Evaluation of anthropogenic impacts in sediments from an aquaculture influenced area: the San Pedro river (Spain)

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Evaluación del impacto antropogénico en sedimentos de una zona con influencia de acuicultura: Río San Pedro (España)

Avaluació de l'impacte antropogènic en sediments d'una zona amb influència d'aqüicultura: Riu Sant Pere (Espanya)

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ABSTRACT

Concentrations of Al, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, and Zn in sediments from San Pedro River were determined to assess the anthropogenic effects. Temporal and spatial variation studies of metal concentrations allowed to identify aquaculture activities as the main metals source. Additionally, Mn was also related with a wastewater treatment plant and Pb with the use of leaded additives in gasolines and its banishment after 2001. Nevertheless, San Pedro River can be considered, in general, as a minor contaminated area, although sampling stations related with aquaculture activities showed a moderate pollution by Cu, Co and Ni. In spite of this, metal concentrations in sediments from San Pedro River presented a low risk for the biota. Only Ni and Cr concentrations were above the probable effect range within which adverse effects frequently occur. In fact, a poor chemical status of San Pedro River was observed for these elements.

Keywords: aquaculture; environmental status; metals; San Pedro River; Sediments

RESUMEN

Se determinaron las concentraciones de Al, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti y Zn en sedimentos del río San Pedro para evaluar los efectos antropogénicos. Los estudios de variación temporal y espacial de las concentraciones de metales permitieron identificar las actividades acuícolas como la principal fuente de metales. Adicionalmente, el Mn también se relacionó con una planta de tratamiento de aguas residuales y el Pb con el uso de aditivos con plomo en gasolinas y su eliminación a partir de 2001. Sin embargo, el río San Pedro puede considerarse, en general, como un área de baja contaminación, aunque las estaciones de muestreo relacionadas con las actividades de acuicultura mostraron una contaminación moderada por Cu, Co y Ni. A pesar de esto, las concentraciones de metales en los sedimentos del río San Pedro presentaron un riesgo bajo para la biota. Solo las concentraciones de Ni y Cr estuvieron por encima del rango de efecto probable dentro del cual ocurren con frecuencia los efectos adversos. De hecho, se observó un pobre estado químico del río San Pedro para estos elementos.

Palabras claves: acuicultura; estado ambiental; metales; río san pedro; sedimentos

RESUM

Es van determinar les concentracions de Al, Co, Cr, Cu, Fe, Mn, Ni, Pb, Tu i Zn en sediments del riu Sant Pere per avaluar els efectes antropogènics. Els estudis de variació temporal i espacial de les concentracions de metalls van permetre identificar les activitats aqüícoles com la principal font de metalls. Addicionalment, el Mn també es va relacionar amb una planta de tractament d'aigües residuals i el Pb amb l'ús d'additius amb plom

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en gasolines i la seva eliminació a partir del 2001. No obstant això, el riu Sant Pere pot considerar-se, en general, com un àrea de baixa contaminació, tot i que les estacions de mostreig relacionades amb les activitats d'aqüicultura van mostrar una contaminació moderada per Cu, Co i Ni. Malgrat això, les concentracions de metalls en els sediments del riu Sant Pere van presentar un risc baix per a la biota. Només les concentracions de Ni i Cr van estar per sobre de la franja d'efecte probable dins el qual ocorren amb freqüència els efectes adversos. De fet, es va observar un pobre estat químic del riu Sant Pere per a aquests elements.

Paraules clau: aqüicultura, estat ambiental, metalls, riu Sant Pere, sediments

1. INTRODUCTION

Metals in sediments have been extensively used as tracers of anthropogenic impacts in marine environment.[1,2,3] This fact is related with the capacity of sediments to retain these elements, being considered as historical archives of metal contamination.[4] In this way, sediment cores can be used to determine contamination episodes in an area as well to establish the evolution of metal contamination from a preindustrial period.[4,5,6] However, metal contents in surface sediments can reflect the actual metal sources in the area and a temporal study of these surface sediments could be useful to detect changes in the sources in a short time scale.[7,8,9]

