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Impact of Acid Mine Drainage on the hydrogeochemical characteristics of the Tinto-Odiel Estuary (SW Spain)

Impacto del drenaje ácido de mina en las características hidrogeoquímicas del estuario de los ríos Tinto y Odiel (SO España)

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Abstract

pH and chlorinity content of estuarine water and behavior in the concentration of some heavy metals characteristics of acid mine drainage in the suspended matter and dissolved phase have allowed the identification of two mixing process in the Odiel-Tinto rivers estuary: a salt-induced mixing typical of marine estuaries and an acid neutralization process as a result of the mixture of acid fluvial water coming from the drainage basins, which are affected by acid mine drainage (AMD). Thus, the estuary is divided into three zones: (1) zone with acid water and with precipitation of sulphate phases during the beginning of the process of neutralization in the absence of salt-induced mixing, (2) zone with pH values between 4.5 and 7 where a removal of heavy metals in their dissolved phase is produced by coexistence of both mixture processes, and (3) zone where water is slightly basic and the salt-induced mixing produces a redissolution of some elements. Spatial location and extent of these zones within the estuarine system have seasonal variations depending on the volume of fluvial discharge.

Keywords: Acid mine drainage, Acid and saline mixing, Tinto-Odiel estuary, hydrogeochemistry

Resumen

El contenido de pH y clorinidad de las aguas de estuario y el comportamiento en la concentración de algunos metales pesados característicos del drenaje ácido de mina en la materia suspendida y en la fase disuelta ha permitido la identificación de dos procesos de mezcla en el estuario de los ríos Tinto y Odiel: una mezcla sal inducida típica de estuarios marinos y procesos de neutralización como resultado de la mezcla de agua ácida fluvial procedente de cuencas de drenaje afectadas por drenaje ácido de mina (AMD). Así, el estuario es dividido en tres zonas: (1) zona con agua ácida y precipitación de sulfatos durante el comienzo del proceso de neutralización en ausencia de la zona de mezcla salina, (2) zona con valores de pH entre 4.5 y 7 donde la eliminación de los metales pesados en la fase disuelta es producida por la coexistencia de ambos procesos de mezcla y (3) zona donde el agua es ligeramente básica y la mezcla salada produce una redisolución de algunos elementos. La posición especial y extendida de estas zonas dentro del sistema estuarino tiene variaciones estacionales dependiendo del volumen de descarga fluvial.

Palabras clave: Drenaje ácido de mina, mezcla ácida y salina, estuario Tinto-Odiel, hidrogeoquímica

1. Introduction

Typically, the hydrochemical characteristics of estuary systems are defined by the mixing processes between masses of fresh water of fluvial origin and masses of salt water coming from the sea.

The hydrochemical markers of salinity and chlorinity concentrations (dissolved Cl^-), more often used to define zones of mixtures in these types of systems, to identify the degree of evolution of the salt-induced process between both masses of water.

The longitudinal variations of these indicators best characterize the intensity of the mixing process, as well as the behaviour of numerous elements such as nutrients, heavy metals, etc. dissolved in the system (Salomón and Fostner, 1984; Seigel, 2002), and changes in environmental conditions.

Inside the mouth of the Odiel and Tinto Rivers describe the typical salt-induced mixture process. Nevertheless, the peculiarity of this system rests in the character of the fluvial contributions received by both rivers from the drainage basins. The rivers are affected by acid mine drainage (AMD) and transmit to the system all the characteristics of these types of processes, e.g., acid waters ($pH<3$) with high heavy metal concentrations (Nelson and Lamothe, 1993; Sáinz *et al*., 2004; España *et al*., 2005).

The discharge in an estuarine system of a mass of fluvial fresh water with acidic character confers special hydrochemical characteristics to the water produced by the convergence of these two processes. The combined salt-induced mixture and acid neutralization will interfere specially with the behaviour of heavy metals and nutrients that are dissolved in the estuary.

The objective of this work is to determine the hydrochemical characteristics of an estuary affected by AMD by studying the seasonal behaviour and longitudinal distribution of the processes of acid and salt-induced mixing.

1.1. Regional Setting

Ría of Huelva is an estuarine system located in the northwest of the Gulf of Cadiz constituted by the mouths of the Tinto and Odiel rivers. This estuary has a strong tidal influence that controls the salt-induced mixture processes of masses of water. The tidal wave moves along the estuary following a hypersinchronic model with an average tidal range of 2.30 m, ranging between 1.63 m during a mean neap tide and 2.90 m in a mean spring tide (Borrego *et al.,* 1995).

Fluvial discharge in the estuary is markedly seasonal and with a great inter-annual irregularity. Usually, the average flow of both rivers is 49 hm^3/month during wet periods (October to March), and less than 5 hm^3/month during the driest months (may to September) (Borrego, 1992). Climate at this latitude is characterized as having a short and warm winter, when most annual rains take place, and warm and dry summers (Cánovas *et al*., 2007). During dry years (rainfall < 400 $mm.y^{-1}$), the average annual discharge of the Tinto river is $5.5x10^6$ $m^3.y^{-1}$ and $79x10^6$ $m^3.y^{-1}$ for the Odiel river, while in wet years (rainfall > 1200 $mm.y^{-1}$), the average values are $99x10^6$ $m^3.y^{-1}$ for the Tinto river and $1670x10^6$ $m^3.y^{-1}$ for the Odiel river (Sáinz *et al*., 2004; in López-González, 2009).

