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Research article

The Anthropocene fingerprint: Hazardous elements in waters of a coastal Mediterranean alluvial plain (Valencia, Spain)

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A B S T R A C T

This study focuses on the alluvial plain spanning between the Turia and Jucar rivers (486 km^2) in Valencia, Spain - a highly productive agricultural area that also involves a Natural Park (La Albufera). Thirty-five points across different water sources and land uses were sampled to map the spatial distribution of 14 heavy metals (Al, As, B, Cd, Co, Cr, Cu, Fe, Li, Ni, Pb, Sr, Tl, and Zn), and to study the potential influence of water characteristics and environmental factors on them. Two pollution indexes were applied, Heavy Metal Evaluation Index (HEI) and Water Pollution Index (WPI), to assess the water quality state in the area. High levels were predominantly found in the southern region, particularly within rice farming areas. For B, Sr, and Tl, all samples exceeded WHO limits, EU legislation, or EPA benchmarks, with 61.76 % and 85.71 % of samples surpassing standards for Al and Li, respectively. Water salinization parameters greatly influenced the dynamics of Al, As, B, Li, Sr, and Tl. Analysis using both indexes (HEI and WPI) revealed poor water quality in the area, particularly in rice fields, posing potential toxic effects on ecosystems and human health. The findings of this work are valuable for understanding elements of concern in coastal wetlands under global change.

1. Introduction

Human-induced activities have notably impacted estuaries and coastal wetlands. They face a multitude of environmental pressures [1,2], such as overexploitation of resources, increasing population and tourism, alteration of hydrological dynamics, etc. In this sense, the presence, distribution and levels of contaminants, such as trace elements, in coastal aquatic environments are influenced by natural phenomena and human activities [3–5]. These last, have their major effects, except in particular cases, on coastal ecosystems and their sources can be diverse, e.g., industrial and urban wastewater discharges, fish farming effluents, agricultural run-off, illegal dumping, and so on [6]. Among all substances that these ecosystems receive, metals have been regarded as potential indicators and fingerprinting of human development across various environmental compartments [7] becoming in a great and global concern [8]. Their impacts on both the environment and human health are widely recognized [9], posing a persistent threat that requires ongoing management in our ever-evolving world.

Coastal areas typically harbor rich biodiversity and distinct ecosystems. They serve as a pivotal factor in the maintenance of the natural equilibrium and produce the highest biological output in world ecosystems [10]. In this sense, to know water quality is paramount in developing and managing of coastal and marine areas [11]. To achieve that, over several decades, great efforts have been

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focused on creating tools for water quality assessment. This has resulted in the development of numerous indices of different types, with differences on objectives, parameters, sample matrix and size, scale of application and complexity. The indexes characterize water quality based on different parameters (physical, chemical, microbiological, sensory perception, etc.) considering risk for human health if their limits are surpassed but their suitability depends on the water use to be applied.

Starting from the initial water quality index (WQI) developed by Ref. [12], numerous methods and indexes have been elaborated with increasing complexity, differing mainly in the statistical incorporation and translation of parameter values [13,14], or the inclusion of qualitative or perceptual aspects. From WQI many other indexes have appeared such as Comprehensive Pollution Index (CPI), Eutrophication Index (EI), Organic Pollution Index (OPI), Trace Metal Pollution Index (TPI), Heavy Metal Pollution Index (HPI), Canadian Council of Ministers of the Environment Quality Index (CCME) WQI), etc. or the more complex one, Global Drinking Water Quality Index (GDWQI) [15]. All of them show their strengths and weaknesses. Among them, WQI and HPI are the most widely used [16,17]. On the other hand, indexes like the Heavy Metal Evaluation Index (HEI) favor equal weightage in formulation, while few indices such as WQI, HPI prefer unequal weightages of parameters to represent the water quality [18,19].

Hussain and Pattra [20] proposed a more adaptive index, Water Pollution Index (WPI), which can be for physical, chemical (major ions or metal ions), or even for biological quality assessment of water sources based on the available water quality standards. The major difference of WPI regarding other indexes, such as WQI or HEI, is that it is not subjected to a particular type of water parameter and assigned weight. It is a versatile index allowing to deal with different waters and a variable number of parameters selected for

