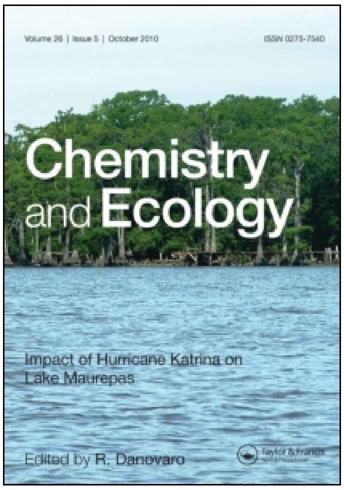

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Pulse-discharges of mining wastes into a coastal lagoon: Water chemistry and toxicity

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Historical mining activities have led to the presence of enormous quantities of mining wastes, which cover large extensions of the Cartagena-La Unión mining district (SE, Spain). In the present work, we study the pulse entrance of mining wastes through two temporary streams (wadis) into the Mar Menor coastal lagoon in two torrential rain events and during a dry period. The characteristics of the runoff pointed to the generation of acid mine drainages in wastes, the acidified stormwater runoff loaded with particulate and dissolved heavy metals causing toxicity in the lagoon waters. The dissolved metals, which mainly affected the sampling stations located close to the wadi discharges, were rapidly eliminated from the water column, whereas the particulate metals were transported further and affected a wider area. Finally, both particulate and dissolved metals are eliminated from the water column and are accumulated in the sediments of the lagoon. The results of the water toxicity tests using sea-urchin embryos indicated that water toxicity disappeared within a few days in the most distant stations, but lasted longer and depended on the climatic conditions of the subsequent days in stations closer to the wadi outlets.

Keywords: Coastal lagoon; Heavy metals; Mining waste; Stormwater runoff; Water toxicity

1. Introduction

Mining activities generate some of the most persistent sources of heavy-metal pollution throughout the world. Such activities involve the generation of great volumes of wastes that are usually stored in a more or less environmentally acceptable manner, although they may occupy huge surface areas. Since mine tailings consist of a slurry of finely ground rock, rich in metals, plus some residual portion of chemicals used during the milling operation, they are very susceptible to erosion, especially in areas where there is heavy rainfall [1, 2]. Therefore, tailings may weather and leach metals for hundreds of years after the mining activity has

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ceased [3, 4]. In addition, one of the major causes of water contamination is the acid generated during the oxidation of sulfur-bearing minerals like pyrites in sulfide mines [4–6], but also dust and soil transported by wind and water erosion [7]. Acid mine drainage (AMD) occurs when the minerals react with water and oxygen in the presence of *Thiobacillus* bacteria to produce sulfuric acid and iron hydroxide or iron sulfate [4]. The low pH values result in the further dissolution of minerals and the release of toxic metals and other constituents into waterways [8]. This can occur on the surface of pyritic waste dumps, ponds, and slag heaps, and is the most persistent environmental impact from the mining industry [3].

The Sierra of Cartagena-La Unión (Murcia, SE-Spain) has long been subjected to mining, and although all mining activities ceased in 1991, the opencast mining practised in this area in the second half of the 20th century has resulted in a highly altered and degraded landscape containing pits, huge dumps, and waste ponds. At the northern edge of the Sierra lies an especially sensitive area, the Mar Menor coastal lagoon, one of the largest coastal lagoons in the Mediterranean region. It is included in the Wetlands Ramsar Convention List, and it is priority habitat no. 1150 (Coastal lagoons) of the Habitats Directive (92/43/CEE). Two main desert-streams (here called wadis) Beal and Ponce (figure 1) flowing from the mining area pour their waters into the lagoon. Due to the semi-arid climate of the area, the wadis remain dry for long periods, and freshwater does not reach the lagoon unless sporadic and torrential rainfall occurs.

The present study focused on the discharge of mining wastes into the Mar Menor lagoon as a result of stormwater runoff during torrential rain events and on their potential toxic effects. When torrential rains occur, the wadis transport drainage and sedimentation wastes associated with old mining activities and abandoned mined lands to the lagoon. Therefore, the lagoon ecosystem will be affected to a degree that depends on the phase in which the metals are carried, since the bioavailability and toxicity of the metals are influenced by the distribution of trace metals in particulate or dissolved phases [9–11]. We analysed the entrance of mining wastes carried by stormwater in the wadis into the lagoon, and assessed the biological effects of these discharges by means of water column toxicity test using sea urchin embryos. Chemical