Among the different anthropogenic activities, metal contamination in sediments is usually related with diverse industrial activities, as tanneries or chemical industry, as well to agricultural activities and urban wastes. [2,5,6,8,10] But in the last years metals appear as non-conventional contaminants in other human activities as aquaculture, usually related with other kind of pollutants as organic matter or nutrients.[11,12] Several authors have reported high levels of copper and zinc in fish farm sediments in relation with undigested feed and faecal inputs, among other sources (Schendel et al., 2004).[12-16]

Nevertheless, distinguish between anthropogenic and natural contributions to metal concentrations in sediments can be difficult, due they could be naturally enriched in several elements.[17,18] For this reason, different approaches have been performed to evaluate the anthropogenic effects on metal concentrations in marine sediments, as the use of the geoaccumulation index or the enrichment factor, which have been widely used with this aim [10,19-26] In addition, sediment quality guidelines provide a useful tool to assess the potential effects on the biota due to the metals content in marine sediments.[27]

The present study has been performed in an aquaculture area near Rio San Pedro (Spain). Its waters bathe a part of the Bahía de Cádiz Natural Park, communicating through the "Caño de la Cortadura", with the "Paraje Natural Isla del Trocadero". Among the main environmental values of this area, the great diversity of maritime-terrestrial transition ecosystems stands out, constituting an important habitat for migratory species of bird fauna. However, this park has several environmental issues. One of the main is its location in an urban-industrial environment, which puts great pressure on the Park, especially in the form of discharges that produce water pollution, in addition to strong tourist pressure. To reduce these adverse effects, a sewage treatment plant was established in this area along the river bank, next to the Río San Pedro industrial zone. This way, waters from the industrial zone are treated before being discharged. Thus, effluents from aquaculture facilities are the only waters that reach the San Pedro River without any treatment.

In this work, the effect of aquaculture activities on the concentrations of several metals (Al, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, and Zn) and organic matter has been determined in sediments from an aquaculture area, the San Pedro River (Spain). The present study complemented a previous work, where enrichments in copper, zinc and lead concentrations in sediments were detected in the study area.[12] In addition, temporal variations in metal concentrations are studied in relation with changes in the anthropogenic sources.

Provided results can be used as a reference to evaluate the posterior influence of aquaculture activities on the metal concentrations in this and in others similar ecosystems. A methodology for evaluating sediment quality is proposed using different suitable indices.

2. MATERIAL AND METHODS

2.1. Study area

Sediments were collected in the San Pedro River, an arm-of-the-sea placed in the south of Spain, where several aquaculture facilities are located (Fig. 1). As has been previously described, five sampling stations were established along the study site. Stations 1 and 2 were located near the mouth of the river, where the influence of fish farms effluents is almost negligible. The sampling station 5 receives the effluents of a farm devoted to intensive land-based aquaculture, meanwhile stations 3 and 4 present minor aquaculture activities. In the inner part, the San Pedro River presents scarce water renovation due its "U" shape, favouring the deposition of particulate matter from aquaculture effluents.

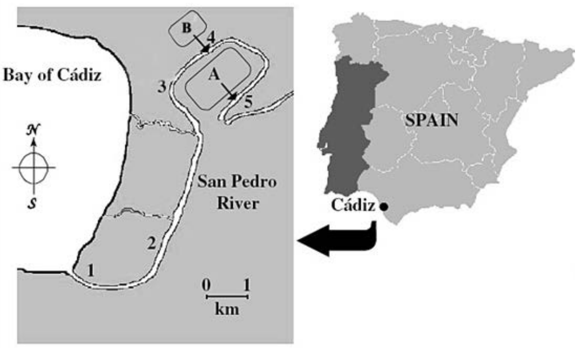

Fig. 1. *Location of sampling stations.*

2.2. Materials and methods

Sediments were taken from a boat using an Ekman-Birge grab during four sampling campaigns, three of them in the years 1997, 1998 and 1999 in order to cover a complete culture cycle in the aquaculture farm located at sampling station 5. The last sampling campaign was carried out in 2010 to evaluated changes in the anthropogenic pollution sources observed in the area.

After sampling, sediments were mechanically sieved (< 500 μm), dried at 105 ºC and homogenised with an agate mortar.