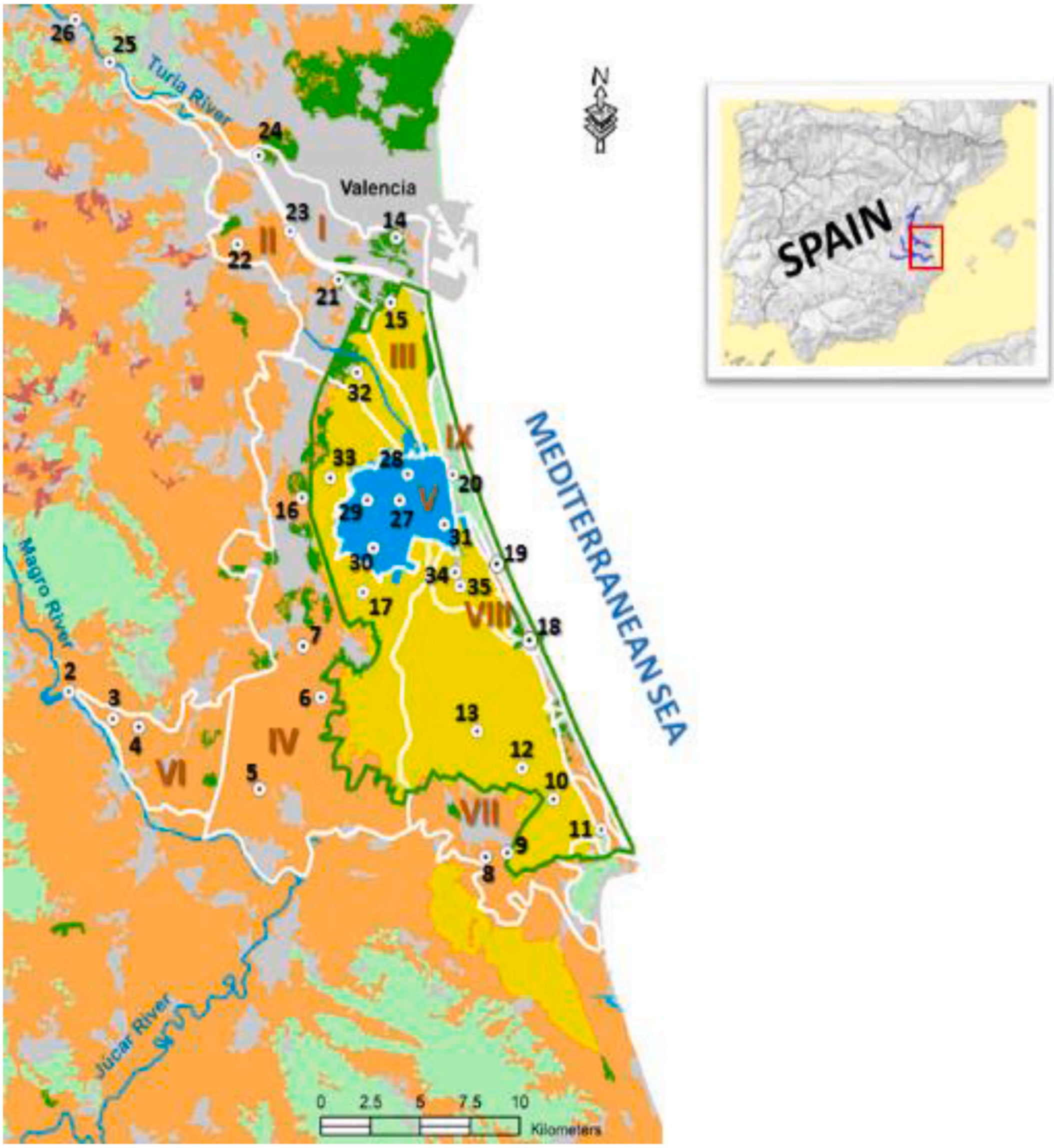

Fig. 1. Location of the study area and sampling points, including the distribution of the LFSs (in roman numerals).

calculation.

The most accepted classification of indexes is whether they are weighted or unweighted. The main difference is that weighted indexes use selected parameters, each weighted based on its importance to overall water quality [20,21]. Parameter selection depends on management objectives and the environmental characteristics of the research area [22]. Then, weights and relative weights are assigned, and raw data parameters are converted to a common scale [23,24]. Finally, sub-index values are aggregated to obtain the final WQI, which is the sum of the ratings and weights of all parameters [25].

Weighted indexes require large databases and complex calculations, often focusing on a specific area over time. Heavily weighted parameters can skew the index, limiting its broader applicability [20]. Additionally, changes in weight assignment can alter the final interpretation of water quality.

In contrast, unweighted indexes use a simple average of the values, giving each observation equal importance. The main difference between weighted and unweighted indexes is how individual values are combined to calculate the overall index.

Heavy metals (HMs) and metalloids are a wide group of elements, many of them scarcely studied in environmental media (B, Li, Sr, Tl, Se, etc.). As a consequence, there are very limited regulations about their toxic concentrations and effects, even in waters. Furthermore, background and/or standard levels have not been ascertained yet for many of them. Data regarding exposure remains incomplete, making it challenging to fully grasp the associated risks within this context [26,27]. However, in the last years, there has been a growing concern about some of them (Tl, Rb, V, Li, Ti, etc.) They are increasingly used in industry worldwide posing a potential risk for human health. These have been included in the category of “elements of emerging concern”.

This study aims to assess the total levels and spatial distribution of 14 elements (Al, As, B, Cd, Co, Cr, Cu, Fe, Li, Ni, Pb, Sr, Tl, and Zn) with varying toxicities and biological roles, in the waters of the coastal alluvial plain between Jucar and Turia rivers (Valencia, Spain). An important aspect of this work is its focus on a coastal wetland, one of the most productive areas in Spain with great ecological value due to the Natural Park (L’Albufera). The area is also designated as a ’Wetland of International Importance’ under the Ramsar Convention on Wetlands and is included in the NATURA 2000 network. Additionally, it holds status as an EU Special Protection Area (SPA) and a Site of Community Importance (SCI). Currently, the study area receives major pressures from traditional agriculture, hinterland industrial and settlement development, as well as reduced hydrological inputs during dry seasons. Special mention should be made to the coastal marshland and Albufera Lake, where major pressures come from the domestic and industrial human activities (1000000 inhabitants living in 13 municipalities within the limits of Natural Park). It is accompanied by the contemporary agriculture practices with the use of agrochemicals in paddy and orchard lands. as an important source of heavy metals. Agriculture has been accredited as largest contributor of non-point source pollution (NPS) of surface water, ensuing in about 75 % of global aquatic pollution [28].