The fluvial basin of these rivers lies, to a great extent, over Paleozoic materials and, more specifically, on formations of the so-called volcano-sedimentary complex, where some of the most important sulfide mineralized masses in Europe can be found. These ore deposits have been mined since at least 4500 B.P. (Leblanc *et al*., 2000). The natural alteration of these sulfide masses, together with the mining activity, has caused the secular pollution of the Tinto and Odiel Rivers, whose waters have high concentrations of heavy metals and extremely low (less than 3) pH values (Grande *et al.,* 2000).

Furthermore, since 1966, fertilizer factories, copper foundries, paper mills, as well as phosphogypsum deposits and plants for cleaning aggregates have been established along the margins of the Tinto and Odiel estuaries (Fig. 1). This industrial activity produces a large volume of effluents, such as phosphogypsum deposits, which find their way into the waters of the estuary and contribute to the already large quantities of heavy metals and nutrients that make this estuarine system one of the most polluted in Western Europe (Ruiz *et al.*, 1998; Grande *et al.*, 2000; Borrego *et al.*, 2002).

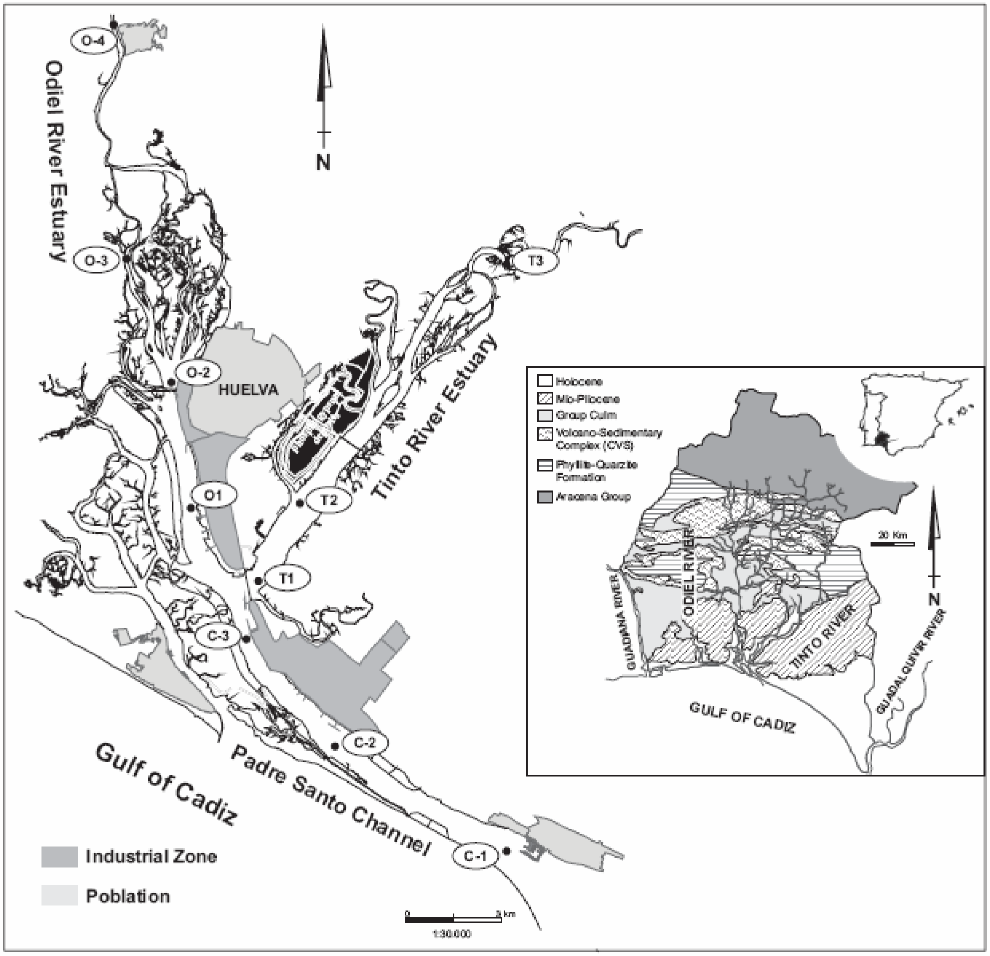

Fig. 1.- Geological setting of the Odiel-Tinto Rivers basins and local setting of the Odiel-Tinto Estuary with indication of sampling stations distributed within this system: in the Padre Santo Channel (C1 C2 and C3 stations) in the Odiel River estuary (O1 O2 O3 and O4 stations) and in the Tinto River estuary (T1 T2 and T3 stations).

Fig. 1.- Localización geológica de las cuencas de los ríos Tinto y Odiel y localización local del Estuario Odiel-Tinto con indicación de estaciones de muestreo distribuidas en este sistema: en el Canal del Padre Santo (estaciones C1 C2 y C3), en el estuario del río Odiel (estaciones O1 O2 O3 y O4) y en el estuario del río Tinto (estaciones T1 T2 y T3).