Determination of organic matter (OM) was performed in triplicate as Loss on Ignition (LOI). One g of sediment, previously homogenised as explained before, was put into a platinum crucible and heated in a muffle furnace (Heraeus Instruments, Germany) at 500ºC until constant weight (approximately for 3 hours). More details can be found elsewhere.[12]

Total concentrations of metals (Al, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Ti and Zn) were determined by a modification of USEPA 3052 digestion method.[28] Samples of 0.25 g were digested in Teflon vessels with 1 mL of hydrofluoric acid and 4 mL of nitric acid using a microwave oven (Milestone Ethos100) with the following programme: 5 minutes at 500 W and then, 16.5 minutes at 1000 W maintaining a constant temperature of 180º C. After digestion procedure, boric acid was added to the samples in order to eliminate the excess of fluoride. Finally, the digested samples were filtered and quantitatively transferred into 50 ml volumetric flask and made up to volume with Milli-Q water.

Metals were analysed by an IRIS Intrepid (Thermo Elemental, United Kingdom) inductively coupled plasma atomic emission spectrometer (ICP-AES), with the exception of Li, that was analysed by a Solaar M (Thermo Elemental, United Kingdom) flame emission atomic spectrometer (F-EAS).

All sediment samples were analyzed in triplicate, and for each series of analysis, blanks were performed. The quality of analysis was controlled by using a marine certified material (GBW 07313, National Research Centre for Certified Reference Material, China). The accuracy of the results obtained was confirmed by applying the t-test at a 95% confidence level.

2.3. Environmental assessment

In the present, there are a variety of pollution assessment methods based on metals concentrations in sediments.[29] Among them, Sediments Quality Guidelines (SQGs) proposed by the American National Oceanic and Atmospheric Administration (NOAA)[30,31] and two quantitative indices, the enrichment factor (EF) and the geoaccumulation index (I_{geo}), has been selected in the present work.

The NOAA guidelines defines the interim sediment quality guidelines (ISQG), also named threshold effect level (TEL), as the concentration above which adverse effects rarely occur, while the probable effects level (PEL) represents the concentrations above which adverse effects are frequently expected. In addition, the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life defines the effects range-low (ERL) as the concentration below which adverse effects rarely occur and the effects range-median (ERM) as the concentration above which adverse effects frequently occur.[32]

The enrichment factor (EF) was evaluated using

$$EF = \frac{(C_{metal}/C_{normalizer})_{sample}}{(C_{metal}/C_{normalizer})_{background}} \quad (1)$$

In this work, Li has been used as normalizer element and the crustal abundance data from Rudnick[33] were used as background values. The results were interpreted as suggested by Acevedo et al.,[19] where EF< 1 indicates no enrichment; < 3 is minor enrichment; 3-5 is moderate enrichment; 5-10 is moderately severe enrichment; 10-25 is severe enrichment; 25-50 is very severe enrichment and > 50 is extremely severe enrichment.

The geoaccumulation index (I_{geo}) was calculated by the following equation:

$$I_{geo} = \log_2\left(\frac{[M]_{sample}}{1.5[M]_{background}}\right) \quad (2)$$

Where, $[M]_{sample}$ is the metal concentration in the sediment sample and $[M]_{background}$ is also the metal concentration in the geochemical background given by Rudnick [33]. The I_{geo} is divided into seven classes or grades[19]: class 0 (unpolluted): $I_{geo} < 0$; class 1 (unpolluted to moderately polluted): $0 < I_{geo} < 1$; class 2 (moderately polluted): $1 < I_{geo} < 2$; class 3 (moderately to strongly polluted): $2 < I_{geo} < 3$; class 4 (strongly polluted): $3 < I_{geo} < 4$; class 5 (strongly to very strongly polluted): $4 < I_{geo} < 5$ and class 6 (very strong polluted): > 5.

Significant spatial and temporal variations in the metals concentrations in the sediments from San Pedro River were evaluated by an analysis of variance (ANOVA) using SPSS 15 for Windows software.