The originality and novelty of the paper lie in (i) analyzing the geo-spatial distribution of the studied elements, (ii) investigating potential environmental influences such as land use and water sources, (iii) exploring the interactions between elements, water characteristics, and environmental factors, and (iv) Utilizing the Heavy Metal Evaluation Index (HEI) and Water Pollution Index (WPI) to assess overall water quality.

Currently, data on the presence of "emerging elements" are scarce in fragile ecosystems like Mediterranean coastal wetlands and there is a gap of knowledge to fully understad the influence of environmental factors (salinization, land use, etc.) on their dynamics.

2. Materials and methods

2.1. Study area and sampling

The study area spans 486 km^2 in Valencia, Spain, situated between the Turia River (north) and the Jucar River (south), both flowing into the sea across a wide coastal plain (see Fig. 1). The landscape features an extensive network of irrigation channels and ditches supporting predominantly agricultural activities, particularly rice farming (covering 223 km^2) and citrus crops, with many fields located within the boundaries of the Natural Park. L’Albufera was declared a Natural Park in 1986, covers an area of 210 $km^{2,}$ and is located 12 km south of the city of Valencia (Spain). The park is part of the hydrographic Xuquer basin, which consists of the large (around 23 km^2) shallow (1–2 m depth) lagoon surrounded by rice fields (140 km2), citrus and orchard crops, pine groves, and dunes, with only a few hectares still in their natural state [29]. This Park is a place of high economic, touristic and scientific interest and it is included in the Ramsar Convention on Wetlands. The lagoon is also very important in regulating the water flow in the rice fields. The lagoon is freshwater-fed by a number of channels associated with the agricultural land uses. These channels are designed to reuse reclaimed water for supplying the ecological flow in the wetland and the irrigation of farm areas. Anyway, the lagoon results in a sink of contaminants coming from the agricultural fields and the treated waters from the different wastewater treatment plants corresponding to the industrial areas and the surrounding cities. Other serious effects are occurring in response to the industrialization of the neighboring areas, demographic expansion in outskirt villages, tourist urbanization in coastal areas, and construction of a dense road network, which takes up over 40 ha [30].

However, the area also experiences significant population growth, industrialization, and urban development, resulting in an average population density of 2000 inhabitants/km^2. These characteristics align it closely with typical Mediterranean fluvio-littoral areas in Europe.

The soils in this region are primarily composed of organic black and gray silts, heavily influenced by agricultural practices. They typically exhibit a basic pH, carbonate-rich composition, with hydromorphic properties near the coast and elevated salinity levels. The main groups of soils are Cambisols, Fluvisols and in the coastal strip, Arenosols [31] some of them can presents gleyc properties because of the variable water table, mainly in the rice fields near the coast.

Water samples were taken from 35 specific locations in the study area (Fig. 1), encompassing key water channels and marshland areas. Prior to sampling, polyethylene bottles (2.5 L) underwent a rigorous cleaning process involving sequential rinsing with nitric acid 20 % v/v and afterwards, several times with deionized water. Bottles were filled to capacity to expel air bubbles, with the addition of a few drops of nitric acid. These samples were then kept at 4 °C until transported to the laboratory, where they were transferred to opaque containers and stored at −20 °C until analysis. All samples were processed within one week of collection.

2.2. Analysis

Physical and chemical properties of water samples were in-situ measured with a water multiparameter HANNA HI9829-01042 (HANNA Instruments, Spain). Concentrations of Al, As, B, Cd, Co, Cr, Cu, Fe, Li, Ni, Pb, Sr, Tl, and Zn were determined using microwave-assisted acid digestion, following the method outlined by the U.S. EPA [32]. Total of concentration were measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Thermo Scientific® ICAP6500 DUO), except As and Cd that were quantified by an Inductively coupled plasma mass spectrometry spectrometer (ICP-MS) (Agilent Technologies. ICPMS7900).

Three replicates were performed per sample, with five readings taken for each replicate. To assess the quality of the applied methodology and the determinations by ICP-OES, various aspects were studied. Matrix interferences were checked using the method of standard addition, and no matrix interferences were observed for the determination of the studied metals. Standard deviations ranged from 6.002e-19 for Cd to 0.9546 for Sr, while standard errors ranged from 6.994e-19 for Cd to 0.9649 for Sr.

2.3. Statistics

Statistical analyses were conducted using IBM SPSS version 22.0. Analysis of variance (ANOVA) and Tukey's multiple range test ($\alpha = 0.05$) were employed to detect differences among treatments. Pearson's bivariate correlation analyses were performed at 95 % and 99 % significance levels to investigate relationships between heavy metal concentrations and water characteristics. Spearman's bivariate correlations were used for variables with non-normal distributions at the same significance levels. Additionally, multiple stepwise linear regression analysis, discriminant analysis, and categorical PCA were utilized to assess variable weight and dependence, differences, and identify behavioral patterns.