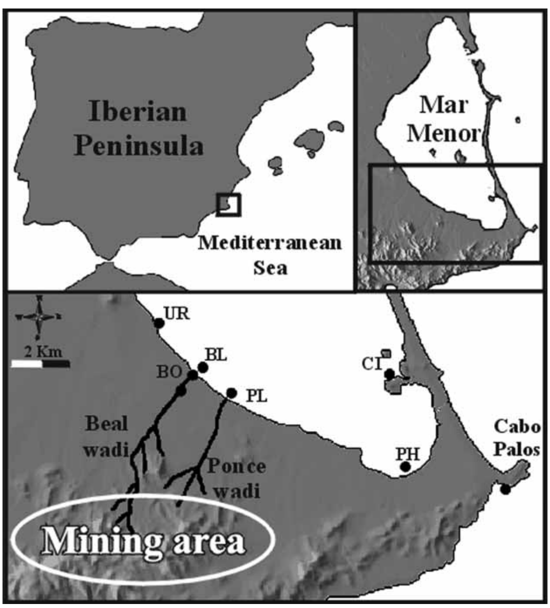

Figure 1. Map of the study area and location of the sampling stations.

analyses alone do not provide evidence of the biological effects [12], and so bioassays are very useful for establishing the biological effects of pollution on marine organisms [13], since such analyses integrate the chemical data and together constitute a tool for pollution assessment.

The objectives of the study were: (1) to characterize the behaviour and distribution of discharged metals in the southern basin of the lagoon, (2) to determine the associated water toxicity, and (3) to compare a wet period (studying two rain events) and a dry period.

2. Materials and methods

2.1 *Study area, sampling stations, and periods*

The study area is located in the Mar Menor, SE Spain, one of the biggest coastal lagoons in the Mediterranean area. It is relatively shallow, with a mean depth of 3.5 m and a maximum depth of just over 6 m. Due to the low freshwater input, which is related to the low annual precipitation (<300 mm), and the high level of water evaporation, the salinity values of the lagoon range between 42 and 47 psu. The water body does not undergo stratification but remains vertically homogeneous, and no hypoxia has been described. The sampling stations were selected in the southern basin of the lagoon, where it was thought they could be affected by the discharge of the two main wadis. Two sampling stations were selected for the Beal wadi, one located at the outlet (BO) and the other approximately 100 m into the lagoon (BL). At a similar distance into the lagoon, but opposite the outlet of the Ponce wadi, PL was sampled. Los Urrutias (UR) station was located to the north of both wadis. Playa Honda (PH) sampling station was located midway between both wadi stations and the relatively distant CI station, which lies to the north of El Ciervo Island. Adults of the sea urchin species *Paracentrotus lividus* and natural sea water for the toxicity tests were collected in Cabo Palos (figure 1), a nearby non-polluted area of the Mediterranean Sea, which was used as control.

As regards the nearby mining region, it is a mixed area containing many mining wastes in ponds and in the wadi riverbeds, but also natural areas, in some cases of high environmental quality. Both catchments are formed by a dense network of ephemeral channels. The Beal wadi catchment has a surface area of 7.6 km^2, a perimeter of 17.3 km, and a bed length of 7.2 km. The difference in height is 242 m with an average slope of 1.9%. For its part, the Ponce wadi catchment has a surface area of 11.9 km^2, a perimeter of 16.6 km, and a bed length of 6.4 km; the difference in height is 384 m with an average slope of 3.1%. These catchments have about 50 waste ponds with different physical and chemical properties containing materials from smelters, mineral laundries, and other mining activities. The total surface area covered by these wastes is more than 0.75 km^2 [14].

Precipitation data were obtained from the closest meteorological station (Roche, Cartagena), located approximately 15 km from the study area, and 70 m above sea level. Precipitation data are represented in figure 2 for the period from October 2003 to March 2004, and although they do not reflect the real quantity of rain falling in each wadi catchment area, they are representative of the area as a whole. Both storms sampled for this study were of moderate to high intensity for this region [15] (CREM, 2002).

To characterize the rainy period, two rain events were sampled, corresponding to the night of 6 October and the night of 19 November 2003 (figure 2). In the morning of the 6 October, we began sampling both stations from Beal wadi. The bed of the wadi was wet, indicating that it had recently flowed. After taking the samples, a torrential rain fell, again causing a new spate in the wadi and giving us the opportunity to sample the water flowing through the wadi upstream of BO before it reached the lagoon. At this moment, with Beal wadi flowing, both Beal stations were again sampled. After the flash spate that only lasted for 1 h, both stations