2. Materials and methods

To study this system, ten sampling stations have been distributed among this system: in the main channel, called Padre Santo Channel (C1, C2 and C3 stations), in the Odiel River estuary (O1, O2, O3 and O4 stations), and in the Tinto River estuary (T1, T2 and T3 stations) (Figure 1). Seven bi-monthly cruises were made from the years 2003 to 2004 to collect superficial water samples and to measure in situ the pH and conductivity values in the control stations. Water samples were collected in 1000 ml polypropylene bottles and filtered through Millipore membrane filters (0.45 µm pore size; 47 mm diameter). Thus, suspended matter samples (with size of particles superior to 0.45 µm) and filtered water samples were obtained. The latter were acidified to pH 2 with Merck supra pure HNO_3 and kept cool until analysis. The suspended matter samples were kept in filters; from each sample, 0.2 g of material was taken and subjected to a triacid attack for total extraction (HF-HCl-HNO_3).

Chemical analysis of the suspended matter samples and filtered water samples were made following the established protocol for these types of samples in the laboratories of the R&D Central Services of the University of Huelva. The concentration of cations was measured by optical emission spectroscopy of the plasma source connected by induction (ICP-MS, HP4500). External calibration was made with the multielemental solution SPEX 1, including periodically a control solution of 10 $\mu g.L^{-1}$ during the analysis. The detection limit was close to 0.01 $\mu g.L^{-1}$, with a precision greater than 5% RSD for all determinations.

The concentration of anions in the filtered water samples were determined by ion chromatography using a DIONEX DX120 machine fitted with an AS9-HC of 4x250 mm column (IonPac) and an ASRS ULTRAII suppressing membrane of 4 mm.

3. Results

The results obtained of the analyses are shown in the table 1 and are represented in the figures 2 and 3.

During the period of study, the pH values ranged from 2.7 to 8.2, showing high gradients in the mixture zones of both rivers (where pH varied between 3 and 7) (Table 1). On the contrary, the pH values in the Padre Santo Channel showed few variations, oscillating between 6.8 and 8.2 (Table 1).

In the mixing zone of the Tinto and Odiel Rivers, greater gradients in chlorinity were observed during winter, spring and autumn, in which the concentrations of dissolved Cl^- oscillate between 0.02 and 16 $g.L^{-1}$. Nevertheless at ebb tides, chlorinity values were uniform in all sampling stations distributed along the estuary, and these were higher than 12 $g.L^{-1}$ (Table 1). In summer, the temperature easily rises above 39ºC in the upper es-

