ORIGINAL PAPER

Assessment of the risk associated with mining-derived arsenic inputs in a lagoon system

Salvadora Martínez-López · María José Martínez-Sánchez · María del Carmen Gómez-Martínez · Carmen Pérez-Sirvent

Abstract Southern Mediterranean lagoons are considered among the systems most vulnerable to anthropogenic activities. In its present condition, the Mar Menor lagoon in south-eastern Spain must be considered as degraded as a result of the pressures to which its shoreline is exposed. These include the transport of arsenic from nearby mining areas, linked to soluble or particulate run-off following rainfall events and flooding. This work studies the solubility and bioavailability of arsenic in the soils of watercourses that drain into the Mar Menor, using nine single chemical extractions with different reagents. The values obtained for As, as well as for Fe and Mn, throw light on the interactions of these metals with As and predict future behaviour patterns for different scenarios. The mineral composition is seen to significantly influence the mobility of the studied elements and shows the relation between the soils and materials of mining origin. It has been suggested that the sediments deposited in the in the watercourses or "ramblas" that transport these materials may act as foci of dispersion.

S. Martínez-López · M. J. Martínez-Sánchez · M. C. Gómez-Martínez · C. Pérez-Sirvent (✉)
Department of Agricultural Chemistry, Geology and Pedology, Campus Mare Nostrum, University of Murcia, 30071 Murcia, Spain
e-mail: melita@um.es

Introduction

Southern Mediterranean lagoons are considered to be among the most vulnerable systems to anthropogenic activity. Studies have pointed to interesting connections between the hydrology and ecology of coastal wetlands; in particular, those of Mediterranean regions such as eastern Spain (Pérez-Ruzafa et al. 2005; López et al. 2003), Portugal (Newton and Mudge 2005), Italy (Marani et al. 2006), Greece (Sylaios and Theocharis 2002) and other countries, including Australia (Marimuthu et al. 2005) and Mexico (Contreras and Zabalegui 1991). Such is the case of the Mar Menor, the largest lagoon on the Spanish Mediterranean coast, which has a high ecological, fishing and tourism value. Furthermore, it is included in several international conservation agreements, including the Ramsar List of Wetlands of International Importance, Specially Protected Area under the EU Wild Birds Directive (SPA), Site of Community Importance (SCI) integrated in the Nature 2000 Network (EU Habitats Directive) and Special Protected Area of Mediterranean Interest (SPAMI) (Tsakovski et al. 2009).

The lagoon is affected by, among other factors, inputs from the Sierra Minera de Cartagena-La Unión,

a centre of mining activity with a history of more than 3000 years of activity (Navarro et al. 2012). During some periods, these activities have been carried out very close to, and sometimes on the very edges, of the Mar Menor, acting as a source of potentially toxic trace elements, including arsenic. These mining wastes can provoke toxic effects both in the source and in the surroundings (González-Alcaraz and van Gestel 2017).

The transport of As linked to soluble or particulate forms is related to rainfall events and flooding and frequently occurs in the watercourses or ramblas (creeks that occasionally carry water after rainfall), which carry a high load of mining wastes containing high concentrations of As and other metals. With the recurrent torrential rains typical of Mediterranean climate, the tailings that remain in the mountains continue to be eroded and washed into the lagoon (Navarro et al. 2008).

The exact degree to which the lagoon ecosystem is affected 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, sediments or dissolved phases (Tsakovski et al. 2009). The bioavailability of sediment-bound contaminants is determined by sediment constituents, overlying and interstitial water chemistry, and the behaviour of organisms (Loring 1991), and can therefore be considered as a dynamic process.

Changes in soil use may provoke changes in environmental conditions, including pH, redox conditions, the organic matter content, among others, which will affect the mobility of As and hence its bioavailability (Adriano 1986).

It is therefore important to determine the fraction of the total element concentration that is available for living organisms and to ascertain the mechanisms which regulate metal bioavailability (Mountouris et al. 2002; Fayiga and Saha 2016).

Estimating the amount of bioavailable As that enters the lagoon will permit its degree of toxicity to be evaluated. It is also important to study the plants within the ecosystem. Some vegetal species have a high capacity to accumulate trace elements, and this may have adverse effects on associated fauna. The same plants may transfer arsenic from the soil to their aerial parts so that these elements may enter the trophic chain, thereby representing a risk to human health. Biotransformation and transfer factors can be used to estimate and predict this trace element transfer capacity from the soil to different plant organs (Pérez-Sirvent et al. 2012).

To assess the solubility and bioavailability of arsenic in the soils of watercourses that drain into the Mar Menor, single chemical extractions with different reagents were carried out. This single chemical extraction methodology can be used to estimate and predict bioavailable As solubility and plant uptake from soils affected by mining activities, since its allows different environmental situations to be simulated (Ure et al. 1992; Martínez-Sánchez et al. 2011). It is also interesting to know the relation that exists between the phases of the major metals, Fe and Mn, and the behaviour of As in the soils and sediments studied since their stability in the face of supergenic processes will influence the mobilisation of this trace element (Montes-Avila et al. 2019).

The aim of this work was to study the current and projected bioavailability of As reaching the Mar Menor in particulate or soluble form as a result of hydrodispersion, taking into account possible changes in environmental conditions.

Materials and methods

Site description

The Mar Menor is a coastal lagoon located in south-eastern Spain (37°42′00″N, 00°47′00″W) with a surface area of 135 km^2. It is separated from the Mediterranean Sea by a narrow sand strip (called "La Manga") and is almost completely dedicated to tourism. Landwards, the lagoon is surrounded by an irrigated agricultural plain of 480 km^2 in a total watershed area of 1275 km^2, with dense urban settlements (Robledano et al. 2011). The lagoon is hyperhaline, with salinity levels (42–47 g/l) that are higher than those of the adjacent Mediterranean Sea because of the low precipitation (around 300 mm per year) and high evaporation rates (mean annual temperature 18 °C) (Tsakovski et al. 2009).