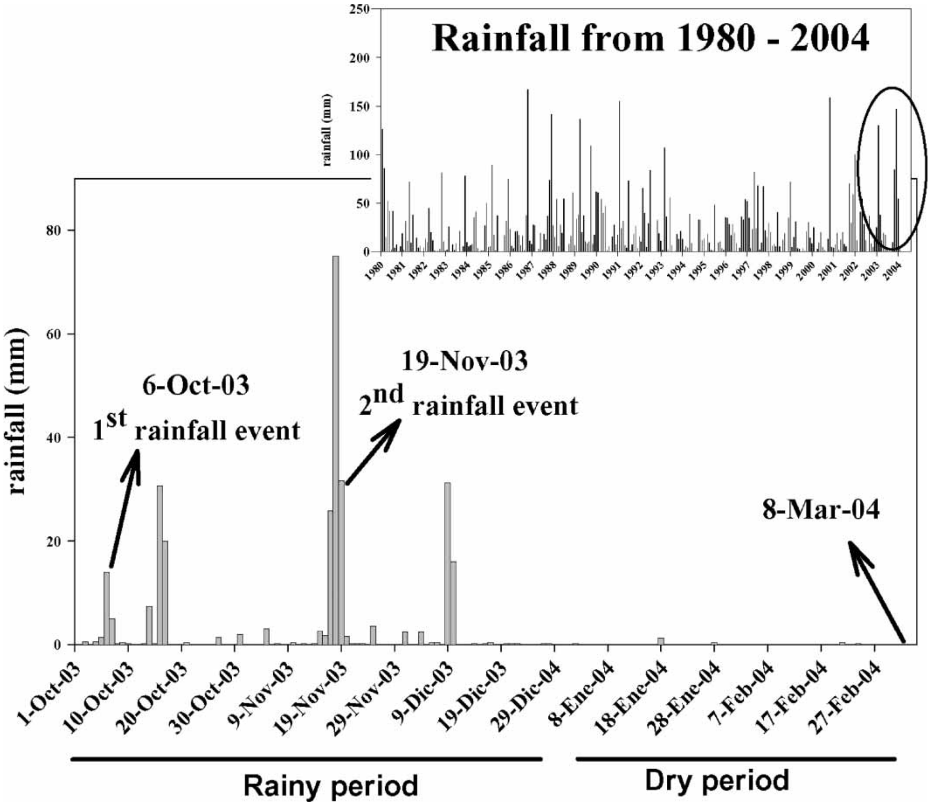

Figure 2. Monthly rainfall data corresponding to the period 1980–2003 with daily data from October 2003 to March 2004 augmented. Arrows indicate the dates of sampling: two rainy events during the rainy period and one day during the dry period. Source of data: Instituto Murciano de Investigación y Desarrollo Agrario y Alimentario (IMIDA).

were again sampled 4 h later (4 h). Therefore, these samples from both Beal wadi stations corresponded to 1 h before the spate (−1 h), during the spate (0 h), and 4 h after the spate, respectively. The rest of the stations were sampled during the spate. Finally, the sampling was repeated at every station after 24 h (7 October) and 48 h (8 October).

In the second rain event on 19 November, every station was sampled, although we do not know the time that elapsed between the flash-flood and the sampling moment (12–14 h). In the dry period, the lagoon stations were again sampled after 3 months without rain, on 8 March 2004.

2.2 *Chemical analyses*

Measurements of water salinity and pH were made *in situ* at each sampling site using a multi-parametric recorder (WTW, MultiLine P4). Water samples were collected in 250 ml polyethylene bottles at 0.5 m depth. All the containers used for the collection and storage of water were thoroughly cleaned with acid (10% HNO_3). Samples were transported refrigerated to the laboratory, where they were stored in the dark at 4 °C. A sample aliquot was filtered through a pre-ashed and pre-weighed GF/F glass-fibre filter and oven-dried at 60 °C to constant dry weight to estimate the suspended solids (SS) content.

For chemical analysis 100 ml of sample was filtered through a 0.45 μm pore size cellulose nitrate membrane filter (Whatman®) previously washed with nitric acid (10%) and rinsed with bidistilled water. Filtered samples were acidified (pH < 2) with concentrated nitric acid (1 ml suprapur Merck®) and stored at 4 °C until analysis. Dissolved Zn, Pb, Cu, and Cd were measured polarographically by anodic stripping voltammetry (Metrohm 646 VA Processor) with a hanging mercury drop electrode. Standard additions were used to determine dissolved metal concentrations and to verify the accuracy of the analytical approach. A blank was introduced every eight samples, and in every series of analyses a duplicate sampling was included at random. The standards used for the calibration were analysed periodically.

For the determination of particulate metals, the filter was digested with suprapur concentrated nitric acid (Merck®) on a hot plate and diluted with Milli Q water (resistivity: 18.2 MΩ) [16]. Zn, Pb, Cu, and Cd concentrations were measured using inductively coupled plasma atomic emission spectrometry (ICP-AES). Blank filters were analysed throughout the analytical procedures to correct the particulate metal determinations.

By dividing the dissolved metal concentration in samples by the reference toxic concentration (EC50) described by Novelli *et al.* [17] for *P. lividus*, we calculated the toxic units (TU) for each of the four metals (Zn, Pb, Cu, and Cd). Assuming additive effects, the total number of toxic units of one sample was therefore the sum of the TU of each metal.

