not disregarded. *In-situ* pH, EC and temperature were measured with a multi-parameter recording device. The 1996 campaign (IGME-MOPTMA, 1996) provided data on the following heavy metal analysis: Pb, Zn, Sr, Ni, Se, Cu, As, Cd and Al.

Natural recharge estimation

Natural recharge was estimated from daily meteorological data (October 2003-October 2004) and identification of potential recharge zones based on outcropping rock mass fracturing lineaments, using an approach similar to that shown by Shaban et al. (2006). Linear structural features (e.g. tectonic rock fracture set or system) identified in the studied area as fracture traces with the aid of geologic maps were stored in a Geographical Information System-GIS (ArcGIS 9.0©, ESRI), and a fracture density map was produced by Spatial Analyst Tools. Frequency density of lineaments per unit area (km of fracture per cell) was defined in a raster map of 45 m x 45 m mesh and a final value was assigned to the centre of the grid (Fig. 3). Up to five class ranges were built and a different weighting factor was assigned according to density values. Weighted effective infiltration estimates were calculated by multiplying the corresponding area weighting factor by the recorded precipitation during the studied period.

In addition, groundwater recharge was estimated based on the chloride mass balance (Kitching et al., 1980):

$$R = P(Cl_p/Cl_w) \qquad (1)$$

where R= recharge rate (mm), P= precipitation (mm), Cl_p= chloride concentration in precipitation (mg/L) and

Cl_w= chloride concentration in groundwater (mg/L). This equation assumes that runoff is zero, that rainfall is the only source of chloride in the area and that no chloride is absorbed, exchanged or transformed within the soil profile. It is considered that steady-state conditions exist.

Estimation of recharge using tracers (e.g. Cl⁻) is based on the conservation of tracer mass. The most successful non-isotopic environmental tracer in hydrologic studies is Cl⁻, specially in coastal areas where aeolian Cl⁻ is deposited from winds carrying precipitation from the sea. Validity of the environmental chloride method for recharge estimation local groundwater recharge in coastal areas has been assessed by a number of researchers.

Open water evaporation from pit-lakes was determined from evaporation pans located at the IMIDA agricultural station (Campo de Cartagena area).

Hydrochemical modelling

Saturation state of groundwater samples (e.g., saturation index, SI) for relevant minerals and ionic speciation were calculated with the PHREEQC Interactive 2.8 code (Parkhurst, 1995). The applied thermodynamic data base was wateq4f.dat (Ball and Nordstom, 1991). Thermodynamic data for Schwertmannite were obtained from Bingham et al. (1996) and Fernández-Caliani (2008). Speciation and equilibrium calculations with respect to mineral phases were carried out in four shafts (C1659, C581, C490, C721) with the 2003 sampling campaign data.

FIGURE 3 | **Fracture density map based on outcropping fracturing lineaments.**

RESULTS OF DATA ANALYSIS

Aquifer unit description/hydrogeological context

Data collected in this study show that the aquifer system in the study area consists of five fractured blocks of the Alpujarride and Nevado-Filábride complexes composed of schist, quartzite, phyllite, limestone and marble, outcropping over an area of 100 km² with thickness between 400 and 800 m. The aquifer units are made of limestone (Alpujarride) and marble (Nevado-filábride) materials; the impervious basement is non-fractured schist and quartzite from the lower Nevado-Filábride unit. Geologic boundaries are difficult to define with accuracy due to the continuity of the unit material beneath the Mediterranean Sea that is unconformably overlain by the Campo de Cartagena hydrogeological unit (Fig. 2). At present, the geometry of the geologic boundaries and relationships between the different geological formations are unknown.

Two factors have particular implications for the rock mass degree of fracturing and the hydrogeological properties of the aquifer system, in particular permeability, as mined ground must be considered as a network of interconnected fractures. The first one is the intense and active tectonic history of the area. The second is related to secondary fracturing induced by mining works (excavation and fracturing). Karstification of carbonate rocks enhanced the permeability of geologic materials to a lesser extent. Transmissivity values estimated from shaft recovery tests range from 10 m²/d (Instituto Geológico y Minero de España-Ministerio de Obras Públicas, Transporte y Medio Ambiente (IGME-MOPTMA), 1996) to 960 m²/d (Rodríguez-Estrella, 2000). The large difference between the two estimates is an indicator of the media's complexity.

