THE UNESCO NATIONAL BIOSPHERE RESERVE (MARISMAS DEL ODIEL, SW SPAIN). AN AREA OF 18,875 HECTARES AFFECTED BY MINING WASTE.

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Abstract

At the mouth of the Odiel river, within the Natural Area "Marismas del Odiel", there has been for years a collection of waste from different mining sites. In the present work an approach has been made to the problem that this supposes, quantifying the pollutants that are poured into the estuary from the mineral collection located on the banks of the river. The study carried out has been able to determine high metal concentrations, comparable to any rubble from the upstream mines, with pH values of 1.66, lower than many other areas affected by Acid Mine Drainage in the same river, and even with concentrations of Fe and As higher than those provided by the rest of the mining facilities of the Odiel basin. This can make us understand the serious situation of the Natural Park, where a great variety of birds and plants of special ecological interest are located.

Keywords: Acid mine drainage, Biosphere Reserve, estuary, metal pollution, water quality, Odiel

1. Introduction

1.1. Acid mine drainage process.

The process of extracting iron sulphide ores (the most common is pyrite - FeS_2) involves a type of hydrogeochemical contamination known as Acid Mine Drainage (AMD). This process appears when pyrite is combined with oxygen in the presence of humidity, which in turn produces a reduction in the pH of the water, reaching values close to 2, an increase in the concentration of sulphate and an increase in the content of heavy metals and other harmful elements. (Lyew and Sheppard 2001; Grande et al. 2005a; de la Torre et al. 2010).

The production of acid leachate takes place in two phases (Grande (ed.) 2016): one of short duration due to rapid runoff, followed by another of variable duration due to slow runoff. Depending on the hydrological regime and the timing of rainfall, one phase or another will be more relevant. Thus, we can affirm that the pollution produced by leachate is the result of the combined action of a mechanism generating pollutants and another responsible for transporting them to the outside of the dump or mineral stockpile (Sainz et al. 2002).

The reactions that occur from the oxidation of pyrite (FeS_2) were explained by Singer and Stumm (1970) and Nordstrom and Alpers (1999):

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

If these reactions take place in a sufficiently oxidizing environment, many of the ferrous ions will change to ferric ions, a process in which acidity is consumed.(Eq. 2)

$$Fe^{2+} + 1/4\ O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \quad (2)$$

The oxidation process can take place in two ways: in a new pyrite, or when pH values below 3.5 are given in the medium and ferric ion (Fe^{3+}) can be found in solution. In this situation, Fe^{3+} hydrolyses and precipitates if the pH increases (Eq. 4) with an added drop in pH.

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{=} + 16H^+ \quad (3)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+ \quad (4)$$

Adding these basic and simplified reactions (Eq. 5), a global reaction is obtained that determines that for each gram of pyrite, approximately three grams of sulphuric acid are generated, which is a clear signal of the potential that this process has to acidify the receptor medium (Sarmiento 2007).

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_{3(s)} + 2SO_4^{2-} + 4H^+ \quad (5)$$

These chemical processes and the consequent pollution of water by these heavy metals, make them in most cases unusable for human consumption, and even for the survival of life in its habitat (Grande (ed.) 2016).

In very acidic waters, the oxidation of ferrous iron can be increased by acidophilic bacteria, such as Acidothiobacillus ferrooxidans, Leptospirillum ferrooxidans, etc., which act as catalysts for the oxidation of the ferrous ion (Leduc et al. 2002).Temperature and pH are two factors of control of the reaction speed very related to the bacterial activity. In general, maximum reaction performance occurs at medium and at high temperatures, between 15 and 35ºC (Blowes et al. 2003) and in a pH range between 2.5 and 3.5 (Sarmiento et al. 2007; Johnson et al. 2008), conditions that occur in a large area of the study area, which is already an indicative factor of how the AMD process affects the biota of the Natural Park.

1.2. Environmental implications

Severity of metal and metalloid contamination can be summarized in three (Grande et al. 2005b): (1) Unlike organic matter, metals are not biodegradable, so they remain in the contaminated environment indefinitely, except by transport processes to other means. (2) The metals, once the microorganisms and the microflora incorporate them, can be retained by the tissues, producing the phenomenon of bioaccumulation. Thus, concentration factors of 290,000 times for zinc, 100,000 times for lead and 35,000 times for copper have been found in accumulating organisms, which can be transmitted to other species located at a higher level of the trophic chain, producing the phenomenon known as biomagnification (Nebel et al. 1999). Through bioaccumulation and biomagnification, much higher values are achieved than those found in the liquid medium. (3) Metal precipitations cause toxic elements to be retained in sediments producing their contamination. Depending on environmental conditions (pH, salinity, redox potential, etc.) some of these elements are bioavailable and pose a major environmental problem when penetrating the trophic chain (e.g. Usero et al. 2004; Morillo et al. 2004; Nieto et al. 2007; Vicente-Martorell et al. 2008; Madejon et al. 2009).

Metals and metalloids, from the point of view of their influence in plant and animal physiology, can be classified as essential and non-essential. Thus, certain elements such as copper, zinc and manganese are essential micronutrients for plants and animals and only become lethal at high concentrations (Begon et al. 1999); the organism needs metals within an optimal range, below which deficiency states occur and above which toxicity.

Similarly, non-essential heavy metals have a value for each individual, below which it is tolerable and above which it is toxic (Sáinz et al. 2002).

2. Location setting.

2.1. Mining affecting the Odiel River Basin.

As it is well known, most of the mines of the Iberian Pyrite Belt (IPB) had already been exploited in Roman times (Pinedo 1963), initially silver was its main source of wealth.
As a result of the development of the chemical industry in the middle of the 18th century, the mining of the IPB suffers an important development, basically due to the growing demands of sulphur. As a consequence of this, from 1855 onwards a multitude of pyrite and manganese exploitations were reopened, which resulted in a great boost to the port of Huelva. Another important factor in the development of the exploitations of the zone was the impulse of the open pit mine, next to the advantage of metals contained in the pyrite, like copper, zinc, gold, silver, etc.