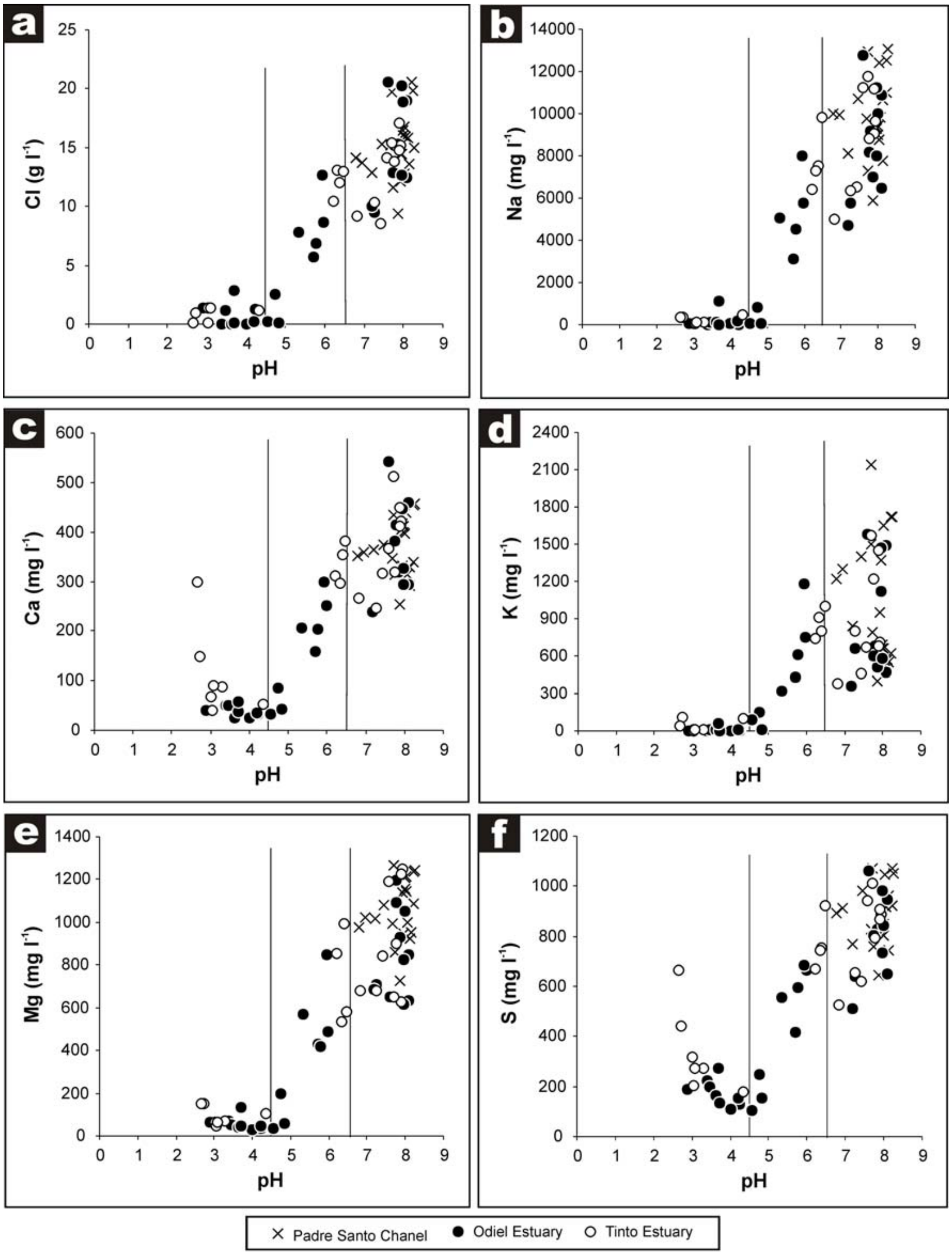

Fig. 2.- Bivariant plots of well-correlated Cl^- Na^+ Ca^{2+} K^+ Mg^{2+} and $SO_4^=$ *vs.* pH of the dissolved phase of estuarine water samples.

Fig. 2.- Gráfico bivariante de correlación de Cl^-, Na^+, Ca^{2+}, K^+, Mg^{2+} y $SO_4^=$ frente a pH en la fase disuelta de las muestras de agua del estuario.

Cruise	**Station**	**pH**	**Cl$^-$ (g.L^{-1})**	**Cu^{2+} (mg.L^{-1})**	**Zn^{2+} (mg.L^{-1})**	**Ca^{2+} (mg.L^{-1})**	**K$^+$ (mg.L^{-1})**	**Mg^{2+} (mg.L^{-1})**	**Na$^+$ (mg.L^{-1})**	**SO$_4^=$ (mg.L^{-1})**
Winter 2003	C1	7.9	14.5	0.5	0.2	405	951	1139	9284	867
Winter 2003	C2	7.7	11.6	0.5	0.3	313	792	863	7273	758
Winter 2003	C3	7.2	12.8	0.6	0.5	364	838	1014	8133	768
Winter 2003	O1	7.3	9.4	0.6	0.3	246	658	710	5748	640
Winter 2003	O2	5.7	5.7	0.8	0.9	158	427	429	3104	416
Winter 2003	O3	4.7	2.5	2.1	3.2	85.4	152	196	850	249
Winter 2003	O4	4.2	1.3	3.2	6.5	31.6	2.3	36.2	13	128
Winter 2003	T1	6.4	12	1.2	1	354	803	992	7526	753
Winter 2003	T2	6.2	10.4	1.3	1.2	310	738	852	6412	669
Winter 2003	T3	3.0	1.4	9.8	23	66.6	10.1	66.6	83	320
Spring 2003	C1	8.1	13.6	1.1	0.1	329	547	954	7772	741
Spring 2003	C2	8	12.8	1.3	0.2	398	656	1145	8766	805
Spring 2003	C3	7.9	9.4	0.8	0.2	254	402	724	5905	643
Spring 2003	O1	8.1	12.4	0.8	0.1	294	469	850	6459	647
Spring 2003	O2	7.2	10.1	0.7	0.5	238	360	686	4724	509
Spring 2003	O3	4.5	0.2	1.9	3.9	33.5	94.2	37.5	67.2	105
Spring 2003	O4	4	0.03	2.4	5.3	26.3	0.9	29.8	35.2	108
Spring 2003	T1	7.4	8.6	0.8	0.3	317	457	842	6553	620
Spring 2003	T2	6.8	9.2	0.8	0.5	265	379	680	5018	525
Spring 2003	T3	3.0	0.1	12.6	10.7	39.7	0.9	44.5	43.8	204
early summer 2003	C1	8	16.4	0.7	0.05	413	692	1209	9429	848
early summer 2003	C2	8	16	0.7	0.1	400	660	1158	9001	805
early summer 2003	C3	7.9	12.1	0.9	0.1	416	682	1220	9399	849
early summer 2003	O1	7.8	15.2	1.4	0.4	414	677	1196	9166	812
early summer 2003	O2	7.8	15.3	1.1	0.3	318	506	930	7006	829
early summer 2003	O3	7.7	12.9	1.7	1.4	381	595	1094	8185	804
early summer 2003	O4	3.4	0.05	2.8	5.9	49.6	0.9	69.5	3	221
early summer 2003	T1	7.9	15.2	1.8	0.4	422	709	1251	9626	888
early summer 2003	T2	7.9	14.8	2	0.2	411	681	1226	9059	869
early summer 2003	T3	2.7	0.9	7.3	9	149	108	149	336	444