For the 2003-2004 hydrologic year natural groundwater recharge was estimated by the two different methods presented above, and results were compared as an accuracy test of the estimation. It is assumed that recharge is only produced by direct infiltration from precipitation through fractures and open shafts as surface watercourses are ephemeral. For the period of interest, the following information was available: mean precipitation was 440 mm and the average chloride content was 20.7, 122, 757 and 227 mg/L in rainfall, springs, shafts and water seepages, respectively. Estimated recharge from fractured recharge zones based on GIS accounts for 5 hm³ (ranging between 4 and 396 mm of annual precipitation), and the higher input is originated in areas characterised by fracture density between 3 and 5 km of fracture per km² (Fig. 3). The estimated recharge value also includes recharge by precipitation through the shafts and open pits where open fractures outcrop. Average recharge estimated by the chloride mass-balance equation (eq. 1) is of approximately 4.8 hm³. Note
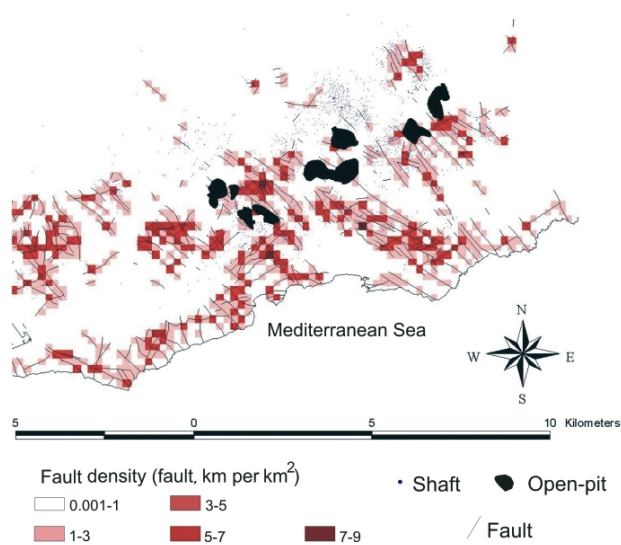
that recharge values (R) vary between 8 and 87 mm according to chloride content, which may account for 0.15 % and 15 % of the annual precipitation. Such variability can be attributed to spatial and temporal distribution of precipitation and variable chloride concentrations recorded in rain gauges. Regarding chloride concentration in the sampled water points (shafts, springs and seepages, see Table 1) a broad range of chloride concentration through time and space is also observed. Although uncertainties or limitations may exist in the accuracy of evapotranspiration estimates, or in the applied methodology, similar values of average recharge were obtained from the two methods.

Aquifer system discharge is difficult to assess due to data uncertainty. For this reason the estimated values presented here should be considered as a first attempt to evaluate the aquifer unit outflow. Discharge from springs and seepages accounts for 0.05 hm^3 (Robles-Arenas, 2007) and outflow to the Mediterranean Sea is 0.55 hm^3 (Confederación Hidrográfica del Segura (CHS), 1997). Net evaporation from water surfaces occurring on permanent open-pit lakes, large diameter boreholes and shallow underground workings is estimated to be 0.1 hm^3. Updates of groundwater abstraction do not exist. The only reliable data provided by Instituto Geológico y Minero de España-Ministerio de Obras Públicas, Transporte y Medio Ambiente (IGME-MOPTMA) (1996) estimates 1.4 hm^3 of abstracted water for water supply, local industries and irrigation for agriculture. Drainage to surface streams does not occur, and some of the permanent open-pit lakes constitute discharge areas

of groundwater flow representing sinks in the groundwater regional pattern. Since the groundwater level records show no trend over time, other than small seasonal variations due to rainfall, it can be assumed that no changes in groundwater storage occurred since the 1970's. The only exception was some dewatering workings developed during the last mining period.

Natural groundwater flow between the different units may also exist, as suggested by geologic investigations on stratigraphic and tectonic features. The water-level contour map developed from water-level measurements in shafts during the field sampling campaign (January-March 2003) is shown in Fig. 2. A dome-shaped topography-driven radial flow pattern elongated along the open-pit lineament indicates the main recharge area. Four springs located at both sides of the dome, shown in Fig. 2, are the field evidence of the system aquifer discharge by the downward-flow component. Inferred groundwater flow direction follows the N-130 fault system and the underground workings trend. Underground workings were developed following the mineralised zone in volcanic breccia, veins and faulted crush zones with the N-130 strike. Therefore, several geologic blocks (mainly controlled by the N-130 fracture set) of different water levels have developed (Fig. 2A, B). Hydraulic connectivity between blocks is extremely low in spite of the high shaft density in the area, and differences in water level greater than 100 m are observed even in closely-spaced shafts (60 m). In some areas, water level differences could be the consequence of water storage in