2.4. Spatial analysis

The study of spatial distribution and zoning was performed using geostatistical and spatial analysis tools (ArcInfo v. 10.3).

2.5. Water quality indexes

To complete the water quality assessment in the studied area, two widely tested indexes have been applied. Given target area conditions (number of samples, zone characteristics, etc.) unweighted indexes were chosen. We preferred indexes more related to metals pollution, flexible for different scenarios, and not too complex to calculate. Thus, we selected the Heavy Metal Evaluation Index (HEI) and the Water Pollution Index (WPI). They were selected, after a deep bibliographical revision, because of its widespread use, flexibility in the selection of parameters application and are not linked to any specific type of water or a particular weight. Another aspect to consider is its relative simplicity facing computation. Both indexes characterized optimal water quality concerning standards permissible limits recommended by the WHO, US EPA, EU or any other agencies being comparatively easier to use and adaptable for different regions.

The Heavy Metal Evaluation Index (HEI) focuses on heavy metal contamination, using equal weightage for parameters. In contrast, indexes like WQI and HPI use unequal weightages [19,21]. HEI values are categorized based on the mean value for the study area [33,34]. HEI [35] gives a value of the overall quality of a given water regarding heavy metal pollution. The HEI is given by (Eq. (1)):

$$\sum \frac{n}{i=1} H_c \Big/ H_{mac} \tag{1}$$

Where H_c is the monitored value of the ith parameter and H_{mac} is the maximum admissible level of the ith parameter.

The obtained global values are given in Table 4, ranging from 0.003 to 178.65 (mean = 26.36). In this case, the values are distinguished into 3 types using a multiple of the rounded mean value differentiating the level of contamination in low (HEI <30), medium (HEI = 30–60), high (HEI 60–100) and very high (>100).

The second index used was the Water Pollution Index (WPI) [36], to obtain a pollution index that can include a high number of variables being compliant with n number of parameters. The WPI avoids confusion from differing assigned weight values in literature and can be applied to various data sets, even if they are skewed. It considers the combined effects of general physicochemical parameters and heavy metals relative to their permissible limits. It is divided in two steps, in the first of them The pollution load (*PLi*) of ith parameters is calculated as (Eq. (2)):

$$\boldsymbol{PLi} = \mathbf{1} + \left(\frac{\boldsymbol{Ci} - \boldsymbol{Si}}{\boldsymbol{Si}} \right) \tag{2}$$

Where *Ci* is the measured level of the *i*th element and *Si* is the standard o highly permissible limit for the respective parameter. Then the water pollution index (WPI) with n number of variables (parameters) can be assessed through the addition of all the pollution loads and finally dividing with n, according to (Eq. (3)):

$$WPI = \frac{1}{n}\sum_{i=1}^{n} PLi \tag{3}$$

The WPI values are classified based on then number of parameters in four categories: excellent (WPI <0.5), good (WPI = 0.5–0.75), moderately polluted (WPI = 0.75–1) and Highly polluted water (WPI >1)

These indexes have been applied based on seven metals (Al, B, Fe, Li, Sr, Tl, Zn) because the remainders metals studied showed values below limits of detection in the sampling zones or were not detected.

For both indexes, the highly permissible limits used were those of [36] and the European Union standards for drinking water [37,38]. However, there is not information or regulations about the admissible levels of some elements (Li, Sr, Tl, etc.) of emerging concern. In this case we have some indications from the US EPA [39–41].

The indexes calculation has been done firstly in a global way including all data corresponding to the sampling points and, secondly, the values of both indexes were calculated regarding to the water sources, land uses and LFZs.

3. Results and discussion

A geostatistical analysis was conducted to distribute the selected area according to land uses, water sources and anthropic pressure. This analysis yielded nine distinct landscape functional sectors (LFS), as illustrated in Fig. 1 and summarized in Table 1. These sectors provided insights into the interplay between various environmental factors and the pollution of water and soils. LFSs I, II, and III are influenced by agricultural activities focused on orchards and rice cultivation and the waters of the Turia River, which also carries inputs from Valencia City (one million inhabitants) and its two wastewater treatment plants (WWTPs). Zones IV, VI, and VII experience significant industrial activity, along with extensive rice farming and tourism, and receive the water of the Jucar River. LFS VIII is predominately dedicated to orchard agriculture and tourism and influenced by both river waters. Zone V is characterized by waters linked to the Albufera Lake (covering 23.96 km2), while Zone IX encompasses the littoral strip.

Most of the metals analyzed (B, Cd, Co, Cr, Cu, Ni, etc.) exhibited concentrations below the thresholds set by both national and international regulations for either irrigation and livestock waters [42,43] or drinking waters [38]. Moreover, they were notably lower than concentrations reported in existing literature for natural coastal wetlands and lakes [44,45] but higher than those measured in reservoirs [46].

Table 1
Environmental influence of waters in the LFSs and land uses for Fig. 1.

