THE BEHAVIOUR OF HEAVY METALS FROM THE GUADALQUIVIR ESTUARY AFTER THE AZNALCÓLLAR MINING SPILL: FIELD AND LABORATORY SURVEYS

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(Received 29 October 2001; accepted 15 April 2002)

Abstract. The spill at 'Los Frailes' caused a large input of metals into the riverine, estuarine and coastal ecosystems. Metal behaviour in natural waters can be studied both by performing field measurements, and by undertaking laboratory simulation experiments. Here is described the behaviour of the heavy metals Zn, Cd, Pb and Cu in the Guadalquivir estuary using incubation experiments and the results compared to those obtained during field assessments. If the toxic waste water had been discharged untreated into the environment, it could have raised the heavy metal concentrations in the estuary water to high values, such as 20.65 μM for Zn and 40×10^{-3} μM for Cd. These values are several times higher than those obtained in samples collected in the area during the monitoring of the early impact. The metals present a non-conservative behaviour, with a high loss to waters of low salinity values.

Keywords: Aznalcóllar acid mine waste, Guadalquivir estuary, heavy metals, laboratory simulation, National Park of Doñana

1. Introduction

On 25 April 1998 part of the tailings pond dike of the 'Los Frailes' zinc mine, situated in Aznalcóllar (SE Spain) collapsed, releasing about 4×10^6 m^3 of toxic acid water and 2×10^6 m^3 of toxic mud with high concentrations of heavy metals over the next 5 days. The mud accumulated along 40 km down river. The polluted water continued its path for 20 additional km, where it was retained by several walls constructed urgently in the Entremuros area (Figure 1). However, approximately 4×10^6 m^3 of the polluted mud and water reaching this site were directly discharged into the Guadalquivir river (Grimalt *et al.*, 1999). The Aznalcóllar accident is one of the worst disasters related to acute pollution ever recorded in Spanish history. It damaged about 4328 ha situated at both shores of the Guadiamar river. It occurred in the vicinity of the Doñana National Park, the major marsh protected area in Europe under national, regional, EU or international law and conventions (Figure 1). A decision to undertake urgent treatment of the toxic water was taken by the Spanish Government, but not without controversy. The final decision was to construct a high capacity treatment pond to clean up the waste water, basically by

Environmental Monitoring and Assessment **83:** 71–88, 2003.

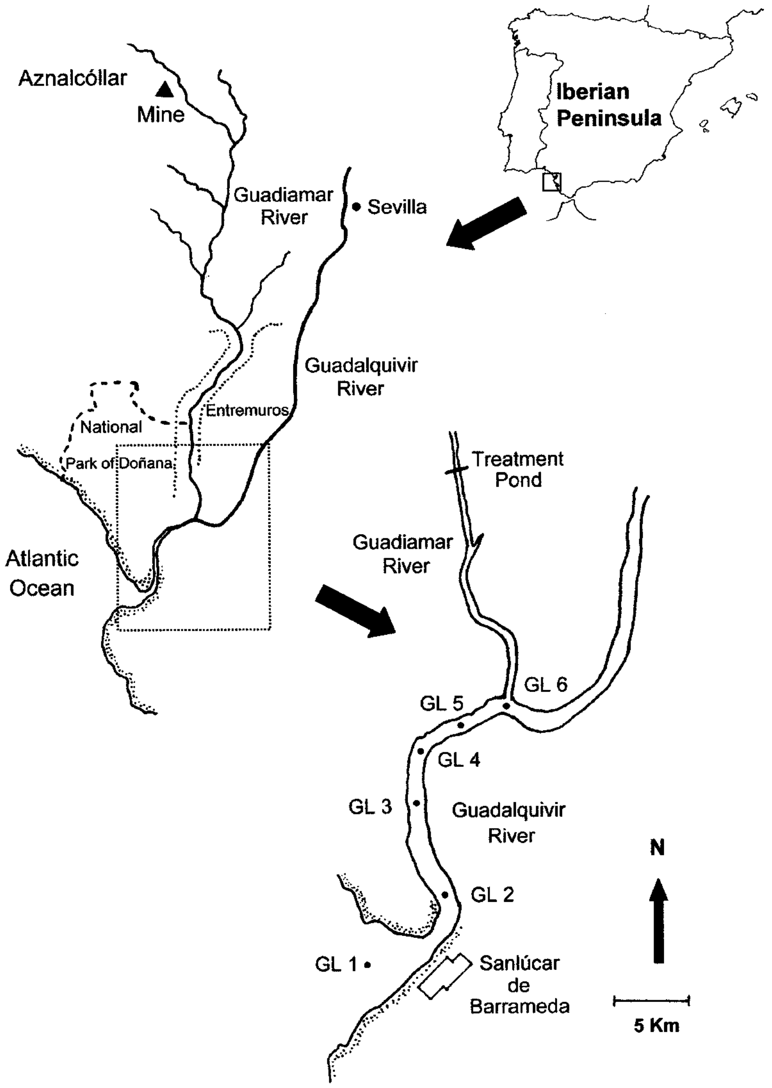

Figure 1. General sampled areas and locations of field sampling stations. GL indicates stations located in the Guadalquivir river and the estuary.

decreasing the concentrations of heavy metals before discharging the treated water into the Guadalquivir estuary. Another option, which was proposed but rejected, would have been to discharge the untreated toxic water, over a relatively short period of time, directly into the river, having first generated a much stronger hydrodynamic regime by releasing large amounts of water upriver. In this article, this theoretical option is evaluated by laboratory simulation techniques and compared to the results obtained under field conditions after the accidental spill.