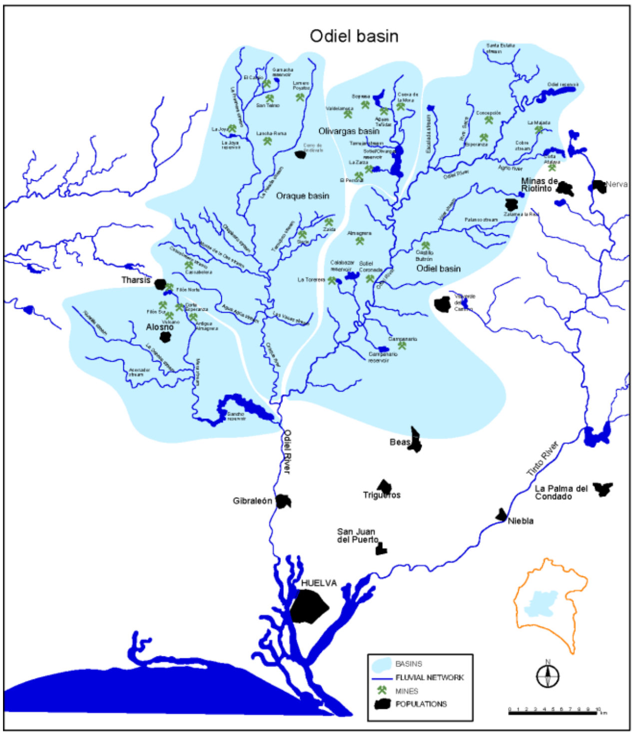


Fig. 1 Mining affecting the Odiel River Basin

During the first decades of the 20th century, the intensification of exploitation and the development of new techniques led to the replacement of the calcination system in the air with that of the canal, in which acid waste was discharged through pipes and ponds into rivers.
From 1982 onwards, the demand for pyrite fell substantially. This, together with the influence that environmental ideas were acquiring, gradually led to the closure of a multitude of installations. However, with the abandonment of the mines, the environmental problems associated with mining operations were maintained, as the polluting substances contained in the dumps and ponds continued to be discharged into the river network by infiltration, mainly during rainy periods.
Fig. 1 shows the Odiel river basin, indicating the position of its main tributaries and mining exploitations.

2.2. Marismas del Odiel Natural Park. Corrales Area.

The province of Huelva is one of the provinces with the greatest natural wealth in Spain, with a great diversity of ecosystems. There is an important number of protected natural spaces (almost 27% of the provincial surface), from the well-known Doñana National Park and the Natural Site of the Odiel Marshes (Fig. 2) on the coast, to the mountainous Mediterranean formations of the Sierra de Aracena and Picos de Aroche Natural Park.