The semi-arid climate of south-eastern Spain means that "temporary water courses" (ramblas) remain dry for long periods of time. However, when torrential rain falls, they flood and transport materials (from the tips and sterile pools) from the mining area and discharge them into the Mar Menor.

Figure 1 shows the study zone and the main watercourses that flow into the lagoon which are affected by mining activities. The hydric transport and sedimentation of trace elements in the Sierra Minera may involve both soluble and particulate forms, and arsenic may reach topographically lower areas, including the Mar Menor lagoon, in either way. The suspended material is generally composed of minerals of clay, iron hydroxides and manganese, together with organic matter, and it is this that transports the arsenic and other elements adsorbed to them due to the large surface area, while other elements may be transported in dissolved form.

Sampling

For this study, 26 soil samples were collected in the proximity of the watercourses that flow into the Mar Menor (Fig. 1). Soil samples 1–8 were taken from zones unaffected by mining and are considered as the control samples. The rest of the samples can be considered as being affected by mining activity.

Sample treatment

The soil samples were air-dried and sieved to < 2 mm for general analytical determinations. The pH was measured in a 1:1 suspension of soil in pure water and in a 1 M KCl solution. Electrical conductivity (EC) was also measured in the extracts obtained by filtering the 1:1 suspension through a 0.45-μm cellulose acetate disc filter. Equivalent calcium carbonate (%) and the organic matter content (% O.M.) were also calculated by means of the usual procedures (Page 1982). High-purity water (18.2 MT cm) obtained using a Milli-Q water purification system (Millipore, Belford, MA, USA) was used throughout. To determine arsenic, the soil samples were first ground to a fine powder using
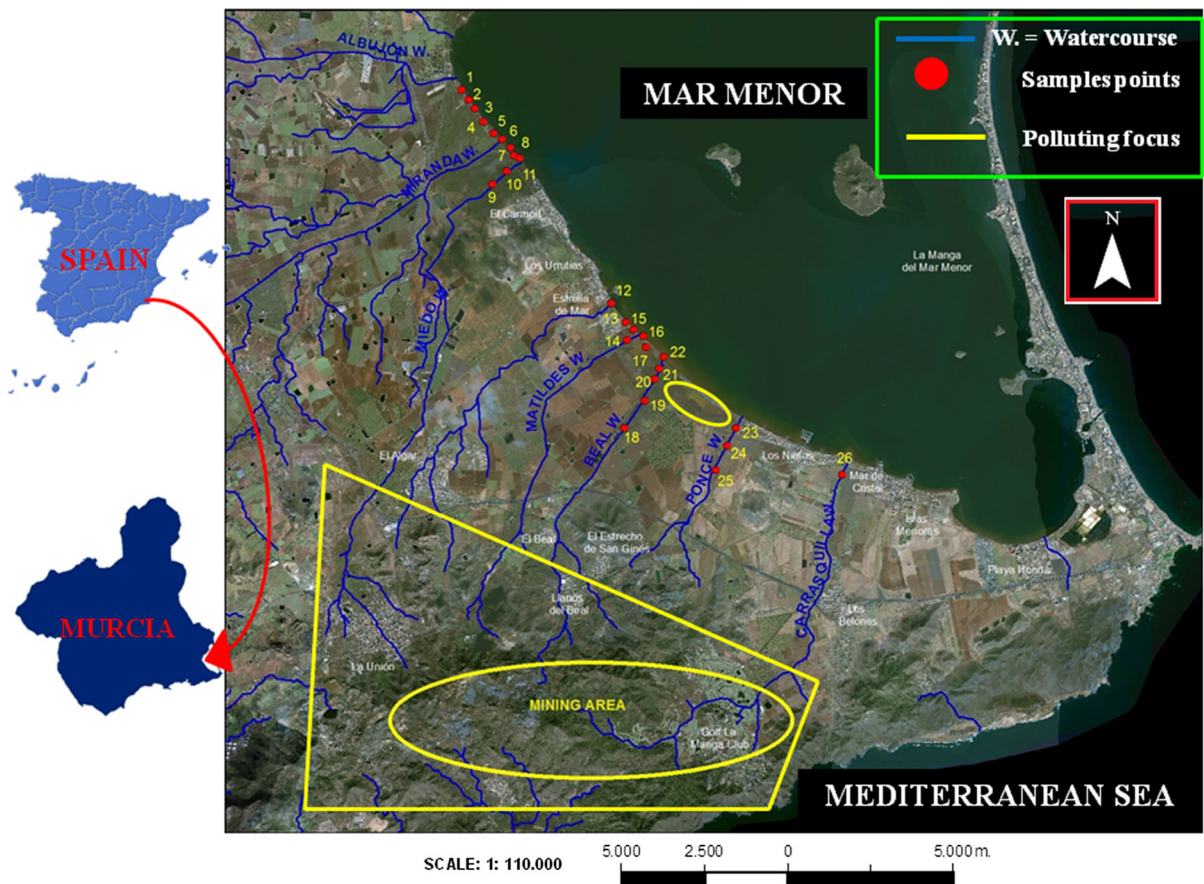

Fig. 1 Location of the zone studied and sampling points

an agate ball mill. Samples were placed in Teflon vessels, and 5 mL of concentrated HF acid solution, 2 mL of concentrated HNO_3 acid solution and 5 mL of pure water were added. When digestion in the microwave system was complete, the samples were transferred to a volumetric flask and brought to 50 mL before measurement. Teflon or other suitable plasticware was used for handling these liquids. The reliability of the results was assessed by analysis of the NIST standard reference materials: NCS DC 73,320 and NCS DC 73,325. The detection limit was found to be 0.01 mg kg^{-1}, 0.002% and 7.0 mg kg^{-1} for As, Fe and Mn, respectively.