TABLE 1 | **Hydrochemical data set samples collected in the 2003-2004 period.**

	Spring samples		Open-pit samples		Seepage samples		Shaft samples (n=102)		Rainwater (n=20)		Runoff (n=6)		R.D. 140/2003
	La Fuente	Chorrillo	Brunita	Los Blancos II	Portman	Lilian	Av	S D	Av	S D	Av	S D	
EC (µS cm $^{-1}$)	791	2040	10390	9110	5010	9010	5081	3610	200	216	5200	1586	2500
pH	7.59	7.67	2.53	3.03	5.67	2.30	6.30	1.60	7.14	0.33	3.67	1.16	6.5-9.5
ALK (mg CaCO$_3$ l^{-1})	189	325	0.00	0.00	17	0.00	184	160	52.42	73.02	0.00		
HARDNESS (mg CaCO$_3$ l^{-1})	224	441	8034	6150	3530	4163	2557	2294	26.42	25.53	2732	585	
TDS (mg l^{-1})	593	1588	12850	11936	5864	12429	5395	5675	159	162	6621	2479	
HCO$_3^-$ (mg l^{-1}))	230	397	0.00	0.00	20	0.00	225	195	57.73	75.87	0.00		
SO$_4^=$ (mg l^{-1})	68	428	9516	9650	4234	10736	3067	4816	22.11	24.81	5472	2455	250
Cl$^-$ (mg l^{-1})	122	290	593	263	227	131	757	942	20.67	19.03	107	69.98	250
NO$_3^-$ (mg l^{-1}))	4.24	0.94	9.43	2.08	0.00	9.11	8.80	18	1.99	2.89	10	7.29	50
Na$^+$ (mg l^{-1})	85	300	390	162	129	44	373	327	9.63	9.22	54.01	42.52	200
K$^+$ (mg l^{-1})	2.27	1.59	10	4.62	6.30	1.13	24.10	37	4.91	9.10	1.76	2.81	12
Ca^{2+} (mg l^{-1}))	36	108.00	449	508	449	139	354	180	6.71	6.67	467	18.70	100
Mg^{2+} (mg l^{-1})	32	41	1678	1185	584	926	396	500	2.54	2.20	381	153	50
NH$_4^+$ (mg l^{-1})	0.01	0.00	0.00	0.00	0.08	0.00	0.90	4.48	9.18	18.17	0.00		0.5
B (mg l^{-1})	0.16	0.43	0.61	0.28	0.26	1.49	0.50	0.66	0.03	0.06	0.35	0.10	1000
P$_2$O$_5$ (mg l^{-1})	3.28	2.60	4.54	3.10	1.3	1.65	2.90	1.80	0.76	0.73	3.10	1.57	5
SiO$_2$ (mg l^{-1})	7.28	15	39	63	7.72	42	25	23	1.68	5.02	29.10	12.54	
Fe tot (mg l^{-1})	0.00	0.01	72	0.00	0.01	2.97	19.30	128	-	0.01	1.62	1.01	0.200
Mn (mg l^{-1})	0.03	0.02	85	93	203	392	26.20	72	0.03	0.07	88	64.60	0.050
Ni (mg l^{-1})	-	-	0.70	1.05	0.50	1.08	0.30	1.07	0.00	0.00	0.69	0.58	
Cu (mg l^{-1})	-	-	-	-	-	-	-	-	0.04	0.05	-	-	
Zn (mg l^{-1})	-	-	159	581	-	838	152	571	0.03	0.04	77.20	40.42	
Cd (mg l^{-1})	-	-	0.16	0.96	-	2.27	2.50	1.91	0.01	0.01	1.30	1.18	
Pb (mg l^{-1})	-	-	0.17	0.77	-	1.08	0.10	0.36	0.01	0.01	0.54	0.33	
Sr (mg l^{-1})	-	-	4.32	4.01	-	0.33	2.44	1.9	-	-	1.34	1.19	

(- unavailable datum; n: number of samples; Av: average; SD: standard deviation; R.D. 140/2003: Spanish guideline for water supply)

collapsed or isolated shafts, or adits located in zones of very low hydraulic conductivity. However, similar flow pattern response of water level over time was observed in previous works (Instituto Geológico y Minero de España-Ministerio de Obras Públicas, Transporte y Medio Ambiente (IGME-MOPTMA), 1996) and unpublished reports (Carulla, 1977; Centro de Edafología y Biología Aplicada del Segura (CEBAS), 1970; Confederación Hidrográfica del Segura (CHS), 1991; García et al., 1978), validating the observed field evidence in this work.

Hydrochemical characteristics of water types

A summary of the physico-chemical characteristics, major and minor ion content of the different sampled waters (rainwater, seepages, springs, runoff and shafts) is shown in Table 1. Sampled water is derived from rainfall recharge and chemical composition is modified as it moves downgradient from the recharge areas (low mineralised rainwater) (Fig. 4). Except for springs and rainwater, 54 % of water samples present neutral-acidic pH, elevated sulphate concentrations, and Zn and Mn are the most dominant ions. As Zn is relatively mobile, it remains largely dissolved through a range of pH. This is likewise observed in mine drainages of polymetallic deposits (Seal and Foley, 2002). Shaft samples show the greatest chemical variation, reflecting not only the aquifer flow path, but also residence time of water. Fig. 5 shows bivariate plots of B, Sr, Mn, Fe, Zn, Pb, Ni and Cd versus pH for the different types of water sampled in the area during the 2003-2004 campaign. It is observed that pH exerts an important control on the selected dissolved selected species (except for Sr) with a significant concentration decrease at pH between 4 and 5. Water samples from open pit-lakes, seepages and shafts of known geologic characteristics have been represented in the Ficklin plot (Plumbee and Nash, 1995). This plot shows the sum of dissolved concentrations of base metals (Cd, Zn, Ni, Pb) as a function of pH (Fig. 6). Water from phyllites and schists is more strongly acid generating than that of open-pit lakes, and more buffering capacity is observed in marls, located within the pH region of 6-7 in the diagram.