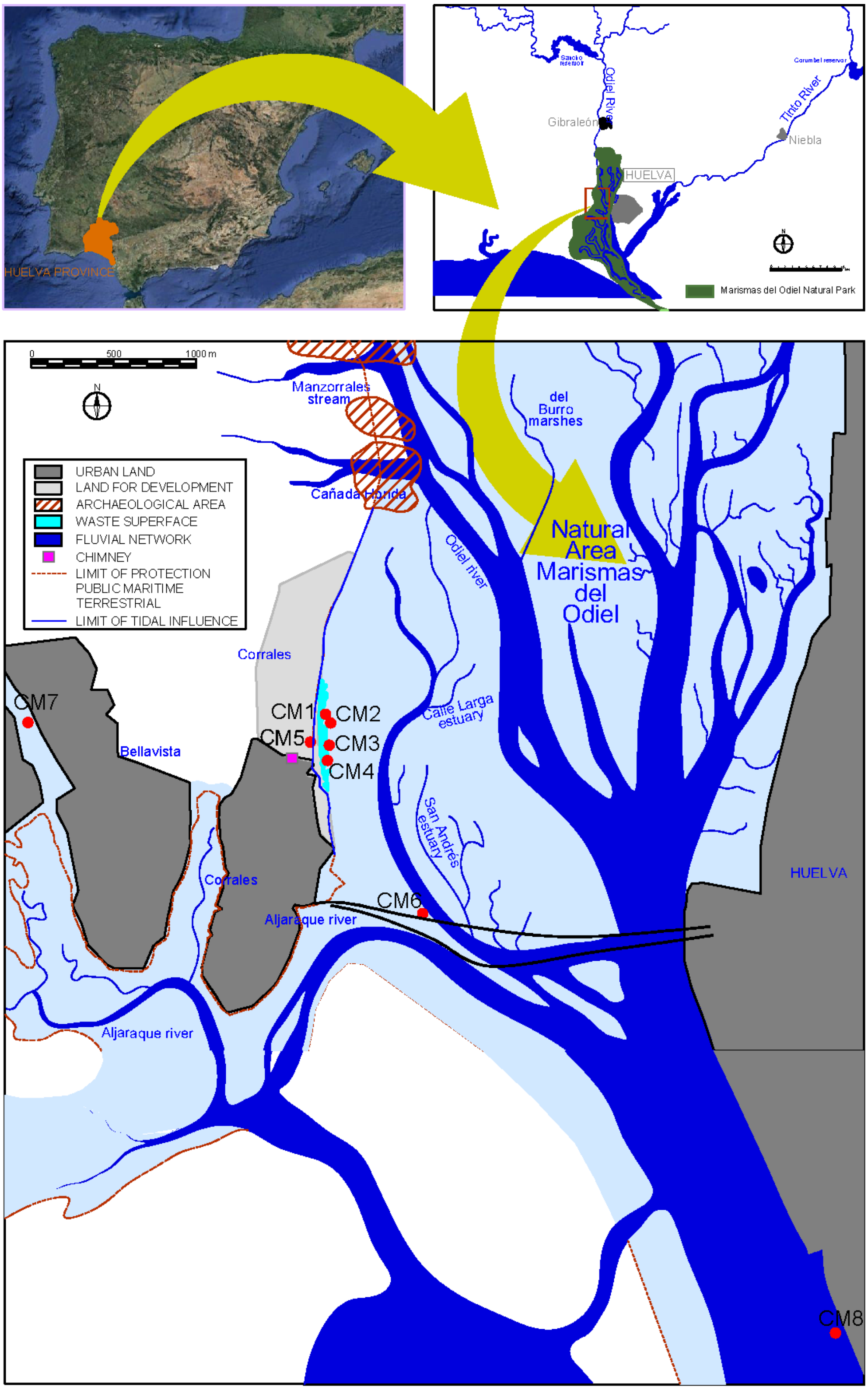


Fig. 2 Location setting

The river Odiel is born in the Sierra de Aracena. The fluvial character of the Odiel is lost in Gibraleón, from where a complex estuary is created forming the Odiel Marshes declared a Biosphere Reserve by UNESCO in 1983. These marshes form an area of 18,875 hectares, being inside the Natural Reserves of the Marshes of El Burro, with 597 hectares, and the Island of Enmedio, with 480 hectares, which stand out for the degree of conservation of their ecosystems. Finally, the Odiel flows into the Northwestern sector of the Gulf of Cadiz along with the Tinto River. Its basin has a surface area of 2,333 km^2 and its main course a length of 140 km (Nieto et al. 2013).
In the second half of the 19th century, the french engineer Deligny reopened the old Tharsis and La Zarza mines (Iberian Pyrite Belt), the latter being located near the mouth of the Odiel river, which was initially used as a

transport route and in which, in 1861, a small loading quay was established between the towns of Gibraleon and Corrales (Huelva), and in the same area, in 1862, a foundry was set up to refine the copper shell.
With the intention of approaching areas of the river located downstream, another jetty was later built in the area of La Punta next to the first worker housing. In 1860 the first project of the railway line between Tharsis and La Zarza was approved with the quay-pier of Puntal de la Cruz, being definitively undertaken by the company The Tharsis Sulfur and Copper Co. Lted, finishing the works in 1870.
The impulse of mining activity led to the development of population centres and industrial use of the Corrales area. A large number of buildings were built and in 1917 a thermal power station was built to electrify the installations. The transport of the ore was made by the railway line and was unloaded in the area of Corrales located in front of the thermal power station, for later, and with wagons of smaller tonnage to be transported up to the wharf. It is in this area where the waste is generated with the collection of material from the mines and it is the area where this work is focused.
Once the wastes have been abandoned after the closure of the facilities at their current location during the 1990s, they function from the hydrogeochemical point of view as a sulphide dump, in this case with a higher contaminating capacity due to the higher average sulphide grade in the stockpiles than in a conventional dump.
The contaminating wastes extend over an approximate surface area of 12,600 m^2 and today remain in the reference area exposed to rain and rising river levels during spring tides. With this, the polluting effects are visible along a 52-hectare supra-tidal surface in which soils altered by the presence of secondary minerals predominate, fundamentally sulphates, oxides, hydroxides and Fe hydroxysulphates, typical of mining environments and coming in this case from the evaporation of leachate arising from ore piles. The leachate resulting from the passage of water through mining waste is a fluid loaded with acidity and sulphates which, at this extreme pH value, dissolves the metals present in the sulphides themselves, whose composition presents high percentages of heavy metals such as Fe, Cu, Zn, etc., and more importantly, other elements which are especially undesirable due to their ecotoxicological nature such as arsenic, cadmium, lead, selenium, etc. In the scenario described above, this leachate occupies the flood plains after rainfall and, subsequently, when the rains cease, it precipitates on the soils giving spectacular images and causing a severe pollution to the environment.
Along with the reactions that have been explained, and associated with the hydrolysis of the ferric ion, there are others through which some oxyhydroxysulphates are formed such as schwertmannite and jarosite, which can be found in the shallow areas of rivers affected by AMD, in tones ranging from intense red to ochre yellow. These precipitates can be seen in the supra-tidal area of the Marismas del Odiel National Park (Fig. 3).

Fig. 3 Precipitates formed in the supra-tidal zone of the work area

The main aims of this work are: to quantify the levels of toxic elements in the supra-tidal area, to evaluate the contributions of pollutants discharged into the estuary and to evaluate the results obtained compared to those of mining areas and those of other IPB estuaries.

3. Materials and methods.

3.1. Sampling network design.

In order to obtain a physicochemical characterization and a proper diagnosis of the pollution caused by the mining waste in the natural place Marismas del Odiel, a sampling network is proposed. In order to obtain a better quality in the sampling, the tidal coefficient statistics for the months of March and April were taken into account together with data from the meteorological station of Gibraleon. Each of the points was georeferenced by GPS. The sampling network had 8 points, as shown in Fig. 2. They are always water samples that were taken in the effluents

of the tailings after the precipitations. These are small springs that run towards the river following the natural slope.
Once the points were defined, the samples were taken on April 23, 2018, with the marking parameter for each one (CM #). The first point (CM1) is in the emergence of the mineral waste dump 30 meters from the chimney without hydrolysis, the CM2 point is taken 20 meters stream below the previous point after the precipitation of Fe (we took 20 meters downstream in the field with a measuring tape and we know that the hydrolysis of Fe had already taken place due to the presence of *yellow boy* and other precipitates that clearly indicate the appearance of insoluble ferric oxide so it precipitates), the CM3 point is taken approximately 80 meters from the immediately preceding, where the major current is born that has already passed through a waste dump removed; 50 meters downstream of point 3 CM4 sample is taken in the same channel. The next point (CM5) is taken along the perimeter road, above the limit of tidal influence and outside the wire fence that limits the developable land; the sample for the flood mat is taken in the so-called San Andres mat (CM6) below the motorway bridge; for the point defined as regional background without affectation called CM7, the sample is taken in the La Dehesa stream and finally, for the regional background with affectation, the CM8 sample is taken in the Odiel river in front of the Huelva football stadium.
When the pH of acid mine drainage is raised past 3, either through contact with fresh water or neutralizing minerals, previously soluble iron(III) ions precipitate as iron(III) hydroxide, a yellow-orange solid colloquially known as *yellow boy*. Other types of iron precipitates are possible, including iron oxides, oxyhydroxides and hydroxysulphates (Grande (ed.) 2016).

