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The role of *Cymodocea nodosa* on the dynamics of trace elements in different marine environmental compartments at the Mar Menor Lagoon (Spain)

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Abstract

During mining activities historically developed at Sierra Minera (Cartagena-La Unión, Spain), high amounts of trace elements were discharged to the Mar Menor coastal lagoon mainly through El Beal Wadi. The objective of this study is to establish the role played by the *Cymodocea nodosa* in the coastal marine dynamics of trace elements at the mouth of the wadi. To this end, the content of nine trace elements (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in different marine environmental compartments (i.e. marine and coastal sediments, *C. nodosa* tissues collected from live seagrass and *C. nodosa* beach cast litter) at two different locations were determined by inductively coupled plasma atomic emission spectrometry. The results showed that the seagrass *C. nodosa* could mobilise part of the elements present in marine sediments and water, thereby causing their re-accumulation in the coastal sediments through the *C. nodosa* beach cast litter.

Keywords

Mining waste; Marine chemistry; Trace metals mobilisation; Analytical chemistry; Seagrass leaf litter beds; Mar Menor coastal lagoon

1. Introduction

The Mar Menor is one of the biggest hypersaline coastal lagoons (salinity ranging between 38 and 51 psu) in the Mediterranean Sea. The lagoon is relatively shallow (i.e. mean depth of 3.5 m) with a surface area of 135 km^2 and a water volume of approximately 580 million m^3 (María-Cervantes et al., 2009; Marín-Guirao et al., 2005c; Pérez-Ruzafa et al., 2005). It is an area with high ecological value and is currently protected by different multi-statement laws and conventions. It was declared a national protected area (Jefe de Estado S. R. M. Juan Carlos I, 1989) and, since 2004, a RAMSAR international site. It has also been declared a *Site of Community Importance (SCI)* and a *Special Area of Conservation* under the Habitats Directive integrated in the Nature 2000 Network (EU habitats Directive). Moreover, it was established a *Special Protected Area of Mediterranean Interest* by Barcelona Convention 2001 (Da Cruz and Consejería de Agricultura, 2003; Gutiérrez and Giménez, 2009).

Despite these regulations, the lagoon is exposed to important environmental threats related to anthropogenic activities. One of these threats is the mining waste from the mining district of Sierra Minera (Cartagena-La Unión, Murcia, Spain) that arrives to the lagoon, even to date. The mining district of Sierra Minera was a very important mining nucleus for more than 2500 years located close to the southern shore of the Mar Menor Lagoon. For hundreds of years, but mainly during the 30 years of mining activity developed in this zone in the 20th century, an important amount of mining wastes was directly discharged to the Mar Menor coastal lagoon mainly through two important temporally water courses (i.e. El Beal and Ponce Wadis)(Conesa and Jiménez-Cárceles, 2007; García-García, 2004; Navarro et al., 2008; Pérez-Ruzafa et al., 1987; Simonneau, 1973). Presently (i.e. 30 years later), sediments with high amounts of toxic elements (mainly Pb, Zn, Fe, Cu and Cd) arrive to the lagoon, even to date, through the typical torrential rains occurring at this region (Conesa and Jiménez-Cárceles, 2007; Gonzalez-Fernandez et al., 2011; Gutiérrez and Giménez, 2009; Marín-Guirao et al., 2007).

Several studies in the last decade have pointed out elevated concentrations of toxic metal elements in this area (i.e. mining district and the coastal lagoon). Most of the studies have been performed across the mining area and at the different wadis that drain these mining zones. The results confirmed that a large proportion of mining wastes, which remain accumulated in this zone, could be dispersed through the surrounded areas because of the weathering processes (i.e. torrential rainfalls and strong winds), thereby releasing great amounts of trace elements through the stream (García-Lorenzo *et al*., 2014, 2012; García *et al*., 2007; González-Alcaraz *et al*., 2013; Gonzalez-Fernandez *et al*., 2011; Navarro *et al*., 2008). These mining wastes, which arrive to the Mar Menor Lagoon through the wadis, transport high amounts of trace elements to water, and this has caused an important impact on the entire coastal lagoon, as mining wastes could be redistributed from the estuary zones to other nearby zones because of variations between different environmental factors such as marine currents, winds, and the existence of temperature and salinity gradients (Dassenakis *et al*., 2010; García and Muñoz-Vera, 2015; Tsakovski *et al*., 2012). However, the most affected areas of the lagoon are the mouths of the wadis, mainly El Beal Wadi. Studies performed at the mouth of this wadi have revealed concentration values of trace elements in sediments and the water column, and these values were found to exceed some of the European limits established in different soil regulations (Gonzalez-Fernandez *et al*., 2011; Tsakovski *et al*., 2009).

The presence of high amounts of trace elements could affect adversely the entire marine environment of the lagoon because of their availability for the different organisms living there. Specifically, seagrasses present significant capacity to incorporate trace elements in their tissues, which might be available to higher trophic levels in the marine food chain (Di Leonardo *et al*., 2017; Lyngby and Brix, 1989). Although some of these elements are considered essential (i.e. Fe, Zn, Mn, Cu and Ni), others can cause adverse effects in the ecosystem, such as the nonessential elements (i.e. Pb, As, Cr and Cd), if they are present at elevated concentrations. In case of the Mar Menor Lagoon, the marine flora and fauna are continuously exposed to high concentrations of trace elements. Some studies have evaluated the toxicity of these elements for different marine organisms and the marine phanerogam *Cymodocea nodosa* (Ucria) Aschers., which is the characteristic seagrass of this zone. Most studies reported a relation between the elemental concentrations found in the marine fauna and those found in the sediment and the different tissues of the *C. nodosa*, thus ensuring the transfer of the elements to the food chain (Conesa *et al., 2011;* María-Cervantes*, 2009;* Marín-Guirao *et al*., 2008, 2005a, 2005b, 2005c; Sanchiz *et al*., 2000).