Rainfall is calcium bicarbonate type, with an important source from marine aerosol. Chemical composition presents significant content of dissolved solids (159 mg/L), neutral pH and presence of heavy metals at the detection level, contrasting with published rainwater chemical data (Appelo and Postma, 2006; Freeze and Cherry, 1979). Generally, rainwater is described as a dilute and acidic solution (pH from 4 to 6), with TDS (mg/L) ranging between few and several orders of magnitude. Anion enrichment of local precipitation is explained by the semiarid characteristics of the area and anthropogenic activities. The constant easterly wind promotes soil erosion, creating dust storms rich in heavy metals and $CaCO_3$, which buffers acidic pH

and affects dry deposition composition (Alcalá and Custodio, 2008). Sea-salt components are Cl, Na and Mg ions. The relative composition of seawater in marine aerosol, according to a fractionation factor, $F_X=(x/Cl)_{rain}/(x/Cl)_{sea}$, for the two rain gauge water samples was estimated for HCO_3^- and SO_4^{2-} relative to Cl^-. The fractionation factor ranges are 64-2070 for HCO_3^- and 1-37 for SO_4^{2-} which shows a strong enrichment with the two anions, indicating that the rainwater of marine origin is modified by land based sources during transport overland. A more complete discussion on rainfall processes is out of the scope of this paper.

One of the characteristics of runoff water is the acidic pH (average 3.67, Table 1) originated from the oxida-
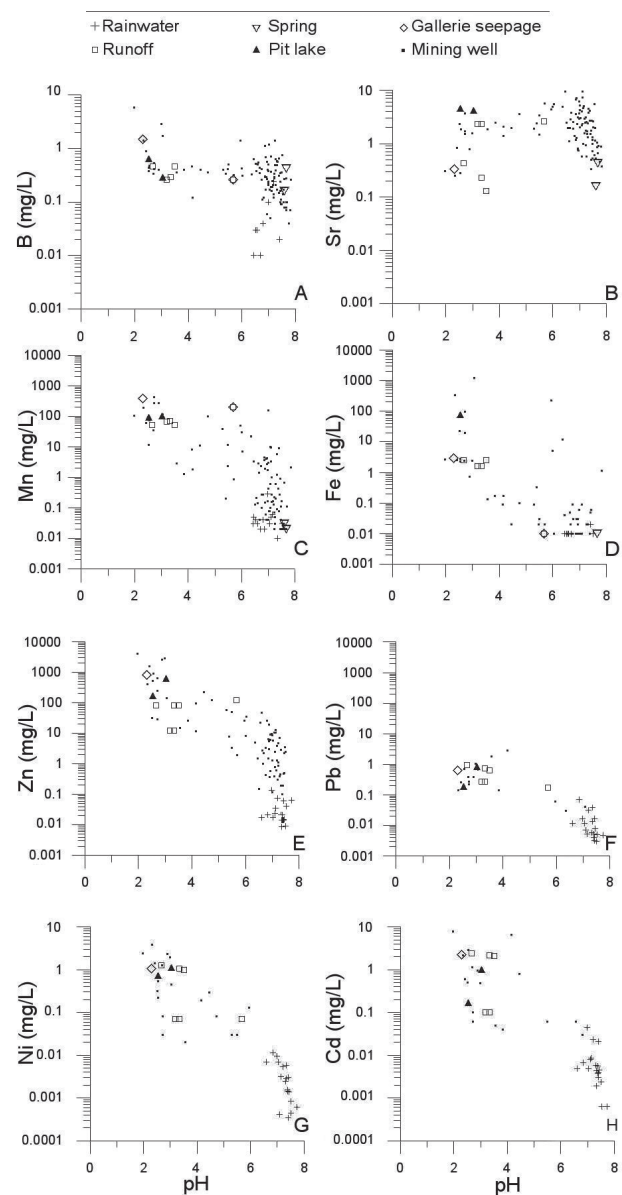

FIGURE 4 | **Selected species concentration of different sampled water vs. pH (2003-2004 sampling campaign).**

tion reaction of sulphide minerals in eroded fine-grained sediments and tailings, and lack of HCO_3^- to neutralise the acidity. As a consequence, SO_4^{2-} is the dominant anion with an average concentration of 5472 mg/L. Regarding heavy metals, an elevated concentration of Zn (77.2 mg/L) and Mn (88 mg/L) is observed which is most likely the result of metal complexation with soil organic matter. Sampling took place during sporadic rainstorms of different intensity and duration, and for this reason a relationship between water chemistry and water discharge cannot be established. Suspended solids ranged between 5,000 and 30,000 mg/L.