LFS	Water influence
I	Turia river and periurban irrigation of Valencia city
II	Turia river and irrigation water from Quart-Benager WWTP
III	Turia river and irrigation water from Pinedo WWTP
IV	Jucar river and “Acequia Real del Jucar” (Royal Jucar Canal)
V	La Albufera Lagoon
VI	Magro River
VII	Lower section of Jucar river
VIII	Mixed irrigation Albufera Lagoon –Jucar river
IX	Littoral strip

Map Colours	
(light grey)	Artificial surfaces
(yellow)	Rice
(light orange)	Citrus
(light green)	Mixed vegetables
(dark orange)	Rainfed farming
(pale green)	Natural vegetation
(blue)	Water bodies

Cd, Co, and Cr were in concentrations bellow the limit of detection (LOD), while Al, B, Fe, Li, Sr, Tl, and Zn were detected at concentrations > LOD in 100 % of the samples (Fig. 2). Maximum concentrations were for Al (1.02 mg/L), Fe (0.96 mg/L), Sr (6.83 mg/L), and Tl (1.22 mg/L). Musgrove [47] noted similar Sr variation in ground waters of the U.S. However, our findings exceed those reported by Peng et al. [48] for certain Chinese cities. It has to be remarked that the average Tl concentration of 0.36 mg/L surpasses levels reported for rivers and groundwater in the literature [49–51]. Li and Sr were also at concentrations higher than those reported for surface and groundwater [52–54].

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In the same way, Li, Sr, and Tl exhibited concentrations exceeding regulatory limits or benchmarks set by various authorities such as WHO, FAO, and EPA for water quality (see Fig. 2). Notably, high levels were observed for Al, As, Fe, Li, Pb, Sr, and Tl. It is noteworthy that for several metals, including B, Co, Li, Sr, Rb, and Tl, there are limited or no regulations regarding their toxic thresholds in water, and because of that is difficult to evaluate their hazard for ecosystems.

From the spatial analysis, we can observe two marked patterns of distribution. On one hand, Al, B, Fe, Li, Sr, and Tl showed high concentrations in LFSs V, VI, and VIII that correspond mainly to the Lagoon and its area of influence characterized by rice farming, together with the zone influenced by Magro river (a tributary of Jucar river) at the South-West. On the other hand, Cu, Ni, Pb, and Zn are concentrated mainly in LFSs I, II, III, and IV at the Western part of the alluvial plain, influenced by the Turia River, the city of Valencia (1 million inhabitants), their important WWTPs and the industrial belt surrounding the rice farming area (Fig. 1).

The statistical analysis revealed limited distinctions between specific LFSs, with only As, Fe, Li, and Tl demonstrating significant differences at the 95 % confidence level. Notably, Ni exhibited significant disparities between lake waters and those used for irrigation in orchard zones (LFS I, II, and IV). In terms of water types, significant differences were observed in the concentrations of Cd, Co, and Cr between water samples from rice fields and those from other areas. Significant differences between river waters and those utilized for orchard irrigation were observed for Zn. Furthermore, Cd, Co, and Cr also showed significant differences between their levels in irrigation channels and the other water types (Fig. 3).

Significant statistical relationships were observed between Al, Sr, and Tl, as well as between B and Li. Al and As were significantly correlated with the Fe content. Only Pb did not show any correlation with the other metals. This anomalous behavior could be due to the periodical inputs of Pb due to duck hunting which represents hundreds of kilograms of lead ammunition each year [55] concentrated mainly in the lagoon area.

The analysis of water's intrinsic characteristics (see Table 2) revealed a strong correlation between salt content (NaCl, Na, electrical conductivity, $SO4^{=}$, $HCO3^{-}$, etc.) and the distribution of B, Li, Sr, and Tl (refer to Fig. 4). Table 3 presents the best-fit equations of metals in relation to water chemical characteristics. Different authors [56,57] observed the impact of salt content in the mobility of metals in waters, reporting also significant positive correlations between HMs and salinity [58–60]. Higher salinity could increase the presence of cations, which could interchange with HMs stored in the sediment, which could be redissolved in water. On the other hand,

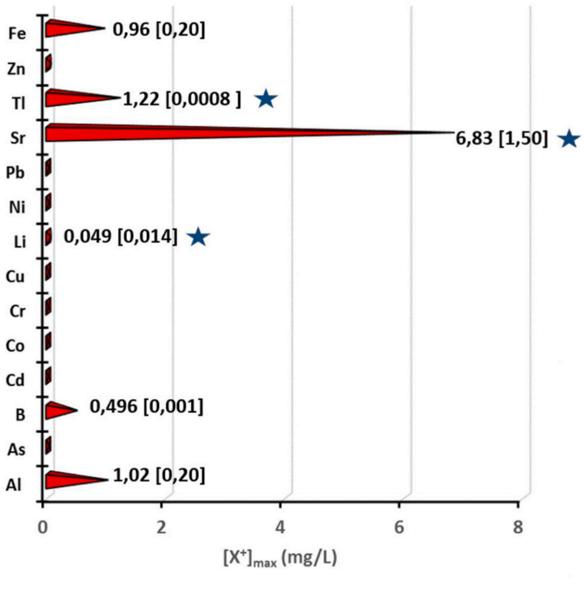

Fig. 2. Maximum values reached for the studied metals in the waters of the study area. The values in the graph correspond to the maximum levels of metals that exceeded legal regulations or EPA benchmarks.