Furthermore, trace elements accumulated in the seagrass could be mobilised or transferred to the marine environment after shedding of the oldest leaves that remain deposited in the seagrass beds. Despite this issue, there are few studies on the impact of detached leaves of seagrass in the marine environment. Hosokawa et al., (2016) evaluated the effects of the leaf litter of the seagrass *Zostera marina L.* (eelgrass) accumulated in the seagrass beds in the mouth of Tokyo Bay (Japan) and observed an exchange of trace elements (Cu, Zn, Pb and Cd) between leaves during decomposition and in the sediments of the seagrass bed. Di Leonardo *et al*., (2017) also evaluated the trace element levels (As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, V and Zn) and organic carbon storage capacity of *Posidonia oceanica* (L.) Delile leaves and its impact on sediments after shedding in the seagrass bed in the Augusta Bay (Italy). They reported that *P. oceanica* banquettes have an important role in the mobilisation of trace elements in the marine environment. Moreover, the oldest seagrass leaves detached from the seagrass might be dragged by the marine currents and the swell to the shore, where leaves could remain accumulated. This seagrass beach cast litter, which contributes to the beach stability, might support high densities of faunal populations and constitutes an important source of nutrients for the organisms (Ochieng and Erftemeijer, 1999). Thus, the trace elements accumulated in the seagrass could be available to the faunal community and the vegetation and the sediment of the coastal environment.

Nonetheless, to the best of our knowledge, none of the studies performed in the Mar Menor coastal lagoon have considered the role of the *C. nodosa* beach cast litter in the mobilisation of trace elements or its impact on the coastal zone. Therefore, the goal of the present work is to establish the role played by the *C. nodosa* beach cast litter on the coastal marine dynamics of trace elements in one of the most affected areas of the Mar Menor Lagoon (Spain). To this end, the content of nine trace elements (i.e. As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) was determined in different marine compartments (marine and coastal sediments, the seagrass *C. nodosa* and *C. nodosa* beach cast litter) at the mouth of El Beal Wadi (Mar Menor Lagoon).

2. Materials and methods

2.1 Study location and sample collection

The study area was sited at two different localities at the Mar Menor coastal lagoon, both separated by a distance of 17 km (Fig. 1): (i) El Beal locality (B) sited at the mouth of El Beal Wadi (37º 39’ 57.4” N, 0º 48’ 47.2” W), which is directly affected by the mining waste of Sierra Minera (Cartagena-La Unión, Murcia, Spain). According to previous literature, this is one of the most contaminated locations at the lagoon (Simonneau, 1973). (ii) San Pedro locality (SP) sited at north of the lagoon, far away from the mining waste discharge point (37º 49’ 4.6” N, 0º 46’ 28.9” W) (Fig.1). Both localities have similar hydrological conditions (e.g. water temperature, nitrate concentration, spatial and temporal dynamics of chlorophyll) with the exception of toxic metal contamination by mining wastes (Pérez-Ruzafa et al., 2005; Umgiesser et al., 2014). With regard to anthropogenic factors, both localities have in their vicinity a marina at a distance of approximately 1 km, and none of them are bathing area for tourists; hence, there is no withdrawal of the seaweed litter washed ashore.

Two zones were studied for each locality: marine and coastal. In each zone, two sites separated from each other by a distance of between 300 and 350 meters and randomly chosen were sampled. Marine sites were characterised by the presence of a *C. nodosa* meadow few meters away from the coastline and an average depth of 60 cm. On the other hand, coastal sites were located in front of the marine sites where accumulations of seagrass beach cast litter were deposited in the shore by wave action. For each site, three replicates of sediments (marine and coastal) and three samples of seagrass (live *C. nodosa* and beach cast litter) were collected using a square box (22.5 x 22.5 cm). In case of the marine zone, the entire shoots of *C. nodosa* (including leaves, rhizomes and roots) and the sediment surrounding the seagrass rhizomes were collected. For coastal samples, both the *C. nodosa* beach cast litter washed ashore and the sediments under those rests were collected. *C. nodosa* beach cast litter was composed of (mainly) leaves and some amounts of both rhizomes and roots. In all cases, coastal and marine sediment samples were collected from the surface (approximately 5 cm depth) of the sediments surrounding the *C. nodosa* samples collected and the marine samples were collected at a depth of between 0.5 to 1 m.

2.2 Reagents

High-purity water with a resistivity > 18 MΩ cm obtained from a Milli-Q water Direct-Q3 purification system (Millipore Inc., Paris, France) was used throughout this work. For sample digestion, 65% w w^{-1} HNO_3, 30% w v^{-1} H_2O_2 (Panreac, Castellar del Valles, Spain) and 65% w w^{-1} $HClO_4$ (Carlo Erba Reagents, Sabadell, Spain) were used. Calibration standard solutions were prepared from 1000 mg L^{-1} multi-elemental ICP reference solution (ICP-IV; Merck, Darmstadt, Germany) and As mono-elemental solution (Merck, Darmstadt, Germany).

2.3 Sample preparation

Sediment samples were air-dried for 2 days and then oven-dried at 60 ºC until constant weight. Once mollusc and pebbles were removed, sediments were grinded in a glass mortar and finally sieved (0.5 mm) and stored in properly labelled polypropylene bottles.

