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Metal contamination in interstitial waters of Doñana Park

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Abstract

The composition of interstitial waters in Spain's Doñana National Park was assessed 4 years after a major pyrite slurry spill occurred from the Aznalcollar Mine. Metal and nutrient concentrations in pore waters from two of the most important watercourses traversing Doñana Park were measured: Guadiamar River (affected by the accident) and Partido Stream (unimpacted by the accident). Concentrations of dissolved constituents in interstitial waters varied according to land use in the two watersheds and to the effects of the mine spill. Levels of dissolved Co, Cu, Mo, Ti, and Zn were higher in pore waters from the Guadiamar River than in the Partido Stream, suggesting that concentrations of trace elements are still influenced by the spill. In contrast, concentrations of dissolved nutrients (NH_4^+, NO_2^-, NO_3^-, PO_4^{-3}) and some trace metals used in fertilizers (e.g. Al and Cr) were higher in the Partido Stream. Levels of dissolved As, Cs, DOC, Ge, Hg, Rb and V in the interstitial waters were equal in both watercourses.

Metal concentrations in interstitial waters of the Guadiamar River floodplain were between 0.3 (As) and 16,000 (Zn) times lower than those previously reported in the river and groundwater a few weeks after the mine spill. Although metals in pore water appear to have reached levels characteristic of the area before the accident, concentrations are 60–150 times higher than those in pore waters from other regions. Metal:Al ratios in Doñana's pore waters suggest a transport of contaminants from the Iberian Pyrite Belt into Doñana Park.

Keywords: Interstitial water; Trace metals; Nutrients; Contamination; Doñana; Aznalcóllar

1. Introduction

Doñana National Park, in Southern Spain, is one of the major protected ecosystems in Europe (Riba et al., 2002). The Park is an important wildlife sanctuary with more than 800 floral and 400 faunal species (Grimalt et al., 1999; Hernández, 1999). Doñana is also the largest bird reserve in Europe (used by 70 percent of all bird species present in Europe; Grimalt et al., 1999), and important habitat for endangered species such as the Spanish imperial eagle (*Aquila adalberti*) and the Iberian lynx (*Lynx pardina*) (Grimalt et al., 1999; Benito, 1999). Because of its ecological importance, Doñana has been declared a Biosphere Reserve and Human Heritage site by UNESCO (UNESCO, 1981, 1994).

Doñana is exposed to strong environmental pressures, due to the intensive agriculture and metal mining activities in the surrounding areas, dating back to the Roman period (Murillo et al., 1999). In 1998, the retention walls of a sludge pond from a pyrite mine bordering the Park (in Aznalcóllar) collapsed, causing the worst environmental disaster ever recorded in Spanish history (Grimalt et al., 1999). The sudden discharge produced by the mine-tailing dam collapse flowed into the Park via the Guadiamar River (Fig. 1), releasing about two million cubic meters of toxic mud and four million cubic meters of acidic water, enriched in Ag, As, Bi, Cd, Co, Cu, Fe, Hg, Pb, S, Sb, Se, Tl and Zn (Grimalt et al., 1999). The spill covered 4286 ha of land surface, of which 66% were within Doñana Park.

