A geochemical and mineralogical study on the impact of acid mine drainage on the water quality of the Odiel River (Huelva, SW Spain)

Sánchez España Javier, López Pamo Enrique, Santofimia Pastor Esther, Reyes Andrés Jesús, Martín Rubí Juan Antonio.

Dirección de Recursos Minerales y Geoambiente.
Instituto Geológico y Minero de España.
Ríos Rosas, 23. 28003. Madrid. España.
E-mail: j.sanchez@igme.es
Keywords: AMD, metal pollution, ochreous precipitates, water quality, Odiel river

ABSTRACT
At 20 km from the riverhead, the Odiel river receives four discharges of acid mine drainage emanating from Concepción, San Platón, Esperanza and Poderosa-El Soldado mines. Two field studies performed in October 2003 and May 2004 showed that these acidic waters (0.2-8.5 L/s, pH 2.3-2.8) transfer to the Odiel river (pH=7-8.3, 220-1,000 L/s) significant quantities of acidity and dissolved metals (Fe, Al, Mn, Cu, Zn, Cd, Co and Ni). As far as the alkalinity of the river (108-155 mg/L $CaCO_3$ eq.) neutralizes the AMD-related acidity and causes the precipitation of Fe and Al in the form of ferrihydrite and Al-oxyhydroxides, the pH of the river remains near-neutral. These poorly crystallized minerals also retain, by sorption and/or coprecipitation, most trace metals (specially Cu and Zn). However, when the Odiel river converges with the acidic Tintillo river (pH=2.5-2.8, 48-240 L/s), the pH decreases to around 3 and the mineral paragenesis is then dominated by schwertmannite, which shows a very limited sorption capacity. Metal concentrations are then increased from near-zero to tens of mg/L (18 mg/L Fe, 76 mg/L Al, 14 mg/L Mn, 10 mg/L Cu, 20 mg/L Zn in May 2004) and the water quality of the river is thus irreversibly damaged.

INTRODUCTION
The water quality of the Odiel river (Huelva, Spain) is intensely affected by acid effluents from abandoned mines of the Iberian Pyrite Belt (IPB). These acidic emissions include seepage from waste-rock piles and tailings impoundments, as well as outflows from mine portals, mine holes and pit lakes (Sánchez España et al., 2005). Their composition and water flow are variable, but always contain high concentrations of dissolved metals (Fe, Al, Mn, Cu, Zn, Cd, Co, Ni), sulphate and acidity, which are finally transferred to the Odiel river, thus causing an important environmental impact. It has been estimated that 29% of the total length of water courses in the Odiel river basin (390 of 1,360 km) are polluted by AMD (Sánchez España et al., 2005). This mine-related contamination affects about 85% of the Odiel river course (104 of 122 km), and is evidenced by low pH (3.0 ± 0.5), and high metallic contents (specially Fe, Al, Mn, Cu and Zn, which are in the order of tens of mg/L).This paper has focused in a 9 km-long segment of the Odiel river, which is comprised between Concepción mine and the confluence with the Tintillo river (Fig. 1). Along this reach, the Odiel river receives the first acidic mine effluents coming from Concepción, San Platón, Esperanza, Poderosa and El Soldado mines, as well as the acidic discharge of the Tintillo river. After intersecting the Tintillo stream, the Odiel river is deeply transformed and irreversibly damaged, and the water quality remains affected until the river mouth in the Huelva estuary.

PROCEDURES
Field work was performed in October 2003 and May 2004 and included the sampling of the different acid mine effluents discharging to the Odiel river, collection of water samples from different sites along the Odiel river course, and sampling of ochreous precipitates from the river banks. Water and precipitate samples were taken upstream and downstream every AMD discharge along the studied reach (Fig. 1).Field parameters such as pH, redox potential (Eh), temperature (T), dissolved O_2 (DO), and electric conductivity (EC), were measured *in situ* with portable instruments properly calibrated. Flow rates were calculated in all cases using digital flow meters (GLOBAL WATER) in previously defined stream sections. Acidity, alkalinity and Fe(III)/Fe(II) iron concentrations were measured on site using digital titration methods.Major and trace metals in water samples were analyzed by AAS, ICP-AES and ICP-MS. Sulphate was gravimetrically measured as $BaSO_4$. Solid samples were analyzed by XRF and ICP-MS (after digestion with HNO_3 and H_2O_2). The solid samples were mineralogically characterized by powder XRD.