later summer 2003	C1	8.3	14.9	2.2	0.1	458	1725	1241	13065	1053
later summer 2003	C2	8.2	20.5	2.2	0.1	454	1717	1239	12525	1069
later summer 2003	C3	8	16.8	2.5	0.1	439	1645	1216	12437	1045
later summer 2003	O1	8.1	19	1.8	0.1	459	1492	632	10866	946
later summer 2003	O2	7.9	20.3	1.8	0.2	448	1469	618	11225	983
later summer 2003	O3	7.6	20.6	1.9	0.5	543	1576	649	12757	1059
later summer 2003	O4	3.5	1.1	12	35.5	50.2	7.2	53.2	122.3	197
later summer 2003	T1	7.9	17.1	1.6	0.1	450	1452	629	11167	908
later summer 2003	T2	7.7	15.4	1.7	0.2	513	1569	649	11753	1013
later summer 2003	T3	4.3	1.1	11	4.7	252	95.5	102	453	178
Fall 2003	C1	7.4	15.3	1.5	1	374	1399	1080	10699	980
Fall 2003	C2	6.9	13.7	1.3	1	359	1296	1022	9914	913
Fall 2003	C3	6.8	14.2	1.4	1.5	352	1223	977	10017	890
Fall 2003	O1	6	8.6	0.9	2.6	251	751	489	5790	666
Fall 2003	O2	5.7	6.9	1.1	3.6	203	609	416	4546	595
Fall 2003	O3	4.2	0.2	11	27	34.1	12.2	45.8	164	153
Fall 2003	O4	3.6	0.05	20	49	24.9	5.2	39.5	117	163
Fall 2003	T1	6.3	13.1	0.9	1.8	295	909	535	7299	746
Fall 2003	T2	6.5	13	1.1	2.3	381	1003	581	9835	921
Fall 2003	T3	2.7	0.1	26.6	65.6	300	44.8	149	325	663
Winter 2004	C1	8.2	19.8	1.1	0.1	339	619	1084	11001	923
Winter 2004	C2	8.1	15.8	0.9	0.2	290	569	924	10619	962
Winter 2004	C3	8.1	16	0.8	0.2	313	561	997	9820	920
Winter 2004	O1	8	18.9	0.8	0.2	325	583	1050	9989	841
Winter 2004	O2	5.3	7.8	1.2	3	206	316	570	5058	555
Winter 2004	O3	4.8	0.1	5.5	4.2	43.2	6.7	57.6	60	155
Winter 2004	O4	3.7	0.1	13.5	35.1	38.7	3.7	48.4	20.1	134
Winter 2004	T1	7.6	14.1	0.9	0.4	366	668	1189	11252	943
Winter 2004	T2	nd	nd	nd	nd	nd	nd	nd	nd	nd
Winter 2004	T3	3.3		43.3	53.9	88.6	11.6	68.8	123	271
Spring 2004	C1	7.7	19.7	17	0.2	435	2136	1264	12953	1072
Spring 2004	C2	7.9	14.5	1.3	0.3	331	1372	945	9287	810
Spring 2004	C3	7.7	15.1	10	0.4	347	1503	995	9745	830
Spring 2004	O1	8	12.7	0.9	0.3	294	1122	826	8024	733
Spring 2004	O2	5.9	12.6	1	0.5	298	1184	849	7979	685
Spring 2004	O3	3.7	2.8	8	17.1	58.4	64.2	133	1095	274
Spring 2004	O4	2.9	1.4	16	36.9	39.7	4.6	62.3	84.6	190
Spring 2004	T1	7.8	13.8	1	0.5	320	1220	901	8820	793
Spring 2004	T2	7.3	10.3	0.7	0.9	247	799	680	6350	654
Spring 2004	T3	3.1	1.4	37	41.4	90.4	7.5	62.5	90	273