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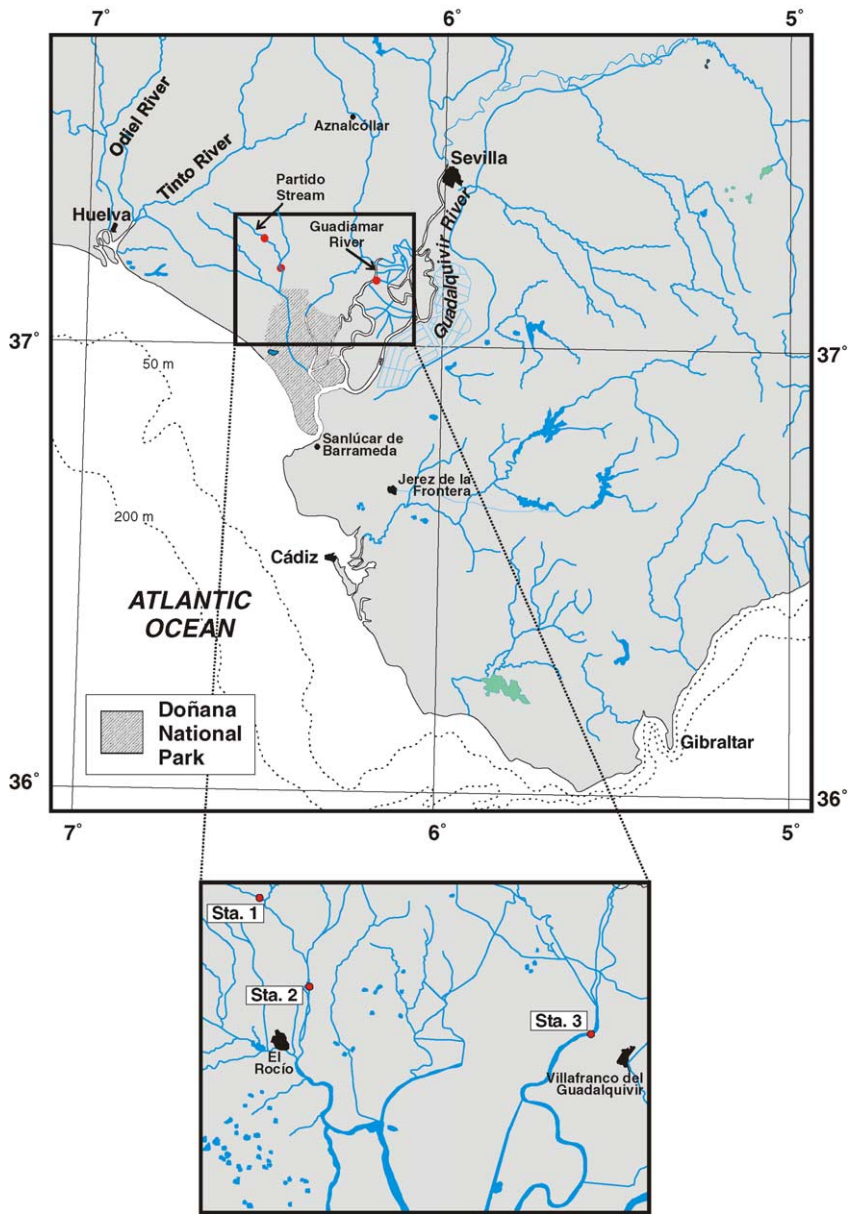

Fig. 1. Location of the sampling stations in the study region. The hatched area represents the National Park of Doñana.

The accident had significant ecological and economical consequences, affecting organisms inhabiting the local environment and more than 2500 ha of cropland (Grimalt et al., 1999).

Considerable efforts by the Spanish Government have been focused to control, minimize and remediate the contamination produced by the mine spill, and numerous analyses of environmental samples have been carried out in the affected region (Garralón et al., 1999; López-Pamo, 1999; Manzano et al., 1999). However, while the 200-million-Euro clean-up effort (Arenas et al., 2002) has considerably improved the environmental conditions in the affected area (CSIC, 2001), contamination from the spill is still pervasive in the upper 30-cm of soils (CSIC, 1999). Those soils are an enormous environmental reservoir of contaminants, where they may remain for hundreds of years (Coulthard and Macklin, 2003). Those soils become then a diffusive source of contaminants, which may release significant levels of toxic metals back to the ecosystem for long periods of time (Flegal and Sañudo-Wilhelmy, 1993).

The transfer of toxic metals from contaminated sediments to the water column occurs via interstitial waters. This flux of metals out of the sediment is responsible for the high metal levels measured in other environments even after the anthropogenic sources have been eliminated (Flegal and Sañudo-Wilhelmy, 1993; Riedel et al., 1997; Topping and Kuwabara, 2003; Kuwabara et al., 2003). Furthermore, the low pH of the mine spill suggests that most of the toxic metals, instead of being associated with soil particles, may be found in the dissolved phase in interstitial waters.

The purpose of this study was to evaluate the metal composition of intertitial waters in Doñana Park in order to better understand the contamination dynamics due to the Aznalcóllar accident. Pore-water samples were collected at three stations located in the two most important waterways traversing the Park (Partido Stream and Guadiamar River). While metal contamination in Doñana soils, surface waters and biota has been extensively studied, measurements of toxic metals in Doñana's interstitial waters have never been reported. Therefore, the results derived from this study are highly relevant.