Research to the state of metals is important, in order to assess the impact of metal discharges into aquatic ecosystems. Metal behaviour in natural waters can be studied by performing field measurements and by undertaking laboratory simulation experiments. Such field measurements have been taken during a study of the early phase of contamination by these heavy metal concentrations in the Guadalquivir estuary (Gómez-Parra *et al*., 2000).

The dynamic simulation of real estuaries was first done by Bale and Morris (1981) and applied to studies of phosphate and iron reactivity. Doering *et al*. (1995) used this technique to evaluate biological activity in estuarine systems. However, simulation under static conditions has been used more frequently (Preston and Riley, 1982; Bilinski *et al*., 1991; Turner *et al*., 1993).

In this article we describe the use of a dynamic automated estuarine simulator to characterize the behaviour of Zn, Cd, Pb and Cu, as well as other physicochemical parameters in the Guadalquivir estuary. Specifically, we have simulated the discharge of untreated toxic water under the typical salinity conditions (gradient) occurring in the area. The results obtained from the simulation experiment are compared with those obtained during field assessment of the impact, caused by variations in heavy metal concentrations. Our ultimate objective is to understand better the chemical reactivity of these heavy metals in natural waters of the Guadalquivir estuary, following an accidental discharge containing the metals.

2. Material and Methods

2.1. SIMULATOR DESCRIPTION

The reactivity of Zn, Cd, Pb and Cu in the Guadalquivir estuary has been studied using dynamic simulation techniques. The simulator system consists of 8 tanks (Plexiglas, cylindrical, and a capacity of ca. 10 L) interconnected under a hydrodynamic regime (Figure 2). The upper tank is supplied with unfiltered fresh water taken from the Guadalquivir river, sampled far away from the waste discharge area (at a distance of 70 km; Figure 1). The lower tank is supplied with seawater sampled in a clean coastal area of the Bay of Cádiz. From the lower to the upper tanks, there is a forced flow of water controlled by peristaltic pumps. In the inverse direction, filling the containers in series with first water generates a down flow. This permits a constant volume of 10 L to be maintained in each tank.

The flow and temperature control is carried out by a Personal Computer using an AID 21-bit translation card. The regulation of flow involves setting-up the peristaltic pumps (Masterflex, 7521–55) in phase with the flow meters (McMillan Company, 111). The temperature is controlled by means of coated dip heaters through thermistor probes. Figure 3 shows the stability of the flow and the temperature.

The used system is a chemical reactivity simulator in a dynamic, continuous fashion. We waited about 14 days to finish the experiment, so adsorption onto the

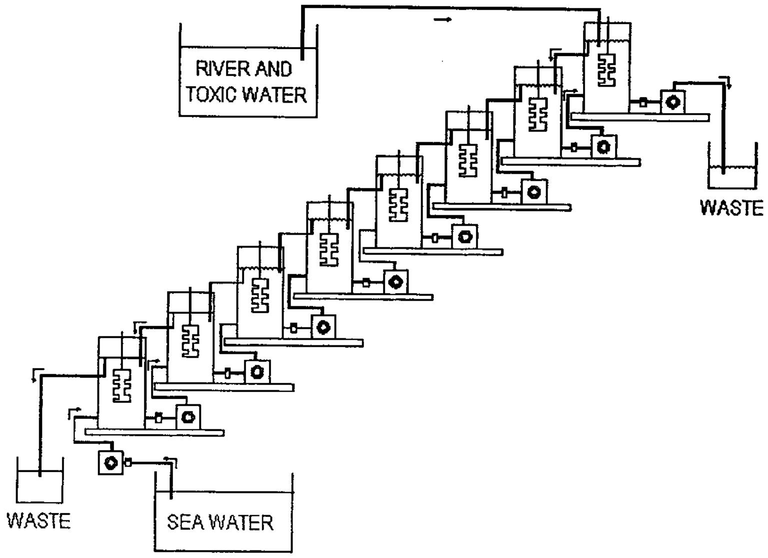

Figure 2. Schematic representation of the estuarine hydrodynamic simulation system used for the study of the heavy metal chemical reactivity in the Guadalquivir estuary.

walls of the tanks is not a problem, because it was produced in the first hours and its influence controlling the heavy metal concentration at the end of the experiment could be rejected.

The mixture is kept homogeneous in each tank by using variable-velocity mechanical stirrers. This system enables vigorous agitation, which keeps all the suspended particulate matter (SPM) permanently in suspension. To ensure that no loss of SPM occurs during the periods of stabilization involved in the simulation, the amount of suspended particulate matter was monitored for each container. The values ranged between 90 and 115 mg L^{-1}, which are similar to those for the original fresh and seawater, therefore there is no loss during the experiment.

2.2. CONDITIONS FOR THE SIMULATION ASSAYS

The system cannot establish a vertical gradient of salinity for each tank. To determine this, the vertical gradient of salinity for the Guadalquivir estuary was measured under field conditions. The salinity variations versus depth are relatively small, therefore the system can be considered to be homogeneous (an estuary type A in the classification of Beer, 1983).