3.2. Field methodology.

The set of samples obtained will be analysed of the following parameters: pH, electrical conductivity, total dissolved solids, Redox Potential and temperature. In situ pH, total dissolved solids, temperature, electrical conductivity and ORP were determined using the portable multiparametric equipment, CRISON-MM 40+. The evolution, as well as its values, allows a general idea of the degree of pollution in the study area by the mining waste. For each one of the points of the sampling network 2 water samples were taken and filtered through filters with 0.2 microns of pore size and packed in polyethylene containers of 100 ml properly sterilized; to one sample was added 1% of nitric acid to avoid the precipitation of dissolved metallic load and to obtain a pH $\leq$ 2 and to allow the analysis of heavy metals; the other sample, non-acidified, was taken for the determination of sulphates.

3.3. Laboratory methodology.

The samples were taken to the laboratory (owned by University of Huelva) and stored at 4°C until analysis. The concentrations of K, Na, Ca, Mg, as well as Pb, Al, Fe, Mn, Cd, As, Cu and Ni were determined, the latter being characteristic of AMD pollutions due to their great toxicity when exceeding certain concentration levels and forming most of the minerals present in sulphides. These elements were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-OES).Internal control standards were analysed every ten samples and a duplicate was run for every ten samples. Reference standards were within 10% of certified values. The precision of all analyses was always within 5%. Sulphates were determined by ion chromatography (IC) with suppressed conductivity detection (Standard Methods, 4110).

3.4. Data treatment.

Data resulting from analytical procedures was submitted to statistical treatment using the software STATGRAPHICS Centurion XVI in order to obtain the statistical summary and cluster analysis. Cluster Analysis is used to define a series of techniques, basically algorithms, whose object is to look for similar groups of variables, which are grouped together in clusters. When we subject a group of variables to this treatment, the cluster analysis orders and classifies them into the most homogeneous groups possible, based on the similarity of the variables among them (Bisquerra 1989). This statistical tool has been widely applied to systems affected by AMD (Borrego et al. 2002; Grande et al. 2003).

4. Results and discussion.

Table 1 lists all in situ measured values of the sampling network.
A first analysis can be made with the results of Table 1: in the first five sampling points (waste collection area and nearest area) very low pH values stand out, with a minimum of 1.66 together with high values of the other parameters, highlighting among them the CM2 point (Eh, 28.1 mS/cm - indicative of a high degree of mineralization; TDS, 17.96 g/L and Redox 440 mV). The pH values at points CM6 and CM8 are compatible with

the precipitation of Fe and other metals (Achterberg et al. 2003; Braungardt et al. 2003) and are even lower than those found in other works (Hierro et al. 2014) in the Tinto and Odiel estuaries, with minimum values of 2.6 and 3.9 respectively, always bearing in mind that sampling points M1 to M4 are within the limit of tidal influence.
It is worth noting the great difference between the values of point CM7 (regional background not affected) compared to the rest, especially the much higher pH value - above 7 and below both conductivity and TDS values. As for sampling points 6 and 8, there is an increasing trend in the physical parameters of conductivity and TDS, according to the influence of seawater.
The results of conductivity and Eh confirm the trend observed by the works of Hierro et al. (2014) with increasing values as we approach the river mouth in the case of conductivity and decreasing values for Eh, already affected by brackish water.

Table 1 List of physical parameters in the sampling network

	pH	EC (mS/cm)	Temperature (ºC)	TDS (g/L)	Eh (mV)	Location	Distance (km)
CM1	1.88	15.32	27.70	9.80	469	N37º 16' 53"; O 6º 59' 1"	0.000
CM2	1.66	28.10	29.00	17.96	440	N37º 16' 53"; O 6º 59' 11"	0.023
CM3	2.16	8.14	27.40	5.15	509	N37º 16' 51"; O 6º 59' 11"	0.105
CM4	1.85	8.09	28.30	5.15	480	N37º 16' 50"; O 6º 59' 11"	0.150
CM5	1.89	12.29	31.90	7.87	518	N37º 16' 52"; O 6º 59' 14"	0.035
CM6	5.78	19.74	27.0	12.63	365	N37º 16' 14"; O 6º 58' 52"	1.409
CM7	7.99	0.31	24.80	0.20	165	N37º 16' 6"; O 7º 0' 32"	3.698
CM8	6.49	20.90	22.50	13.39	198	N37º 14' 47"; O 6º 57' 24"	4.977

EC: electrical conductivity; Eh: redox potential: TDS: total dissolved solid

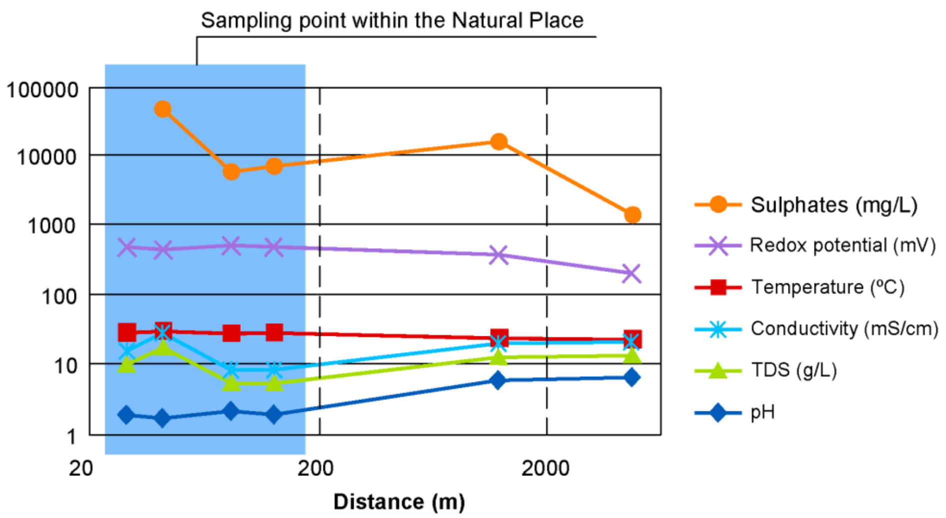


Fig. 4 Longitudinal evolution of physical parameters "in situ" established in the "Marismas del Odiel Natural Place" and up to 4.9 km (CM8)

Fig. 4 shows increasing values for pH, TDS and conductivity (the latter two with very similar behavior) and decreasing values of sulphate content, Redox Potential (Eh) and temperature, as we move away from the points of maximum disease, included within the Odiel Natural Park, and we approach the river mouth, therefore more influenced by the presence of seawater. There is a very regular behaviour in the four samples taken in the Corrales area in terms of pH values, temperature and electrical conductivity. In this figure, points M5 (above the limit of tidal influence) and CM7 (regional background without pollution) have been eliminated to facilitate their interpretation.