2. Sampling and analytical methods

Pore-water samples were collected in the flood plains of the Partido Stream and the Guadiamar River in September 2002 (Fig. 1). Samples were collected using PVC-piezometers inserted into the sediments to a depth of 30 cm and left in place for 11 days to equilibrate with the surrounding interstitial waters. Pore-waters were then withdrawn from the piezometers using a pumping system equipped with acid-cleaned C-Flex and Teflon tubing and polyethylene filter cartridges (0.22 μm). The filtered samples were poured directly into acid-washed polyethylene (LDPE, for metals and nutrients) or glass (for DOC) bottles. Nutrient and DOC samples were frozen and stored in the dark until analysis. Samples for trace metal analyses were acidified to pH <2 with quartz-distilled HCl and stored for at least one month prior to analysis. Nutrients (NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, SiO_2) were quantified spectrophotometrically using the methods described by Parsons et al. (1984), and DOC was measured using a Shimadzu DOC 5000 instrument. Metal concentrations (Al, As, B, Ba, Co, Cr, Cs, Cu, Ga, Ge, Hg, Mn, Mo, Ni, Rb, Sr, Ti, V and Zn) were determined by high-resolution, magnetic-sector, inductively coupled plasma mass spectrometry (ICP-MS, Finnigan MAT Element 2) at the Marine Sciences Research Center at Stony Brook University. The accuracy of the analysis was established using Riverine Water Reference Material for Trace Metals (SLRS-4), with recoveries ranging from 89% for Mn to 104% for As and Sr.

3. Results and discussion

Toxic metal levels in the flood plains are likely to vary because of differences in land use in the Partido and Guadamiar watersheds. For example, the Partido Stream drains intensive agricultural areas and receives the waste generated by local industries and sewage from several small communities (with a total population of 35,000; Arambarri et al., 1996). The Guadiamar River also receives sewage from small villages located within its watershed ($\sim$40,000 inhabitants), and the waste generated by industries processing oil, wine and fruits (Arambarri et al., 1996). However, the Guadiamar River also drains through the Iberian Pyrite Belt, eroding old mine tailings, and leaching important quantities of trace metals in the process (Arambarri et al., 1996). Furthermore, while the mine tailings from the Aznalcóllar accident contaminated the Guadiamar River (Grimalt et al., 1999), the Partido Stream was not affected by the spill. In the absence of data on pore-water composition before the spill, sampling in those two areas is an alternative way to establish the impact of the spill on the chemical composition of regional pore-water.

3.1. Effect of land use on levels of dissolved constituents in pore-waters of Doñana park

All of the concentrations of dissolved constituents measured in the pore-waters collected in the two water-courses of Doñana Park are reported in Table 1. In order to establish the effect of land use and the Aznalcóllar mine spill on the chemical composition of the interstitial waters, we compared our metal results from the samples collected in the flood plains of the Guadiamar River to the levels measured in the Partido Stream (Fig. 2).

Our results indicate that approximately 4 years after the Aznalcóllar accident, the concentrations of some elements (B, Ba, Co, Cu, Ga, Mn, Mo, Ni, Sr, Ti and Zn) remain high in the pore-waters of the Guadiamar River relative to the Partido Stream (Fig. 2). Concentrations of those elements in the pore-waters were 2.2 times higher (for B) to 8.6 times higher (for Mn) in the Guadiamar River. Hence, of the 25 dissolved constituents measured in this study, 11 (or 44% of the total) showed concentrations that were higher in the area impacted by the mine spill. Enrichments of Co, Cu and Zn at the River site are likely to be directly attributable to the mine spill, as those three elements are among those previously reported to be enriched in the pyrite mud (Grimalt et al., 1999). Furthermore, these elements are preferentially mobilized during the oxidative dissolution of solid sulfides (Morse, 1994; Domènech et al., 2002), which were present in the Aználcollar sludge (Garralón et al., 1999). We cannot draw any major conclusions about the enrichments of B, Ba, Ga, Mn, Mo, Ni, Sr, and Ti in the flood plains of the Guadiamar River, because information regarding their concentrations before the Aznalcóllar accident is unavailable.