Chemical extraction methods

Nine chemical extraction methods were used to assess As, Fe and Mn availability in soil, namely water medium (1:5 extract), nitric acid medium (1 g of solid in 50 ml 0.1 M HNO_3), hydrochloric acid medium (1 g of solid in 25–50 ml 0.5 M HCl) (an adaptation of the chemical extraction method of Adriano 2001), complexing–reducing medium (Mehra and Jackson 1960), oxidising medium [step 3 BCR (Community Bureau of Reference)] (Sutherland and Tack 2002), 0.5 M $HNaCO_3$ (Olsen et al. 1954), ammonium acetate (5 g of solid in 112.5 ml 1 M CH_3COONH_4) (Adriano 2001), 0.05 M $(NH_4)_2SO_4$ (Wenzel et al. 2002) and 0.005 M DTPA (Lindsay and Norvell 1978).

Analytical determinations

A semiquantitative estimation of the mineralogical composition of the samples was made by X-ray diffraction (XRD) analysis, using Cu-Kα radiation with a PW3040 Philips Diffractometer. X-powder software (Martín 2004) was used to analyse the X-ray diffraction diagrams obtained by the crystalline powder method. The powder diffraction file (PDF2) database was used for peak identification, taking into account that the determination of minerals from soils by XRD analysis is not accurate below a limit of 1% of the total weight in a sample (depending on the crystallinity of individual minerals). Arsenic was determined using atomic fluorescence spectrometry with an automated continuous flow hydride generation (HG-AFS) spectrometer (PSA Millennium Excalibur 10,055). The experimental conditions and

instrumental parameters used were as follows: wavelength (nm) = 197.3, primary current (mA) = 27.5, boost current (mA) = 35, delay time (s) = 15, analysis time (s) = 30, memory time (s) = 30, air flow rate (ml/min) = 300.

Fe and Mn were determined by flame atomic absorption spectrometry (FAAS) using a CONTRA AA700 High-Resolution Continuum Source Atomic Absorption Spectrophotometer.

The digestion of the samples was carried out using a Milestone ETHOS Plus Microwave system operating with a standard program (applied power in watts 150, 0, 150, 0, 150, 0, 350, 400, 0, 450 and 0 for 1, 1, 1, 1, 2, 1, 5, 5, 1, 1 and 20 min., respectively).

Statistical analysis

The statistical analysis of the data was performed with MINITAB 14 and IBM, SSP ver 20. The Pearson product-moment correlation test was used to establish possible relationships between the arsenic content and the mineralogical composition of the soil samples.

Results and discussion

General characteristics of the soils

Table 1 shows the general characteristics of the soil samples considered in this work. The samples had an alkaline pH value, in both water and potassium chloride extracts. Electrical conductivity varied widely (range 0.38–23.01), the samples with the highest conductivity values reflecting the marine influence. In general, the salt content increased as the distance to the shoreline fell.

Most of the samples had a low organic matter content (mean value of 3.1%). The calcium carbonate content varied (range 0.0–62.4%), although most samples had a low active content. Soil texture was generally coarse and, in some samples, ranged from sandy to silt loam.

The mineralogy is indicative of the influence of the different materials in the soils and of the processes taking place during their formation. The mineralogical analysis (see Table 2) showed that the main minerals were aragonite, quartz, dolomite, calcite, gypsum and phyllosilicates (kaolinite, illite and clinochlore), while the minority minerals were feldspar, mining products

Table 1 General characteristics of the soil samples

| Sample	pH (H$_2$O)	pH (KCl)	E.C. (mS cm^{-1})	Eh (mV)	O.M. (%)	CaCO$_3$ (%)	CaCO$_3$ Activ (%)	Clay (%)	Silt (%)	Sand (%)
1	7.63	7.48	17.10	130	2.6	34.1	1.2	0.4	12.7	86.9
2	8.02	8.05	17.30	120	2.6	32.2	1.1	0.1	2.1	97.8
3	9.02	8.96	15.84	89	1.2	36.1	0.9	5.3	22.6	72.2
4	8.27	7.63	20.57	140	2.5	18.3	0.6	0.1	20.2	79.7
5	7.98	7.92	21.01	130	3.1	19.3	0.7	0.2	40.3	59.5
6	8.88	8.78	23.01	115	2.1	57.1	0.5	0.1	1.7	98.2
7	8.70	8.7	22.60	110	2.2	62.4	0.5	0.1	1.5	98.4
8	9.27	9.27	11.56	93	1.9	57.8	0.4	0.1	2.3	97.6
9	7.51	7.15	1.65	199	4.1	3.8	0.3	0.1	17.5	82.4
10	7.77	7.53	1.81	162	3.1	3.0	0.3	0.2	31.9	67.9
11	7.98	7.8	9.18	183	4.2	35.4	9.0	0.1	4.9	95.0
12	7.75	7.61	11.60	230	5.0	15.4	4.0	0.1	2.5	97.4
13	8.12	7.42	0.85	201	6.1	60.2	4.8	0.1	0.1	99.8
14	8.04	7.7	3.31	185	5.3	50.1	4.1	0.1	1.5	98.5
15	8.14	7.79	3.71	189	3.6	50.3	6.0	0.1	3.2	96.7
16	8.09	7.95	9.03	191	1.8	15.0	9.7	0.1	15.0	84.9
17	8.09	7.95	9.03	191	1.4	19.0	7.8	0.1	15.0	84.9
18	7.75	7.73	1.78	207	3.2	0.0	0.0	0.1	0.9	99.0
19	7.71	6.42	1.89	276	4.4	0.0	0.0	0.1	3.9	96.0
20	7.44	7.21	8.60	203	3.1	2.0	1.0	0.1	15.6	84.3
21	7.39	7.34	5.67	196	1.8	2.0	0.3	0.1	4.5	95.4
22	7.95	7.57	1.27	230	0.8	35.2	2.1	0.1	5.0	94.9
23	7.64	7.4	0.95	277	2.6	13.1	6.3	0.2	10.0	89.9
24	8.18	7.37	0.38	173	2.4	1.1	0.3	2.6	20.8	76.6
25	7.51	7.16	1.38	202	4.2	6.1	2.1	0.1	18.1	81.8
26	7.65	6.89	1.23	249	6.1	6.3	0.2	0.1	5.9	94.0
Median	8.0	7.7	8.5	179.7	3.1	24.4	2.5	0.4	10.8	88.8
Range	7.4–9.3	6.4–9.3	0.4–23.0	89.0–277.0	0.8–6.1	0.0–62.4	0.0–9.7	0.1–5.3	0.1–40.3	59.5–99.8
SD	0.5	0.6	7.8	51.8	1.4	21.4	3.0	1.1	10.4	10.9

(hematite, jarosite, pyrite and goethite) and amorphous materials.