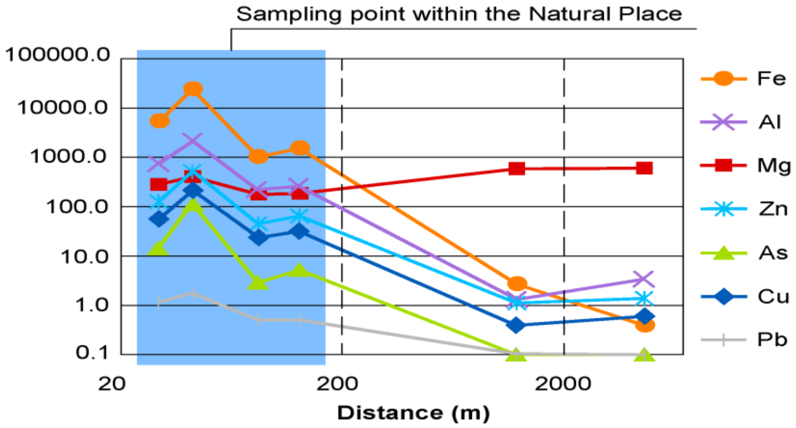


Fig. 5 Longitudinal evolution of concentrations of the most representative metals in the "Marismas del Odiel Natural Place" and up to 4.9 km (CM8).

Fig. 5 shows a graphical representation similar to the previous one, but taking into account the concentrations of metallic elements, decreasing values being observed in all the elements represented, except again in the Mg affected by the increasing presence of brackish water (the same would happen with K and Na), according to what was indicated by Borrego et al. (2002). It can be appreciated that all these elements (except the Mg) have their maximum peak in the CM2 point belonging directly to the dump after the precipitation of iron oxides and on the contrary, the lowest point is the CM6 belonging to the Estero de San Andres.

Table 2 Statistical summary of physical-chemical parameters

Variables	Average	Standard deviation	%Variance	Minimum	Maximum
Al (mg/L)	476.34	726.36	152.49	0.59	2,157.00
As (mg/L)	19.50	39.93	204.78	0.01	117.00
Ca (mg/L)	362.93	179.84	49.55	109.20	621.20
Cd (µg/L)	222.00	0.29	129.61	0.00	850.00
Co (mg/L)	2.15	2.90	135.13	0.01	8.64
Cu (mg/L)	59.05	78.94	133.69	0.07	213.13
Fe (mg/L)	4,587.27	8,092.19	176.41	0.42	23,889.43
K (mg/L)	47.71	78.71	164.98	0.36	175.20
Mg (mg/L)	328.54	200.55	61.04	44.30	603.40
Mn (µg/L)	8.02	6.73	83.88	220.00	16,840.00
Na (mg/L)	1,438.25	2,339.58	162.67	152.00	5,277.00
Ni (µg/L)	351.00	0.338	109.17	0.00	1,120.00
Pb (µg/L)	539.00	0.66	121.94	0.00	1,800.00
Zn (mg/L)	113.48	169.17	149.08	0.18	504.20
pH	3.71	2.59	69.84	1.66	7.99
SO_4^{2-} (mg/L)	11,807.00	15,337.20	129.90	0.00	45,500.90
EC (mS/cm)	14.07	8.86	62.92	0.30	28.10
T (ºC)	26.91	3.08	11.43	22.50	31.90
TDS (g/L)	9.02	5.63	62.41	0.20	17.96
Eh (mV)	393.00	139.09	35.39	165.00	518.00

As for the spatial evolution of sulphides, the point with the highest concentration is CM2 (45,500.90 mg/L), with a subsequent decrease to the lowest peak at CM6 (15,540.00 mg/L).

Table 2 presents the statistical summary of the most significant physical-chemical parameters of the analysed samples.

Very high values are observed for some metals, such as Fe, Al, Cd, Cu, Mg, Mn, As and the sulphate content, especially significant in the maximum values. Table 3 compares these values with the maximums permitted by RD 817/2015, the European Directive 98/83/EC and with the maximums recommended by Ayers and Westcot (1985), appreciating how some metals greatly exceed these maximums. Although the last two criteria refer to drinking water, they give us a clear idea of the level of pollutant matter in the water.

In order to verify the interdependence between the physical-chemical parameters, a cluster analysis was carried out using the Ward Euclidean method. The Dendrograms (Fig. 6) show the grouping of the sampling points according to their proximity defined by the Pearson correlation coefficient (Bisquerra 1989).

Table 3 Recommended maximum values

	Units	Marismas del Odiel Reserve (max/average)	R.D. 817/2015	Directive 98/83/CE	Ayers and Westcot
SO_4^{2-}	mg/L	45.5 / 11.8		250.0	---
Al	µg/L	2,157,000.0 / 476,341.0		200.0	5,000.0
Cu	mg/L	213.2 / 59.1		2.0	0.2
Fe	mg/L	23,889.4 / 4,587.3		0.2	5.0
Mn	µg/L	16,840.0 / 8,023.0		50.0	200.0
Zn	mg/L	504.2 / 113.5			2.0
As	µg/L	117,000.0 / 19,496.0		10.0	100.0
Cd	µg/L	850.0 / 222.0	1.5	5.0	10.0
Co	µg/L	8,644.0 / 2,146.0		---	50.0
Ni	µg/L	1,120.0 / 351.0	20.0*	20.0	---
Pb	µg/L	1,800.0 / 539.0	7.2*	10.0	---

* referred to the annual average

Fig. 6 shows two large clusters of chemical parameters: on the one hand, K, Na and Mg and the next group belonging to the other variables. Within the second group several subgroups are observed: Ca and Mn; Ni and Pb; Fe, As, Al, Zn, Cd, Co and something more distal Cu; which shows us its independence from other elements, since these are characteristic of the minerals and its metallic load. Observing Figure 6, we can appreciate the interconnection between the following parameters: electrical conductivity, dissolved solids and SO_4^{2-} on the one hand, and Redox Potential and temperature on the other. The pH shows a different behaviour to the other physical parameters, so that, as the water flow increases far away from the dump, it has room to evolve and more sulphur is dissolved, leading to sulphates. To the extent that H is released, causing the pH dropping, it is observed that the pH drops by 2 tenths in less than 30 metres.