In contrast to the enrichments of some metals (e.g. Co, Cu, Zn) observed in the Guadiamar River, high concentrations of Al and Cr, as well as the nutrients NH_4^+, NO_2^-, NO_3^-, PO_4^{3-} and SiO_2, were found in interstitial waters of the agricultural watershed of the Partido Stream (from two times higher for Cr to 106 times higher for NO_3^-, compared to the Guadiamar River; Fig. 2). The high levels of those constituents in the Partido Stream are consistent with the application of fertilizers (inorganic and organic) to agricultural lands in this watershed, which increases the concentrations of nutrients (e.g. N, P, K; Alva, 1992;

Table 1
Concentrations of trace metals, nutrients, pH and dissolved oxygen (DO) in interstitial waters from the Partido Stream (stations 1 and 2) and the Guadiamar River (station 3)

Location		Element (all in μg/L, DO in mg/L) (mean ± 1SD)								
		Al	As	B	Ba	Co	Cr	Cs	Cu	Ga
Partido stream	Station 1	11.8 ± 5.3	20.6 ± 5.5	178.4 ± 10.7	33.5 ± 2.6	0.4 ± 0.2	1.82 ± 0.75	0.014 ± 0.012	0.92 ± 0.09	1.38 ± 0.86
	Station 2	1.43 ± 0.55	24.2 ± 2.4	201.1 ± 18.1	21.7 ± 2.3	1.29	2.8 ± 0.07	0.011 ± 4.5e-3	0.40 ± 0.37	1.26 ± 5.4e-3
Guadiamar river		2.24 ± 0.46	25.8 ± 0.4	410.4 ± 66.3	83.6 ± 4.6	2.81 ± 0.30	1.12 ± 0.51	0.013 ± 4.5e-3	5.47 ± 1.08	3.45 ± 0.95
		Ge	Hg	Mn	Mo	Ni	Rb	Sr	Ti	V
Partido stream	Station 1	0.09 ± 0.03	0.118	280.7 ± 19.0	0.16 ± 0.05	1.61 ± 1.14	6.34 ± 0.54	189.8 ± 1.5	255.0 ± 10.1	76.6 ± 16.1
	Station 2	0.11 ± 0.05	0.233	136.5 ± 12.1	0.46 ± 0.13	1.34 ± 0.18	4.18 ± 0.57	216.5 ± 23.5	270.3 ± 25.6	69.0 ± 6.4
Guadiamar river		0.17 ± 0.01	0.232	1815.2 ± 473.0	1.66 ± 0.24	5.74 ± 0.16	2.89 ± 0.60	938.9 ± 207.1	1118.6 ± 94.1	106.7 ± 12.5
		Zn	DOC	NH_4^+	NO_2^-	NO_3^-	PO_4^{3-}	SiO_2	pH	DO
Partido stream	Station 1	3.22 ± 1.03	98940.0	3427.0	21.62	321.2	7193.0	9302.0	7.05	3.65
	Station 2	3.44 ± 0.42	74050.0	141.6	1105.0	7286.0	5202.0	16720.0	7.20	2.60
Guadiamar river		10.13 ± 1.61	60190.0	10.0	7.36	36.0	612.6	457.8	6.55	2.55

Agrawal, 1999) and metals (such as Al, Cd, Cr, Ni, Zn; Garralón et al., 1999; Mortvedt, 1996; Debreczeni et al., 2000) in nearby waters and soils.

Levels of dissolved As, Cs, DOC, Ge, Hg, Rb and V were approximately equal in the Guadamiar River and Partido Stream pore-waters (equivalent to 28% of the total analyzed constituents). The similar concentrations of these elements in both areas suggest that those dissolved constituents were not affected by the mine spill. However, these data suggest that relatively high concentrations of some toxic elements (Table 2) are present in both watercourses, of unknown origin.

Although the differences in metal levels observed in the pore waters of Doñana could be the result of different redox conditions in the interstitial waters, we believe that that was not the case for the following reasons: 1) pH and dissolved oxygen levels found in the pore waters (range: 6.55–7.05 and 2.55–3.65 mg/L, respectively; Table 1) were one order of magnitude lower than the pH (>8) at which oxidation of Mn^{2+} occurs in alkaline aerated solutions (McBride, 1994); 2) levels of redox-sensive As were not significantly different in the 3 locations (Table 1), suggesting that metal precipitation due to the exposure of reduced waters to the atmosphere was not occurring. Furthermore, the metal pattern presented in Fig. 2 is consistent with the land use dynamics of the region and the anthropogenic perturbation caused by the mine spill.