A cluster analysis was performed first in order to classify the samples into mineralogical groups. Next, after the corresponding discriminant analysis, the samples were divided into three groups according to mineralogical composition and texture (Fig. 2). The first group was made up of 8 soils, the most mineralised samples, localised in the first quadrant of the figure. These soils contained minerals of primary contamination such as jarosite, pyrite, goethite and weather-resistant minerals like quartz

(Table 2). They contained no minerals of marine influence like aragonite and were the least carbonated soils. The second group was formed of 10 samples between the second and third quadrants. This group clearly showed marine influence, as reflected by the high aragonite content. These samples had the lowest phyllosilicate content, an average carbonate content and no minerals like jarosite and goethite. The third group was made up of 8 samples from the fourth quadrant. As can be seen from Table 2, these samples had the highest carbonate and feldspar content. They contained moderate levels of phyllosilicates and no

Table 2 Characterisation of mineralogical groups (mean values)

Variable	Group 1	Group 2	Group 3	Range	Median	SD
Clinochlore	16.50	5.90	8.50	1–22	8.19	6.375
Illite	17.37	12.90	18.75	1–42	14.42	9.287
Kaolinite	15.5	4.40	7.75	1–22	9.34	7.200
Quartz	17.25	11.50	11.50	6–48	23.03	13.101
Gypsum	5.37	4.50	7.12	0–28	8.50	8.262
Feldspar	1.62	1.60	10.38	1–16	4.23	2.984
Jarosite	7.25	0.00	0.00	0–17	3.38	4.850
Aragonite	0.00	30.00	1.22	0–47	11.53	16.543
Hematite	2.75	6.40	3.00	1–15	3.00	3.805
Goethite	7.37	0.00	2.12	0–14	4.50	3.905
Calcite	4.00	5.20	5.75	0–37	11.26	10.802
Dolomite	3.62	16.60	27.75	0–58	4.76	11.718
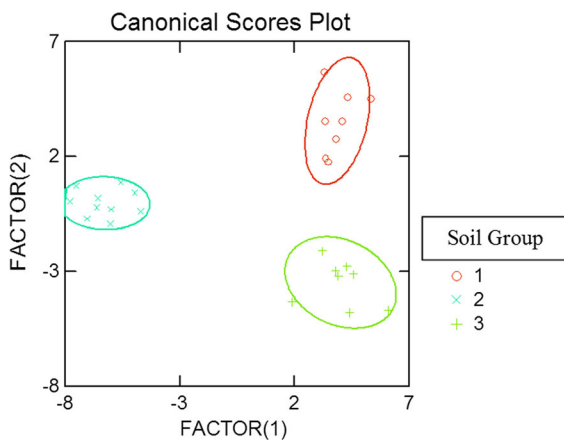
Fig. 2 Results for the grouping of samples by discriminant analysis

minerals resulting from mining contamination such as jarosite and pyrite. As regards the texture of the soils studied, groups 1 and 3 contained the samples with the finest texture.

The overall correct classification average obtained with a Jackknifed classification matrix pointed to 81% correct assignations to groups.

Levels of trace elements determined in soils

Particulate levels of arsenic, iron and manganese

The total content of the trace elements determined varied greatly, with high standard deviation values, as can be seen from Table 3.

Soils samples (1–8) are from the stretch of coast affected by the Miranda watercourse. These contain

calcareous Fluvisols formed of materials brought down from the nearby soils, mainly calcareous Regosols and calcic and petrocalcic Xerosols. The area is hardly influenced by mining and contains very low levels of trace elements. It is an uncontaminated zone and was therefore considered as a control.

Two transects almost permanently under water (9, 10) on red soils and others very near the lagoon (11, 12), which can be considered highly or moderately influenced, given their high content of As, Fe and Mn, respectively, were studied. These points can be considered small foci of dispersion given the high levels of elements they contain.

Soils samples 13–17 are luvic Xerosols, calcic Xerosols and, occasionally, calcic Luvisols and lie against the zone of Arenosols which makes up the coastal belt. The total level of trace elements determined is not very high given that they are transported materials that have been mixed.

Soils samples 18–22 have a high total trace element levels and are strongly influenced by mining, with two sources of contamination: one, the Beal watercourse, which transports mineralised materials from the Sierra Minera, both naturally and in canals (based on the placement of old canals), while the other source is the present day Lopoyo pool (an old mining installation that stored mine wastes, and which is now in a protected zone (ZEPA) near the beach on the lagoon).

Soil samples 23, 24 and 25 have high trace element levels, and the soils are directly and strongly influenced by the Sierra Minera. Soil sample 26, in which the soils have been transformed to make them suitable for growing crops, showed a medium–high