All *C. nodosa* samples were first rinsed with tap water and then scraped with a glass slide to remove the leaves fouling and then, rinsed again with deionised water. Finally, samples were cut, oven-dried at 60 ºC until constant weight and then stored in properly labelled polypropylene bottles.

Prior to the analysis, samples were digested using a microwave oven (model Start D, Milestone S.r.l., Sorisole, Italy) at conditions recommended by the manufacturer (Programmes HPR-EN-33 and HPR-AG-02 for sediments and seagrasses, respectively). Digestion of samples collected at each sampling point was done in triplicate. Hence, at the end of the digestion process, for each sampling point, 9 solutions were available for each sediment or seagrass sample. For the digestion of sediments, 6 ml of HNO_3 65% w w^{-1}, 1 ml of $HClO_4$ 65% w w^{-1} and 1 mL of H_2O_2 30% w v^{-1} were added to 0.25 g of sample in Teflon vessels. Samples were heated for 30 minutes at maximum power. After the digestion process, the solutions obtained were totally clear, and no sediments or deposits were observed.

For the digestion of seagrass samples, 6 ml of HNO_3 65% w w^{-1} and 2 mL of H_2O_2 30% w v^{-1} were added to 0.5 g of sample. The heating programme used was same as that of the sediment digestion procedure.

After digestion, samples were brought to a final weight of 25 g with ultrapure water. For analysis of most concentrated elements (i.e. Fe, Pb and Zn), these solutions were diluted 1:10 with ultrapure water prior to the analysis, while the rest of the elements (i.e. Mn, As, Cd, Cr, Cu and Ni) were analysed directly.

2.4 Trace metal analysis

2.4.1 Analysis by ICP-AES

The concentration of trace elements (i.e. As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES; model 720, Agilent, Santa Clara, CA, USA). Details of operating conditions and emission lines selected are presented in Table 1.

Internal standardisation (IS) was employed as a calibration strategy to perform the ICP-AES determination to minimise the signal variations during the analysis as a consequence of the complex matrix samples (mainly acid and easily ionised elements). (Todolí and Mermet, 1999; Todolí *et al*., 2002) Yttrium (Table 1) was used as the internal standard throughout the work (Ivaldi and Tyson, 1996; Shirdam *et al*., 2008; Zachariadis and Vogiatzis, 2010). Two Yttrium emission lines, ionic and atomic, were selected to correct for the possible differences in ionisation and/or excitation mechanisms for each line. Hence, the internal standard emission line employed for As, Cr, and Cu determination was the atomic one (Y 410.237 nm), whereas the remaining elements were determined using the ionic one (Y 324.228 nm).

2.4.2 Method Validation

The analyte methodology developed for metal analysis in sediment and seagrass samples was validated by recovery because of the lack of a proper certified material. To this end and considering the concentrations previously reported in the literature (Conesa et al., 2011; García-García, 2004; Marín-Guirao et al., 2005c), sediment and seagrass samples were spiked at different concentrations (i.e. major elements 100 mg kg^{-1}, minor elements 0.5 mg kg^{-1}) with a multi-element ICP reference solution before the mineralisation step. In all cases, recovery values were quantitative (100 ± 30%). The method detection limits (see Table 1) determined for the elements analysed were calculated attending to the 3σ criterion (Miller and Miller, 2002).

2.4.3 Statistical analysis

The content of nine trace elements (i.e. As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the seagrass and sediment samples was analysed separately using a nested 3-factor mixed ANOVA model to determine differences among two littoral zones (coastal and marine) at two localities using site replication factor as it is shown by the sampling design (site within locality by zone).

The following factors were considered: (1) L: Locality, a fixed factor, with two levels (B: El Beal and SP: San Pedro); (2) Z: Zone, fixed and orthogonal to the previous one, with two levels (C: coastal; M: marine); (3) S: Site, a random factor and nested in the interaction term Locality x Zone, with two levels (Underwood, 1997). From each site, three samples were collected (n=3). The model of source of variation was as follows:

$$X = \mu + L + Z + S(L \times Z) + (L \times Z) + Residual$$

Prior to ANOVA, heterogeneity of variance was tested with Cochran's C-test (Sokal and Rohlf, 1981). Data were transformed with the square root of x+1 if variances were significantly different from $P=0.05$, and log (x+1) transformed if variance was still heterogeneous. Where variances remained heterogeneous, untransformed data were analysed, as ANOVA is a robust statistical test and is relatively unaffected by heterogeneity of variances, particularly in balanced experiments (Underwood, 1993, 1994). However, in such cases, special care was taken in the interpretation of results. Furthermore, in such cases, to reduce type I error, the level of significance was reduced to <0.01. *A posteriori* multiple comparison was carried out with the Student–Newman–Keuls (SNK) procedure (Underwood, 1997).

3. Results

The concentrations obtained for all elements in the sediment and seagrass samples at the two localities tested are summarised in Table 2 and Fig 2. As expected, samples from the El Beal (B) locality present higher metal concentrations than samples from the San Pedro (SP) locality. Results also indicate that coastal samples (sediments and seagrass) show higher concentration levels than marine ones.