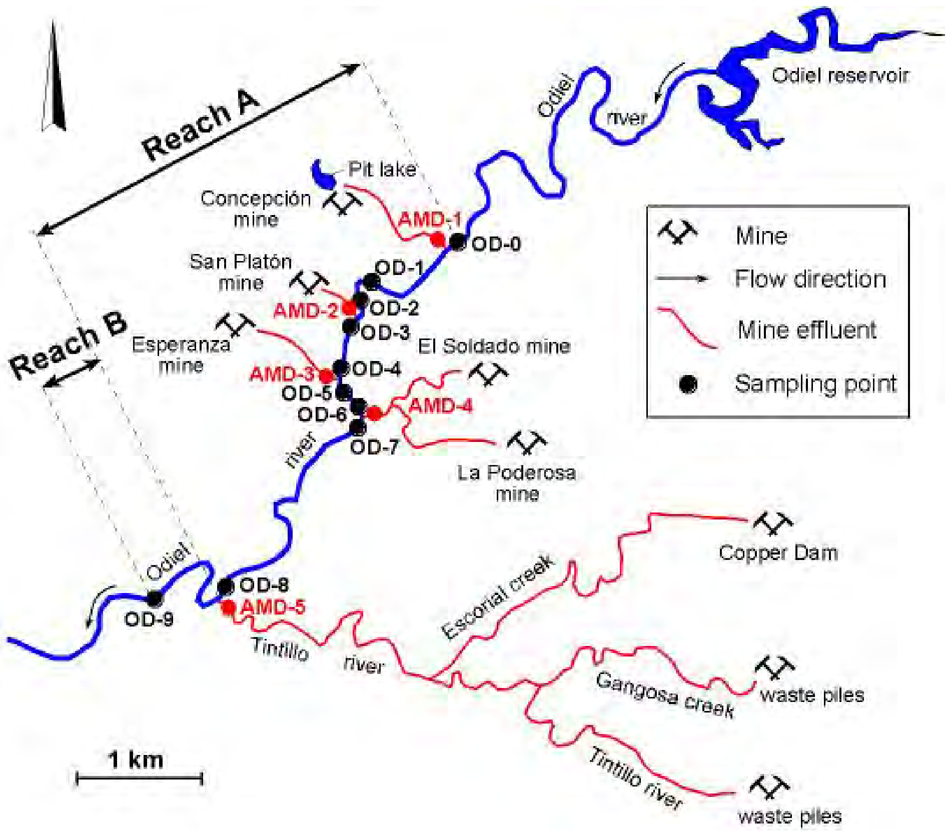

Figure 1: Hydrological configuration of the studied segment in the Odiel river.

RESULTS AND DISCUSSION

Mineralogy and chemistry of the AMD-related precipitates

The strong pH contrast between the mine effluents (pH 2.3-2.8) and the Odiel river (pH 7.0-8.3), provokes the precipitation of dissolved metals and the formation of a plume of ochreous to whitish precipitates which are either settled and accumulated in low-flow segments and/or transported downstream as particulate load. Before the Tintillo confluence, the precipitates formed in the water column from are mainly composed of ferryhidrite ($Fe_5HO_8 \cdot 4H_2O$). This mineral shows two broad peaks at around 34 and 62 º2θ Cu K□(1.51 and 2.54 Å, respectively; Fig. 2) and low S content (S=0.16-0.26%). On the other hand, the Fe(III) precipitating mineral after the confluence with the Tintillo river is schwertmannite ($Fe_8O_8(SO_4)(OH)_6$), which shows an XRD pattern with eight characteristic bands and a chemical composition of around 60% Fe_2O_3 and 5% S (with $(Fe/S)_{molar}$~5.0), which contrast with that of ferrihydrite (34-39% Fe_2O_3, $(Fe/S)_{molar}$=54-92; Table 1).