2.3 *Water toxicity*

Water samples for toxicity testing were centrifuged to eliminate the particulate material, and the salinity was adjusted to that of the control (natural Mediterranean water, 37.6 psu) with bidistilled water or hypersaline brine prepared from natural sea water. A brine control was also used during the development of the toxicity tests. Short-term chronic toxicity tests were performed with adults of the sea urchins *Paracentrotus lividus* collected in Cabo Palos according to [18] and accepted guidelines [19]. Adult female and male urchins were stimulated to spawn by the injection of 5 ml of 0.5 M KCl, and their gametes were collected separately: eggs in 200 ml beakers containing dilution sea water, and the sperm collected directly from the sea urchin gonopore. Gametes obtained from at least three organisms of each sex were combined and their densities determined. Pre-trial testing was conducted in order to determine the fecundation ratio, and only rates higher than 90% were employed. The volume of solution added to the test tubes for each experiment was calculated according to the number of fertilized eggs required, adding approximately 300 to each test chamber. This volume did not exceed 100 µl. Four replicates were used per treatment. Tests were conducted in 15 ml polystyrene tubes placed in a constant temperature chamber (ASL-Snijders) at 20 °C, with a 16 h/8 h light/dark photoperiod. The tests ended when control embryos reached fully developed four-arm pluteus larva stage, each test tube being fixed with buffered formalin. The exposure period was approximately 38 h. Using a microscope, the first 100 embryos encountered in each tube were counted for normal or abnormal development, also recording general observations such as the high proportion of embryos in earlier developmental stages (first and second cleavages, blastula stage, gastrula stage, prism stage).

2.4 *Data analysis*

Data from the physico-chemical analyses were log-transformed and subjected to Dunnet's test (ANOVA, $p < 0.05$) to check differences between stations and periods. A Pearson correlation analysis was carried out to search for correlations between metal concentrations and the physico-chemical parameters. Data were standardized by subtracting the mean and dividing by the standard deviation before running the analysis. The results from the water toxicity tests were arc sine-root-transformed prior to statistical analysis using the Toxstat® V.3.3 statistical program [20]. Data passed both the Shapiro–Wilk's and Hartley's test to check the normality and homogeneity of variances of the data, respectively, and were then subjected to Dunnetś test (ANOVA, $p < 0.05$).

3. Results and discussion

During the torrential rain events studied (October and November 2003), Beal and Ponce wadis discharged stormwater runoff loaded with solids resulting from the erosion of mining ponds and contaminated soils. The lagoon water parameters salinity, pH, and SS content (table 1) indicated that an undetermined amount of acidified freshwater with a heavy load of solids was suddenly discharged into the coastal lagoon.

One hour before the flash-flood (−1 h) in October 2003, the pH and salinity values of the lagoon waters reflected the rain that had fallen the previous night. It was during the flash spate (0 h) that we observed a drastic fall in salinity and pH, and an increase in the SS concentration at the outlet of Beal wadi (BO), which was also reflected in the station further out into the lagoon (BL). Although the flash discharge through Beal wadi was still evident in its outlet (BO) 4 h after the spate, it was not evident in the lagoon station (BL) due to mixing and dilution processes. One and 2 d after the spate (7 and 8 October), only the slightly low pH values determined in BO station still reflected the discharge of the stormwater runoff, while the SS content remained high in every station.

The second rainfall event studied occurred on 19 November 2003 and was more intense than that of October (figure 2). This heavier rain was also reflected by the physico-chemical parameters measured in the lagoon water (table 1), those stations most influenced by wadi discharges (UR, BO, BL, and PL) presenting lower pH and salinity values and a higher SS content than those located further away (PH and CI). On this occasion, both Beal and Ponce wadis drained into the lagoon.

For their part, samples taken on 8 March 2004 during the dry period, following 3 months without rain, pointed to no clear differences between stations. Although, in this dry period, the salinity measured was lower than during the rainy season, this was due to the natural seasonal hydrological balance of the lagoon waters.

The runoff sampled during the spate on 6 October was characterized by its high content of suspended solids and particulate metal concentrations, which provided firm evidence that the metal-rich eroded material reaches the Mar Menor lagoon through the wadis; the low pH values and high dissolved metal concentrations that it presented (table 2) point to the generation of AMD [21]. The pyrite mining wastes are oxidized by water and oxygen in the presence of *Thiobacillus* bacteria, the final result of these reactions being a set of soluble pollutants deposited on the mineral [22]. This process occurs throughout the year, and the pollutants are accumulated on the surface of ponds and mining soils to be subsequently dissolved and carried away by rainfall and runoff water [4, 6]. The yellow efflorescent salt commonly observed in wadi beds during dry periods indicates the presence of soluble and sparsely soluble sulfate minerals [23].