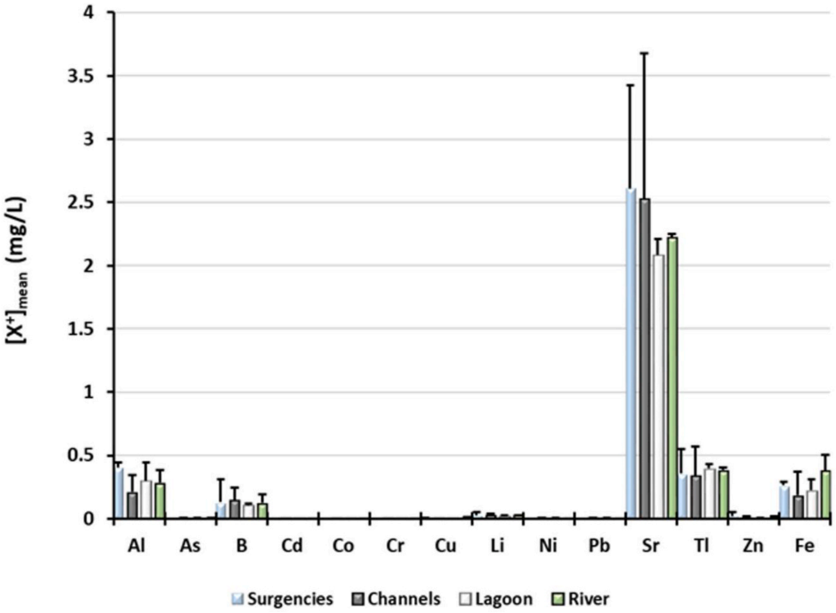

Fig. 3. Mean values of the studied metals according water types, with the standard errors.

the increase in salinity could also favor metal cations to form stable compounds with other cations. Their stability and solubility were higher than the affinity of the particulate phase for metals, leading to desorption and mobility of them from the particulate phase [58,61]. In natural waters, boron forms stable species and exists primarily as undissociated boric acid [$B(OH)_3$] and complex polyanions (e.g., $B(OH)_4^-$) [62,63]. These forms of boron are highly soluble and not easily removed from solution by natural mechanisms. Borate and boric acid are in equilibrium depending on the pH of the water, at the alkaline pH of the Albufera water (7.8) it is present as borate ions [62,64].

Casiot et al. [65] and Coup and Swedlund [66] reported that Tl^+ sorption may be only noticeable at alkaline pH values, which explains the high mobility of Tl^+ observed in aquatic environments. Other studies found that dissolved Tl concentrations may decrease as long as the Cl^- concentrations increase (Table 3). However, Cánovas et al. [67] observed an increase in Tl concentration with salinity, which could be related to suspended particle-water interactions as also occurs with Sr [68]. In the same way, increase in B and Sr concentrations with salinity could be related to suspended particle-water interactions [67].

In our case, the significant impact of marine intrusion resulting from aquifer overexploitation, especially for agricultural purposes, and the increasing drinking water demand, has led to seawater intrusion in numerous coastal aquifers across the Mediterranean region [69,70]. Similarly, Wen [71] in their study of the heavy metal pollution of the coastal groundwater of Laizhou Bay, noted the correlation between groundwater salinization and increased heavy metal pollution, leading to ecological and health risks. Different studies have found that seawater intrusion has major control over concentration of pollutants in aquifers [72].

Another common process associated to salinity, increment of reduction reaction and ion exchange mechanism, is the release of Cd and Zn–S complexes [73]. On the other hand, Gantayat and Elumalai [64] found that the formation of stable Cl^- and OCl^- and organic ligands under alkaline conditions (Ph > 8) had higher control over Zn, Pb and Cd toxicity in a highly ionic reactive condition. In other cases, seawater intrusion enhances the absorption of ions at metal absorption sites, making them more mobile [74]. These authors reported that in alkaline conditions, soluble PbCl, CdCl and ZnCl stared to appear at 35 mg/L Cl^-. In our case, water pH and Cl^- levels ranges between 7.1- 8.6 and 55.1–389.4, respectively, which could promote the increase of these soluble MCl^+ complexes (where M represents the different HMs).

One of the consequences of seawater intrusion is the transport of HMs along with salts leading to an increase in the health risk [75] and accelerating the hydrochemical and biogeochemical reactions in aquifers [76,77], leading to the desorption of adsorbed ions in aquifers, increasing the reactive species into groundwater that increase the toxicity to humans after exposure [76]. However, some authors reported that increasing salt concentration due to seawater intrusion increases the metal load but reduces the toxicities of several trace metals [75].

For Cu and Ni, strong inverse relationships were noted with nitrite levels, which was already observed by Deng et al. [78] and Giannopoulos [79]. However, it was observed only in four samples, and may be related to the bacterial decomposition of OM giving place to $NO2^-$ generation [80]. $NO2^-$ is easily converted to $NO3^-$. However, the nitrate values in these samples were low (between 15 and 22 mg/L). Similar relationships were observed between Al and Fe with dissolved oxygen levels. Kang et al. [81] observed similar relationships in river waters and surface sediments depending on the oxic/anoxic conditions. anoxic conditions decrease the potential bioavailability risks of Pb, Zn, Ni, Cu, Mo, and Fe. The most significant relationships observed have been confirmed by the PCA analysis (Fig. 5) explaining the 81.21 % of the variance.

Water quality status was assessed through the application of HEI and WPI indexes. From the complete pool of data corresponding to

Table 2
Intrinsic characteristics of the studied waters according LFSs.