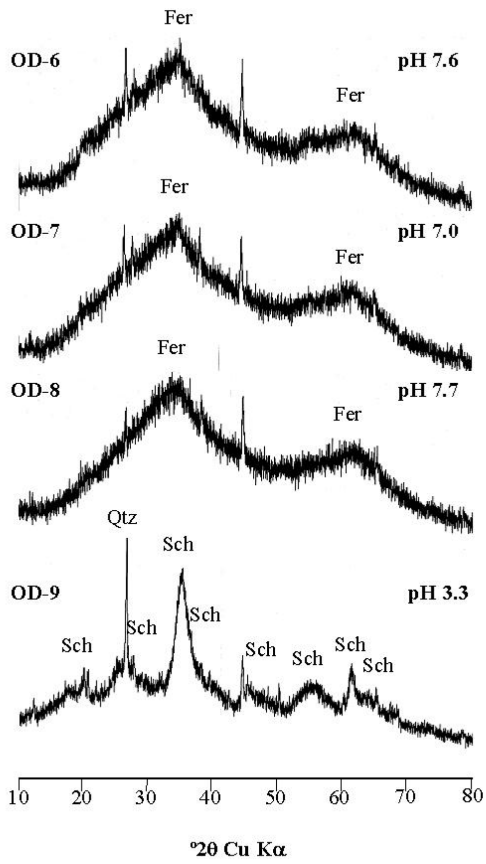

Figure 2: XRD profiles of selected mine drainage precipitates.

Sample Nº	Mineralogy		SiO_2	Al_2O_3	Fe_2O_3	CaO	LOI	S	Fe/S*	As	Ba	Cd	Co	Cu	Cr	Ni	Pb	V	Zn
OD-3	Fer	Al ox.	17.03	12.64	32.59	1.27	34.59	0.25	54.8	162	161	23	65	6,651	23	12	543	86	11,898
OD-4	Fer	Al ox.	13.73	12.71	34.02	1.53	34.88	0.18	79.4	179	186	28	84	7,602	20	14	60	92	16,114
OD-5	Fer	Al ox.	13.41	13.38	34.12	1.51	-	-		153	201	27	64	7,796	20	14	124	73	14,756
OD-6	Fer	Al ox.	13.54	13.41	35.19	1.26	35.08	0.16	92.4	188	170	35	71	8,668	21	13	87	77	21,096
OD-7	Fer	Al ox.	11.12	12.98	39.26	1.05	35.05	0.24	68.7	279	119	29	42	14,409	17	11	63	57	12,176
OD-8	Fer	Al ox.	17.00	9.59	36.09	1.35	34.17	0.26	58.3	236	180	31	79	11,772	20	20	77	39	11,735
OD-9	Schw	Qtz	2.91	1.89	60.36	0.48	39.54	5.09	5.0	168	11	6	15	496	30	7	17	7	706

Table 1: Mineralogical and chemical composition of selected precipitates along the studied reach. Fer, ferrihydrite; Al ox., Al oxyhydroxides; Schw, schwertmannite; Qtz, quartz; Major elements and S in %, trace metals in ppm.

Thus, the mineralogy of Fe(III) is modified as a response to changing geochemical conditions. From OD-0 to OD-8 (reach A in Fig. 1), the pH of the river is comprised between 7 and 8.3, and the redox potential (Eh) is always very constant and around 270 mV. After receiving the acidic waters of the Tintillo river, the pH-Eh conditions change drastically (pH 3.3, Eh 490 mV) and ferrihydrite is no longer stable. These results are in agreement with solubility calculations performed with the PHREEQC code, which predict saturation with respect to ferrihydrite in reach A, and undersaturation with respect to this mineral in reach B.

A number of Al (oxy)hydroxysulfate minerals are also stable under the pH conditions found in the Odiel river (e.g., basaluminite, hydrobasaluminite, aluminite, meta-aluminite, gibbsite; Nordstrom, 1982; Bigham and Nordstrom, 2000). The XRD patterns of Fig. 2 show no reflections characteristic of Al minerals, and the saturation indices predicted by PHREEQC for the Al minerals ($SI_{Basal}<0$, $SI_{Al(OH)_3}<0$, $SI_{Gib}>0$) suggest that the Al content present in the precipitates is probably a combination of nearly amorphous to cryptocrystalline gibbsite, and Al_2O_3 adsorbed by ferrihydrite.