Samples taken from the two permanent open-pit lakes present low pH (2.5 and 3.0), high EC and SO_4^{2-} concentration, absence of HCO_3^- and a noticeable heavy metal concentration (Zn, Mn, Ni, Table 1). Sulphate is the major dissolved solid produced by sulphide oxidation due to the water level fluctuation at the lakeside, which is the only area where oxidation reactions may happen. Anoxic condi-

tions are expected to prevail under the water surface. Concentration of total Fe only appears in Brunita (72 mg/L), while in Los Blancos II samples it is completely oxidised (0.0 mg/L); Zn presents the maximum concentration (581 mg/L) in Los Blancos II. Water evaporation in Brunita lake has led to elevated concentrations of Cl^- and Na^+. This process is assessed by isotope measurements (data not shown in this paper). According to isotopic data of water samples (Robles-Arenas, 2007), open-pit water is composed of rainwater, runoff and groundwater mixture of different residence time that are affected by direct evaporation and stagnant conditions, leading to chemical differences. These findings are also supported by previous works carried out in Brunita lake (Instituto Geológico y Minero de España-Ministerio de Obras Públicas, Transporte y Medio Ambiente (IGME-MOPTMA), 1996).

At the regional scale, the degree of mine water mineralisation indicated by the groundwater system of shafts
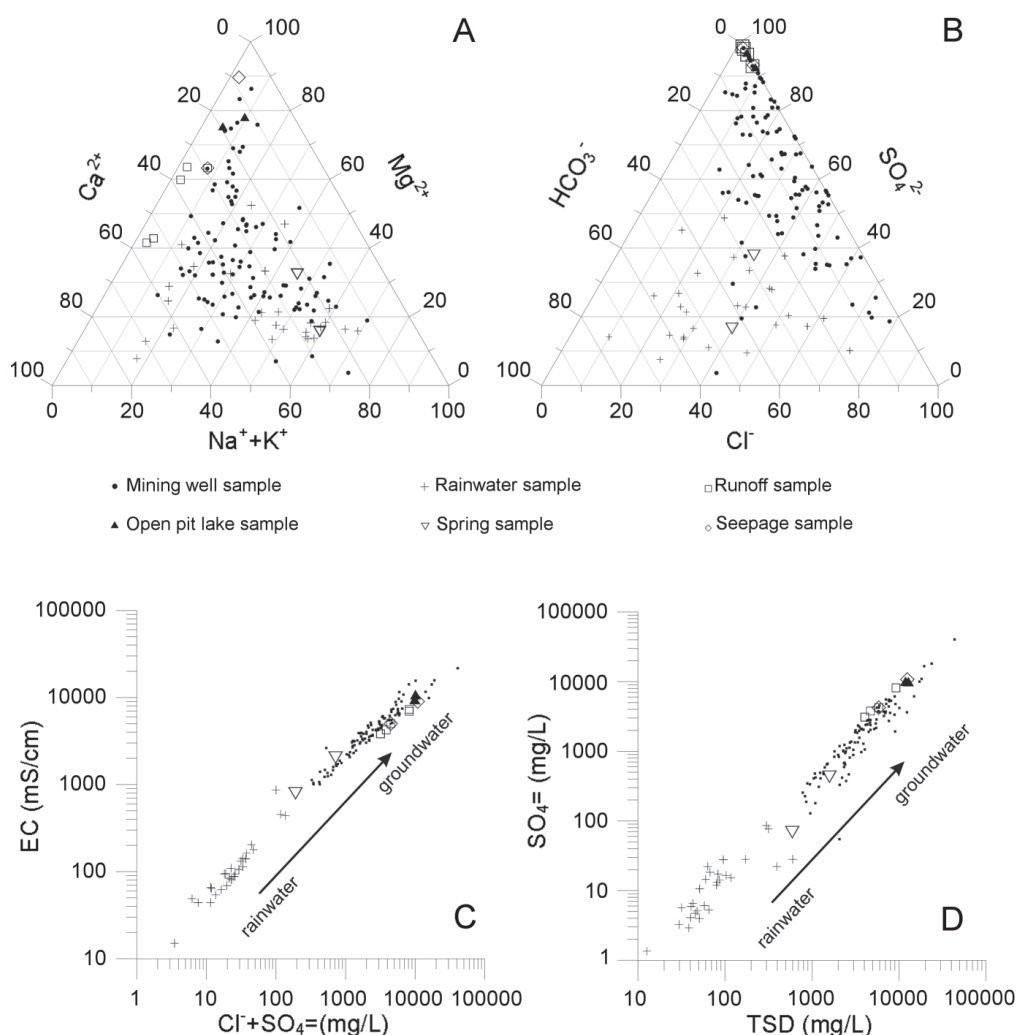