Regarding metal concentration values in sediment samples, Fe, Pb, Zn and Mn are the most concentrated elements, independent of the locality and zone. Nevertheless, the lowest concentration of elements depends on the locality considered. Thus, irrespective of the type of sediment (i.e. coastal or marine), Cd is the element with the lowest concentration value reported at the El Beal locality. With regard to the San Pedro locality, As, Ni and Cd are not detected in any sediment sample, while Cr, with a concentration of approximately 3 mg kg^{-1} in both sediments (marine and coastal), is found at the lowest concentration detected. Chromium concentration levels in sediments from the San Pedro locality are significantly lower than those found in the El Beal locality (i.e. sevenfold to tenfold). Although natural phenomena could affect metal levels in sediment samples (i.e. year and season of sampling, sampling location, meteorological conditions, etc.) (García and Muñoz-Vera, 2015), the values obtained in the present work for El Beal samples are comparable with those previously reported by other authors (Table 3). To evaluate the current degree of contamination of this area, after the mines were closed 30 years ago, the concentrations determined in the coastal sediments from the El Beal locality have been compared with the current limits established by different regulations. Table 4 reports the concentration limits established for different types of soils according to regulations by some European countries and the concentration limits established in the region of Murcia (where the study is performed) that were considered (European Parliament, 2008; Faz et al., 2009). When comparing data in Tables 2 and 4, it can be derived that, despite potential differences in soil characteristics, Pb, Zn, Cu and Cd levels in the coastal sediment at the El Beal locality exceed, in terms of not only the limits established by the different European countries (García-García, 2004; María-Cervantes, 2009) but also both the background levels and those established for contaminated soils in the Mar Menor area (Faz *et al*., 2009). These results clearly indicate the high pollution level by toxic metals at the El Beal locality.

In the case of seagrass samples, similar to that observed for sediment samples, the elements that presented higher concentration values are Fe, Pb, Zn and Mn, whereas As, Cu and Ni are found at trace levels. Interestingly, As is detected only in samples from the El Beal locality. The remaining elements (i.e. Cr and Cd) are not detected in any seagrass sample. In this case, the results obtained for *C. nodosa* samples are also comparable with those reported in previous studies (see Table 3); however, there are no concentration values for *C. nodosa* beach cast litter, as it has not been previously studied in the Mar Menor Lagoon.

To evaluate the differences in the elemental concentration pattern of sediment and seagrass samples from El Beal and San Pedro, a nested 3-factor mixed ANOVA model was applied. For sediments, the ANOVA test was applied to those elements present in all samples investigated (Fe, Pb, Zn, Mn, Cu and Cr). Arsenic, nickel and cadmium were discarded, as they are not present in the sediments from San Pedro. Similarly, the ANOVA test for seagrass samples was applied only to elements present in the El Beal and San Pedro samples (i.e. Fe, Pb, Zn, Mn and Cu). Table 5 shows the results obtained in the ANOVA analysis for both sediment and seagrass samples at the El Beal and San Pedro localities. Fe concentration values in the sediment samples are consistently higher at the El Beal locality (L), but they showed no difference between zones (coastal and marine, Z). With regard to Pb, Zn, Cu and Cr, concentration values in the coastal sediments are 330, 520, 20 and 10 times higher, respectively, in the El Beal locality than in the San Pedro locality. Moreover, the concentration pattern of these elements in the sediment samples shows significant differences in the interaction (LxZ). While in the San Pedro locality, there are no differences between zones, in the El Beal locality, the values obtained on the coastal samples are higher than those obtained in the marine zone (SNK: $p<0.01$). Finally, Mn concentration values in sediment samples from the El Beal locality are significantly higher than those in the San Pedro locality. Nevertheless, concentration values in marine sediment samples are significantly higher than those in the coastal ones from the El Beal locality (SNK: $p<0.01$), unlike what is observed for the other elements. On the contrary, there are no significant differences between zones in the San Pedro locality. For seagrass samples, Fe concentration values do not show significant differences, between neither zones nor localities. For the rest of the elements (Pb, Zn, Mn, and Cu), the concentration values in *C. nodosa* beach cast litter are significantly higher in the El Beal locality than in the San Pedro locality, and these values are also higher than those in *C. nodosa* samples for each locality (SNK: $p<0.01$).

4. Discussion

The localities selected in this study (El Beal and San Pedro) have similar characteristics (i.e. hydrological, external factors, etc.); hence, it is feasible to evaluate the influence of *C. nodosa* on the mobilisation of trace elements in one of the most contaminated areas of the Mar Menor Lagoon regarding an area not directly affected by mining activity.

To this end, it is important to analyse and evaluate the elemental composition of the sediments in which the *C. nodosa* has grown. Given that mining wastes were discharged to the lagoon through El Beal Wadi, it was totally expected that the metal concentration values obtained were significantly higher in the El Beal locality than in the San Pedro locality (Dassenakis et al., 2010; García-García, 2004; Navarro et al., 2008). Moreover, the concentration values obtained for each element analysed are in good agreement with the original composition of the ore mine, as Fe, Pb, Zn and Mn showed higher concentration levels than As, Cu, Ni, which appeared as trace elements in the ore mine (García-García, 2004; María-Cervantes, 2009; Marín-Guirao et al., 2005a). Differences in the metal level could also be attributed to soil characteristics. The discharge of mining wastes through El Beal Wadi has changed the original granulometry and composition (SiO_2) of lagoon sediments at this locality. It has been found that sediments at the El Beal locality contain clay, which favours the retention of elements in the soil dissolved fraction (Conesa et al., 2011; Marín-Guirao et al., 2008, 2005a, 2005b; Zaaboub et al., 2014). Differences in the composition of both coastal and marine sediments could be explained considering that elements in marine sediments are partially dissolved with time into the lagoon. Umgiesser et al. (2014) estimated that the water renewal time of the lagoon is longer than 1 year because of its choked nature. On the other hand, it is essential to consider the formation of soluble metal sulphides that occurs because of either the high concentration of organic matter present in the Mar Menor Lagoon or the mining wastes rich in sulphide ions (Chapman *et al*., 1983). The specific pattern shown by Mn in the marine samples collected from the El Beal locality can be explained considering that Mn is present in three different forms, i.e. in its insoluble forms (Mn^{3+} and Mn^{4+}), in the superficial aerobic layer and in its soluble form (Mn^{2+}) in a deeper layer where manganese is retained by oxidation–reduction cycling, diffusing between these two layers, which will depend on the reactivity of this element and the abiotic factors of the media (i.e. pH, redox potential, etc.) (Anschutz et al., 2005; Delfino and Lee, 1968; Grygo-Szymanko et al., 2015; Hierro et al., 2014; Jara-Marini et al., 2015).