Some co-precipitation of Fe(II) hydroxides ("*green rust*") along with ferrihydrite could have taken place near the Concepción discharge (pH 8.3), although precipitation of Fe(II) is considered to have been negligible along the rest of the segment. From a chemical perspective, the change in pH conditions leads to significant differences in trace metal concentration between the ferrihydrite formed at pH>7.0 and the schwertmannite precipitated at pH 3.3 (Table 1). This is especially true for Cu (6,651-14,409 ppm in ferrihydrite, 496 ppm in schwertmannite) and Zn (11,735-21,096 ppm in ferrihydrite, 706 ppm in schwertmannite), although these differences are also noticeable for other metals such as Pb, Cd, V, Co and Ba. In consequence, the hydrous Fe(III) oxides formed in the Odiel river show very distinct sorption capacity between the upstream and downstream sites of the Tintillo confluence. At circumneutral pH, ferrihydrite and the Al-oxihydroxides present negatively charged surfaces and sorb nearly 100% of dissolved metals like Cu, Zn, Cd, Pb, Ni and others. Conversely, schwertmannite formed under pH 3.3 shows a limited sorption capacity due to its net positively charged surfaces. On the other hand, the metals which can be present in the acidic solutions as oxyanions ($SeO_4^{=}$, VO_4^{3-} or $CrO_4^{=}$; Smith, 1999; Bigham and Nordstrom, 2000) should be more intensely sorbed in schwertmannite under pH 3.3 than in the ferrihydrite and Al-oxyhydroxides at pH>7.

Evolution of water chemistry

The aqueous metal concentrations of the Odiel river are not significantly increased during reach A. The four AMD discharges received by the Odiel river invariably contain high concentrations of metals and acidity (Table 2). However, the flow rate of the acidic effluents is very low. Therefore, metal concentrations are strongly diluted, the acidity of the effluents is neutralized, and the water pH is maintained around 7.5-8.3 (Figs. 3A-B). Both Fe(III) and Al are rapidly hydrolyzed and precipitated (as ferrihydrite and Al-oxyhydroxides), forming large plumes of colloids which are transported downstream and/or sedimented in the river banks. These precipitates provoke the virtually total loss of dissolved Fe and Al along the OD-0 to OD-8 segment, but also retain, by sorption and/or coprecipitation, large amounts of trace elements like As and Pb (92 and 99% sorption respectively in October 2003), and metals like Cu, Mn and Zn (respective losses of 80%, 82% and 50% in May 2004). Other elements like Na, K, Ca, and Mg behave as conservative.

Sample Nº	Description	Q	pH	EC	SO_4	Na	K	Ca	Mg	Mn	Fe	Al	Cu	Zn	Alkalinity
Units		L/s		µS/cm	g/L					mg/L					*mg/L*
Odiel river															
OD-0	Before mines	1,000	8.3	257	0.11	1.17	11.91	28.20	11.33	0.02	0.25	0.09	0.05	0.01	108
OD-1	After Concepción	1,008	7.5	269	0.09	1.16	11.83	27.53	12.38	0.16	0.04	0.15	0.04	0.07	96
OD-4	After San Platón	1,011	7.6	285	0.11	1.28	11.81	28.06	12.65	0.20	1.02	0.11	0.07	0.43	83
OD-6	After Esperanza	1,013	7.6	273	0.10	1.22	11.92	27.80	12.72	0.12	1.47	0.17	0.10	0.45	82
OD-8	After Poderosa	1,027	7.7	282	0.10	1.20	12.06	29.14	12.72	0.22	0.05	0.11	0.07	0.40	64
OD-9	After Tintillo	1,265	3.3	1,670	1.25	1.45	17.97	48.34	116.84	14.01	18.31	76.29	10.11	20.60	0
															Acidity
AMDs															*mg/L*
AMD-1	Concepción	8	2.7	1,850	1.27	1.24	15.89	30.75	53.43	85.83	200	60.43	21.31	52.30	990
AMD-2	San Platón	0.5	2.8	5,700	5.97	3.49	27.71	147.71	194	54.5	1,750	219.73	12.30	30.29	5,050
AMD-3	Esperanza	2	2.5	2,820	7.53	1.92	28.38	93.32	123	64.43	195	79.35	15.60	39.75	1,360
AMD-4	Poderosa	8.5	2.5	2,400	1.88	3.28	17.41	41.90	46	52.73	412	73.85	12.85	31.89	1,750
AMD-5	Tintillo river	238	2.8	6,730	7.53	2.87	49.59	131.19	760	41.48	430	75.07	9.12	22.20	6,900