	Landscape Functional Sectors																	
	I		II		III		IV		V		VI		VII		VIII		IX	
	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD
pH	7.62	0.31	7.95	0.38	7.11	0.29	7.85	0.39	7.95	0.33	8.05	0.17	8.04	0.31	7.66	0.32	7.63	0.35
EC[a] (dS/m)	1.37	0.09	1.35	0.08	1.79	0.35	1.49	0.41	1.55	0.13	2.58	0.06	1.90	0.37	2.06	0.45	1.59	0.80
TDS[b] (mg/L)	728.33	49.86	600.30	222.07	950.00	176.22	670.88	182.10	818.93	66.77	1355.00	12.73	1008.92	196.91	580.65	151.11	835.83	410.36
NaCl (mg/L)	662.60	53.67	635.60	44.94	890.50	189.27	726.13	192.79	731.76	72.32	1334.00	11.31	907.67	234.18	946.95	223.52	783.70	413.43
DO[c] (%)	89.00	14.46	85.67	5.06	94.10	10.20	83.38	20.55	90.41	7.65	74.55	2.90	70.67	8.95	61.10	27.29	77.00	18.02
Cl^-[d] (mg/L)	140.17	23.79	135.17	17.80	229.00	38.74	111.15	49.17	205.35	38.11	376.13	0.11	250.06	73.24	312.63	90.26	174.09	146.21
NO_2^-[e] (mg/L)	1.63	2.12	1.14	1.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO_3^-[f] (mg/L)	18.61	3.12	20.40	0.96	36.20	7.51	54.84	58.83	11.68	4.17	17.15	0.14	20.90	17.56	0.00	0.00	12.34	8.78
$SO_4 =$[g] (mg/L)	271.03	6.78	266.04	17.90	321.15	16.38	273.69	79.06	295.91	14.87	603.13	0.46	329.06	157.21	249.50	61.02	361.68	186.34
Na^+ (mg/L)	87.70	18.28	85.93	12.07	138.10	25.21	78.52	31.44	113.96	13.97	221.75	7.42	152.03	40.63	185.70	61.52	105.95	92.61
K^+ (mg/L)	4.90	2.52	4.70	1.49	13.70	3.21	4.90	3.23	7.69	0.93	9.25	0.07	4.90	0.70	11.70	8.20	4.38	3.55
Mg^{+2} (mg/L)	31.47	0.90	29.93	0.96	39.10	3.89	42.15	7.31	41.36	2.58	79.80	1.84	57.83	21.39	65.85	19.73	45.10	27.61
Ca^{+2} (mg/L)	74.77	6.04	71.63	4.12	83.40	5.92	90.83	31.23	52.03	3.22	112.25	8.84	80.23	14.35	58.30	11.31	81.40	24.37
TH[h] (mg $CaCO_3$/L)	316.27	17.92	302.13	12.21	369.26	31.57	400.38	100.99	300.24	18.19	608.90	29.64	438.50	119.50	416.75	109.49	388.98	172.31

* Standard deviation.
[a] Electric conductivity.
[b] Total dissolved solids.
[c] Dissolved oxygen.
[d] Chlorides.
[e] Nitrites.
[f] Nitrates.
[g] Sulphates.
[h] Total hardness.