When the elemental concentration pattern for both sediments and *C. nodosa* is compared, it is clearly observed that the metal content in the live *C. nodosa* reflects the composition of the sediment bed where it has grown. This means that *C. nodosa* samples collected in the El Beal locality have higher metal levels due to the mining wastes. In general, bioconcentration factors (defined as the ratio between the concentration of metal in the seagrass and that in the sediments) (Mountouris et al., 2002) for *C. nodosa* samples are lower at the El Beal locality than in the San Pedro locality. Thus, for instance, Fe bioconcentration factor was 0.03 and 0.16 for *C. nodosa* samples from El Beal and San Pedro, respectively. These differences in bioconcentration factors are explained considering the high metal levels for the marine sediments at El Beal. In the case of Fe, concentration levels in *C. nodosa* at the El Beal locality are tenfold higher than those at the San Pedro locality, whereas levels in sediments are 65-fold higher. Similar conclusions could be obtained for the remaining elements studied.

Differences in elemental composition between the seagrass beach cast litter and *C. nodosa* can be explained by considering different factors. First, trace elements accumulated into the leaves of live seagrass could be leaked from them to the water (Brix and Lyngby, 1982). Second, the elemental concentration in seagrass beach cast litter depends on the proportion of leaves and roots dragged to the shore. It is well known that inside the live *C. nodosa,* the elements undergo translocation processes, which involve the transport of the trace elements to different organs of the plant according to the necessities thereof (Malea and Haritonidis, 1999). Indeed, two groups of elements can be distinguished attending to their function in the seagrass. The first group comprises elements linked to plant physiological functions, i.e. Fe, Zn, Mn, Cu and Ni, while the second one comprises elements that are toxic for plants, i.e. As and Pb. Furthermore, previous studies have demonstrated that As, Cu, Zn, Ni and Mn are accumulated into *C. nodosa* leaves and Fe and Pb into roots (Llagostera *et al*., 2011; Malea and Haritonidis, 1999; Malea and Kevrekidis, 2013). Third, the higher elemental content shown in the beach cast litter could also be explained considering metal bioadsorption ability of the detached leaves (Sánchez et al., 1999) and the organic matter loss by the meteorological conditions and the coastal fauna, which contribute to increase in the elemental concentration by biomass unit of beach cast litter (Di Leonardo et al., 2017; Ochieng and Erftemeijer, 1999). Finally, when the seagrass beach cast litter begins to decompose, the exchange of elements from these detached leaves to the sediments contributes to the increase in metal concentration in the coastal sediment. Muñoz-Vera et al. (2016, 2015) reported similar conclusions in different bioaccumulation studies with two different jellyfish species. They highlighted the hazard associated with the deposition of these organisms in soils and landfills, as the bioaccumulated metals may produce toxic effects because of pollution on soil (marine and coastal sediments), water, and food chain. Considering experimental data and previous considerations, Figure 3 shows a representation of the hypothetical role of the *C. nodosa* seagrass in the mobilisation of trace elements in the marine environment of the Mar Menor Lagoon. Trace elements accumulated in the marine sediments (1) are partially dissolved in water and partially mobilised by the seagrass, which accumulates some of these elements in roots (Fe and As) (2) and others in leaves (Cu, Ni, Pb, Zn and Mn) (3). When seagrass is dragged to the shore by the marine currents (4), it begins to decompose; consequently, elements present in the beach cast litter are reaccumulated in the coastal sediments, and they could be available for the coastal fauna (5). Experimental data in this work show that metal mobilisation by *C. nodosa* beach cast litter occurs in both the El Beal and San Pedro localities, but this effect is more significant for the area directly affected by the mining wastes. Although metal concentration in the *C. nodosa* beach cast litter is much lower than that in the coastal sediments and this does not suppose an important impact on the coastal sediments from the mouth of El Beal Wadi, it is an important variable to consider, as it could be a source of contamination if it is deposited in unpolluted surrounding areas.

5. Conclusion

The results of the study show that, as expected, El Beal Wadi, which has been affected by mining waste, presents higher concentrations of trace elements than the unaffected zone. Moreover, results obtained also show that, irrespective of the locality considered, the samples from the coastal zones present higher concentrations than samples from the marine ones. This fact could be a consequence of the interaction between different marine environmental compartments, as a portion of the trace elements accumulated in the marine sediments could be dissolved in the water and another portion could be mobilised by the *C. nodosa,* which could keep them retained in leaves.

Consequently, when the detached leaves of this seagrass are accumulated in the shore, their interaction with the coastal fauna and the meteorological conditions could promote the mobilisation of the trace elements retained in the leaves to the coastal sediments. Thus, it is essential to consider the possibility of removing the seagrass beach cast litter to minimise the impact of elevated trace element concentration levels in surrounding unpolluted zones.