Prior to the simulations assays, some field measurements were carried out in the Guadalquivir estuary. The salinity gradients along the estuary were studied, in different tidal times, in the area between the mouth of the estuary and the Guadalquivir's confluence with the Guadiamar river (Figure 1). Figure 4 shows the salinity variations versus the distance from the ocean, for different tidal conditions;

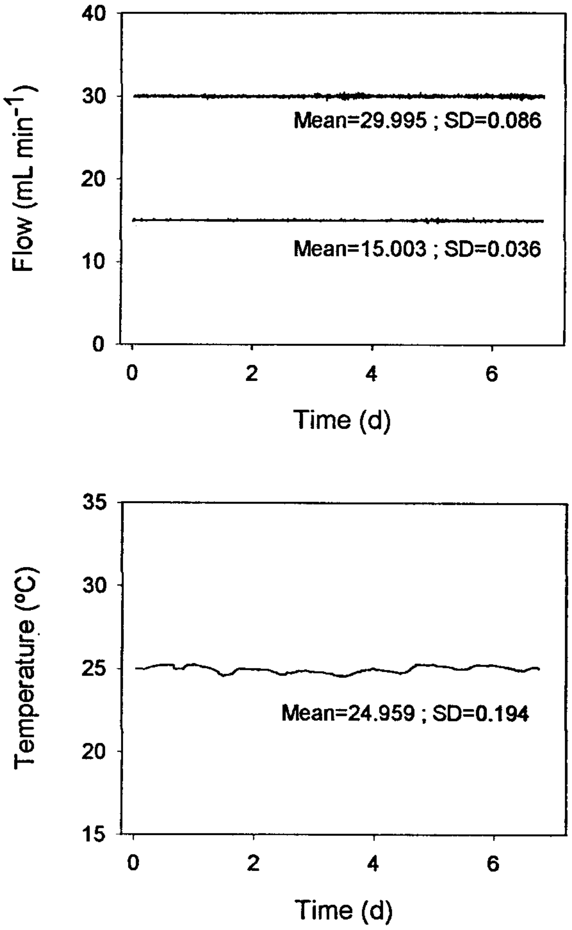

Figure 3. Peristaltic pumps and temperature flows stability during simulation assays.

the salinity gradient used in the simulation assays, which is associated with an intermediate tidal coefficient, is also shown.

These conditions are simulated in the experiments by mixing unfiltered fresh water and seawater flows of 15 and 30 mL min^{-1}, respectively. The flow between the tanks is also 30 mL min^{-1}. Initially all the tanks were filled and the salinity values were monitored until a stable condition was achieved. The stabilization period, necessary to reach the gradient of salinity equal to that actually found in the Guadalquivir estuary, under the particular hydrodynamic conditions used, was 6.5 days. After that period had elapsed, a continuous flow of unfiltered and untreated toxic water was introduced into the system. The toxic water, coming from the Aznalcóllar mine, was collected in the retained water pond upstream the treatment pond. Again a stabilization period of 6.5 days was needed to re-create the heavy metal gradient throughout the simulated estuary. The toxic water entry flow

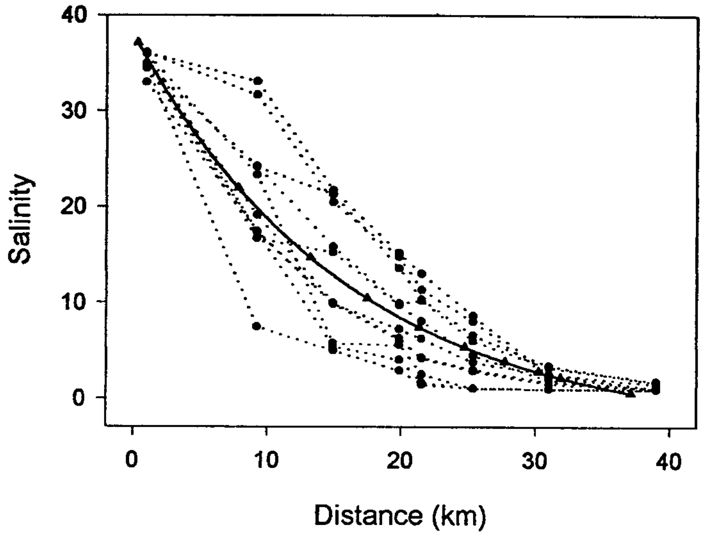

Figure 4. Longitudinal gradients of salinity in the Guadalquivir estuary for different tide times. The continue line shows the salinity gradient used in the simulation assays.

was fixed at 0.72 mL min^{-1}, which after a scale translation is similar to the most likely conditions in the case of the discharge of the 5×10^6 m^3 originally stored in the toxic reservoir over a 20 day period, and taking 60 m^3 s^{-1} as the average flow rate of the Guadalquivir river between the point of theoretical discharge and the ocean. Specifically, three assays like described above were carried out in the laboratory to obtain three replicates. At the end of the laboratory experiments, water samples were collected from each tank in acid-washed 5 L polyethylene vessels. All samples were acidified after collection, stored in the dark at 4 °C and analyzed immediately.

Table I gives the fresh water, seawater and toxic water composition, used for the simulation. From these values and using the salinity gradients observed in each container after the first period of stabilization (i.e. after the first 6.5 days), the initial heavy metal concentration in the river and estuary water before the spill at ‘Los Frailes’ was determined from the various containers. To determine the final heavy metal concentrations, it was necessary to operate the system for another 6.5 day period, to achieve stabilization, before taking the measurements, which marked the end of the experiment.

The mass balance results made tank by tank of the simulator, for each of the four heavy metals, are shown in Table II. It can be observed that the input and output values are similar in all the cases. It confirms previous results. Therefore, the adsorption process of the metals onto the walls of the tanks are relatively fast (hours), so the obtained results after the stabilization period (some days) are not affected by this kind of process.