In order to determine the relative level of metal contamination in Doñana's interstitial waters, we compared the concentrations of the dissolved constituents measured in this study, to those reported for local waters collected within a few weeks after the mine spill (Fig. 3). In general, metal levels measured soon after the accident in the Guadiamar River and in other local waters (e.g. groundwater and the Agrio River; Garralón et al., 1999; Manzano et al., 1999; Prat et al., 1999) were comparable to the concentrations measured in the Tinto and Odiel rivers, both historically contaminated with mine wastes from the Pyrite Belt (Elbaz-Poulichet et al., 1999; Van Geen et al., 1999; Fig. 3).

In contrast, our interstitial water values in the Guadiamar River were between 0.3 (As) and 16,000 (Zn) times lower than the metal concentrations measured a few weeks after the accident ($Zn < Co < Ni < Mn < Al < Cu < Sr < B < Ba < As$; Fig. 3). Furthermore, current levels of metals in pore-waters collected in the flood plains of the Guadiamar River are within the range of values previously reported for areas unaffected by the mine spill (Manzano et al., 1999; Prat et al., 1999; Van Geen et al., 1999; Fig. 3). This suggests that metal concentrations in the interstitial waters of that River may have reached levels characteristic of the area before the accident.

While levels of dissolved trace metals in the interstitial waters of Donaña's tributaries are lower than those measured immediately after the pyrite mud slide (Fig. 3), current metal levels are still considerably high compared to pore-water values measured in other areas of the world (Table 2). For example, concentrations of Co, Cu and Hg measured in this study were about 150, 77 and 60 times higher than

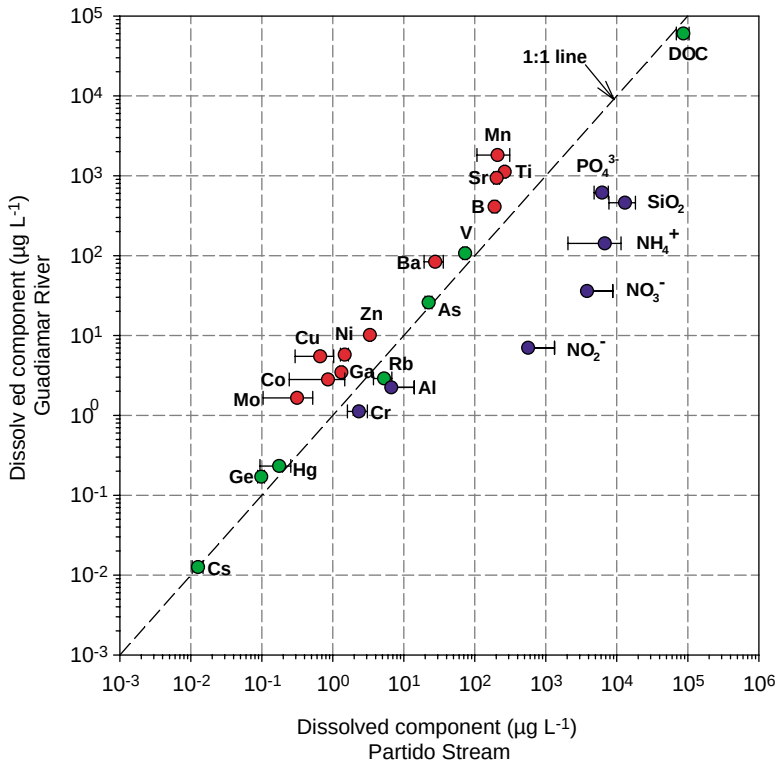

Fig. 2. Trace metal and nutrient concentrations in pore-waters from Guadiamar River plotted against their respective average concentrations in Partido Stream. The error bars represent one standard deviation. Comparison of concentrations in the pore-water between the two studied watercourses indicated an effect of the agriculture activities on the Partido Stream, and a remaining of metals in the Guadiamar River due the mine spill.

the values reported for other non-contaminated environments (e.g. Long Island, New York). Some of the metal values used for this comparison were obtained from samples collected using the same piezometers deployed at Doñana and analyzed concurrently with our samples (Tsukamoto, 2003). This comparison shows that the relatively high metal levels found in pore-waters of Doñana were not due to the analytical protocols used in this study.