Table 3 As, Fe and Mn extracted by different reagents

Total content		H_2O	HNO_3	HCl	Oxidisable	M–J	Olsen	NH_4Ac	$(NH_4)_2SO_4$	DTPA
As	Quantification limit (ql)	0.01	0.1	0.1	0.1	0.1	0.02	0.04	0.05	0.004
	Median	108.6	0.005	2.3	8.6	0.9	61.3	0.4	0.1	0.1	0.03
	Range	6.9–347	0.01–0.04	0.1–10	1.2–22	0.10–2.5	0.1–235	0.02–1.2	0.04–0.2	0.05–0.1	0.004–0.1
	SD	105.2	0.01	2.7	7.1	0.7	70.9	0.3	0.05	0.04	0.03
Fe	Quantification limit (ql)	0.002*	2.8	27.1	0.002	0.6	0.002	5.6	3.3	4.0	0.3
	Median	5.7*	0.4	1159.0	0.6	22.9	2.8	4.9	1.5	1.3	168.3
	Range	0.1–18.2*	0.0–2.8	27.1–4438	0.03–2.9	0.6–135	0.02–7.2	5.6–24.3	3.3–6.3	0.0–4.0	16.0–911
	SD	5.21	0.2	1419.0	0.7	36.2	2.5	5.5	1.4	0.7	185.4
Mn	Quantification limit (ql)	7.0	0.8	8.0	6.0	8.0	7.0	5.6	3.5	4.0	1.1
	Median	2291	0.6	749.0	968.0	64.0	1091.0	1.5	5.4	1.8	169.9
	Range	166.0–6975.0	0.8–7.4	8.0–2412	53.0–2409	8.0–495.4	7.0–4680	5.6–6.9	3.5–14.4	4.0–6.0	1.1–1823.5
	SD	1997	1.5	713	790	98.1	1137.0	1.6	4.3	1.3	383.2

level of influence by the Sierra Minera, with a medium content of As and high Fe and Mn contents.

To study the relation between the total concentrations of the trace elements in the soil in the study area, a Chi-squared test was made, formulating two hypotheses to be compared (Table 4). The results obtained with the Chi-squared test can be summarised as: As–Fe (Chi-squared = 970.632, GL = 25, $P = 0.000$), As–Mn (Chi-squared = 2602.762, GL = 25, $P = 0.000$) and Fe–Mn (Chi-squared = 13,017.444, GL = 25, $P = 0.000$).

The results point to a P value of 0.000 for the three trace elements studied. This means that for a level of significance of $\alpha = 0.05$ or $\alpha = 0.01$ the trace elements are mutually dependent; that is, there is evidence of an association between As and Fe, between As and Mn and between Fe and Mn.

The total As content was positively correlated with total Fe ($r = 0.617$, $p = 0.001$) and total Mn ($r = 0.700$, $p = 0.000$). In the case of soil Fe and Mn, a strong positive correlation was found ($r = 0.896$, $p = 0.000$).

Further significant correlations of the three elements with the mineralogy and general characteristics of the soils can be observed in Table 5.

There was no strong correlation between As, Fe and Mn with minerals such as jarosite, suggesting that they may be related to Fe and Mn oxides. The soils with the highest concentrations of As, Fe and Mn did not contain calcite or other carbonates, but did contain high levels of clay minerals and iron oxides and hydroxides. Taken together, the data underline the similar behaviour of As, Fe and Mn in the soils of the study zone.

Mobilisation of trace elements in different environmental scenarios

To study and simulate the different inputs that may reach the Mar Menor lagoon in future, the environmental scenarios depicted in Table 6 were considered.

- **E1: Particulate and soluble material dispersion**

Through run-off and erosion, rainfall carries the particles away from the contamination source to disperse them along the watercourses, which act as the transmission pathways.

Table 4 Variables of Chi-squared test

Variables	Hypothesis	X and Y are independent?	P value (level of significance of α = 0.05 or 0.01)
X = Presence of "trace element 1" in the soil	H0	Yes (no association)	P is > α
Y = Presence of "trace element 2" in the soil	H1	No (association)	P is $\leq$ α

Table 5 Correlations of the As, Fe and Mn elements with the mineralogy and general characteristics of the soils

Correlation coefficient (r)

Element	Clinochlore	Kaolinite	Calcite	pH(H$_2$O)	E.C	CaCO$_3$
As	0.841**	0.639	− 0.681*	− 0.586*	− 0.708**	− 0.678**
Fe	0.494*	0.557*	− 0.552*	− 0.593*	− 0.552*	− 0.748**
Mn	0.536*	0.465*	− 0.639*	− 0.577*	− 0.630*	− 0.739**

*$P < 0.05$; **$P < 0.001$

Table 6 Conceptual model of contamination

Scenario	Method	Simulation	Mobilisation
E1.1: Particulate and soluble	Water medium (a)	Rain	Natural
E1.2: Rainwater	Rainwater		
E2.1: Acid and oxidant	Nitric acid médium (a)	Acidic waters	Potential
E2.2: Acid	Hydrochloric acid médium (b)		
E3: Oxidising medium	Step 3 BCR (c)	Oxidants conditions	Potential
E4: Reducing conditions	Complexing–reducing medium (d)	Presence of organic materials and permanent flooding	Potential
E5: Assimilation by plants	DTPA. Lindsay and Norvell (1978) (e)	Transferable to plants	Plant-available
	NH$_4$Ac. Ammonium acetate (b)		
	(NH$_4$)$_2$SO$_4$. Wenzel et al. (2002) (f)		
	HNaCO$_3$ Olsen et al. (1954). (g)		

(a) Martínez-Sánchez et al. (2011); (b) Adriano (2001); (c) Sutherland and Tack (2002); (d) Mehra and Jackson (1960); (e) Lindsay and Norvell (1978); (f) Wenzel et al. (2002); (g) Olsen et al. (1954)

In these natural mobilisation conditions (Martínez-López 2010), the arsenic may move in two forms—particulate or soluble—although torrential rain is more likely to provoke input in particulate form.

The concentrations of soluble arsenic released by extraction in liquid medium (1:5 extract) were, in general, below quantification limits (Table 3), and only in isolated points did they reach 0.04 mg/kg. Arsenic is not mobilised when it comes into contact with the basic pH soils.

The concentrations of soluble Fe and Mn in the studied soils were very low, and most of the samples contained both metals in concentrations below the quantification limit (Table 3).

To study the natural mobilisation of As, Fe and Mn by run-off waters, a chemical characterisation of the waters of the study area was carried out by reference to the pH, EC and the soluble ions measured.