Metal analyses of the runoff indicated that, before reaching the lagoon, 54% of Zn and 28% of Cd transported by the runoff were associated with particles, whereas in the case of Pb and Cu, the values reached 99% and 84%, respectively. Once the runoff reached the outlet of the wadi (BO), this percentage increased to 79 and 43% for Zn and Cd, respectively, and was still high for lead and copper (99 and 95%, respectively). At the same time, in the Beal lagoon station (BL), Pb and Cu remained mainly in particulate form (98 and 99%, respectively), while the percentages for Zn and Cd were lower at 72 and 14%, respectively (table 3). This increase in dissolved Zn and Cd observed may be explained by the 'salinity shock' which occurs when

Table 1. Summary of water physico-chemical analyses.

	1st rainfall event															2nd rainfall event			Dry period		
	6 October 2003 (−1 h)			6 October 2003 (0 h)			6 October 2003 (4 h)			7 October 2003 (24 h)			8 October 2003 (48 h)			19 November 2003 (12–14 h)			8 March 2004		
	sal	pH	SS	sal	pH	SS	sal	pH	SS	sal	pH	SS	sal	pH	SS	sal	pH	SS	sal	pH	SS
UR	–	–	–	45.9	8.09	480	–	–	–	46.1	8.28	387	46.6	8.2	400	36	8.29	158	43.3	8.47	38
BO	14.2	6.73	1320	5	4.38	3849	18.2	6.47	1,502	46.7	7.88	336	47.8	7.79	406	33.2	8.14	536	44.9	8.54	55
BL	46.5	7.86	320	41.1	6.57	483	47.1	8.04	406	46.2	8.15	332	47.1	8.08	337	35.8	8.26	230	43.9	8.51	45
PL	–	–	–	46.7	8.3	304	–	–	–	46.5	8.4	305	46.3	8.36	292	36.1	8.16	429	43.1	8.51	41
PH	–	–	–	48.1	8.42	291	–	–	–	46.4	8.47	288	46.8	8.33	296	43.4	8.56	48	42.5	8.53	37
CI	–	–	–	48.2	8.49	306	–	–	–	47.4	8.58	291	47.1	8.42	281	44.3	8.6	61	42.9	8.52	40

Note: sal: salinity in psu; SS: suspended solids content ($mg\,l^{-1}$). In parentheses: the time elapsed between the spate and sampling.

Table 2. Summary of the physical and chemical characteristics of the runoff sampled on Beal wadi, 250 m upstream of the outlet, during the spate of 6 October 2003.

	Beal wadi runoff						
	Metals (mg l^{-1})				Physico-chemical parameters		
	Zn	Pb	Cu	Cd	Salinity (psu)	pH	SS (mg l^{-1})
Dissolved	26.6	0.89	0.3	0.35	1.9	4.1	4901
Particulate	31.65	141.41	1.64	0.15			

Note: Concentrations of metals are given in mg l^{-1} for both dissolved and particulated forms; SS: suspended solids content.

Table 3. Percentage of metals in the particulated form, in the runoff before reaching the lagoon 250 m upstream of the outlet (runoff), at Beal wadi outlet (BO) and in the station corresponding to the lagoon (BL) during the first rain event studied (October 2006).

Percentage particulated	6 October (0 h)		
	Runoff	BO	BL
Zn	54.4	78.7	72.6
Cd	28.8	42.9	13.9
Pb	99.4	98.6	97.8
Cu	84.3	94.9	99.5

suspended particulate material meets saltwater, the rapid initial zinc and cadmium desorption that takes place being due to the competition between the main sea water cations and the metals for binding sites in the suspended material [24, 25]. In contrast, due to its particle reactive nature, dissolved lead shows important removal at low salinities and low pH values [26].

The finding that the lead contained in the runoff was principally in particulate form while the dissolved concentrations were low, contrary to that observed for zinc and cadmium, is in accordance with a recent study of metal mobility in a mining pond of Beal wadi catchment, where Marguí *et al.* [27] found that, while lead was well retained in the wastes, zinc and cadmium were the more mobile metals and therefore most liable to be released to the environment.

The hydrography of the wadis is characterized by abrupt rises and falls, meaning that AMD occurs as a pulse which lasts only a few hours. As regards the metal concentrations in the lagoon waters, the highest concentration of dissolved metal was always that of zinc, while lead showed the highest concentration of the particulate metals (figure 3). During both rain events studied, the concentration of dissolved metals exceeded water-quality standards and background reference concentrations [28, 29], whereas during the dry season, trace-metal concentrations were within ranges found in other Mediterranean areas [28], as previously reported during mine exploitation by De Leon *et al.* [30]. In the first rain episode studied (October), both Beal wadi stations presented the highest metal concentrations in the lagoon waters. One day after the rains, metals were mainly found in particulate form in all the lagoon stations. The slight increase in particulate metal concentrations observed in the stations influenced by the wadi discharges 2 d after the spate seems to be related to the wind of that particular day, which came from the first quadrant (dominant wind in the area), causing sediment resuspension by the swell generated in the south shore of the lagoon.