3. RESULTS AND DISCUSSION

3.1 Influence of aquaculture activities in sediments from San Pedro River

Organic matter

It is well-known that organic matter is associated with the effluents of aquaculture activities, so it could be useful to determine the impact of this activity in the San Pedro River.

As Fig. 2 shows, the organic matter (OM), determined by LOI, presented a similar trend for all the sampling campaigns, with higher values in the inner part of the river, were aquaculture facilities are located. This increase can be related with the deposition of suspended matter from aquaculture effluents, mainly uneaten food and faeces, in this area that is characterized by calm waters. In fact, the OM content in a clean culture pond at the beginning of a culture cycle (1.43%) was similar to those observed in the sampling stations far away to the aquaculture facilities, meanwhile the OM concentrations in the area under aquaculture influence were similar to the values observed in the culture pond at the end of a culture cycle (4.3%).

It can be note that higher values were observed in the inner part of the river for the last sampling

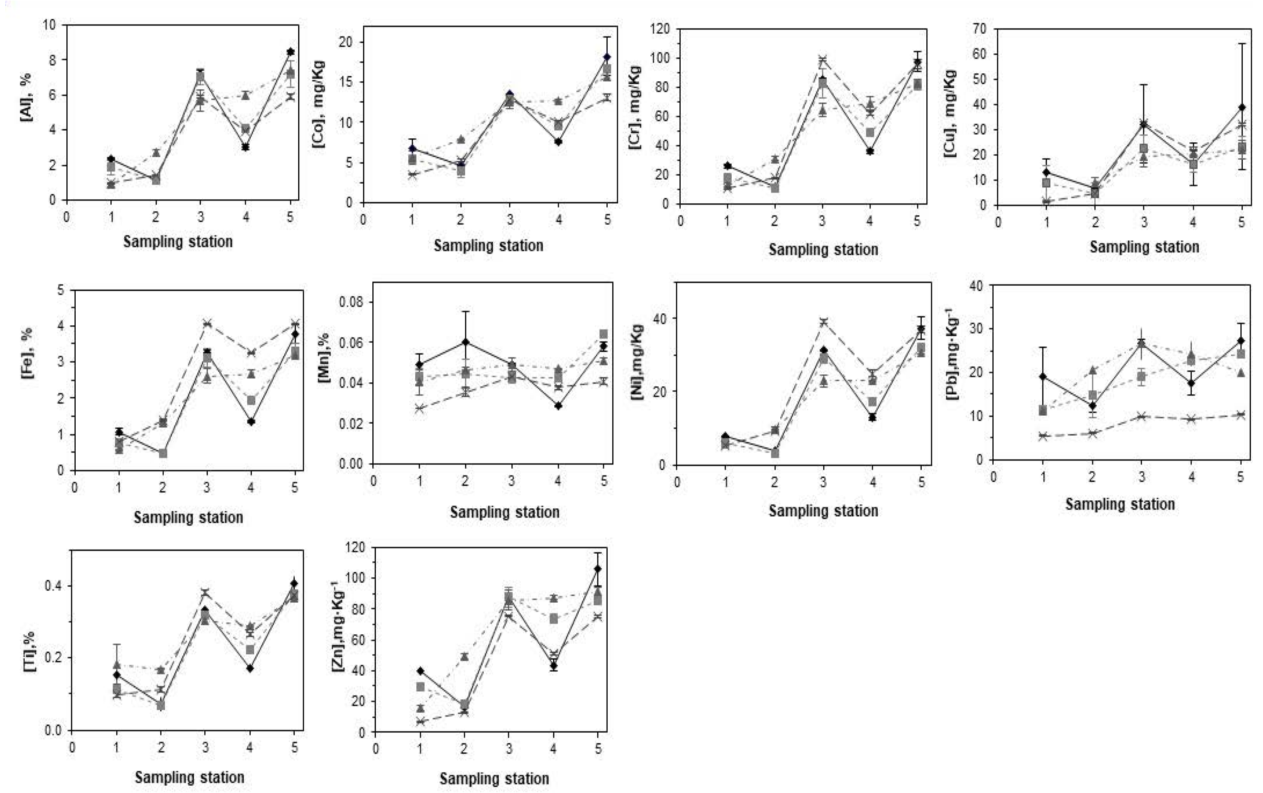

Fig. 2. *Organic matter and metals concentrations in sediments from the San Pedro River.*

campaign, probably due to the accumulation of the suspended matter from aquaculture effluents along the last decade.