TABLE I

Chemical composition of the fresh water, seawater and toxic water used for simulation assays

	Fresh water	Seawater	Toxic water
Salinity	0.586	37.098	6.448
pH	8.5	8.1	7.7
Inorganic carbon (mM)	3.12	2.27	1.62
Suspended solid (mg L^{-1})	90.7	112.6	852.3
Oxygen (mg L^{-1})	7.31	5.66	2.95
Chloride (mM)	4.93	598.91	56.61
Sulphate (mM)	2.64	31.36	52.97
Calcium (mM)	2.45	9.70	11.39
Zn (μM)	0.319	0.404	457.98
Cd (μM)	$1.06e^{-3}$	$2.58e^{-3}$	0.846
Pb (μM)	0.027	0.019	1.216
Cu (μM)	0.057	0.040	1.454
Ammonia (μM)	1.5	3.3	20.7
Nitrite (μM)	0.9	0.8	1.2
Nitrate (μM)	391.5	2.0	1.7
Phosphate (μM)	4.7	2.5	0.7
Silicate (μM)	102.9	6.6	118.2

TABLE II

Mass balance with particulate and dissolved trace metal results during the simulation assays. The mass balance has been done tank by tank

	Zn		Cd		Pb		Cu	
	In	Out	In	Out	In	Out	In	Out
Tank 1	45.989	45.688	0.104	0.104	0.144	0.144	0.472	0.471
Tank 2	40.371	39.077	0.093	0.087	0.139	0.138	0.449	0.430
Tank 3	36.009	32.394	0.078	0.074	0.136	0.133	0.395	0.394
Tank 4	31.987	31.407	0.072	0.070	0.128	0.126	0.390	0.387
Tank 5	28.941	27.706	0.066	0.064	0.119	0.116	0.383	0.376
Tank 6	26.462	22.948	0.057	0.056	0.112	0.109	0.375	0.373
Tank 7	19.971	19.091	0.050	0.046	0.107	0.107	0.345	0.342
Tank 8	15.506	12.799	0.042	0.040	0.106	0.104	0.303	0.295

2.3. FIELD SAMPLINGS

Sampling for water and SPM was conducted during May, July, August and September 1998. Water samples were collected in acid-washed ruttner bottles, made of polycarbonate, acidified and transferred to 5 L polyethylene vessels. Then transported to the laboratory to be stored in the dark at 4 °C, until the analyses. In all cases, the sample analysis began within three days after collection. Three replicates of each sample were made. Samples were collected at each of the 6 selected stations along the Guadalquivir river (Figure 1).

2.4. ANALYTICAL TECHNIQUES (FOR FIELD AND LABORATORY SAMPLES)

The salinity of the samples was determined by means of an induction salinometer (Beckman, RS-10). The amount of suspended particulate matter (SPM) for each container was calculated by filtration (Millipore, AP40). The initial pH (NBS) and the inorganic carbon content were measured by potentiometric titration (Metrohm, 670). The sulphate concentration was determined by gravimetry (Grasshoff *et al.*, 1983). Chlorinity was determined by silver potentiometric titration. Dissolved oxygen was measured by the Winkler method. The concentration of calcium in the containers was analyzed by flame atomic absorption spectrophotometry, using matrix correctors (Loring and Rantala, 1992).

Samples for nutrient and metal analyses were filtered through Nuclepore 0.4 μm polycarbonate filters (Millipore, HTTP047). The nutrient concentrations were quantified using an automated analyser (Bran Luebbe, Traacs 800). The dissolved heavy metal concentrations (Zn, Cd, Pb and Cu) were determined by DPASV (Metrohm, VA646 and VA647) after a digestion procedure using UV radiation (4 hr) at 85 °C (Metrohm, 705UV). The analytical procedure for dissolved metals was checked using reference material CASS3 with an accuracy of ±10%. The heavy metal concentrations in SPM were measured, using the same technique after total digestion of the membrane filters, following the procedures outlined by Loring and Rantala (1992). The acid mixture used in the total digestion was aqua regia: HF at 1:1. The blanks used for the analysis were filters, which had undergone the same treatment, but without SPM, these were digested in the same acid matrix. The analytical procedure for solid extracts was checked, using reference material (MESS-1NRC and CRM277 BCR) and allows agreement with the certified values higher than 90%.

Prior to sampling and setting-up the simulations, all equipment, filters, beakers and containers used, were thoroughly cleaned with acid (10% HNO_3) and then rinsed in reagent grade water (Milli-Q).

3. Results and Discussion

The variations of main physicochemical parameters (chloride, sulphate, inorganic carbon and pH), obtained during the simulation assays are shown in Figure 5. The

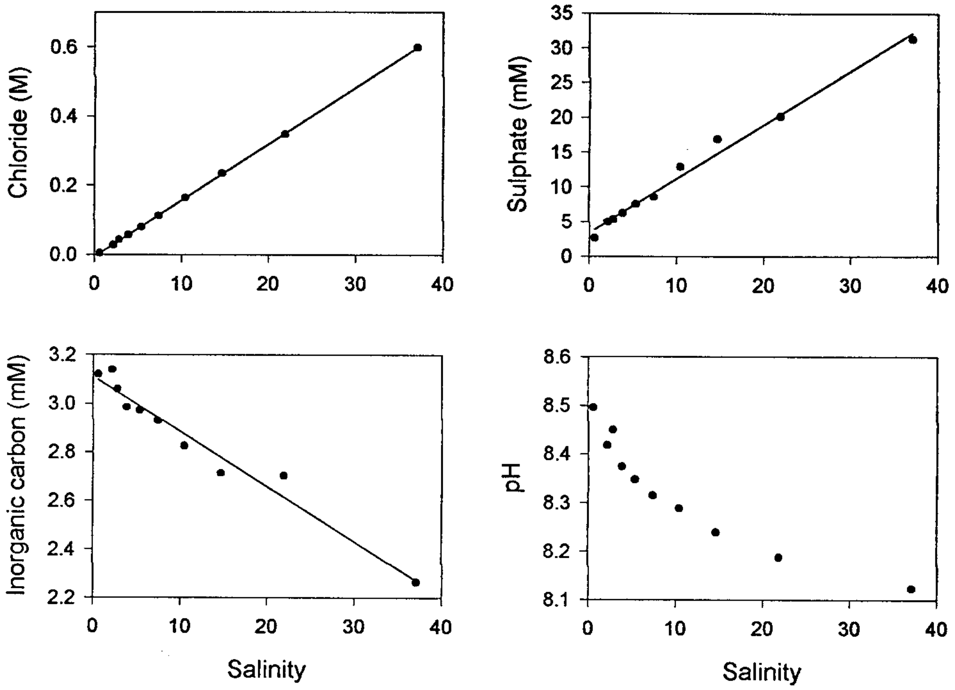

Figure 5. Variations in the concentrations of chloride, sulphate, inorganic carbon and pH versus the salinity during the simulation assays.