3.2. Impact of the iberian pyrite belt on metal contamination in Doñana

Metal concentrations found in this study (e.g. Co, Cu, Mn, Ni, SiO_2 and Zn; Fig. 3) were within the range of concentrations reported for ground waters from the Iberian Pyrite Belt by Pauwels (2002). In order to further substantiate the impact of the Iberian Pyrite Belt on the high metal levels measured in the interstitial waters of Doñana, we calculated the Metal:Al ratios for the interstitial waters collected in this study and compared them to the ratios reported for the Tinto and Odiel Rivers (Elbaz-Poulichet et al., 1999). Metals/Al normalization compared with the crust mean composition is generally used to estimate the natural background and as pollution indicator (Benninger and Wells, 1993; Freydier et al., 1998).

Dissolved As, Cu, Ni, Cr, Zn, and Mn:Al ratios measured in the pore-waters of the Partido Stream and Guadiamar River were similar to those reported for those two rivers

Table 2
Comparison of concentrations of interstitial water constituents measured in Doñana Park (this study) with available values reported in the literature from non-contaminated sites

Dissolved constituent	This study (µg L^{-1})	Non-contaminated sites from other regions (µg L^{-1})	Times over non-contaminated sites
Al	1.4–11.8	0.83–6.5[a]	1–2
Co	0.42–2.8	0.0028–0.095[a]	29–150
Cu	0.40–5.5	0.0052–1.8[a]	3–77
Hg	0.12–0.23	0.002–0.004[b]	58–60
Mn	136–1815	0.18–22[a]	83–756
Ni	1.3–5.7	0.11–0.51[a]	11–12

[a] West Neck Bay, New York (Tsukamoto, 2003).
[b] Pallette Lake, Wisconsin (Krabbenhoft and Babiarz, 1992).