FIGURE 5 | **Major dissolved ionic constituents in the different sampled points: A, B) Ternary diagrams, concentration in meq/L; C, D) Sources of EC (mg/L) and TDS (mg/L) in the sampled water.**
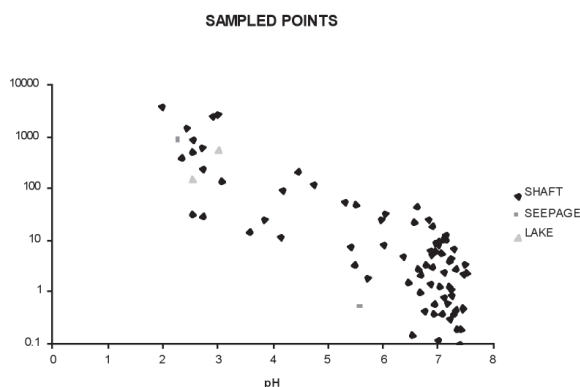
FIGURE 6 | **Flicklin diagram. Spring values are out of the plot range due to low mineralization.**

and seepages chemistry, shows important differences depending on their spatial location and host rock. Largest values are associated with schist and phyllites. In the shaft samples (Table 1), the important values of standard deviation clearly indicate heterogeneity of groundwater chemistry. Most of water samples present an acidic pH, lower than 5.5 (21% of the samples). Sulphate is always the dominant anion, while Mg^{2+}, Ca^{2+}, and Na^+ constitute the most representative cations originating from dolostones, limestones and silicates. The presence of Fe and Mn at detectable concentration indicates that anoxic conditions must prevail in the majority of shafts. Heavy metal concentration in shafts follows the sequence: Zn > Mn > Fe > Cd > Ni > Sr > Pb with values ranging between several orders of magnitude. Mn, which is present in almost all samples, ranges from below detection limit up to 436 mg/L. Maximum concentration of Zn in shafts was 4,100 mg/L, while the average is 152 mg/L (Table 1; Fig. 5). Variability of Mn and Zn concentration in samples from shafts illustrates the heterogeneity of flow paths produced by underground mining.

Seepages constitute a slow, regional groundwater system outflow through underground workings (adits). Concentration of major ions and heavy metals in the two sampled seepages is controlled by pH, where the Lilian seepage has the highest TDS (12,429 mg/L) and the lowest pH (2.3). Spring water samples present the lowest TDS and EC values of mine water. Measured pH values are neutral and heavy metal concentration was under detec-

tion limit, except for Fe and Mn. Nevertheless, physico-chemical characteristics of water depend on the spatial location of the sampled point. La Fuente spring, located at the northernmost part of the study area, tends to have the lowest ion concentration (see Fig. 2), which represents the rapid and shallow groundwater flow mostly originated from direct rainfall infiltration and with small residence time. This assumption is also supported by its tritium content (4.25 UT).

Calculated saturation indexes of waters of the four selected mine shafts using PHREEQC code show that water is generally subsaturated with respect to almost all possible mineral phases at the pH range existing in the study area (1.9-7.8) (Table 2). Anoxic conditions are always present (except in C721). When groundwater emerges to the surface, where oxidising conditions prevail, subsequent precipitation of metal oxides, hydroxides and oxy-hydroxides is produced (Sánchez-España et al., 2005). This fact is supported by field observations of ochre precipitates of oxide and hydroxides found in open-pits and seepages. Water with the lowest pH (C581 and C1659, Table 2) presents a magnesium sulphate facies, and both samples are in equilibrium with respect to gypsum ($CaSO_4$ x $2H_2O$). At pH 1.97 it is also in equilibrium with respect to $Fe(OH)_{2.7}Cl_3$, and at pH 2.72 saturation with respect to Fe oxides and hydroxy-sulphates occurs. As pH increases (5.49), water is in equilibrium with respect to SO_4Ca and $SrCO_3$, and is supersaturated with respect to Mn oxides and hydroxides. At basic pH (7.83) under sodium bicarbonate facies, water is supersaturated with respect to calcium and magnesium carbonate, Fe and Mn oxides and hydroxides, and Fe hydroxy-sulphates.

Spatial and temporal distribution of chloride and sulphate (groundwater hydrochemical characteristics)

In order to assess hydrochemical changes in the area, the spatial and temporal distribution of sulphate and chloride concentration was selected to be the most representative ions in water samples. Chloride ion was selected as it behaves conservatively and it does not interact with the media (Appelo and Postma, 2006), while sulphate is the best pollution indicator in a sulphide mining environment (Gray, 1996; Heikkinen et al., 2002). As it is depicted in Fig. 7, the spatial distribution of sulphate and chloride content in mine water seems to be conditioned by both

TABLE 2 | **Hydrochemical data of four selected shafts (C1659, C581, C490, C721).**

Shaft	EC (1)	pH	ALK (2)	Hard (2)	TDS (3)	HCO₃⁻ (3)	SO₄⁼ (3)	Cl⁻ (3)	NO₃⁻ (3)	Na⁺ (3)	K⁺ (3)	Ca²⁺ (3)	Mg²⁺ (3)	NH₄⁺ (3)	B (3)	Fe (3)	Mn (3)	Cd (3)	Ni (3)	Pb (3)	Sr (3)	Zn (3)
C1659	21700	1.9	0	8565	43600	0	40310	560	1.5	218	25	404	1835	0	5.8	2.7	106	8.0	2.4	nd	0.3	4093
C581	6580	2.7	0	3636	7636	0	5394	483	3.1	276	16	449	610	0.2	0.5	96	266	0.1	0.1	0.2	1.7	251
C490	5500	5.5	28	3482	5780	34	3757	542	0	364	20	487	550	1.0	0.5	nd	12	0.1	0.0	nd	3.4	50
C721	2630	7.8	855	514	2074	1042	55	474	0	213	80	53	93	1.1	0.3	1.1	2.1	nd	nd	nd	0.4	nd