- **E2.1: Acid mine water**

Acid mine drain waters have a naturally high potential to mobilise arsenic (Table 3). If these waters interact with particulate material in which arsenic is bound to

carbonates, the trace element is released. This could be the case with samples from zones 11 and 12, in which the arsenic is closely associated with the calcium carbonates. The acid mine waters can release the As retained by insoluble minerals such as sulphides and jarosite, which in some soils, like those of the Beal watercourse, is poorly or badly crystallised.

There were large differences in the amount of Fe and Mn extracted from the samples, as reflected by the high SD values of Table 3.

- **E2.2: Acidic condition**

Arsenic is readily mobilised when the effect of very acid waters is simulated by means of HCl extraction (Table 3). In such conditions, the carbonated phases, oxides and oxyhydroxides are strongly attacked. The sulphates (gypsum and jarosite) are also attacked, with the consequent mobilisation of the As associated with them, as occurs in points 9, 11, 12, 16, 18, 19, 20 and 25. However, mobilisation is very low in the soils close to the Miranda watercourse, probably because the As is retained in a residual form and only that part associated with the carbonated phases is mobilised.

The concentration of Fe extracted was high, especially in soils of the watercourses showing signs of primary contamination (central part of the study zone). Mn behaved similarly to Fe.

- **E3: Oxidising medium**

Most of the As extracted in oxidisable medium was from soils showing primary contamination (central part of the study zone) (Table 3). In mildly acid conditions, when the environmental conditions are highly oxidising, As release is lower than at pH < 1, and the As released is bound to reduced forms of iron II, carbonates and sulphides. Both Fe and Mn were extracted more readily from samples containing iron oxides in their mineralogy.

- **E4: Reducing conditions**

The Mehra and Jackson extraction method (Mehra and Jackson 1960) simulates the change from reducing to complexing conditions, in which complexation processes may release the As associated with carbonated phases and amorphous or poorly crystallised particles, or those bound or associated with jarosites or iron oxides (mainly hematite).

Reducing or complexing conditions may arise in the following two cases:

(1) The soils are permanently flooded and the poorly evolved organic matter forms complexes with As, Fe and Mn.
(2) The watercourse sediments are deposited on the seabed with its reducing conditions and high organic matter content. This situation is highly likely at present and so there is imminent hazard of As being mobilised.

Our assay was carried out at 80 °C, but it would be convenient to repeat it in conditions reflecting seabed conditions.

As was present in very high mean concentrations (Table 3), confirming that in most of the samples the element is mainly bound to amorphous or poorly crystallised particles.

Arsenic is also released when it is bound or associated with jarosite or iron oxides (hematite) in samples in which the mineral crystallinity is low (soils belonging to group 1).

As can be seen (Table 3), iron concentrations were high in all the samples, pointing to the existence of non-crystalline phases of the element. It seems that the iron is found in its free form and not associated with silicated phases. Mn is also present in very high concentrations in the type 1 soils.

- **E5: Plant-available**

Four different extraction methods were used to evaluate the availability to the plants, with very different results for the samples studied.

In DTPA extraction (pH neutral and complexing medium), the trace elements mobilisation was low at all the sampling points, although slightly higher in the soils showing primary contamination (Table 3).

DTPA was originally designed for determining micronutrients for plants, including Fe and Mn among others, and so is suitable for studying the mobility of both these elements, which are found in high concentrations in the samples (Table 3).

With ammonium acetate (pH = 7) and ammonium sulphate (pH = 5) extraction, mobilisation was very low (Table 3). These reagents are widely used for studying cationic exchange and so it can be assumed that the As is not found in cationic form (As^{3+}, As^{5+}) in any of the soils studied.

Table 7 Factors obtained after principal component analysis between the As, Fe and Mn concentrations in soil, concentrations of the As, Fe and Mn extractible in soil (with different extractants) and mineralogical composition of the soils

Factor	Variable	%Variance
F1	+ [Mn] E4, + [Mn] Total, + [Fe] Total, + [Fe] E4 , + [Mn] E2.2, + [Mn] E3, + [As] E4 + [As] Total, [Mn]E2.1, − Aragonite, − Hematite, − pH	29.91
F2	+ [Mn] DTPA, + [Fe] DTPA, + [Fe] E3, + [Fe] E2.2, + [Fe] E2.1	18.31
F3	+ [As] E2.1, + [As] E2.2, + Goethite, + [Mn] E.5, + Jarosite, + [Fe] E2.1, − As] E3, Calcite	16.95
F4	+ [As] E5	7.20

Iron and Mn concentrations in the ammonium acetate and ammonium sulphate extracts of these soils were very low and below the quantification limit in most samples. However, mention should be made of the Mn extracted in the control zone and from the Miedo and Carrasquilla watercourses, where the Mn is associated with the fine particles—possibly active forms of calcium.

Based on the method described by Olsen in 1954, extraction in bicarbonate medium (pH = 8.5) simulates the conditions reigning in the rhizosphere and mobilises the trace elements bound to carbonates and probably exchangeable.

The As concentrations in this medium were low (Table 3), samples 5, 6, 12, 15, 20 and 24 being of note for the small amount of As they contained bound to carbonates in anionic form in the exchange complex.

The concentration of Fe in bicarbonate medium was very low but highest in the soils of the Miedo, Matildes and Beal watercourses. In the case of Mn, most samples contained amounts below the limit of quantification.

Principal component analysis

To determine whether there were significant relationships between the concentration of As, Fe and Mn in the fraction obtained after different selective chemical extractions and the mineralogical composition of the soils, a principal component analysis was carried out, using the "varimax" orthogonal rotation option, to facilitate the analysis and to minimise the number of variables with a high loading factor. The result of assigning a group number to each sample was contrasted by means of a linear discriminant analysis. Four factors explained 72.4% of the variance (Table 7).