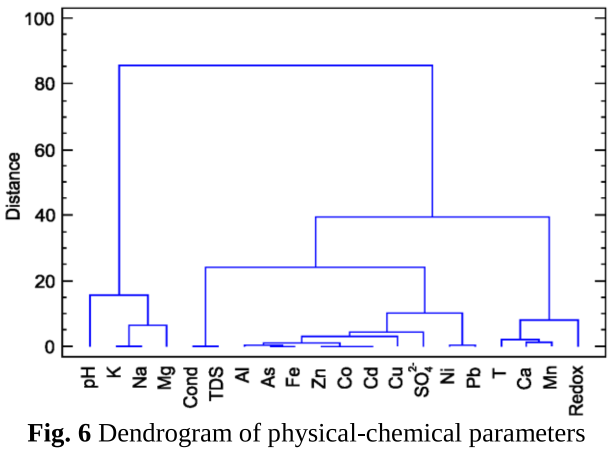


Fig. 6 Dendrogram of physical-chemical parameters

Two large groups can be observed in Fig. 6: one formed by electrical conductivity, TDS, Al, As, Fe, Zn, Co, Cd, Cu, SO_4^{2-}, Ni, Pb, T, Ca, Mn and Redox potential; and a second group with great affinity formed by the pH, K, Na and Mg. In the same figure, a singularity is observed in the relationship established between the pH and the sulphates, being in this case ratified the inexistence of a relationship. This is due to the fact that the pH is totally linked to the tidal influence without leaving aside the mining influence. Sulphates are linked to the mining indicators that are directly affected by the river that transports the metallic load along the mineral stockpile.

Redox potential is linked to Ca and Mn concentrations. Regarding the presence of Ca in the waters of Odiel, the justification is as follows: the value of the concentration of 362.93 mg/L in these waters cannot be considered to be in paragenetic associations with the proper mineralization of polymetallic sulphides, but with the subvolcanic host rocks (tuffs, volcanic ash or cinerita and the very slate quartzite of the Culm (Santisteban et al. 2019). On the other hand, being within the intertidal zone (Grande et al. 2003) that causes that the deposits of phosphoyeses (more than 1,000 ha of unrestored deposits that emit leachates to the union of the rivers Tinto and Odiel) at the mouth of the Tinto river, provide notable amounts of gypsum (SO_4Ca), which are dragged with the rise of the tide to the sampling points of this work. Moreover, the supra-tidal section was defined as "Alluvial Upper Level" by Pendon and Rodríguez Vidal (1986) in Grande (1995) and includes sandy and clayey materials. Moreover, during the oxidation process the hydrolysis of other minerals is accelerated, producing large amounts of its constituent elements such as Ca (Sarmiento et al, 2009).

This is a characteristic of the external mining waste stockpiles, since these stockpiles are on a clay soil typical of the study area, which does not happen in the stockpiles at the foot of the mine. In addition, the waters are very acidic, they dissolve everything in their path. Additionally, this relationship between the redox potential, Ca and Mn shows us the maturity of the water and reflects its spatial evolution since it leaves the dump with a few mili-volts, increasing as it moves away.

Mg, as well as K and Na are marine indicators that are present throughout the study area due to the tidal influence, which limits the hydrogeochemical behavior, being this a phenomenon characteristic of the land Huelva.

The physicochemical alterations in the environment of the Marsimas del Odiel Natural Park, typical of mineral stockpiles, produce sediments with high polluting potential and bioavailable metal charges. This availability can occur with fluctuating environmental variations, typical of tidal systems subjected to periodic flooding (Beeftink et al. 1982). Thus, given the high concentrations of heavy metals found, the removal of sediments and their distribution due to tidal and fluvial hydrodynamics, all organisms, regardless of their location in the Odiel marshes, may be affected by the incorporation of heavy metals (Bonnevie et al. 1994).