For its part, the metal concentrations measured during the second rain event sampled on 19 November 2003 point to a higher rate of mine waste discharge through Ponce wadi than in Beal wadi, with both particulate and dissolved concentrations being higher in PL than in BL. The metals in the lagoon were mainly found in the particulate form, the dissolved concentrations

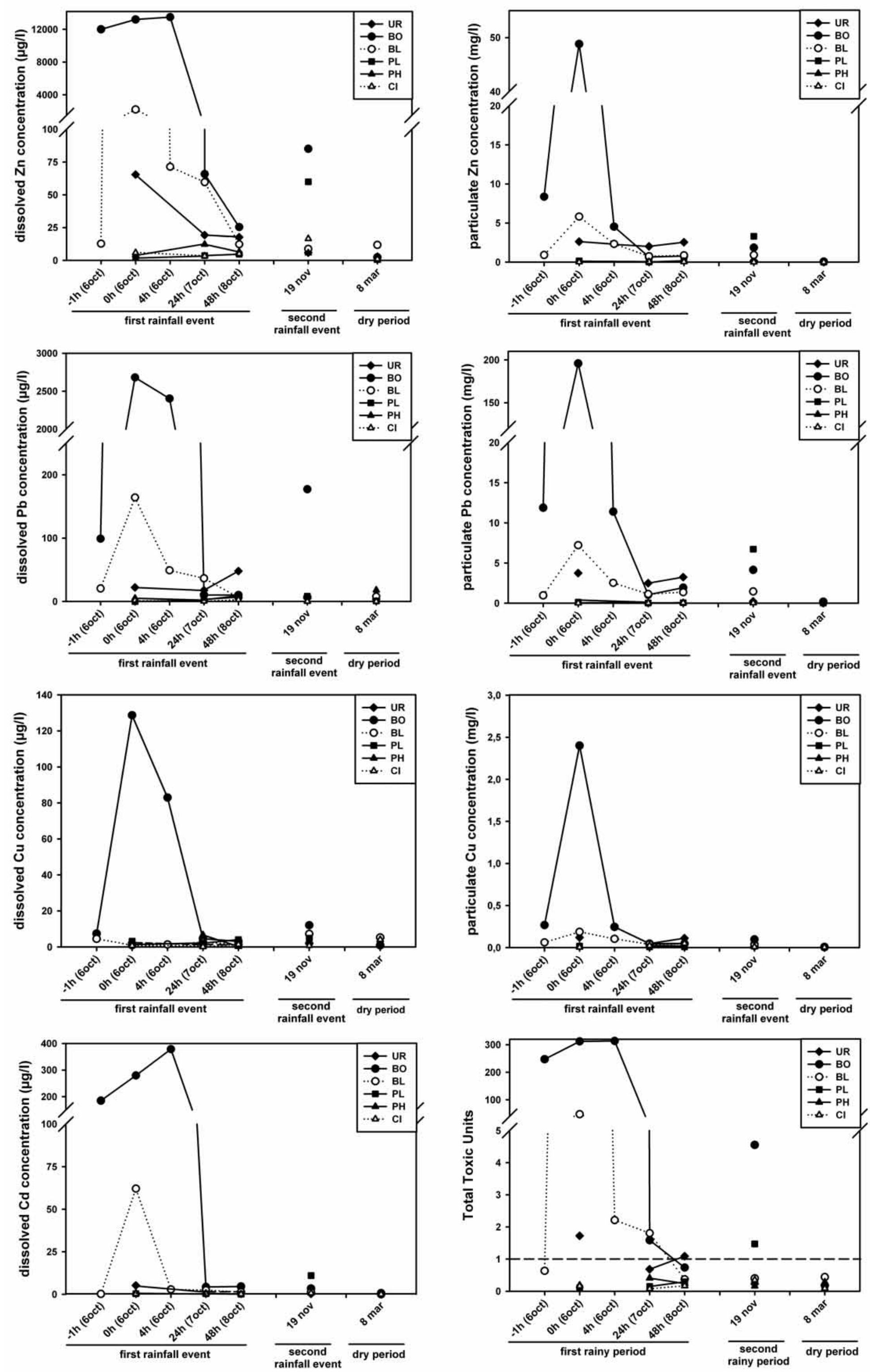

Figure 3. Summary of dissolved and particulate metal analyses (Zn, Pb, Cu, and Cd) and the total number of toxic units. Concentrations are given in $\mu g\, l^{-1}$ for dissolved metals and $mg\, l^{-1}$ for particulate metals.

being similar to that found 24 h after the spate of October. On the other hand, metals measured in the dry period (8 March 2004) presented the lowest values in this study. On this occasion, the highest dissolved concentrations were found in the PH station (lead, 17.9 $\mu g\,l^{-1}$) and in BL (zinc, 11.7 $\mu g\,l^{-1}$), the rest of stations showing levels below 2 and 7 $\mu g\,l^{-1}$ for zinc and lead, respectively. Particulate metals showed the highest concentrations in both Beal wadi stations.