Table 1.- pH, Cl$^-$ (g.L^{-1}), Cu^{2+}, Zn^{2+}, Ca^{2+}, K$^+$, Mg^{2+}, Na$^+$ and SO$_4^=$ (mg.L^{-1}) in water samples of Odiel-Tinto Rivers Estuary.

Tabla 1.- Valores de pH y concentración de Cl$^-$ (g.L^{-1}), Cu^{2+}, Zn^{2+}, Ca^{2+}, K$^+$, Mg^{2+}, Na$^+$ y SO$_4^=$ (mg.L^{-1}) en las muestras de agua del estuario de los ríos Tinto y Odiel.

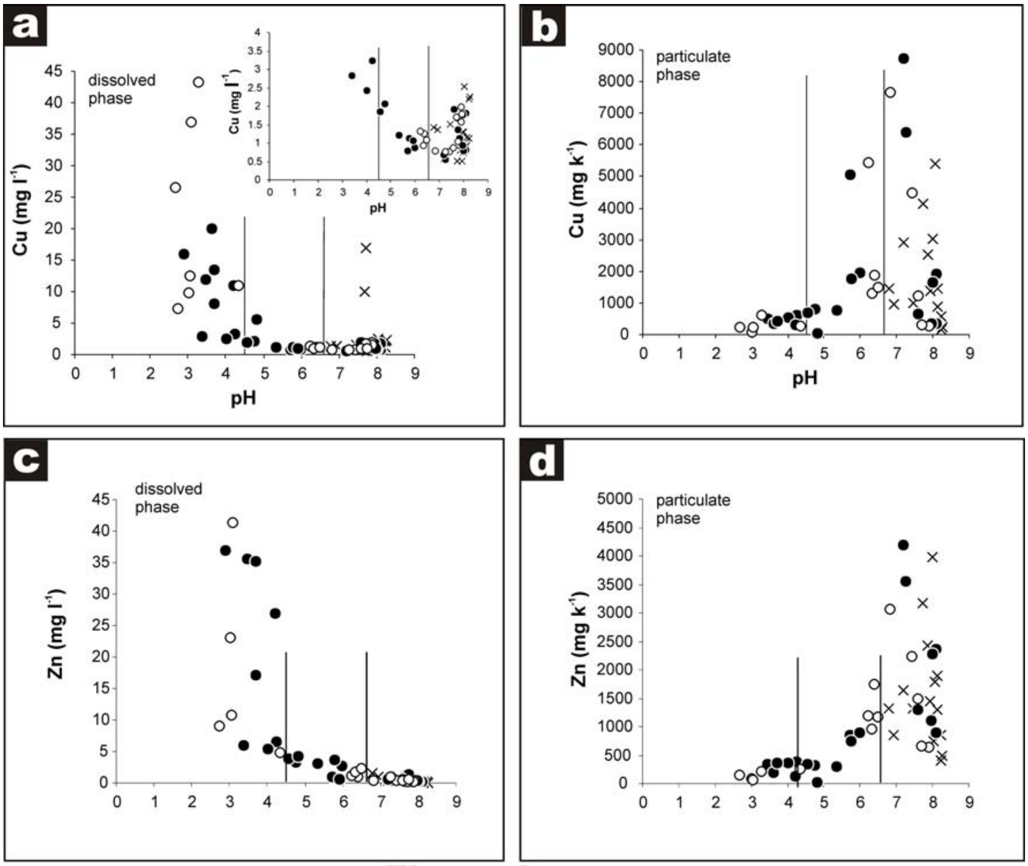

Fig. 3.- Relationships pH vs. Zn^{2+} and Cu^{2+} concentration in water samples: (a) dissolved Cu^{2+} vs. pH (b) particulate Cu^{2+} vs. pH (c) dissolved Zn^{2+} vs. pH and (d) particulate Zn^{2+} *vs*. pH.

Fig. 3.- Relaciones entre pH y concentración de Zn^{2+} y Cu^{2+} en las muestras de agua: (a) Cu^{2+} disuelto frente a pH (b) Cu^{2+} particulado frente a pH (c) Zn^{2+} disuelto frente a pH y (d) Zn^{2+} particulado frente a pH.

tuary zone, inducing intense evaporation of water (Borrego *et al*., 1995). Thus, greater chlorinity values can be observed in this sector than in the marine sector (Padre Santo Channel) where temperatures are smoothed.

4. Discussion

4.1. pH and Chlorinity of the Water

The most outstanding characteristic of the water in Ria of Huelva is the longitudinal variation of the pH values, which can be attributed to the mixing of acid water contributions from the Tinto and Odiel Rivers and the marine water introduced by the tide (Borrego *et al*., 2004).

The largest longitudinal variations in the pH values were observed during winter, spring and autumn, when the fluvial inputs were greater. Whereas during summer, the pH of the estuary was more uniform, with values higher than 6.5 in most of the stations, except for the O-4 and T-3 stations where the tidal influence was minor and the pH values were lower than 4 (Table 1). In this case, the low volume of fluvial contributions in summer allowed fast neutralizations of the acid water in the upper sector of the mixing zone of both rivers. It is necessary to point out that during periods of strong and abundant rains at the source of the Odiel and Tinto Rivers, the acid water inputs that reached the estuary gave rise to pH values lower than 7 in the Padre Santo Channel, as it happened in the autumn cruise of year 2003.

4.2. Relationship of pH Values to Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+} and $SO_4^=$ concentrations

As for the relationship between pH values and Cl^- and Na^+ concentrations dissolved in water (characteristic marine water elements), it was observed that when pH values were lower than 4.5, the concentrations of Cl^- and Na^+ did not exceed 4 and 1 mg.L^{-1}, respectively. Neither did these elements show a direct relation with pH of water (Figure 2a-b). These behaviours indicate that, during the first stages of neutralization of acid water, pH did not respond to an increase in the volume of seawater in the mixture and therefore was not related with the salt-induced mixture process. Likewise, the concentrations of Ca^{2+}, K^+ and Mg^{2+} dissolved in water did not display any response related to this increase of pH (Figure 2c-d-e), one reason why the neutralization of the fluvial water could not be related to the weathering of carbonates or aluminium silicates phases. Nevertheless, for equal range of acidity in estuarine water, an inverse relation of pH with the dissolved $SO_4^=$ concentration was observed (Figure 2f). This progressive loss of dissolved $SO_4^=$ took place via the precipitation of sulphated salts in the upper inter-tidal zones of the estuary (Borrego *et al*., 1995; Carro *et al*., 2006) (Figure 4).

At an advanced stage in the process of acid water neutralization inside the estuary (sectors with pH values between 4.5 and 6.5), a direct linear relation of pH with concentrations of dissolved Cl^-, Na^+, Mg^{2+}, Ca^{2+}, K^+ and $SO_4^=$ was observed. It is shown that the increase of pH in this sector was directly related to a process of dilution between the acid water coming from fluvial discharge and the marine water introduced by the tide in the system. These neutralization processes took place in the mixture zones of the Odiel and Tinto Rivers, between the sampling stations of O-1 and O-4, and T1 and T-3, respectively (Table 1).