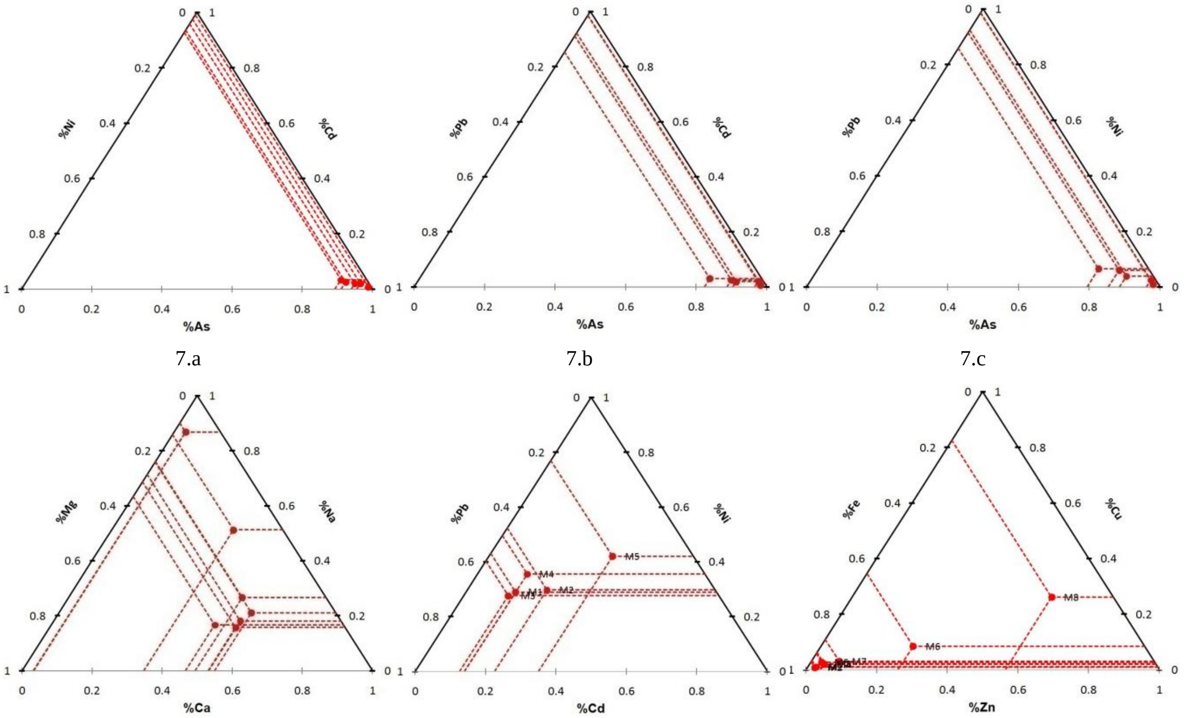
Studies carried out in New Jersey (Bonnevie et al. 1994) show that concentrations of heavy metals significantly lower than those found here, with the exception of nickel, may cause risks to biota in general, and in particular to the spatula, a species in danger of extinction and which has a colony in the Odiel Marshes Natural Area which accounts for 30% of the European population.

Fig. 7 shows, in percentage, the relationships between some of the most representative metals, in which arsenic is absolutely predominant over other metals such as nickel, cadmium and lead (figure 7.a, 7.b and 7.c), with percentages above 80%, which gives an idea of the high content of predominant elements. A contrary effect can be appreciated in the figure 7.d, 7.e and 7.f, where closer percentages are confirmed between the different elements, with the clear exception of the percentage of Fe versus Cu and Zn, which in the samples taken close to the waste stockpiles present values higher than 90%.

4.1. Regional Background.

To conclude the analysis, the results obtained were compared with those of other areas of interest, such as those of mining operations in the same basin (in particular Tharsis mines), with other estuaries that can be considered in similar situations, as their waters are also affected by exploitations of the IPB (Odiel, Tinto and Guadiana rivers), and finally, the results obtained were compared with those that other authors (Hierro et al. 2014) have determined a few kilometres upstream of the Odiel, which will therefore serve to objectively assess the effect produced by the mining waste in the Corrales area.

This analysis begins by comparing the physical parameters obtained in the four samples closest to the mining waste (CM1 to CM4 included in tables 1 to 4) with those of Tharsis mines (Filon Norte, Centro and Sur), observing pH values similar to those obtained by Valente et al. (2013), and even lower at one of the sampling points (1.66 as opposed to 1.79 obtained in Filon Norte). The conductivity values are much higher than those found in Tharsis mines with a maximum value of 28,100 μS/cm compared to the maximum of 3,470 obtained in Filon Norte. Looking at the chemical parameters, we see much higher values in the concentrations of most metals, with a maximum of 23,889.00 mg/L at point CM2 compared to the maximum of Filon Norte, which reaches a value of 2,715.00 mg/L in Fe concentration; 213 mg/L of Cu versus 87 mg/L; 1.80 mg/L of Pb versus 0.28 mg/L; 504.20 mg/L of Zn versus 7.04 mg/L; 2.157.00 mg/L of Al versus 0.56 mg/L and 117.00 mg/L of As versus 3.54 mg/L. In the rest of the determined metallic concentrations (Cd, Mn, Co and Ni) the values are similar to those of Tharsis mines without reaching its maximum values. All this clearly indicates that this area has characteristics similar to those of a dump of any exploitation of the IPB.



7.a 7.b 7.c

7.d 7.e 7.f

Fig. 7 Ternary diagrams of different metals

Comparing the results obtained by Delgado et al. (2009) at the mouth of the Guadiana, with those obtained in the four samples already indicated in the previous paragraph (CM1 to CM4 - tables 1 to 4), much lower pH values are observed in the Corrales area (minimum value of 1.66 compared to the minimum of 7.49 in the Guadiana estuary). The electrical conductivity values are between the minimum and maximum of the Guadiana. For the chemical parameters we find the following: all the concentrations of metallic elements analyzed are higher than those of the Guadiana, in particular, a maximum of 23,889 mg/L in the CM2 point as opposite to the maximum in the Guadiana area that reaches a value of 2.00 mg/L in Fe concentration; 213 mg/L of Cu; 1.80 mg/L of Pb versus 0.01 mg/L; 504.20 mg/L of Zn *versus* 0.01 mg/L; 2,157.00 mg/L of Al; 117.00 mg/L of As *versus* 0.12 mg/L; 0.85 mg/L Cd vs. 0.01; 16.84 mg/L Mn; 8.65 mg/L Co and 1.12 mg/L Ni vs. 0.43. All these results clearly indicate a totally anomalous and differentiated situation opposite to the Guadiana mouth, when one could think that both are in similar situations, affected by AMD and located in the IPB.

Furthermore, if we compare these values with what was obtained by other authors (Hierro et al. 2014), the concentrations offer much higher results in CM1 to CM4 samples, in particular: a maximum of 23,889.00 mg/L at the CM2 point as opposed to the maximum in the area of the Odiel that reaches a value of 1.20 mg/L in Fe concentration; 213 mg/L of Cu as opposite to 2.90; 1.80 mg/L of Pb as opposed to 0.05 mg/L; 504.20 mg/L of Zn as opposed to 12.00 mg/L; 2,157.00 mg/L of Al vs. 27.00; 117.00 mg/L of As vs. 0.06 mg/L; 0.85 mg/L of Cd vs. 0.03; 6.84 mg/L of Mn vs. 5.70; 8.65 mg/L of Co vs. 0.19 and 1.12 mg/L of Ni vs. 0.10.); emphasizing further that while Al predominates in the Odiel estuary, Fe is the predominant element in the area under study. These differences are even more noteworthy if the concentrations are compared with those found in other estuaries (Hatje et al. 2003 and Audry et al. 2007). Similarly, the mean value of conductivity is of the order of nine times the mean value of the estuary and the sulphate content around 15 times the mean value of the estuary of the Odiel river (20 times higher if we only take into account the sampling points near the mining waste). Finally, the lowest pH value found in the Odiel estuary is 3.9, compared to 1.66 in the area studied.