oxygen saturation percentage was almost constant during the assay for each container (ca. 90–95%). The amount of suspended solids measured in the containers ranged between 90 and 115 mg L^{-1}. The chloride concentration shows a linear variation with the salinity, therefore the relationship between salinity and chloride concentration in the Guadalquivir estuary is

$$S = 1.740\ \mathrm{Cl}\ (‰) + 0.337 \qquad (r^2 = 0.9999)\ .$$

Comparing this expression with those previously reported (see e.g., Millero and Sohn, 1992) we observe a relatively low slope as well as a high value for the independent term. This finding is related to lower equivalent conductivity for the major ions in the fresh water, such as bicarbonate, carbonate and calcium (Table I). Nevertheless, the high correlation coefficients obtained for both variables confirm the use of the salinity as the correct mixture index. Also, the sulphate concentration presents a conservative behaviour as is usual for estuaries (see e.g., Hosawaka *et al.*, 1970).

The Guadalquivir water simulated in the laboratory experiment presents high concentrations of inorganic carbon and a clear linear decrease of these concentrations seaward of the estuary. This is a non-typical behaviour for inorganic carbon, but it has been reported earlier for some estuaries, such as San Antonio in the

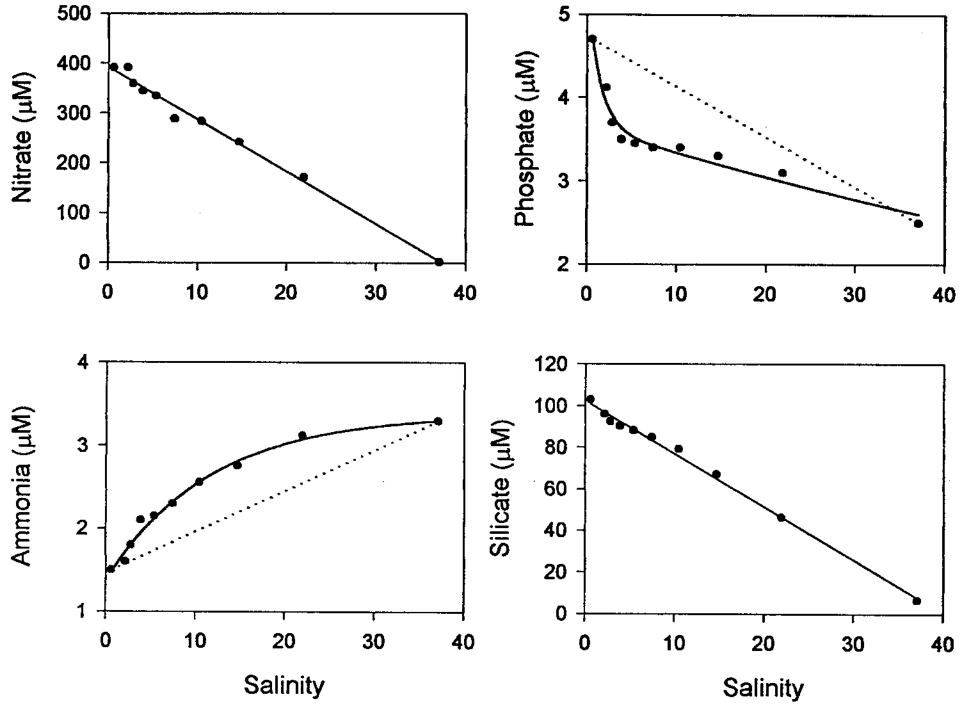

Figure 6. Variations in the nutrient concentrations versus the salinity during the simulation assays.

U.S.A. (Benoit *et al.*, 1994). The pH shows a clear non-conservative pattern with high values in the fluvial area of the estuary. Both factors make the carbonate concentrations high (about 0.17 mM) at low salinity values.

Figure 6 shows the nutrient concentrations during the estuarine simulation in the laboratory. It is clear the presence of a sharp gradient of inorganic nitrogen in the estuary. In the fluvial area, those tanks nearby the fresh water feeding, the nitrate concentration is high (about 400 μM) and there exists a linear decrease seaward of the estuary, represented by the tanks located nearby the seawater end-member of the simulation experiment. This conservative behaviour of nitrate has been described in other estuarine systems (Shengquan *et al.*, 1993). The nitrite levels were almost constant along the estuary. The ammonium concentrations increase from the fresh water to the seawater and it is the chemical specie, predominant in the seawater, for inorganic nitrogen. This process could be related to the existence of a denitrification process under anoxic microenvironments occurring in the surface of the suspended particulate matter.