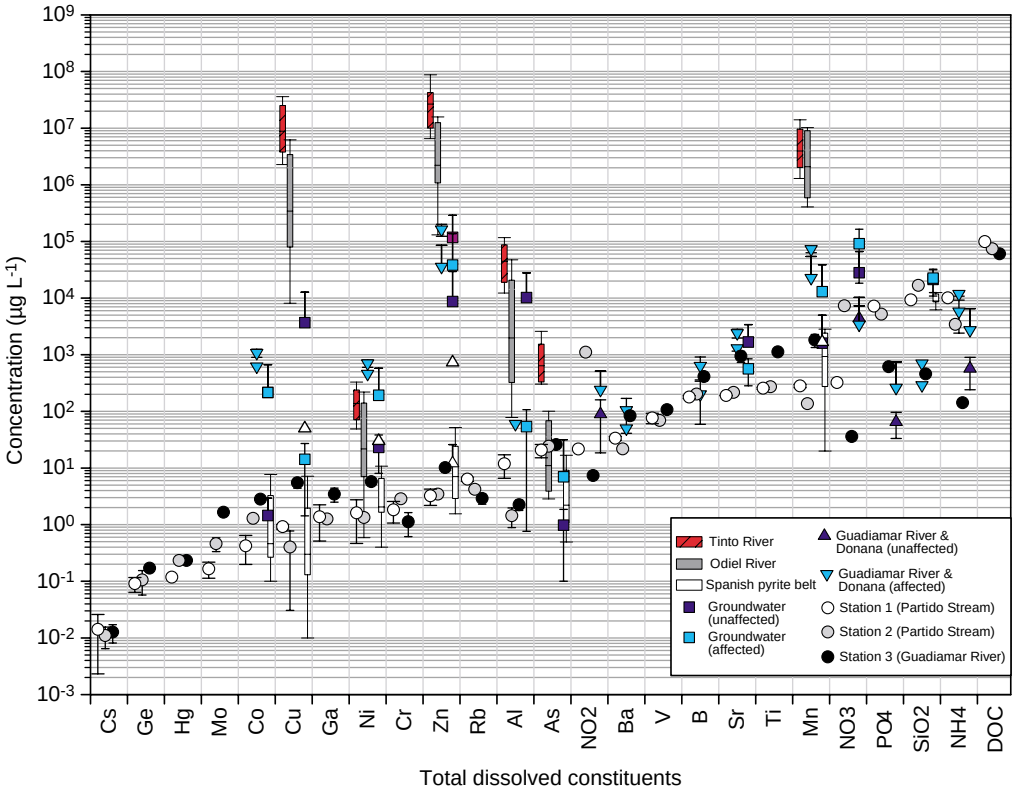

Fig. 3. Concentrations of trace metals and nutrients in the Doñana Park: interstitial waters from this study arranged arbitrarily by increasing order of abundance (stations 1, 2 and 3: white, gray and black circles, respectively); groundwater unaffected (dark blue squares) and affected (cyan squares) by the spill (Manzano et al., 1999); water from the Guadiamar River and other water channels in Doñana area unaffected (dark blue triangles: Manzano et al., 1999; Prat et al., 1999; Van Geen et al., 1999) and affected (cyan triangles down: Garralón et al., 1999; Manzano et al., 1999; Prat et al., 1999) by the spill; water from the Tinto (red dashed boxes: Elbaz-Poulichet et al., 1999; Van Geen et al., 1999) and Odiel rivers (gray boxes; Elbaz-Poulichet et al., 1999); groundwater from the Iberian Pyrite Belt (white boxes; Pauwels, 2002). Boxes represent the interquartile range and their error bars represent the 5th and 95th percentiles. A substantial decrease in the levels of trace metals concentrations is observed in the area affected by the mine spill 4 years after the accident (For interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).

(Fig. 4). Although further studies are needed to identify the transport mechanisms (seasonal floods, groundwater seepage, etc.), the similar Metal:Al composition in the four waterways suggests a transport of contaminants from the Iberian Pyrite Belt into Doñana Park. However, similar Metal:Al ratios in Doñana's interstitial waters and those calculated for groundwater in the Guadiamar River (Fig. 4), suggests that metal contamination could be caused by groundwater intrusions.

Consistent with an allochtonous source of metals to Doñana, Metal:Al ratios in soils contaminated by the mine spill and in Aznalcóllar sludge were an order of magnitude lower than the ratios calculated for pore-water samples in this study (Fig. 4). Lower Metal:Al ratios in areas impacted by the spill are consistent with the high levels of Al found in the sludge (Simon et al., 2002). These different ratios further suggest that high metal levels in the pore-waters cannot be completely attributed to desorption processes from local soils or from the mine spill sludge. This conclusion is important, especially in the case of the Partido Stream (which has been very poorly studied), as it could imply that a substantial amount of trace metals is being transported to Doñana from the Iberian Pyrite Belt, through the Partido Stream and Guadiamar River.

Consistent with a strong impact of mining activity on the area of study, all of the pore-water Metal:Al ratios were higher than the 1:1 concordance line (between 19 and 146, 000 times the crust values; Fig. 4), suggesting that pore-waters were enriched in metal concentrations relative to the average crustal levels. Similarly, spill-contaminated soils and mine sludge were also enriched with respect to the shale (Fig. 4).

In contrast, ratios reported for alluvial and marsh soils in the Guadiamar River and other soils unaffected by the mine spill (those sampled outside river beds; López-Pamo, 1999) closely followed the 1:1 line of concordance, suggesting that the chemical composition of those soils is similar to the average earth crust shale. While high metal levels in the alluvial and marsh soils in the Guadiamar River were attributed to metal contamination occurring before the Aznalcollar mine accident (López-Pamo, 1999), when we normalized those metal concentrations with Al levels, they were comparable to the ratios calculated for the crust shale (Fig. 4). Therefore, the high metal concentrations found in