Finally, when pH values in the system reached between 6.5 and 8, Cl^- and concentrations of Na^+ and $SO_4^=$ dissolved did not show any relation to pH and maintained relatively constant values in each sampling. Nevertheless, a significant variation in the concentrations of these elements dissolved in water was observed during the seven sampling cruises that were made. This increase of pH where values next to neutrality were reached did not seem to have a direct relation with the increase of the concentrations of dissolved Cl^-, Na^+ and $SO_4^=$. This same effect has been observed in previous work (Carro *et al*., 2006) and has been interpreted as the result of the mixing of estuarine water with water with greater concentrations of dissolved salt (respect to fluvial water) and with pH values near neutrality and slightly basic marine water. This mixing process was limited to the sector of the Padre Santo Channel where these levels of pH were reached.

4.3. Relationship of pH Values to Cu^{2+} and Zn^{2+} in the Water and in Particulate Suspended Matter (SPM)

Concentrations of dissolved Cu^{2+} and Zn^{2+} in the water of this estuary showed a decrease in pH of less than 4.5 (Figure 3a-c) not associated with the transference processes from the dissolved phase to the particulate one (SPM) since the concentrations of both metals in the SPM remained constant at this pH level. As explained previously, this removal of metals cannot be associated with the salt-induced mixture processes because it has a different level of pH values. However, it can be associated with decrease of dissolved $SO_4^=$ produced by the precipitation of sulphated salts by intense evaporation in the upper inter-tidal zones, because these salts work like a temporary warehouse of metals and atoms of hydrogen (acidity) (Cánovas *et al*., 2007).

In the acidity interval ranging from 4.5 and 7, concentrations of Cu^{2+} and Zn^{2+} in the dissolved phase also improved by a significant removal, wherein Cu^{2+} concentrations decreased from greater than 2000 µg.L^{-1} to concentrations lower than 550 µg.L^{-1}. Concentrations of Zn^{2+} went from 4000 µg.L^{-1} to 1500 µg.L^{-1}. In these cases, the removal of these metals in the dissolved phase can be explained by the coexistence of two processes. The first is a removal associated with a mixture process brought about by acid water dilution with tidal water (indicated

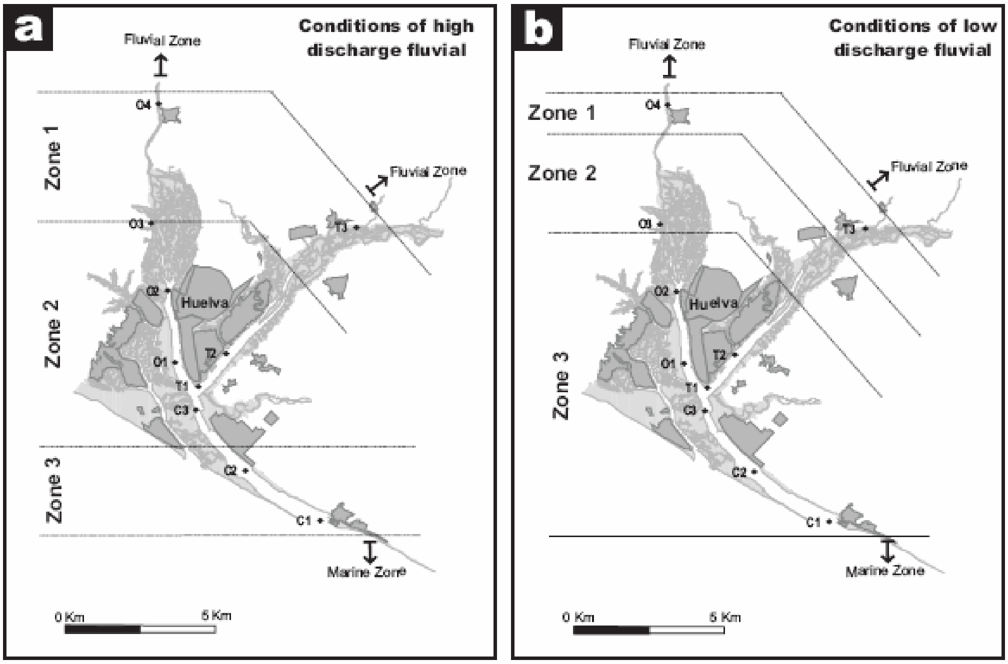

Fig. 4.- Spatial location and extent of zonation of the estuarine system affected by seasonal variations depending of volume of fluvial discharge: (a) Conditions of high discharge fluvial and (b) low discharge fluvial.

Fig. 4.- Localización especial y extensión de la zonación del sistema estuarino afectado por variaciones estacionales dependiendo del volumen de descarga fluvial (a) Condiciones de alta descarga fluvial y (b) Baja descarga fluvial.

by the reduction of Na^+ and Cl^- and an increase of pH). The second is by transfer of a fraction of Cu^{2+} and Zn^{2+} dissolved in water towards the SPM by sorption or coagulation (Turner and Millward, 2002; Braungardt *et al.,* 2003), since under this pH level, an important increase in the concentration of these metals in this phase was observed (Figure 3b-d).

4.4. Hydrochemical Zonation

Based on the mixture processes that occur in the estuary of Ria of Huelva, we have mapped out a hydrochemical zonation in the system.