The presence of several high loads on a given component was taken to indicate that there is a
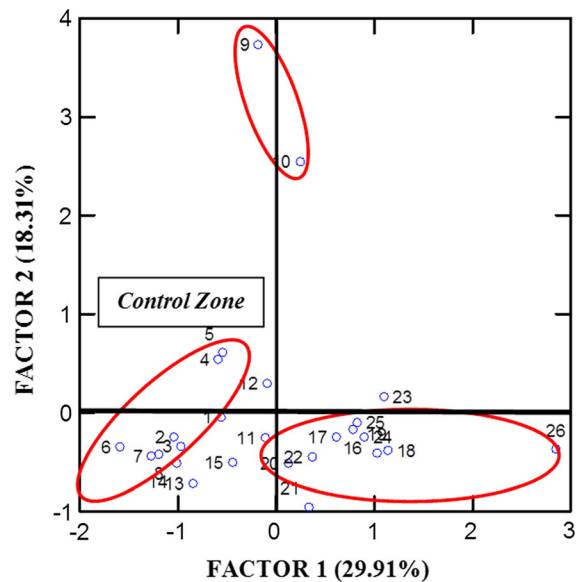
Fig. 3 Graphic representation of factor 1 versus factor 2

correlation between the variables and the component, the sign of the load indicating whether the correlation is direct or inverse. When the loads on a component are high and positive, the component indicates quantity, and when the signs are mixed, the component indicates contrast between the properties or basic variables (Ramis and García 2001).

The scores referring to each factor and for each sample are represented below (Figs. 3 and 4) in order to establish the correlations. Figure 3, which represents F1 versus F2, points to the separation of the samples mainly grouped in the third and fourth quadrants. In general, the negative quadrant contains samples with lower concentrations of As, Fe and Mn extractable in acid medium (HNO$_3$ and HCl) and in complexing–reducing medium. They mainly correspond to the samples from the control zone and the Matildes watercourse. The fourth quadrant contains
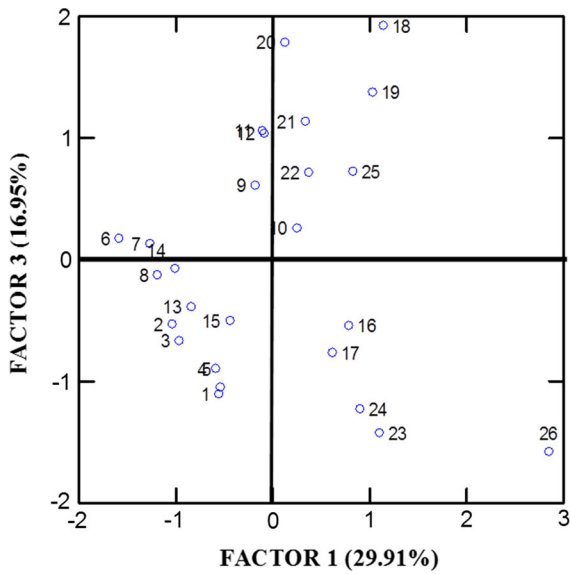
Fig. 4 Graphic representation of factor 1 versus factor 3

the samples with the largest content of elements extractable in the above media, but the lowest content of Fe extractable in acid and oxidisable medium and DTPA. These mainly correspond to the samples from the watercourses. Samples 9 and 10 from the Miedo watercourse are grouped differently. These samples have high concentrations of As, Fe and Mn, but also high concentrations of As, Fe and Mn extractable in complexing–reducing medium, a low hematite content and no aragonite in their mineralogical composition.

Figure 4 (F1 versus F3) points to a uniform distribution of samples in each of the quadrants. The positive quadrant contained samples 10, 18, 19, 20, 21, 22 and 25, which are characterised by the higher concentrations of total As, Fe and Mn and the same elements extractable in complexing–reducing medium. All, except sample 22, which comes from the coastal belt, are from the watercourse heads. The samples from the control zone and Matildes watercourse, which has a low total arsenic concentration, are distributed between the second and third quadrants. These samples have the lowest concentrations of As, Fe and Mn extractable in acid and complexing–reducing media and the highest aragonite concentration in their mineralogical composition. The last quadrant contains samples with the highest calcite concentration in their mineralogical composition and arsenic extractable in oxidant medium.

Conclusions

A clear correlation was evident between the three elements studied. The sediments deposited in the watercourses or ramblas that transport these materials may act as foci following rainfall.

The mineralogical composition of a soil is a very important factor that determines the mobility of the studied trace elements, as a function of environmental conditions. For example, increasing soil acidity may mobilise the As associated with carbonates and the As retained by insoluble minerals such as sulphides and jarosites. If the medium is strongly attacked by acidic agents, the As associated with oxide and oxyhydroxide phases may also be mobilised.

The high values of As extracted by the Mehra and Jackson method show that the particulate arsenic that enters the Mar Menor lagoon through the watercourses is susceptible to mobilisation when the organic matter content is high, for example, as a result of an accidental spill from a sewage treatment plant or intensive agricultural practices.

At present, the Mar Menor lagoon can be considered a research laboratory for different disciplines and organisms involving a multitude of research methods and research teams, all dedicated to understanding and, hopefully, finding a response to the causes that have led to the serious degradation of the lagoon. The findings of the present study show that the lagoon is affected by trace elements from the Sierra Minera de Cartagena-La Unión and steriles pools located in the surroundings. This leads to a diffuse contamination around the mouth of several of the watercourses that enter the lagoon after rainfall.

It is also concluded that the trace elements (As, Fe and Mn) contained in the sediments from the watercourses that enter the Mar Menor are susceptible to mobilisation and will therefore be incorporated into the aquatic medium if there are substantial changes in acidity, oxidation or reduction in the environmental conditions.

References

Adriano, D. C. (1986). *Trace elements in the terrestrial environment*. Heidelberg: Springer.

Adriano, D. C. (2001). *Trace elements in terrestrial environments: biogeochemistry, bioavailability and risks of metals* (2nd ed.). Heidelberg: Springer.

Contreras, F., & Zabalegui, L. M. (1991). *Hidrología, nutrientes y productividad primaria en la laguna La Joya-Buenavista, Chiapas, México*. México: Anales del Instituto de Ciencias del Mar y Limnología.

Fayiga, A. O., & Saha, U. K. (2016). Arsenic hyperaccumulating fern: Implications for remediation of arsenic contaminated soils. *Geoderma, 284*, 130–143.