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Table 1. ICP-AES operating conditions, emission lines (nm) and detection limits for each element (mg kg-1 dry weight). (I)/ (II): Line type, atomic and ionic, respectively.

	ICP-AES
Plasma forward power/ W	1400
Argon flow rate/ L min^{-1}	
Plasma	15
Auxiliary	1.5
Nebulizer (Q_g)	0.7
Sample uptake rate (Q_L)/ mL min^{-1}	1.5
Sample introduction	
Nebulizer	Meinhard, type K
Spray chamber	Standard cyclonic
View mode	Axial
Integration time /s	1
Readings/replicates	3

Element	**Emission line*/nm**	**Method detection limits/ mg kg^{-1}**	
		Sediment	**Live *C. nodosa***
As	193.696 (I)	20	10
Cd	226.502 (II)	5	2
Cr	357.868 (I)	1	0.5
Cu	327.395 (I)	2	1
Fe	238.204 (II)	20	10
Mn	257.610 (II)	8	4
Ni	216.555 (II)	6	3
Pb	220.353 (II)	0.8	0.4
Zn	202.548 (II)	6	3
Y	324.228 (II)	-	-
Y	410.237 (I)	-	-

*(I)/ (II): Line type, atomic and ionic, respectively.

Table 2. Elemental concentrations in samples mg kg^{-1} dry weight; Mean ± confidence interval; n=18; 95% confidence level). LoD: Limit of Detection.

	Sediment				***C. nodosa***			
Element	**Coastal**		**Marine**		**Coastal**		**Marine**	
	Beal	**San Pedro**	**Beal**	**San Pedro**	**Beal**	**San Pedro**	**Beal**	**San Pedro**
Fe	141000 ± 2000	2800 ± 180	104000 ±12000	1610 ± 80	3000 ± 200	570 ± 7	2600 ± 1400	250 ± 80
Pb	8700 ± 70	26 ± 2	2530 ± 30	27 ± 3	4350 ± 14	264 ± 4	810 ± 60	8 ± 3
Zn	8300 ± 800	16 ± 6	3700 ± 300	9 ± 3	1030 ± 8	322.6 ± 0.9	279.3 ± 1.2	44 ± 9
Mn	2450 ± 70	214 ± 3	3500 ± 40	210 ± 30	3160 ± 70	1040 ± 50	447 ± 9	100 ± 30
As	485 ± 19	< LoD	203 ± 7	< LoD	16.4 ± 0.8	< LoD	19 ± 9	<LoD
Cu	155 ± 4	7.0 ± 0.8	25.2 ± 0.7	4.88 ±0.13	43.0 ± 0.4	20.26 ± 0.03	12 ± 2	8.0 ± 0.4
Cr	30.3 ± 0.5	3.2 ± 0.3	22.8 ± 0.4	3.45 ± 0.03	< LoD	< LoD	< LoD	< LoD
Ni	29.25 ± 0.11	< LoD	21.7 ± 1.4	< LoD	6.77 ± 0.08	3.758 ± 0.003	< LoD	< LoD
Cd	19 ± 3	< LoD	8.6 ± 1.1	< LoD	< LoD	< LoD	< LoD	< LoD

Table 3. Elemental concentration published for the different samples from the Beal wadi (mg kg^{-1} dry weight).

Elements	Sediments		*C. nodosa*
	Coastal	Marine	
Pb	7100 ± 3900 [a]	950 [c]	126 [e]
	4990 ± 261 [b]	4673 ± 310 [d]	300 [f]
	-	-	551 ± 3 [d]
Zn	8700 ± 8300 [a]	650 [c]	78 [e]
	5120 ± 263 [b]	3858 ± 870 [d]	350 [f]
	-	-	269 ± 2 [d]
As	312 ± 154 [a]	-	-
	310 ± 24 [b]	-	-
	-	-	-
Cu	107 ± 49 [a]	35 [c]	-
	101 ± 7 [b]	59.0 ± 0.1 [d]	-
	-	-	16.7 ± 0.6 [d]
Cd	22 ± 23 [a]	15 [c]	0.2 [e]
	13 ± 1 [b]	16.0 ± 0.3 [d]	0.2 [f]
	-	-	0.2 ± 0.3 [d]

a: María-Cervantes, 2009; b: Conesa et al., 2011; c: García-García, 2004; d: Marín-Guirao et al., 2008; e: Marín-Guirao et al., 2005c; f: Marín-Guirao et al., 2005b.

Table 4. Concentration values established for soils by different European countries (mg kg^{-1}).

Element	Europe				Spain	
	Netherland [a]	Denmark [a]	Turkey [b]		Reference levels in Mar Menor lagoon [c]	Background levels in Mar Menor lagoon [c]
			Contaminated	Extrem. contaminated		
Fe	-	-	-	-	-	-
Pb	> 530	> 400	150	600	77	44
Zn	> 720	> 1000	500	3000	51	39
Mn	-	-	-	-	-	-
As	> 55	> 20	-	-	-	-
Cu	> 190	> 500	100	500	49	30
Cr	-	-	-	-	-	-
Ni	-	-	-	-	-	-
Cd	> 12	> 5	5	20	0.2	0.2

a: María-Cervantes, 2009; b: García-García, 2004; c: Faz *et al.*, 2009.

Table 5. Summary of three-way multifactorial variance analysis (ANOVA) of different elements concentration value on sediments and *C. nodosa* samples. Factor Locality (L) was fixed, factor Zone (Z) was fixed and Factor Site (Si) was random within the interaction Locality x Zone. Df: degrees of freedom; MS: Mean Square; F: value of F statistic. ns: non significant; *Significant at p<0.05; **p<0.01; ***p<0.001; ns: no significant differences; NT: no transformation performed.