(Hierro et al. 2014) also analysed the estuary of the Tinto river, being, against the samples M1 to M4 that follows: maximum of 23,889.00 mg/L of Fe *versus* 59; 1.80 mg/L of Pb compared with 0.1 mg/L; 2,157.00 mg/L of Al vs. 57.00; 117.00 mg/L of As vs. 0.08 mg/L; 0.85 mg/L of Cd vs. 0.08; and 1.12 mg/L of Ni vs. 0.14, with higher values in the rest of concentrations. The minimum pH value found in the Tinto Estuary is 2.6, compared to 1.66 determined at the CM2 sampling point.

A similar analysis has been carried out comparing the results obtained in the Corrales area with those determined by Hierro et al. (2014) in a sampling point located 2 km upstream of this area, which will allow to assess the level of disease involved in mining waste, finding the following values: the minimum pH value is 3.8, compared to the minimum of Corrales which reaches a value of 1.66; ORP about 23% lower than the sample taken above; conductivity is about 8 times higher in Corrales; Al concentration between 7 and 70 times higher, depending on the sampling point (samples CM1 to CM4); As up to 14,000 times higher (CM2); Cd up to 25 times higher (in

CM2); Cu concentrations between 7 and 70 times higher; Fe up to 16,000 times higher (CM2); Mn between 3 and 60 times higher; Ni up to 10 times higher and Pb between 5 and 17 times higher.
Finally, we believe it is important to highlight the pollutants discharged into the estuary by the waste located in Corrales, and comparing with those determined by Olias et al. (2006) for the Odiel river basin, in order to understand the degree of pollution that the former imply for the Natural Area.
By means of a GPS system, the surface occupied by mining waste has been determined, being 1,260,000 m^2 and an average height of 2 m has been estimated for the waste.
The annual discharge of pollutants caused by the tailing of the study area, is calculated from the annual average local precipitation value of 580 mm/year (Grande, 1995 and "El Tolajillo" nearest weather station - 8 km away from the study area). This precipitation, multiplied by the concentrations of each pollutant under study, gives us the annual average value of the discharges. We consider the value of the ETP (exchange traded products) to be null since the dump surface lacks of vegetation and, on the other hand, the high permeability does not allow the existence of surface water on them, thus considering a total infiltration in a similar way. These infiltration waters will be the same ones that we consider as outflow after a short/moderate residence time inside the dumps (Sainz et al, 2002) since only during a few spring tides the water of the river reach the surface of dump. The behaviour of these dumps is perfectly detailed in the works of Sainz et al (2002) and Viers et al (2018). These mineral accumulations work the same way as a mine sterile tailing but with a higher pollutant capacity since they are already preconcentrated sulfides and classified by particle size for commercialization.
An estimate has been made of the metallic discharges to the Marismas del Odiel Natural Park, the results of which are included in Table 4, the last row includes data on discharges (in ton/year) from the Odiel river, with the Fe discharges (the Corrales discharge is twice the amount found in most of the mines in the Odiel basin), Al (around 13% of the discharges from the Odiel basin) and As, with a slightly higher discharge than in the rest of the basin and twice as much as in the Tinto river.

Table 4 Metallic spills to the Natural Area Marismas del Odiel produced by waste from the Corrales area in front of other mining exploitations of the Odiel river and Tinto River (Olias et al 2006).

	Fe	Al	As	Pb	Cd	Ni	Cu	Zn	Co
Average efluents study area (CM1-CM4) (mg/L)	7,900.8	848.5	34.9	0.5	0.4	0.4	325.7	185.0	3.5
Area discharges (Ton/year)	5,574.9	598.7	24.7	0.8	0.3	0.5	230.0	130.6	2.4
Tinto Basin discharges (Ton/year)	5,075.0	1,224.0	12.4	14.8	3.9	2.2	469.0	863.0	8.7
Odiel Basin discharges (Ton/year)	2,847.0	4,557.0	23.1	11.8	7.1	33.9	1,252.0	2,612.0	62.5

5. Conclusions

The Marismas del Odiel Natural Park has very special characteristics that until now had not been analysed and which constitutes a fundamental factor for understanding the physical-chemical behaviour of the Odiel estuary, which until now has not been completely addressed. In fact, following the zoning defined by Carro et al. (2011) for estuaries, the area under study could be defined as a subzone (pH <2.0) within zone 1 (with pH values lower than 4.5).
As a consequence of the foregoing, it is clear that the presence of mining waste within the space covered by the Marismas del Odiel Natural Park means direct contamination of the waters into which the leachate is dumped, bearing in mind that the waste is within the limits of tidal influence, which requires rapid action by the competent authorities to remedy the affected area. These pollutants represent a high risk for biota and, in particular, for some species in danger of extinction.
The physical-chemical parameters found in the Corrales area, within the Marismas del Odiel Natural Park, are comparable to those from the waste dumps of IPB mining exploitations, many of them even more unfavourable (pH values and many metallic concentrations).
The physicochemical parameters of the Marismas del Odiel Natural Park have been compared with several estuaries of rivers affected by AMD, both in the IPB and in other mining areas. In all cases low pH values and higher metallic concentrations (Fe, Pb, As, Cd, etc.) were found. Likewise, the contributions of pollutants transported by the Odiel river upstream of the estuary have been compared with those found in the Corrales area, being able to conclude that the latter reach values of the same order in comparison with the contributions upstream,

reaching in some cases, such as Fe and As, values even higher than those of the mining exploitations that discharge their leachate into the Odiel basin.

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