González-Alcaraz, M. N., & Van Gestel, C. A. M. (2017). Changes in soluble metal concentrations induced by variable water table levels as response to liming and Phragmites australis growth in metal-polluted wetland soils: Management effectiveness. *Geoderma, 289*, 20–28.

Lindsay, W. L., & Norvell, W. A. (1978). Development of a DTPA test for zinc, iron, manganese and copper. *Soil Science Society of America Journal42*, 421–428.

Loring, D. H. (1991). Normalization of heavy-metal data from estuarine and coastal sediments. *ICES Journal of Marine Science,48*, 101–115.

López, R., Quintana, X. D., Salvado, V., Hidalgo, M., Sala, L., & Moreno, R. (2003). Comparison of nutrient and contaminant fluxes in two areas with different hydrological regimes (Emporda Wetlands, NE Spain). *Water Research,37*, 3034–3046.

Marani, M., Silvestri, S., Belluco, E., Ursino, N., Comerlati, A., Tosatto, O., et al. (2006). Spatial organization and ecohydrological interactions in oxygen-limited vegetation ecosystems. *Water Resource Research, 42*(6), W06D06.

Marimuthu, S., Reynolds, D. A., Salle, La, & C. L., (2005). A field study of hydraulic, geochemical and stable isotope relationships in a coastal wetlands system. *Journal of Hydrology, 315*, 93–111.

Martín, D. (2004). *Qualitative, quantitative and microtextural powder X-ray diffraction analysis*. https://www.xpowder.com

Martínez-Sánchez, M. J., Martínez-López, S., García-Lorenzo, M. L., Martínez-Martínez, L. B., & Pérez-Sirvent, C. (2011). Evaluation of arsenic in soils and plant uptake using various chemical extraction methods in soils affected by old mining activities. *Geoderma, 160*, 535–541.

Martínez-López, S. (2010). *El arsénico en suelos con influencia minera en ambientes semiáridos*. Doctoral thesis. University of Murcia.

Mehra, O. P., & Jackson, M. L. (1960). Iron oxide removal from soils and clays by a dithionite–citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals, 7*, 317–327.

Montes-Avila, I., Espinosa-Serrano, E., Castro-Larragoitia, J., Lázaro, I., & Cardona, A. (2019). Chemical mobility of inorganic elements in stream sediments of a semiarid zone impacted by ancient mine residues. *Applied Geochemistry, 100*, 8–21.

Mountouris, A., Voutsas, E., & Tassios, D. (2002). Bioconcentration of heavy metals in aquatic environments: the importance of bioavailability. *Marine Pollution Bulletin, 44*, 1136–1141.

Navarro, C., Pérez-Sirvent, C., Martínez-Sánchez, M. J., García-Lorenzo, M. L., & Molina, J. (2012). Weathering processes in waste materials from a mining area in a semiarid zone. *Applied Geochemistry, 27*, 1991–2000.

Navarro, C., Pérez-Sirvent, C., Martínez-Sánchez, M. J., Vidal, J., Tovar, P. J., & Bech, J. (2008). Abandoned mine sites as a source of contamination by heavy metals: a case study in a semi-arid zone. *Journal of Geochemical Exploration, 96*, 183–193.

Newton, A., & Mudge, S. M. (2005). Lagoon-sea exchanges, nutrient dynamics and water quality management of the Ria Formosa (Portugal). *Estuarine, Coastal and Shelf Science, 62*, 405–414.

Olsen, S. R., Cole, C. V., Watanabe, F. S., & Dean, L. A. (1954). Estimation of available phosphorus in soils by extraction with sodium bicarbonate. *US Department-Agriculture, 939*, 1–19.

Page, A. L. (1982). *Methods of Soil analysis* (2nd ed.). Madison, WI: American Society of Agronomy.

Pérez-Ruzafa, A., Fernández, A. I., Marcos, C., Gilabert, L., Quispe, J. I., & García, J. A. (2005). Spatial and temporal variations of hydrological conditions, nutrients and chlorophyll a in a Mediterranean coastal lagoon (Mar Menor, Spain). *Hydrobiologia, 550*, 11–27.

Pérez-Sirvent, C., Martínez-Sánchez, M. J., Martínez-López, S., Bech, J., & Bolan, N. (2012). Distribution and bioaccumulation of arsenic and antimony in Dittrichia viscosa growing in mining-affected semiarid soils in southeast Spain. *Journal of Geochemical Exploration, 123*, 128–135.

Ramis, G., & García, M. C. (2001). *Quimiometría* (p. 238). Madrid: Editorial Síntesis.

Robledano, F., Esteve, M. A., Martínez-Fernández, J., & Farinós, P. (2011). Determinants of wintering waterbird changes in a Mediterranean coastal lagoon affected by eutrophication. *Ecological Indicators, 11*, 395–406.

Sutherland, R. A., & Tack, F. M. G. (2002). Determination of Al, Cu, Fe, Mn, Pb and Zn in certified reference materials using the optimized BCR sequential extraction procedure. *Analytica Chimica Acta, 454*, 249–257.

Sylaios, G., & Theocharis, V. (2002). Hydrology and nutrient enrichment at two coastal lagoon systems in Northern Greece. *Water Resources Management, 16*(3), 171–196.

Tsakovski, S., Kudłak, B., Simeonov, V., Wolska, L., García, G., Dassenakis, M., et al. (2009). N-way modelling of sediment monitoring data from Mar Menor lagoon, Spain. *Talanta, 80*, 935–941.

Ure, A. M., Quevauviller, P. H., Muntau, H., & Griepink, B. (1992). Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International Journal of environmental Analytical Chemistry, 51*, 135–151.

Wenzel, W. W., Brandstetter, A., Wutte, H., Lombi, E., Prohaska, T., Stingeder, G., et al. (2002). Arsenic in field-collected soil solutions and extracts of contaminated soils and it implication to soil standards. *Journal of Plant Nutrition and Soil Science, 165*, 221–228.