The correlation analysis carried out between the physico-chemical parameters and the metal concentrations showed that both dissolved and particulate concentrations were significantly (and negatively) correlated ($p < 0.001$) with salinity and pH values, whereas they were significantly (and positively) correlated ($p < 0.001$) with the suspended solids content (table 3). As we found in the Mar Menor lagoon, negative correlations have previously been found between dissolved metals and salinity and pH values in estuaries influenced by AMD [8, 31, 32]. In such systems, metal behaviour appears to be controlled by strong pH variations, as well as changes in salinity [24]. As regards our results, when the acidified runoff mixes with the buffered and saline lagoon waters, the pH suddenly rises. This pH increase will translate into a significant reduction in the dissolution capacity of the mining waters [6], which causes the metal load carried by AMD to precipitate into the lagoon. Furthermore, the particulate matter found in similar estuaries has been shown to play an important role in the transport and attenuation of trace metals, regulating dissolved metal concentrations through adsorption and desorption processes [31, 33]. Consequently, metals rapidly begin to be removed from solution at neutral pH and high salinity levels. Therefore, dissolved metals are rapidly eliminated from the water column and only seem to affect those stations located near the wadi outlets, whereas particulate metals are transported further and are accumulated in high concentrations in the sediments of the lagoon, affecting a wider area. In fact, the influence of particulate metals could be detected in the most distant stations, PH and CI (approximately 6 km), as a result of diffusion and transport of the stormwater plume, which was visually noticeable during the sampling from the colour of the plume. Something similar was observed in a study of trace-metal impact in the Baltic Sea during an exceptional flood [34], where the bulk of discharged metals was associated with suspended solids, which were eliminated from the water column and accumulated in the sediments. In this sense, the high metal levels reported in the sediments of the Mar Menor lagoon in recent decades [30, 35–37] indicate that a great proportion of the metals lost from solution, both dissolved and particulate, is retained within the lagoon.

Due to the salinity adjustment for the development of the toxicity tests, samples were diluted in a range of 1.8–28.3%. Every station sampled at the time of the Beal wadi spate on 6 October showed water toxicity and presented significant differences with the control ($p < 0.05$) (table 4). The highest toxicity values were determined in UR and Beal stations,

Table 4. Summary of the correlation coefficients obtained between metal concentrations (both dissolved and particulated) and the physico-chemical parameters salinity, pH, and concentration in suspended solids.

		N	Salinity	pH	SS
Zn	Dissolved	34	−0.91***	−0.86***	0.84***
	Particulate	34	−0.75***	−0.87***	0.95***
Pb	Dissolved	34	−0.78***	−0.83***	0.87***
	Particulate	34	−0.56***	−0.59***	0.68***
Cu	Dissolved	34	−0.80***	−0.84***	0.92***
	Particulate	34	−0.72***	−0.85***	0.94***
Cd	Dissolved	34	−0.86***	−0.83***	0.81***
	Particulate	8	−0.79*	−0.88**	0.97***

Note: Cadmium in the particulate form was only detected in eight samples ($N = 8$). Significance level: $^{*}p < 0.05$; $^{**}p < 0.01$; $^{***}p < 0.001$.

Table 5. Percentage of fully developed four-arm pluteus larvae (% pluteus) and standard deviation (SD).

	1st rainfall event										2nd rainfall event		Dry period	
	6 October 2003 (–1 h)		6 October 2003 (0 h)		6 October 2003 (4 h)		7 October 2003 (24 h)		8 October 2003 (48 h)		19 November 2003 (12–14 h)		8 March 2004	
	%pluteus	±SD	%pluteus	±SD	%pluteus	±SD	%pluteus	±SD	%pluteus	±SD	%pluteus	±SD	%pluteus	±SD
UR	–	–	0.0*	0	–	–	0.0*	0	0.0*	0	85.8*	5.3	87.5*	1.3
BO	0.0*	0	0.0*	0	0.0*	0	0.0*	0	0.0*	0	2.8*	1.3	84.5*	1.7
BL	0.3*	0.5	0.0*	0	2.5*	1.7	0.5*	0.6	0.3*	0.5	28.5*	3.3	89*	3.6
PL	–	–	13.5*	2.5	–	–	76.5	3.1	62.3*	6.4	0.0*	0	87.3*	3.9
PH	–	–	58.3*	2.8	–	–	74.0*	2.9	82.5	2.1	96.8	1	84.5*	2.6
CI	–	–	46.3*	2.5	–	–	76.3	5.6	77.3	2.2	97.8	0.5	95.3	1
Reference	89.5	4.8	89.5	4.8	89.5	4.8	89.5	4.8	90.5	5.1	98	1.6	96.5	0.6
Brine control	84	5.9	84	5.9	84	5.9	–	–	–	–	96.7	1.3	–	–

Note: In parentheses: the time elapsed between the spate and sampling.
*Significant difference from control ($p < 0.05$).