Table 2: Aqueous composition of the Odiel river and the mine effluents. Data from May 2004

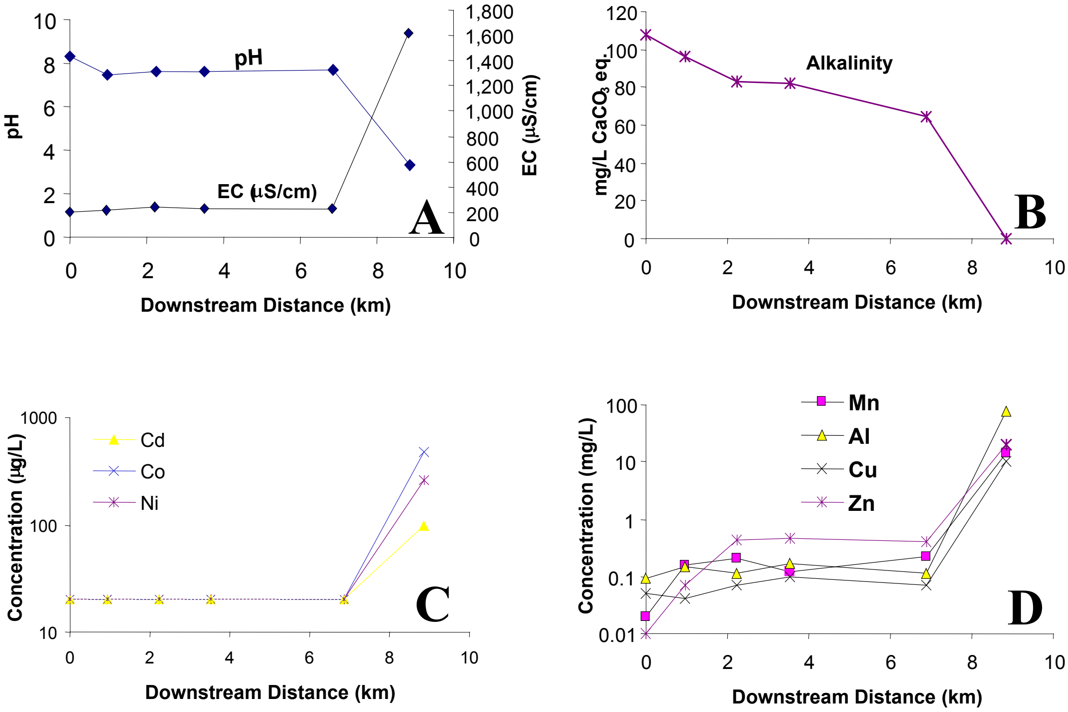

Figure 3: Downstream evolution of pH, electric conductivity (EC), alkalinity and metal concentrations. Data from May 2004.

The confluence with the Tintillo river represents, however, a dramatic change for the water quality of the Odiel river (Fig. 3). The flow rate of this acidic river (48 L/s in October 2003 and 238 L/s in May 2004) is much more important than those of the small AMD discharges received by the Odiel river before this confluence. The acidity load transported by the Tintillo river (5,912 Kg/h $CaCO_3$ eq. for sample AMD-5) is overwhelmingly high when compared with the alkalinity load of the Odiel (236 Kg/h $CaCO_3$ eq. for sample OD-8). Therefore, the alkalinity of the Odiel is totally consumed at the mixing zone, and the remaining acidity load of the Tintillo river is transfered to the Odiel river, thus causing a pH decrease down to 3.3.