Metals concentrations

In general, metals presented the same behaviour than organic matter in the sediments of the San Pedro River, as it was observed in a previous work for Cu, Zn and Pb.[12] In Fig. 2, it can be observed higher metal concentrations in the inner part of the river, where aquaculture activities are developed. In fact, an analysis of variance (ANOVA) determined significant spatial differences for most of the metals, with the exception of Mn ($p=0.203$) and Pb ($p=0.155$) suggesting a different origin for these elements. In general, sampling stations 1 and 2 were similar and different to the other sampling stations confirming two different areas in the San Pedro River. Nevertheless, Mn concentrations were very similar in the five sampling stations, probably due to high values in the outer part of the river related with a wastewater treatment plant in this area. As can be seen in Fig. 2, the manganese concentrations in the sampling stations 1 and 2 were even higher than those observed in the culture ponds before and after the culture cycle, meanwhile other metals presented similar concentrations for these two sampling stations and the culture pond before the culture cycle.

In addition, ANOVA was also used to determine temporal changes in metal concentrations in the sediments of the San Pedro River. As can be expected from the results, most of metals present no significant differences between the different sampling campaigns, with the exception of Pb ($p=0.018$). The concentrations of this element were significant different in the last sampling campaign in comparison with the other ones due to the lower concentrations found for all sampling stations in 2010. This fact suggests the existence of other source for this element, different to the aquaculture activities, during the previous sampling campaigns. Probably, this source can be related with the use of leaded gasoline in automobiles before the banishment of the leaded additives in the year 2001. In the Bay of Cádiz, Ligero et al., observed that the introduction of unleaded gasoline diminished the concentration of Pb in sediments, although this study has not data after the banishment.[34] A similar trend was also observed in the Seine River, where a fast decreased in the lead concentrations in suspended particulate matter was related with the banishment of gasoline leaded additives.[35]

3.2. Environmental status of the San Pedro River

As Fig. 3(A) shows, the enrichment factor (EF) was below 1 for most of the metals, with the exception of Mn in sampling stations 1 and 2, and Ti and Pb in sampling station 1. Nevertheless, these elements showed a minor enrichment, suggesting the San Pedro River is a minor contaminated area. Geoaccumulation index confirms this result due to it was lower than 0 in all cases (Fig. 3(B)).

It can be notice that metals with EF higher than 1 showed higher value in the two first sampling stations, were aquaculture activities are not presented, in spite of the higher concentrations were observed in the other sampling stations. It can be related to the fact that the reference element (Li) also presented higher concentrations in the inner part of the San Pedro River. Some authors have pointed out the limitations of this index due to its arbitrary "cut-off value" and the assumption of the constancy of heavy metal/reference element ratios in nature as well as its dependence on the background and the reference element selected.[29]

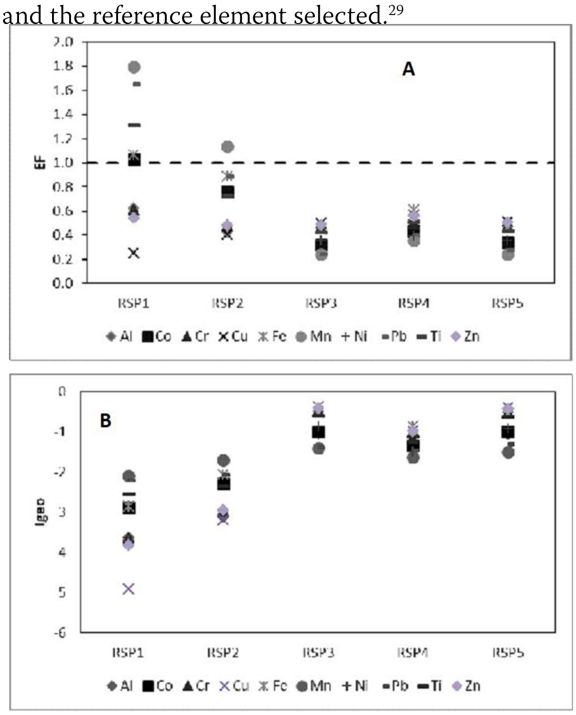

Fig. 3. *Pollution assessment indexes: (A) Enrichment factor, (B) Geoaccumulation index.*