where no fully developed larvae were observed, whereas water toxicity in PH and CI stations was lower than in the rest of the stations. In these latter stations (PH and CI), which were further from the wadi discharges, water toxicity diminished one day after the spate and, after two days, there was no evidence of water toxicity. On the other hand, 2 d after the rains, high toxicity levels were still present in water samples from UR and Beal wadi stations. Although Ponce wadi seems not to have discharged great amounts of stormwater compared with Beal wadi, PL showed high toxicity levels during this spate, the values diminishing after 24 h. For the four metals analysed, the dissolved levels recorded in the mouth of Beal wadi during the spate and 4 h after were higher than the median effective concentration (EC_{50}) reported in the literature for *P. lividus* [17, 38–40]. Except for that moment, dissolved Cu and Cd were never found in concentrations higher than their EC_{50}. In the Beal lagoon station, 24 h after the spate, dissolved zinc was higher than the EC_{50}, and after 48 h both lead and zinc were in higher concentrations than their corresponding non-observable-effect concentration (NOEC) [17].

In November 2003, the station located opposite Ponce wadi (PL) presented the highest toxicity values with no normal fully developed larvae being observed, and, although on this occasion and contrary to the observations made in the previous rainy event, the discharge from Ponce wadi was higher than that of Beal, both Beal stations (BO and BL) also presented high toxicity levels. These stations showed dissolved lead and zinc concentrations higher than their EC_{50}. At this moment, UR station showed low toxicity levels and only the most distant stations (PH and CI) did not present significant differences from the control ($p < 0.05$). The water toxicity results from the dry period (8 March 2004) showed that, although every station presented percentages of fully developed larvae higher than 84.5%, only the distant CI station did not differ significantly from the control ($p < 0.05$).

Every metal analysed in this study (Zn, Pb, Cu, and Cd) has been described as causing embryotoxic effects in *P. lividus* [17]. Because an additive effect of the mixture of metals is considered in the calculation of toxic units (TU), we observed that water samples with $\sum \mathrm{TU} < 1$ presented high toxicity levels, perhaps due to a synergic effect of the mixture of metals in such samples [38, 41], as well as to the existence of other toxic elements not analysed (e.g. Ni and As). Whatever the case, the correlation analysis indicated a significant negative correlation ($p < 0.05$; $N = 34$) between the percentage of pluteus and the total number of toxicity units, the TU for Zn and the TU for Cd.

Although the selected test end-point was the fully developed four-arm pluteus larva stage, we observed similar inhibitory effects in the state of development of the embryos between both Beal wadi stations (BO and BL) to those recently described by Kobayashi and Okamura [42] in a mine effluent. During the spate of October, samples from BO showed that most of the fertilized eggs had not undergone any division, whereas zygotes corresponding to BL had reached the first and second cleavage stage. It was only 24 h after the spate that we observed the presence of some zygotes in the blastula stage in BO station, the proportion increasing 48 h after. On the other hand, BL at 24 h showed most of the embryos to be in the gastrula stage with some embryos reaching the prism stage, this proportion increasing after 48 h. Moreover, as seems to be our case, Kobayashi and Okamura concluded in a later work [43] that zinc was one of the elements responsible for causing malformations, and its effects were intensified by the presence of other metals such as lead and copper, among others.

4. Conclusion

In conclusion, the present work looks at the pulse entrance of mining tailings into the Mar Menor coastal lagoon during torrential rain events characteristic of the region. The torrential nature and the fact that rains are unpredictable in time and are very localized in space mean that great differences might occur in the amount of rain falling in a few kilometres and therefore in the amount of water discharged between wadis. The generation of AMD due to the oxidation of the wastes implies that, together with the particulate metals, a great quantity of metals in dissolved form was discharged into the lagoon. The lagoon water parameters, such as salinity and pH, recovered to reach normal values within a few days, causing the precipitation of dissolved metals, whereas particulated metals lasted longer and affected a wider area, depending on the climatic conditions on subsequent days. The flash discharges caused toxicity in the lagoon waters and negatively affected the health of the ecosystem. Although this water toxicity affects the southern basin of the lagoon, its duration seems to be low and depends on, among other factors, the climatic conditions and the amount of rain that has fallen. Since the coastal lagoon is a cumulative system, metals are retained in sediments due to the saline and buffered conditions of the waters and due to the high amount of particulate metals discharged through the wadis. Hence, this entrance of mining wastes into the lagoon and their accumulation within it implies a risk to the general lagoon ecosystem and to human health. Besides the high ecological value of the Mar Menor coastal lagoon, which is recognized by several protection measures (Wetlands Ramsar Convention List, Habitats Directive, Barcelona Convention), the lagoon waters have many socioeconomic uses and provide many recreational activities. Therefore, it is important to eliminate or mitigate the entrance of these mining wastes into the lagoon through remediation strategies that should be developed by the relevant authorities.

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