The phosphate concentrations show a non-conservative behaviour with high loss of this chemical specie at low salinity values. This high chemical reactivity of phosphorus has been reported in several estuaries (Aston, 1980; Flegal *et al.*, 1991; Lebo, 1991; Windom *et al.*, 1991; Clark *et al.*, 1992; Lebo *et al.*, 1994; Pitkänen

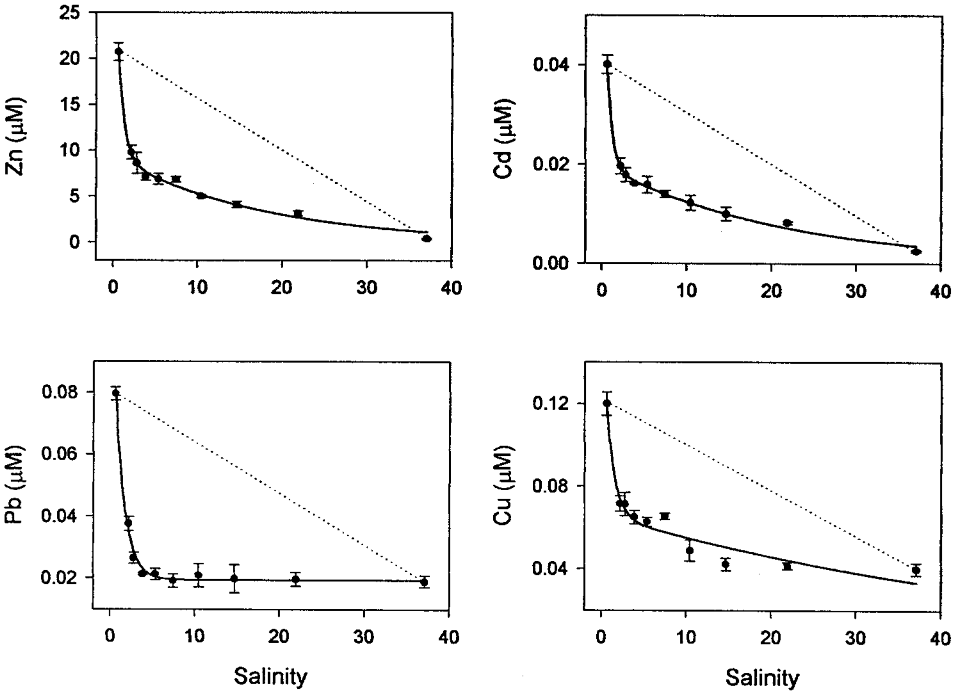

Figure 7. Variations in the Zn, Cd, Pb and Cu concentrations versus the salinity during the simulation assays. Error bars of the mean values represent standard deviations of the data.

and Tamminen, 1995), and could be associated with the biological activity or with the chemical adsorption onto Fe and Al hydroxides. It has a continental origin with levels about 100 µM for silicates in the fluvial area of the estuary. Its variation versus salinity is approximately linear, explained by the low reactivity showed by this nutrient in estuarine areas (Burton *et al.*, 1970; Flegal *et al.*, 1991; Shengquan *et al.*, 1993).

3.1. BEHAVIOUR OF THE HEAVY METALS (FIELD AND LABORATORY CONDITIONS)

Figure 7 shows the mean concentrations for Zn, Cd, Pb and Cu obtained during the assays. In all cases the variations are below the theoretical dilution pattern, therefore there is a high chemical reactivity, principally at low salinity values. The non-conservative behaviour of these metals has been reported for other estuaries (e.g., Holliday and Liss, 1976; Duinker and Nolting, 1978; Flegal *et al.*, 1991; Van der Berg, 1991; Windom *et al.*, 1991; Benoit *et al.*, 1994), and, in general, this is related to adsorption processes onto the SPM of both organic and inorganic origin (Bilinski *et al.*, 1991; Kozar *et al.*, 1992; Dai *et al.*, 1995; Wood *et al.*, 1995). Nevertheless, other authors have reported linear gradients with salinity for some of the measured metals (Paulson *et al.*, 1989; Harper, 1991).

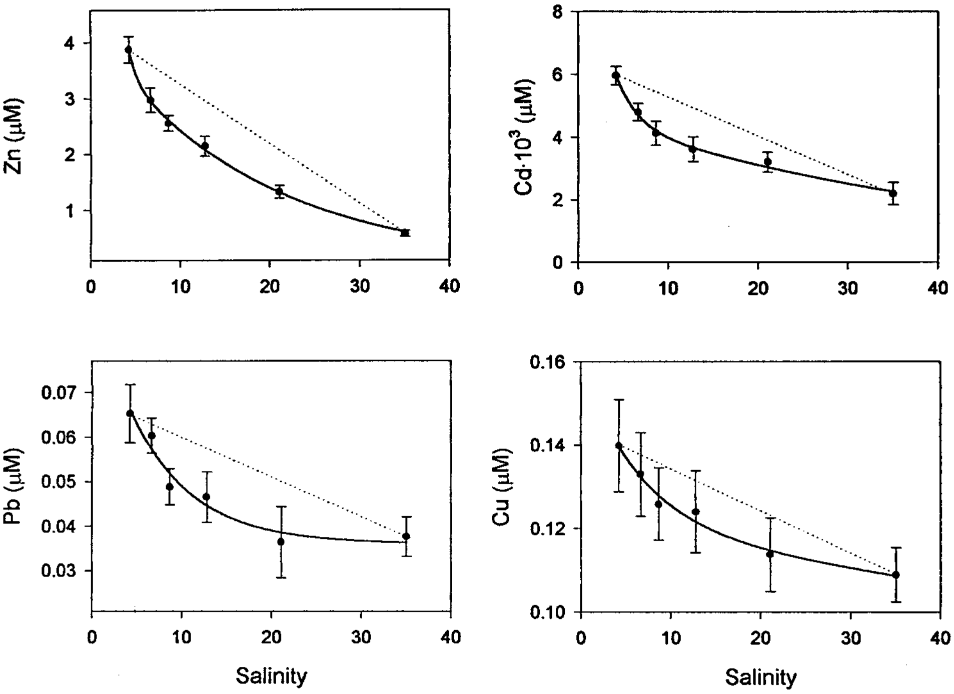

Figure 8. Variations in the Zn, Cd, Pb, and Cu mean concentrations versus the salinity in 6 stations located in the Guadalquivir estuary. Error bars of the mean values represent standard deviations of the data.