Then, a comparison has been made with the sediment quality values for the Gulf of Cádiz proposed by Choueri.[36] All sampling stations related with aquaculture activities (sampling stations 3, 4 and 5) can be considered as moderately polluted by Cu, Co and Ni, as well sampling station 2 by Ni. The rest of metal concentrations were in no polluted range.

In addition, a comparison of metal concentrations (Cu, Cr, Ni, Pb, Zn) with the sediment quality guidelines was also performed to evaluate the possible toxic effects on the biota (Fig. 4). As can be expected from the EF and the I_{geo} values, metal concentrations in sediments from San Pedro River present low risk for the biota due to concentrations were below the ERL for most of the cases, and even below TEL for Zn and Pb in all sampling stations and for the rest of metals in sampling stations 1 and 2. Only Ni and Cr showed concentrations above PEL in the inner sampling stations (3, 4 and 5).

Finally, the chemical status of San Pedro River was also evaluated using the World Wide Natural Background levels (WWNBLs) and the World-Wide Threshold Values (WWTVs) proposed by Gredilla et al.[37] These authors proposed an alternative to evaluate the quality of surface water bodies according to the chemical status of their sediments. If less than 20% of sampling stations present concentrations higher to the WWTVs for a specific contaminant, a good chemical status can be concluded regarding to this contaminant. On the contrary, if more than 20% of sampling stations present concentrations higher of WWTVs, a poor chemical status can be concluded. As shown table 1, a good chemical status was observed in the San Pedro River for Cu, Pb and Zn, meanwhile a poor chemical status was observed for Cr and Ni. In this case, the stations with concentrations higher than the WWTVs were those closed to the aquaculture facilities.

Table 1. *Chrome, cooper, nickel and lead status concluded for the San Pedro River. All concentrations are given in mg.kg^{-1}*

	Cr	Cu	Ni	Pb
Average concentration	57.1	18.3	23.2	8.2
Maximum concentration	99	32.3	39.1	10.4
Minimum concentration (mg·Kg^{-1})	11	1.4	5.4	5.5
World-Wide Natural Background Levels (WWNBL)	31.1	73.2	19.9	59.3
World-Wide Threshold Values (WWTV)	55.6	73.2	20.4	59.3