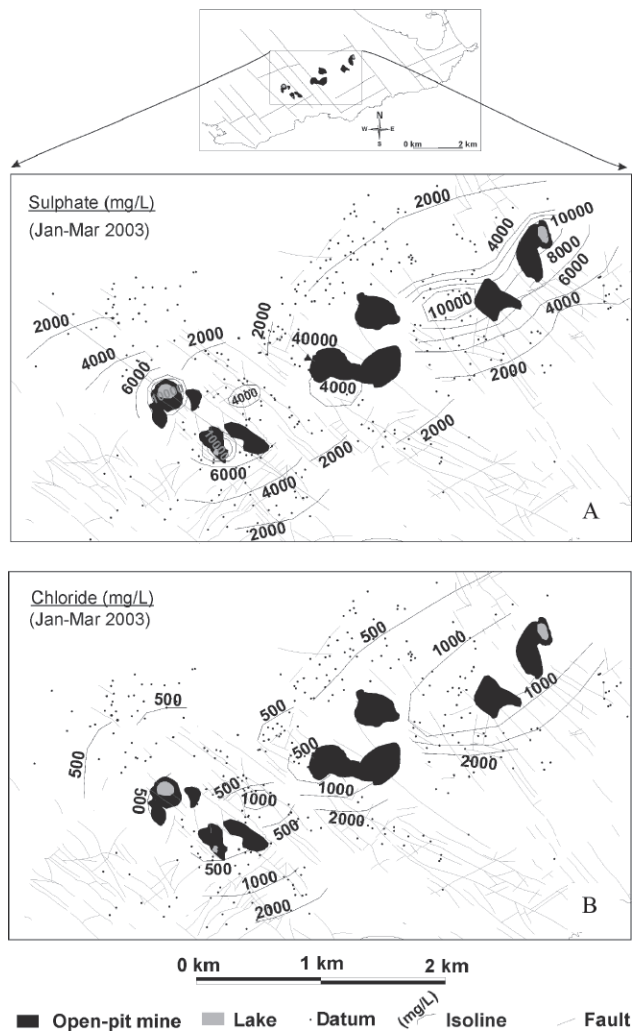nd: not detected; (1) (μS cm $^{-1}$); (2) (mg Ca CO₃ l⁻¹); (3) (mg l⁻¹)

FIGURE 7 | **Spatial distribution of concentration of A) sulphate and B) chloride in the study area.**

the tectonic fractures and the mining-induced fractures, as previously observed for the water level contour map (Fig. 2).

Maximum values of sulphate, up to 10,000 mg/L, correspond to the open pit-lake water and nearby shafts, where sulphide oxidation was probably promoted by mining activities during the final exploitation period (beginning of the 1990's). However, the high sulphate concentrations are probably partly due to sulphuric acid used in the milling process. Chloride content in the aquifer decreases from South to North being originated by atmospheric bulk deposition. The marked increase concentration in the downstream direction, south of the groundwater divide, could be the effect of the known (or unknown) sludge with seawater dump in the pits. Impacts from the Tomasa mine are still observed in some isolated shafts (10) located south of the divide. The important chloride concentration and the Na/K ratio between 0.02-0.025 clearly identifies its seawater origin.