The discharge of untreated toxic water would have produced high heavy metal concentrations in the area of confluence of the rivers Guadiamar and Guadalquivir, especially by Zn (20.65 μM) and Cd (40 $\times$ 10^{-3} μM). This is a direct consequence of the toxic water composition in which the Zn and Cd present high concentrations, approximately 1000 times higher than the natural levels in the Guadalquivir fluvial area. For Pb and Cu, these differences are lower (only 50 times higher) and dilution gives maximum values measured in the simulation assays similar to those actually measured in the Guadalquivir estuary. Figure 8 shows the average values of the heavy metal concentrations measured in the field, versus the salinity for 6 stations located between the confluence of the rivers Guadalquivir and Guadiamar, and the mouth of the estuary (Figure 1), between May and September 1998. It can be observed that standard deviations are higher than those calculated in the simulation assays (Figure 7). The reason is the natural variations of the system, principally related to the strong hydrodynamic regime and the velocity of discharge of the treated toxic water from the treatment pond. The observed behaviour is also non-conservative for the heavy metals, but the Zn and Cd concentrations are lower than those measured during the simulation assays (4 μM and 6.22×10^{-3} μM, respectively). On the other hand, Pb and Cu concentrations are similar for both natural samples and simulation assay samples. Therefore, it is clear that Pb and Cu concentrations are of little influence, whether the toxic water is treated or untreated. From these data, it can be observed that the proposed direct discharge of the untreated toxic water would have produced unacceptably high levels of Zn and Cd contamination.

Although the behaviour of the studied metals in the simulation assays and in the field samples is non-conservative, the decreases in concentration with salinity show different trends. For the untreated waste, the gradient of heavy metal concentration with salinity is described by the next double exponential equation:

$$C = ae^{-bS} + ce^{-dS} ,$$

where C is the heavy metal concentration, S is the salinity, and a, b, c, and d are the fitted parameters for each metal. For real samples with treated waste, the heavy metal concentration gradients versus the salinity are described by the following exponential equation:

$$C = a + ce^{-dS} .$$

Table III gives the values for the fitted parameters, as well as the correlation coefficient for both equations. It can be observed that the fitted parameters in the second exponential term from the simulation assays are similar to those fitted to the exponential equation associated with the field samples. This indicates that the behaviour is similar for salinity values higher than 5, both in the simulation assays and in real conditions. Nevertheless, the high value of 'b' for the simulation assays describes the sharp decrease of the heavy metal concentrations for low salinity values. Windom *et al.* (1999) describe a similar behaviour for some metals in the zone with lower salinity values of the estuarine region of the 'Patos Lagoon' (Brazil).

These expressions allow us to calculate the dissolved heavy metal loss along the length of the estuary. The heavy metal flow through a fixed section of the estuary is established as:

$$F = Q(C - SdC/dS) ,$$

where Q is the river flow, fixed at 60 $\mathrm{m}^3\ \mathrm{s}^{-1}$. The losses depend on the salinity values and they are obtained by:

$$\mathrm{loss} = dF/dS ,$$

with the final expression depending on the values of the fitted parameters. Figure 9 shows a comparison of the losses of Zn, Cd, Pb, and Cu along the estuary under both simulated and real conditions. At the mouth of the estuary, where salinity is at maximum values, the accumulated losses of Pb and Cu are similar for both conditions, but in the simulation assays, the losses of Zn and Cd are higher. The evolution

TABLE III

Fitted parameters calculated for the heavy metal (Zn, Cd, Pb and Cu) concentrations versus salinity values during the simulation assays and for the field samples

		a	*b*	*c*	*d*	r^2
Zn	Simulation	25.62	1.340	9.350	0.0565	0.9854
	Real	0.3896	–	4.634	0.0825	0.9709
Cd	Simulation	0.0534	1.603	0.0197	0.0456	0.9812
	Real	2.3750	–	5.7700	0.1229	0.9134
Pb	Simulation	0.0996	0.854	0.0195	0.0001	0.9852
	Real	0.0361	–	0.0559	0.1460	0.8069
Zu	Simulation	0.0984	1.0234	0.0664	0.0184	0.9352
	Real	0.1072	–	0.0472	0.0920	0.6487

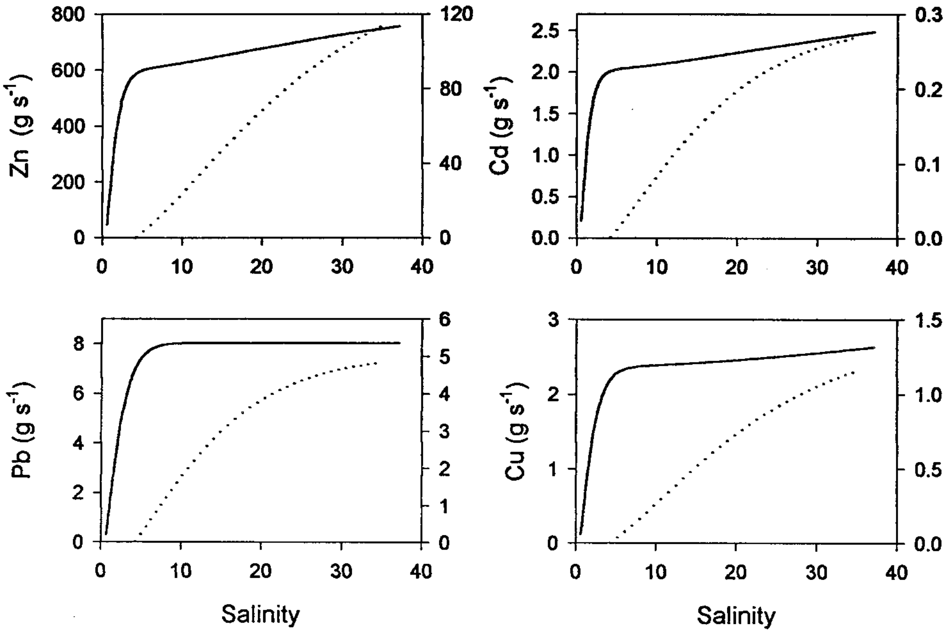

Figure 9. Heavy metal accumulated losses in the Guadalquivir estuary (continue line) and during the simulation assays (discontinue line).