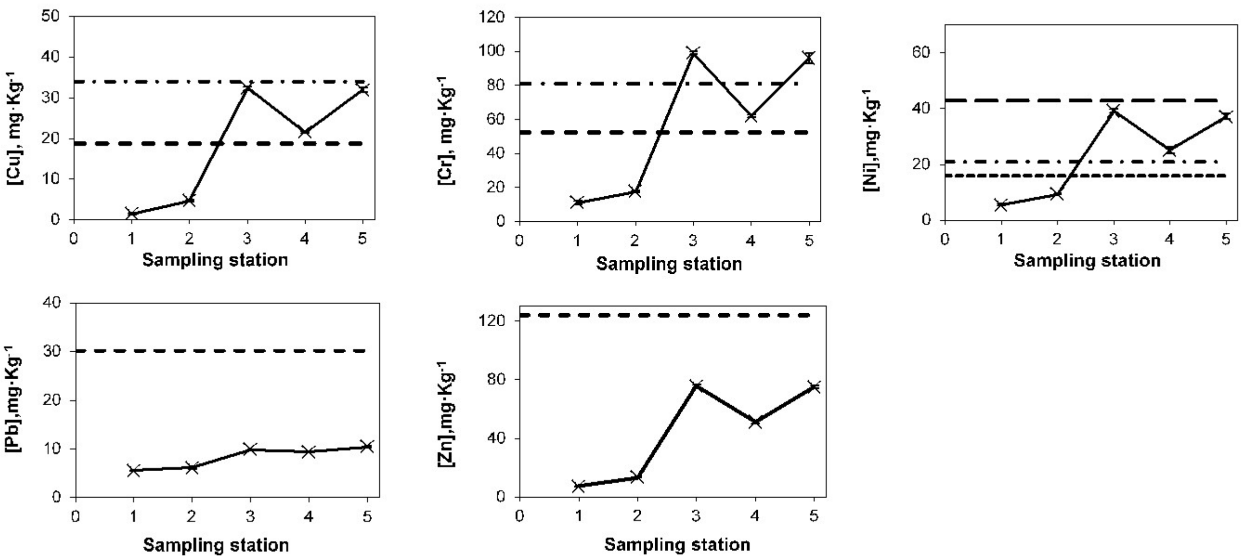

Fig. 4. *Comparison of metal concentrations in San Pedro river with the sediment quality guidelines: TEL; ERL; PEL*

3.3. Comparison of sediments of Rio San Pedro with sediments from other rivers influenced by aquaculture activities

Organic matter content in sediments from Rio San Pedro was between 2.6-5.9 times lower than that from sediments in Batan Bay, Aklan, Philippines[38] and estuarine sediments in Guadiana, Spain[39]. Both ecosystems are also influenced by aquaculture activities.

On the other hand, Cr and Co concentrations were, generally, between 6 and 17 times higher, while Ni was between 15 -17 times higher as well in Rio San Pedro[39].

Variability of Cu, Pb and Zn concentrations in other ecosystems was significantly high respect to concentrations found in the present study, meaning that sometimes metal concentrations were higher in Rio San Pedro, while in other cases it was lower than that reported elsewhere. Thus, Cu was 1-3.4 times higher in Rio Tinto and Rio Odiel than that in Rio San Pedro[40,41]. In the same way, Cu concentration was more than 100 and 3-5 times higher than that reported by Poersch et al.[42], Pal and Maiti[43] and Aslam et al.[44]. Lead was also 1 time higher in Rio Odiel[40] and between 6.8-32 times higher in Dhanbad (India)[43] in comparison with Rio San Pedro. Similarly, Zn was around 10-14 and 6-12 times higher than that in Rio San Pedro in both ecosystems, respectively. While it was around 10 times higher than that reported in Rio Tinto[41].

Contrastingly, Pb was similar in Rio San Pedro than that reported by Junejo et al,[45], while it was higher in those sediments than reported elsewhere[38,39]. Finally, Zn was also around 3 and 23 times higher in Rio San Pedro than that reported in estuarine sediments from Rio Guadiana[42] and in Southern Brazil[44].

In summary, the comparison of metal concentrations found in Rio San Pedro with those found elsewhere did not show a clear picture. In some cases, concentrations were higher and in other cases were lower. Several factors could explain the diversity of observed results, for instance, the applied sediment digestion preparation, which can vary among different studies. In this context, enrichment factor and geoaccumulation index used to classify the pollution level as such as the comparison of found metal concentrations with reference concentration, which evaluated the occurrence probability of adverse effect on the biota confirmed their usefulness as effective tools in metal pollution assessment of sediments.

CONCLUSION

Aquaculture activities have been identified as the main anthropogenic source of metals in San Pedro River. Sampling stations close to aquaculture facilities have been considered as moderately polluted in Cu, Co and Ni when metal concentrations were compared with the sediment quality values for the Gulf of Cádiz. Nevertheless, Pb concentrations in sediments are mainly controlled by the use of leaded gasolines, since a considerable decrease was observed after the banishment of gasoline leaded additives. In addition, Mn concentrations were also related with the activities of a wastewater treatment plant located in the outer part of the river.

In spite of this, San Pedro River can be considered as a minor contaminated area in relation to the enrichment factor and geoaccumulation index. Only Ni and Cr presented concentrations above the probable effects level (PEL), so adverse effects on the biota could be frequently expected for these metals. In addition, a poor chemical status of San Pedro River was also observed only for these elements.

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DATA AVAILABILITY STATEMENT (DAS)

The authors confirm that the data supporting the findings of this study are available within the article [and/or] its supplementary materials.

COMPLIANCE WITH ETHICAL STANDARDS

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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