Under the new pH conditions, ferrihydrite and the Al-oxyhydroxides are not stable and tend to be re-dissolved. The re-dissolution of the colloids formed in reach A and transported downstream as particulate load implies not only the re-incorporation of Fe and Al to the aqueous solution, but also the desorption of trace metals (e.g., Cu, Zn, Mn, Cd) from the mineral surfaces (Smith, 1999). Further, the precipitates accumulated during months as recent sediments in the river banks in reach B, would actuate as a continous input of dissolved metals to the aqueous solution. Iron seems to be rapidly re-precipitated in the form of schwertmannite. However, more soluble metals like Al, Mn, Cu and Zn should be partly (or totally) removed from the solid to the aqueous phase. Also, most of the sulphate and metal loads of the Tintillo river (which do not precipitate in segment B) are incorporated to the aqueous phase of the Odiel river course. Thus, the concentrations of most metals (especially Al, Mn, Cu and Zn, but also Cd, Co and Ni), sulphate and acidity are sharply increased (Fig. 3), and the water quality is strongly impacted and exceeding the existing standards for drinking and irrigation water (e.g., 50 □g/L for As, Cu, Pb, Mn and Cr, 5 □g/L for Cd, 3 mg/L for Zn, 0.3 mg/L for Fe; *EU Council Directive 75/440/EEC of 16 June 1975*).

Beyond the OD-9 point, the Odiel river presents a constant pH around 3.3 and is close to equilibrium with respect to schwertmannite (SI~0). Further, the hydrolysis of Fe(III) acts as a strong chemical buffer, as it releases free H^+ ions when the pH is locally increased by dilution with other streams, and the water pH remains essentially constant. In consequence, despite the Odiel river is subsequently diluted with waters from the Olivargas (pH~7), Oraque (pH~3-4) and Meca (pH~4-4.5) rivers, the pH at Gibraleón (50 km downstream from OD-9) remains around 3.0±0.5. During the summer (when very little dilution occurs), metal concentrations are usually rather constant. This statement is supported by chemical analyses conducted in the Odiel river, where average metal contents of 16 mg/L Fe, 12 mg/L Mn, 7 mg/L Cu, 20 mg/L Zn and 66 □g/L Cd are usually measured in Gibraleón (Confederación Hidrográfica del Guadiana, *unpublished data*).

Evolution of the sulphate and metal loadings

In order to illustrate the significance of the AMD-related pollution to the water quality of the Odiel river, the loadings of sulphate and selected metals (Fe, Al, Mn, Cu and Zn) being daily discharged by the mine drainage systems to the Odiel river in October 2003 are summarized in Table 3. Overall, these data indicate an average daily input of around 50 tons of sulphate, 3 tons of Fe, and 2.9 tons of Al, in addition to 665 Kg of Mn, 489 Kg of Cu and 910 Kg of Zn. With these average data into consideration, the four small AMD discharges received by the Odiel river along reach A, plus the discharge of the Tintillo river along reach B, represent an average yearly input of about 18,000 tons of $SO_4^{=}$, 1,100 tons of Fe, 1,000 tons of Al, 240 tons of Mn, 180 tons of Cu and 330 tons of Zn. These metal loadings can be transported either as dissolved load (specially Al, Mn, Cu and Zn) and/or as particulate load (mostly Fe). The particulated material (essentially schwertmannite and/or ferrihydrite) can be transported downstream as colloids suspended in the water column and/or sedimented on the river banks. In the latter case, these chemical sediments may act as a temporal store of Fe and acidity which are readily incorporated to the aqueous solution during high flow conditions.