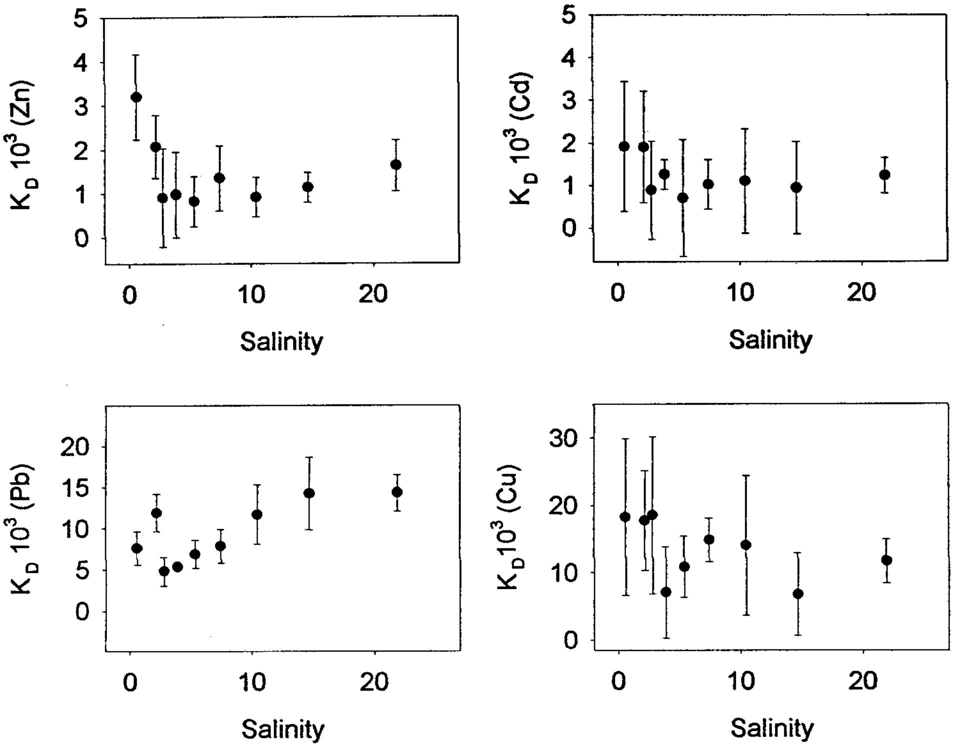

Figure 10. Calculated ratios between concentrations of heavy metals (Zn, Cd, Pb and Cu) in suspended particulate matter and water (K_D) as a function of the salinity for the simulation assays.

of these losses with the salinity values is notably different; for the simulation assays 80% of losses are related to salinity values of about 5 but under real conditions the losses are move evenly distributed across the salinity values. These differences are explained by the location of the actual waste discharge point being 17 km up the Guadiamar river, from its confluence with the Guadalquivir. Part of the chemical reactivity measured during simulation in the laboratory can be related to reactions undergone by these metals principally while they are associating with SPM in the transition area between the discharge point and the Guadalquivir itself (i.e. in the 'Entremuros' channel; Figure 1). On the other hand, the very high concentrations of metals in the assays simulating the rapid direct discharge of untreated toxic water are responsible for the high chemical reactivity observed at low salinity values.

The K_D values, defined as the ratio between the concentrations in the SPM and in the water, are ranged between 10^3 and 10^4, and they are similar to those reported by various authors (see e.g., Benoit *et al.*, 1994; Wood *et al.*, 1995). Assuming the association with particulate material to be the principal mechanism controlling the elimination of heavy metals, the residence times for each tank (about 650 min) are long enough for equilibrium between the two phases to be reached (Millward *et* *al.*, 1992). It cannot be observed a clear tendency owing to the average values for K_D are affected by a high variability because of the high standard deviation in the measurement of the particulate heavy metal concentrations (Figure 10).

4. Conclusions

The dynamic simulation assays of the theoretical discharge of untreated toxic water from the Aznalcóllar mining spill have provided an evaluation of the effectiveness of the treatment pond and plant established to clean up the heavy metals. The average concentrations of dissolved Zn and Cd actually measured along the Guadalquivir estuary are 6 times lower than those measured in the simulation of the system in the laboratory.

The heavy metals present a non-conservative behaviour showing a high chemical reactivity and high levels of losses to the aqueous phase at low salinity values. This was mainly due to the incorporation of these metals into the suspended particulate matter. The accumulated losses in the Guadalquivir estuary could have reached values of 750 g s^{-1} for Zn, in the event of a theoretical discharge of this toxic water without treatment.

Acknowledgements

Thanks are due to the Consejo Superior de Investigaciones Cientificas for supporting this study. We thank the staff of the Estación Biológica de Doñana for their help during the sampling of the seawater, fresh water and toxic water. Thanks are due to the Consejená de Medio Ambiente de la Junta de Andalucía (Grant No. 8 of Corredor Verde Program).

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