In an attempt to evaluate the temporal evolution (referred to the 2003 field campaign) and spatial distribution of concentration of sulphate and chloride in groundwater, available data of both anions from shafts at different geographic areas of the study site have been represented. Representative and reliable data were obtained from the campaigns on 1977 (south western part), 1978 (northeast part), 1991 (eastern part), 1995 (western part), and 2005 (isotope sampling). The plot in Fig. 8 shows the sulphate and chloride concentration, referred to the 2003 values, in
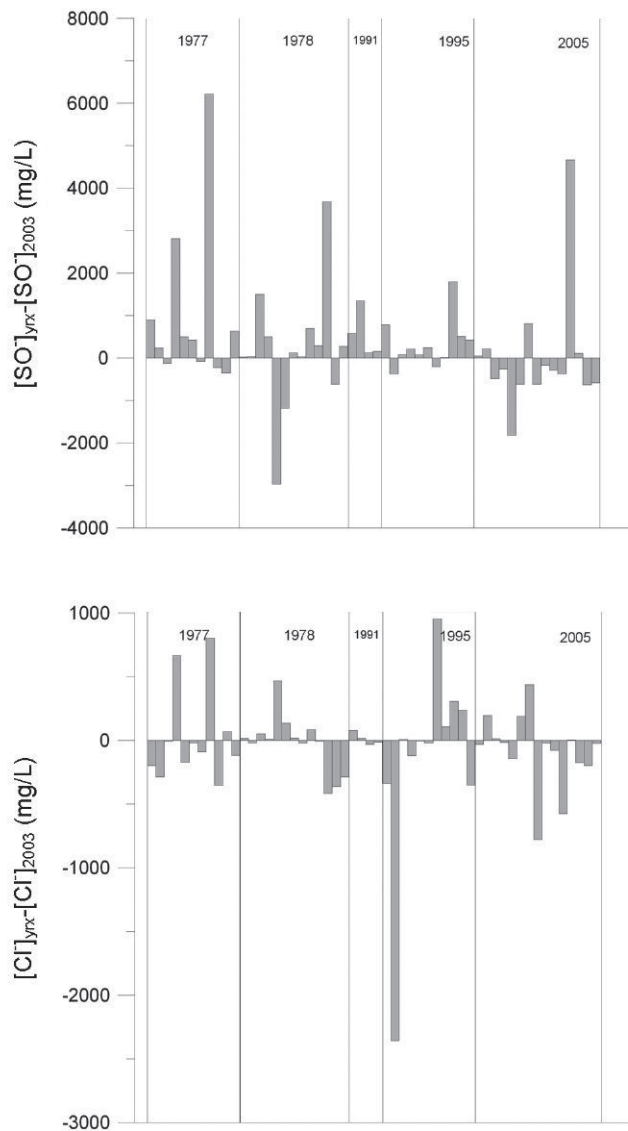

FIGURE 8 | **Sulphate and chloride concentration (referred to the 2003-2004 sampling campaign) in groundwater with time. Each vertical bar graph represents a sampled water point located at the south western (1977), north eastern (1978), eastern (1991), and western (1995) part of the study area. Data from IGME Instituto Geológico y Minero de España-Ministerio de Obras Públicas, Transporte y Medio Ambiente (IGME-MOPTMA), (1996) and unpublished reports (Carulla, 1977; Confederación Hidrográfica del Segura (CHS), 1991; García et al., 1978).**

shafts sampled over several years (1977, 1978, 1991, 1995 and 2005). The negative values of the plotted bars indicate a trend of sulphate concentration decrease with time over the aquifer. This is due to the dilution effect and the present saturated conditions of the main mineralization, which impairs sulphide oxidation and dissolution processes. Although the available records are fragmentary over time, a decrease in chloride concentration seems to occur in the northern part (1978) compared to other areas where no trend is observed.

SUMMARY AND CONCLUSIONS

Open-pit and underground mining activity in the Sierra de Cartagena-La Unión area has originated the occurrence of high concentrations of Zn, Pb, Ag and Fe yielding a metal-rich groundwater system and a modified natural landscape. Interpretation from geologic and tectonic settings, combined with groundwater field data and hydrochemical tools, has led a better understanding of the area and establishment of the conceptual model.

Data analysis revealed the aquifer system to be defined by five groundwater units of limited size formed along fracture zones. Nevertheless, North and South aquifer boundaries and hydraulic relationships with other units are difficult to establish and geophysical and geologic studies are still needed. Under undisturbed regime, the local groundwater flow would probably follow the natural South gradient to the Mediterranean Sea. At present, the contour map of groundwater level shows closed contours as in dome-shaped topography along pit-lakes; the local groundwater flow direction is both, north and south. Groundwater is controlled by fractures, joints and faults with limited to moderate interconnectedness. Piezometric surface presents similar pattern along time, supporting the aquifer conceptual model. It also indicates that presence of groundwater is not the result of precipitation storage in shafts and pits as reported in previous works. Based on fracturing lineaments and hydrochemical data, aquifer natural recharge that is geologic-structural controlled is mainly produced by direct rainwater percolation through fractures and shafts. Recharge is highly variable along space and time as assessed by chloride content in the sampled points and fracturing density. Being a semi-arid area, evaporative processes constitute an important percentage of the hydrologic budget. Due to the lack of data of aquifer discharge, especially in the Mediterranean Sea and Campo de Cartagena unit, estimation of the annual hydrologic budget presents an important degree of uncertainty.

The resulting different hydrochemical facies are due to water interaction with silicate, carbonate and sulphide minerals bearing deposits (pyrite, marcasite, galena, chalcopyrite and pyrotine). Oxidation of sulphide minerals caused by groundwater level fluctuations or rainwater infiltration through wastes and the unsaturated zone, and dissolution of weathering products along different flow pathways lead to elevated aqueous concentrations of sulphate, magnesium and manganese, acidic pH and high EC. The significant level of metals is favoured by the intense evaporative concentration in open-pit lakes. Over time, sulphate concentrations in groundwater tend to diminish due to the aquifer dilution effect and dissolution after groundwater rebound. Oxidation processes are not promoted as the major mineralisation outcrops in the saturated zone of the aquifer. Chloride content does not show a clear evolution along space and time. Although an adequate understanding of the regional system was provided, further detailed hydrochemical study is necessary to assess the undergoing geochemical changes in mine water.

ACKNOWLEDGMENTS

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