Sample Nº	Description	Q	pH	EC	SO_4	Fe	Al	Mn	Cu	Zn
		L/s		µS/cm	Kg/day					
AMD-1	Concepción	7.0	2.7	2,490	786	160	44	4	2	4
AMD-2	San Platón	0.2	2.8	5,530	102	34	4	0.2	0.5	4
AMD-3	Esperanza	0.6	2.3	4,250	159	17	7	0.3	0.8	0.8
AMD-4	Poderosa	1.4	2.5	3,480	426	118	19	1.2	8	6
Total metal loads Reach A					**1,473**	**329**	**74**	**6**	**11**	**15**
AMD-5	Tintillo river	48	2.55	8,660	48,025	2,751	2,811	659	478	895
Total metal loads Reach A + Reach B					**49,498**	**3,080**	**2,885**	**665**	**489**	**910**

Table 3: Daily loadings of sulphate and selected metals (in Kg/day) transferred by the different AMD discharges to the Odiel river along reaches A and B. Data from October 2003.

Seasonal variations of the water quality evolution

The evolution in water chemistry and precipitate mineralogy depends on the Odiel to AMD water volume ratio. This variation results from the fact that the mine effluents are basically formed by groundwater outflows emanating from mine portals, and these flows are volumetrically more constant than the surface water courses. For example, the water flow of the Odiel river can be in the order of several cubic meters per second in winter, and as low as 60 L/s in summer, whereas the variations in flow rate of the mine effluents is much less important.

Comparing data from May 2004 with data from October 2003, the flow rate of the acidic emissions varied from 0.5 to 0.2 L/s in San Platón, from 8 to 7 L/s in Concepción, from 2 to 0.6 L/s in Esperanza, from 8.5 to 1.4 L/s in Poderosa-El Soldado, and from 238 to 48 L/s in the Tintillo river. The flow ratio between the Odiel and Tintillo rivers ([Flow $rate_{Odiel}$]/[Flow $rate_{Tintillo}$]) was 4.6 in October 2003 and 4.3 in May 2004, although based on different studies conducted along 2003 and 2004, the average flow ratio has been calculated to be around 5.5. This average flow ratio is in perfect agreement with estimations based on the respective catchment areas and rainfall discharge for both rivers (26,500 Ha and 1,000 mm/year for the Odiel, 5,700 Ha and 800 mm/year for the Tintillo), which also indicate an average flow ratio of 5.7.

Seasonal changes in water flow result in pH variations along the Odiel water course and, therefore, the geochemical and mineralogical evolution can be notably different from the situation described for May 2004. Under low flow conditions (specially during the summer), the AMD volume being discharged to the Odiel river is quantitatively more important than during the winter, and the downstream evolution can be temporally distinct. As an example, in 26th September 2003, the pH of the Odiel river in OD-7 was 3.2. During a heavy rainfall episode, the pH increased to 4.6 in 1st October, and to 6.1 in 2nd October. The pH after the Odiel-Tintillo confluence increased accordingly from 2.1 to 2.9 during the same period.

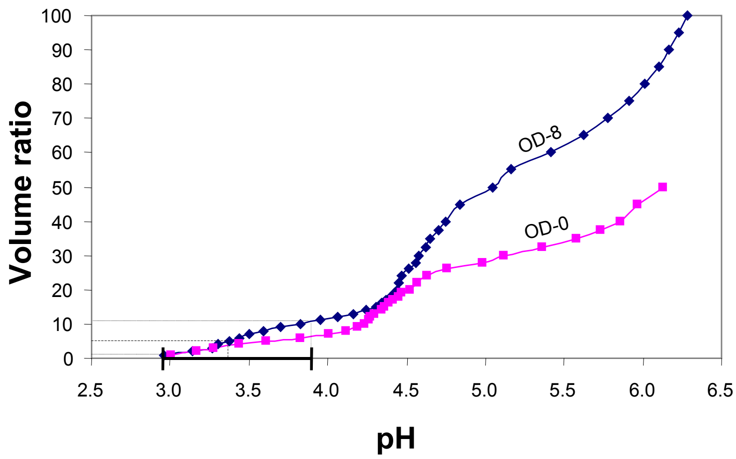

Figure 4: Titration curves for a water sample from the Tintillo river, which as progressively mixed with water from the Odiel river before (OD-0) and after (OD-8) the mining area. The black solid line represents the common pH range for the Odiel river.