Source of variation		Fe sediment				Fe *Cymodocea nodosa*		
	df	MS	F	P	F versus	MS	F	P
L	1	3242346.81	180.59	0.000***	Si (LxZ)	3347482.81	5.41	0.081 ns
Z	1	3607681.60	4.50	0.101 ns	Si (LxZ)	842003.60	0.14	0.73 ns
Si (LxZ)	4	3486049.14	27.88	0.000***	Res	6164513.44	78.94	0.000***
LxZ	1	9848886.73	3.95	0.118 ns	Si (LxZ)	16222.31	0	0.962 ns
Res	16	7340955.37				78089.69		
Tot	23							
Cochran's Test		C = 0.4344	n.s.			C = 0.7287	< 0.01	
Transformation		none				none		

Source of variation		Pb sediment				Pb *Cymodocea nodosa*		
	df	MS	F	P	F versus	MS	F	P
L	1	158.98	430.29	0.000***	Si (LxZ)	5863661	238.53	0.000***
Z	1	1.98	42.68	0.003**	Si (LxZ)	1605811	951.03	0.000***
Si (LxZ)	4	0.05	2.49	0.085 ns	Res	11074	0.14	0.966 ns
LxZ	1	2.53	54.6	0.002**	Si (LxZ)	6170331	460.20	0.000***
Res	16	0.02				80740		
Tot	23							
Cochran's Test		C = 0.4719	n.s.			C = 0.642	< 0.01	

Transformation	Ln (x+1)	none

Source of variation		Zn sediment				Zn *Cymodocea nodosa*		
	df	MS	F	P	F versus	MS	F	P
L	1	9212523	32.38	0.005**	Si (LxZ)	1333214	568.43	0.000***
Z	1	2631272	15.47	0.017*	Si (LxZ)	1589024	3061.30	0.000***
Si (LxZ)	4	2755236	57.34	0.000***	Res	219	0.09	0.986 ns
LxZ	1	2397626	15.39	0.017 ns	Si (LxZ)	333291	642.08	0.000***
Res	16	48053				6089		
Tot	23							
Cochran's Test		C = 0.3960	n.s.			C = 0.642	< 0.01	
Transformation		none				none		

Source of variation		Mn sediment				Mn *Cymodocea nodosa*		
	df	MS	F	P	F versus	MS	F	P
L	1	5681407	860.17	0.000***	Si (LxZ)	9192968	303.59	0.000***
Z	1	1650748	67.20	0.001***	Si (LxZ)	20012975	660.90	0.000***
Si (LxZ)	4	24557	0.42	0.792 ns	Res	30280	0.44	0.776 ns
LxZ	1	1668924	67.96	0.001***	Si (LxZ)	4757789	157.12	0.000***
Res	16	58489				68466		
Tot	23							
Cochran's Test		C = 0.4634	n.s.			C = 0,6363	< 0.01	
Transformation		none				none		

Source of variation		Cu sediment				Cu *Cymodocea nodosa*		
	df	MS	F	P	F versus	MS	F	P
L	1	30.06	390.36	0.000***	Si (LxZ)	1041.79	57.89	0.002*

Z	1	6.43	190.43	0.000***	Si (LxZ)	2851.64	158.46	0.000***
Si (LxZ)	4	0.03	2.36	0.097 ns	Res	18	3.75	0.025 ns
LxZ	1	3.34	99.09	0.001***	Si (LxZ)	550.8	30.61	0.005 ns
Res	16	0.01				4.8		
Tot	23							
Cochran's Test		C = 0.5103	n.s.			C = 0.7287	< 0.01	
Transformation		Ln (x+1)				none		

Source of variation		**Cr sediment**			
	df	**MS**	**F**	**P**	**F versus**
L	1	3222.24	2.19	0.000***	Si (LxZ)
Z	1	80.21	48.84	0.002**	Si (LxZ)
Si (LxZ)	4	1.61	0.42	0.7889 ns	Res
LxZ	1	89.99	55.92	0.001***	Si (LxZ)
Res	16	3.79			
Tot	23				
Cochran's Test		C = 0.4455			
Transformation		none	n. s.		

Figure captions

Figure 1. Location of the studied area with the Sierra minera of Cartagena – La Unión, Mar Menor coastal lagoon and the two sampling localities (Beal: mouth of the Beal wadi and San Pedro: San Pedro del Pinatar).

Figure 2. Trace elements concentrations in *Cymodocea nodosa* (A) and sediments (B) samples from the two locations (El Beal (B) and San Pedro (SP)) and for marine (Grey) and coastal (White) samples. Elemental concentrations in mg kg^{-1} dry weight versus the location.

Figure 3. Hypothetical scheme of *Cymodocea nodosa* role on the dynamic of trace elements in the Mar Menor lagoon.