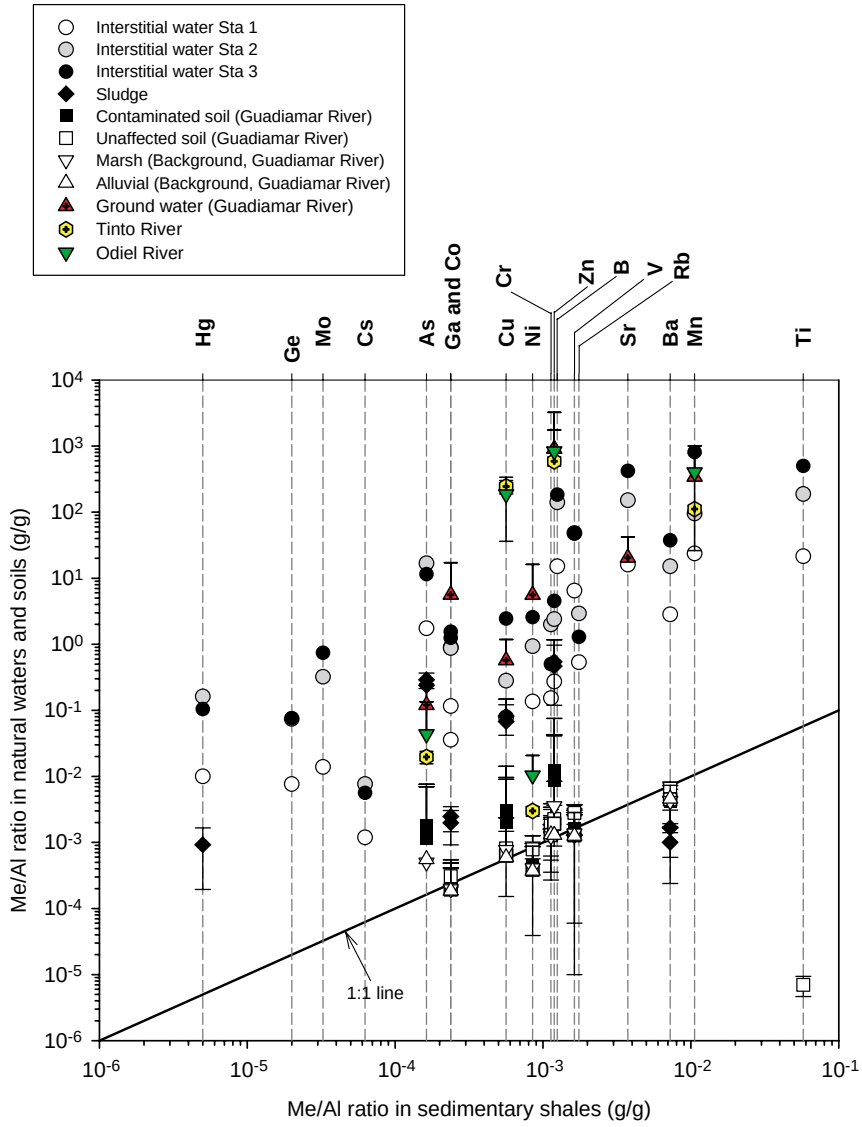

Fig. 4. Metal/Al ratios in average sedimentary rock shale from the earth crust (Turekian and Wedepohl, 1961) versus those calculated in: interstitial waters from the Partido Stream (stations 1 and 2) and the Guadiamar River (station 3) (white, gray and black circles, respectively; this work), ground water affected by the mine spill from Guadiamar River (red triangles; Manzano et al., 1999), waters from the Tinto (yellow hexagons) and Odiel Rivers (green inverted triangles) (Elbaz-Poulichet et al., 1999), sludge spill (black rhomboids), soils affected by the mine spill (black square), soils unaffected by the mine spill (open square), marsh soils (inverted triangles) and alluvial soils (white triangles) from Guadiamar River (López-Pamo, 1999). The error bars represent one standard deviation. The continuous line represents the 1:1 concordance line (For interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).

those soils might not be due to human activities, but rather to natural weathering processes. This metal normalization suggests that some areas within Doñana Park have not yet been impacted by mining and agricultural activity in the surrounding area.

4. Conclusions

Levels of dissolved metals in Doñana's interstitial waters were higher in the Guadiamar River, suggesting that concentrations of those trace elements are still influenced by the mine spill. Metal levels in pore waters of the Partido Stream were also high when compared to levels reported for other environments. Our results suggest that there is a transport of contaminants from the Iberian Pyrite Belt into the Park, although the transport mechanism requires further investigation.

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