Mixing modelling

An interesting approach to the variation of the Odiel water quality at different mixing proportions with the Tintillo river is given by experimental work in the laboratory. The results of several mixing experiments performed with water samples from both rivers are illustrated in Fig. 4. This figure represents a titration experiment conducted in May 2004. A progressive titration of the Tintillo river water (represented by sample AMD-5) with water from the Odiel river (exemplified by samples OD-8 and OD-0) was carried out with systematic pH measurement. These waters were aliquots of the samples described in Table 2.

A sharp slope brake of both titration curves in the 4.2-4.7 pH range indicates strong buffering of the aqueous solution by Al hydrolysis. Also, this experiment illustrates the effect that the small AMD discharges received by the Odiel river along reach A cause in the further evolution of the water quality. These acidic emissions decrease the alkalinity from 108 mg/L $CaCO_3$ eq. in OD-0 to 64 mg/L $CaCO_3$ eq. in OD-8 (Table 2, Fig. 3B). An immediate consequence of this alkalinity decrease is that the Odiel river presents a lower acid-neutralizing capacity and, consequently, undergoes a greater acidity and metal pollution, than in the case of a theoretical interaction with unaffected water. For example, from Fig. 4 it can be deduced that a proportion of around 45:1 would be required to obtain a final pH of 6.0 in the case of the OD-0 sample, whereas the volume ratio needed to obtain the same pH approaches 80:1 in the case of sample OD-8 (which represents the actual field conditions).

The minimum, average and maximum water flow ratios (as observed in the field) and the resulting pH values from such ratios, are also indicated in Fig. 4. The predicted pH value of 3.3 for the most common (average) water flow ratio of 4:1 compare very well with observations made by the authors during the last two years.

CONCLUSIONS AND OUTLOOK

The Odiel river receives the effluents emerging from the Concepción, San Platón, Esperanza, and Poderosa-El Soldado mines along a 7 km-long reach. Although metal and sulphate concentrations are not substantially increased, the water alkalinity is decreased to about a half of its initial value, and the precipitation of poorly crystallized secondary minerals (Fe and Al hydrous oxides) provokes a high turbidity and avoids the presence of aquatic life. The further interaction of the Odiel river with the highly acidic and metal-rich Tintillo river constitutes a critical point at which acidity and metal pollution are exponentially increased. Downstream from this confluence the pH of the Odiel river is buffered to around 3 ± 0.5 by the hydrolysis of Fe(III), so that dissolved metals like Fe, Al, Cu, Zn and Mn remain mostly in the aqueous phase during the rest of the course to the Huelva estuary.

This situation can be modified by seasonal changes in flow rate of the Odiel river and the mine effluents, although the ultimate effects for the Odiel river are rather constant and persist even at very high [Odiel]/[AMD] volume ratios.

ACKNOWLEDGEMENT

This project has been finantially supported with funds from CICYT project number REN2003-09590-C O4-04, and from Junta de Andalucía (Consejería de Innovación, Ciencia y Empresa).

REFERENCES

Bigham, J.M., Nordstrom, D.K., 2000. Iron and Aluminum Hydroxysulfates from Acid Sulfate Waters. In Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance (Alpers, C.N., Jambor, J.L., Nordstrom, D.K. (Eds.). Reviews in Mineralogy & Geochemistry, 40, 351-403.

Nordstrom, D.K., 1982. The effect of sulphate on aluminum concentrations in natural waters: some stability relations in the system Al_2O_3-SO_3-H_2O at 298 K. Geochim. Cosmochim. Acta, 46, 681-692.

Sánchez España, F.J., López Pamo, E., Santofimia, E., Aduvire, O., Reyes, J., Barettino, D., 2005. Acid Mine Drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): Geochemistry, Mineralogy and Environmental Implications. Applied Geochemistry, DOI: 10.1016/j.apgeochem.2005.01.011.

Smith, K.S., 1999. Metal sorption on mineral surfaces: an overview with examples relating to mineral deposits. In: Plumlee, G.S., and Losdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Rev. Econ. Geol., 6A, 161-182.