Figure 1

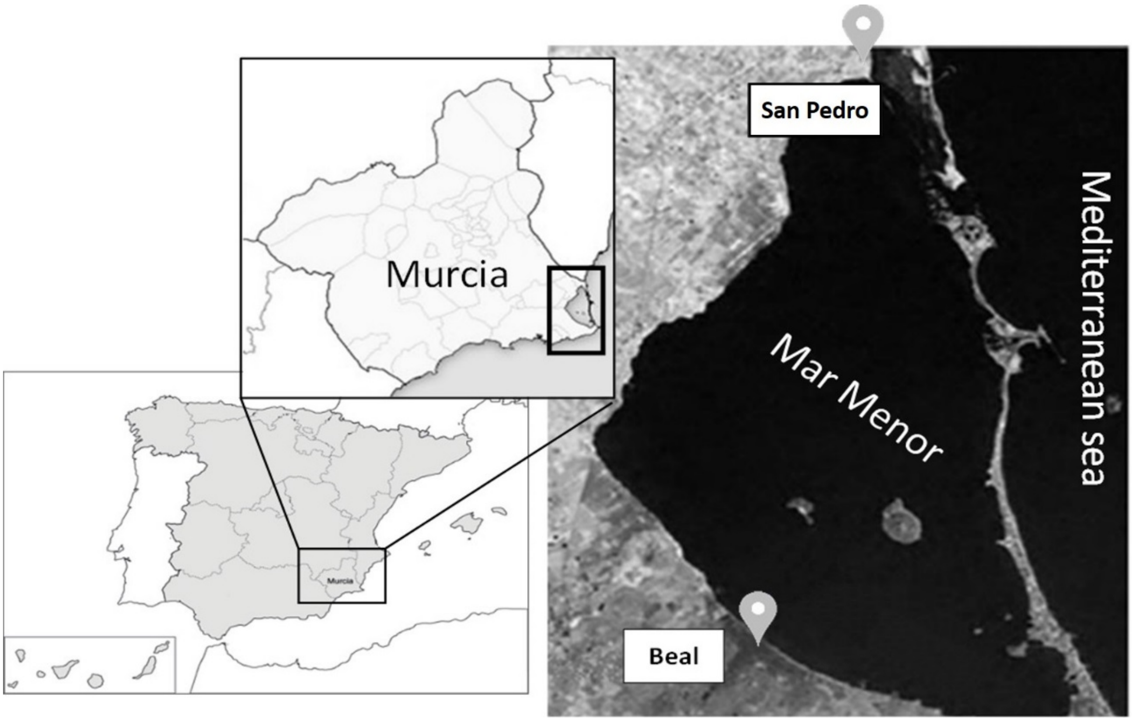


Figure 2

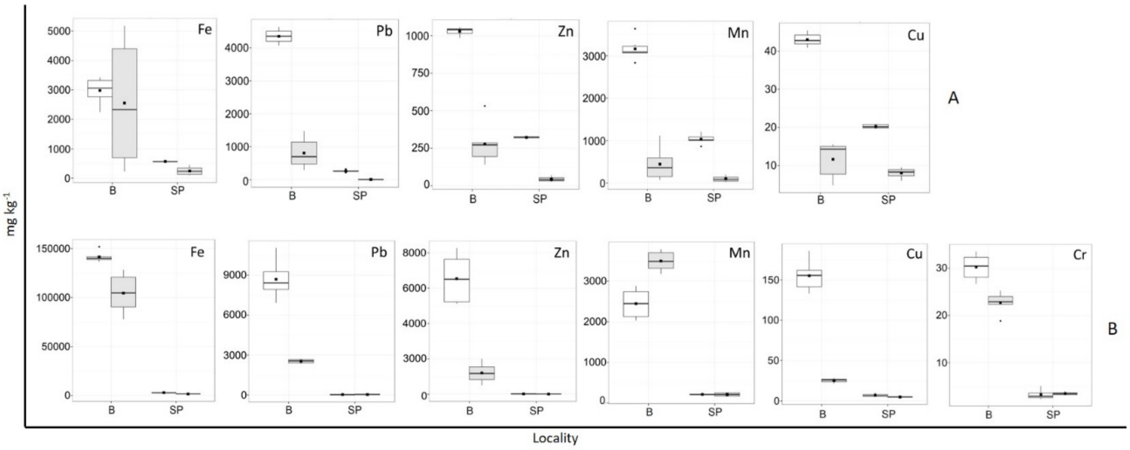
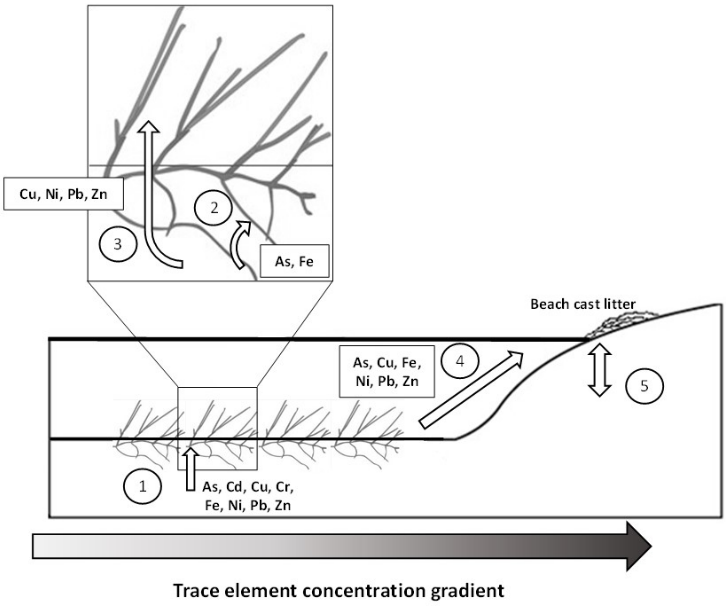


Figure 3


Cu, Ni, Pb, Zn
2
3
As, Fe
Beach cast litter
As, Cu, Fe,
Ni, Pb, Zn
4
5
1
As, Cd, Cu, Cr,
Fe, Ni, Pb, Zn
Trace element concentration gradient

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