Zone 1. In this sector, pH increases from the most typical acid values of acid fluvial water (from 2.4 to 3) to pH values of 4.5. The chlorinity does not rise above 3 $g.L^{-1}$, keeping relatively constant values during each one of the cruises. The same behaviour has been observed in the concentrations of dissolved Na^+, which in this zone does not exceed 2 $g.L^{-1}$. Concentration of dissolved S displays an inverse relation with the values of pH, reaching values lower than 0.2 $g.L^{-1}$ with lower pH values. One of the main characteristics of acid water derived from sulphide oxidation is the greater concentration of dissolved metals and sulphates in its composition. The process of neutralization of this water in the absence of salt-induced mixing gives rise to the precipitation of sulphates and therefore a fast removal of dissolved $SO_4^=$ and Cu^{2+}. The precipitated sulphates scavenge an important fraction of the concentration of some heavy metals transported by water in the dissolved phase (Cu^{2+}, Zn^{2+}, for example), since these sulphated salts are a temporary warehouse of heavy metals and atoms of hydrogen (acidity). Together with this process could be oxidation of Fe^{2+} to Fe^{3+}, which generates water and consumes acidity with the following reaction (Younger *et al*., 2002):

$$4\ Fe^{2+} + O_2 + 4\ H^+ \rightarrow 4\ Fe^{3+} + 2\ H_2O$$

The Fe^{3+} released could react with any other element and precipitate in the form of colloid, so that no hydrogenions would be released since the following reaction would be interrupted:

$$4\ Fe^{3+} + 8H_2O \rightarrow 4Fe(OH) + 12H^+$$

On the other hand, the existence of an anoxic environment in the river channel could also account for the lack of acidity generation.

Neutralization by mixing of water masses is not related to the weathering of carbonates or aluminium silicates in their mineral phases, as charts indicate the absence of any relation in the concentration of elements such as dissolved Ca^{2+}, Na^+, Mg^{2+} or K^+ versus pH values. Neither does this process show an effect of the dilution of marine water with pH values greater than 7, since this would typically give rise to an increase in the concentration of dissolved marine elements such as Cl^-, Na^+, Ca^{2+} and $SO_4^=$.

Zone 2. This zone is limited to pH values ranging between 4.5 and 7.5, and chlorine concentration with values between 3 and 15 $g.L^{-1}$. Both parameters have a lineal relation suggesting that neutralization in this sector is induced by the direct dilution of acid fluvial water and marine water with pH values greater than 7. The same behaviour that shows pH values and chlorinity also indicates that other dissolved elements that have been described, such as Na^+, Ca^{2+}, K^+, Mg^{2+} and $SO_4^=$, are contributed by dissolved salts in marine water.

During this mixing dilution, a noteworthy decrease in the concentrations of some dissolved heavy metals in fluvial water derived from acid mine drainage has been observed. This was the case of Cu^{2+} and Zn^{2+}, which had lower concentrations in the dissolved phase, from 1500 to 600 $\mu g.L^{-1}$ and, from 4000 to 1000 $\mu g.L^{-1}$ respectively. Likewise, a part of these dissolved metals is absorbed as solid particles that compose the SPM and cause a progressive increase of the concentration of these metals in this phase. This process has been observed in laboratory of neutralization of waterproof (Achterberg *et al*., 2003; España *et al*., 2006).

Zone 3. In this zone, pH values range from 7.5 to 8.2, and average increase of the dissolved concentrations of Cl^-, Na^+ and $SO_4^=$ occurs. In this sector, distribution of the concentration of heavy metals dissolved in water changes depending on chemical element. Whereas some elements such as dissolved Mn or Zn^{2+} experience a strong loss in concentration because of the dilution of estuarine water with water derived from the open sea, other elements such as dissolved Cu^{2+} or U increase in concentration. This event is caused by the remineralisation produced by saline shock, wherein a part of the concentration of the chemical element in its particulate phase is re-dissolved and transferred to the dissolved phase.

Spatial location and extent of these zones within the estuarine system are affected by seasonal variations depending on volume of fluvial discharge (Figure 4). Therefore, in dry season, there is a shift upstream of these areas, reducing considerably the area of Zone 1 and expanding Zone 3 (Figure 4b), while in periods with great fluvial discharge, there is an opposite effect (Figure 4a).

5. Conclusions

The hydrogeochemical characteristics of the water in an estuary where acid fluvial water and marine water are mixed allow us to define the intervention of two geochemical processes: a typical process of salt-induced mixing and a process of neutralization of acid water derived from AMD. The product of the convergence of these mixture processes will not only affect the behaviours of heavy metals and nutrients that form the system. It allows us to make a hydrochemical zonation of the estuary. The definition of these zones depends on the behaviour of pH values and chlorinity concentration of the water, as well as on the heavy metal concentrations in their dissolved and particulate phases.

The three zones are:

Zone 1. Sector with pH values that increase from 2.4 to 4.5, where chlorinity concentration of the water does not rise above 3 g.L^{-1}. In this zone, starting the neutralization process produces the precipitation of particulate sulphates, which scavenge an important fraction of the metal concentration that is transported in a dissolved phase by the acid water.

Zone 2. In this zone, pH and chlorinity have a direct relation (fluctuating from 4.5 to 7.5 and from 3 to 15 g.L^{-1}, respectively). This indicates that the neutralization process is induced by the dilution of the water derived from Zone 1 with salt water, which introduces dissolved elements (typically marine) into the mixture.

Zone 3. This zone is characterized by slightly basic pH water, where the salt-induced mixture process typical of estuarine systems takes place and some dissolved elements such as Cu^{2+} or U increase in concentration due to the remineralisation produced by saline shock.

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