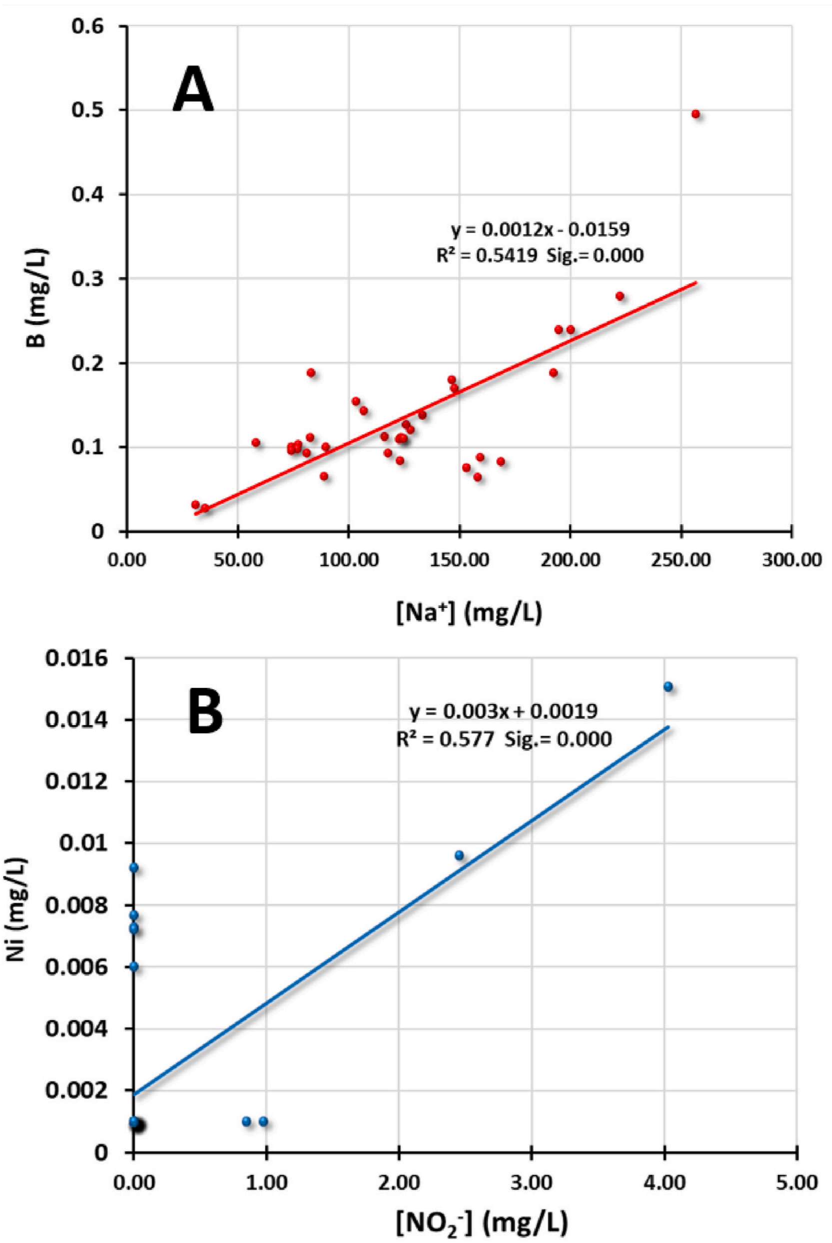

Fig. 4. Linear correlations between B and Na contents (A) and Ni and nitrites (B).

the sampling points the value found was 184.49 (very high degree of pollution) (Table 4). Only three sampling points gave values lower than 100 (8.57 %), the remainders show values between 100 and 200 (51.3 %) and the 40 % were higher than 200. The maximum value was for the sampling point 34 (625.41) followed by points 33 and 35, with 298.15 and 359.98, respectively (Table 2). These three points correspond to rice farming zones. Two of them (34 and 35) are located at the South-east of the lagoon in a zone that suffers high urban pressure and different roads with a dense traffic, together with the proximity of agricultural crops, mainly orchards. Point 33 is at the North-west of the lagoon is an area that receives the discharge of several industries related to fireworks, metal alloys and ceramics, between others. This could be the reason why these high scores appear, mainly for Tl and Li.

This very poor quality of the waters is also reflected by the values of HEI in contrast with values given for other authors [20,82]. LFZ 8 reaches the highest value of 492.69, where points 34 and 35 are located. This value is significantly higher than those of the other zones. In the same way, rice fields showed the highest value.

The profile shown for HEI values is almost similar for the Water Pollution Index (WPI), which showed a global value of 26.36. In all cases the WPI showed values were far beyond 1, which indicates a very polluted waters. The lagoon for water sources and the rice fields (for land uses) gave the highest values 29.07 and 361.88, respectively. As occurred with the HEI, Landscape Functional Zone 8

Table 3
Multiple stepwise regression models and best fit equations for metals versus water characteristics. Y= B0 +B1X1 + ….BjXj

Element (Y)	B_0	B_i	X_j	r^2	Sig.[a]
Al	0.541	$B_1 = 0.468$	$X_1 = [Fe^{2+}]$	0.669	$1.9930e^{-9}$
As	−0.005	$B_1 = 0.018$	$X_1 = [Fe^{2+}]$	0.642	$7.2918e^{-8}$
B	−0.098	$B_1 = 0.006$	$X_1 = [Na^+]$	0.852	$5.6487e^{-13}$
		$B_2 = -4.770\ e^{-0.006}$	$X_2 = [Na^+]^2$		
		$B_3 = 1.380\ e^{-0.007}$	$X_3 = [Na^+]^3$		
Li	−0.016	$B_1 = -1.870\ e^{-0.007}$	$X_1 = [NaCl]^2$	0.568	$7.8603e^{-6}$
		$B_2 = 8.420\ e^{-0.011}$	$X_2 = [NaCl]^3$		
Ni	0.002	$B_1 = -0.006$	$X_1 = [NO_2^-]$	0.547	$1.5904e^{-5}$
		$B_2 = 0.006$	$X_2 = [NO_2^-]^2$		
		$B_3 = -0.001$	$X_2 = [NO_2^-]^3$		
Sr	−0.190	$B_1 = 0.530$	$X_1 = [Mg^{+2}]$	0.904	$7.0171e^{-16}$
		$B_2 = -0.001$	$X_2 = [Mg^{+2}]^2$		
		$B_3 = 9.870\ e^{-0.006}$	$X_3 = [Mg^{+2}]^3$		
Tl	−1.227	$B_1 = 0.072$	$X_1 = [Mg^{2+}]$	0.867	$6.5000e^{-12}$
		$B_2 = -0.001$	$X_2 = [Mg^{+2}]^2$		

[a] Sig.: Significance.

Table 4
Values of the heavy metal evaluation index (HEI) and the water pollution index (WPI).

	HEI	HEI –Tl[a]	WPI	WPI –Tl[a]
Land Uses				
Streams	144.45	4.78	20.64	0.8
Rice fields	2533.19	75.26	361.88	12.54
Orchard	113.81	5.19	−215.70	−36.28
Citrus	153.57	4.90	21.94	0.82
Lagoon	230.35	5.73	32.91	0.96
Wetland	158.78	5.23	22.68	0.87
Water Sources				
Surgencies	185.21	7.15	26.46	1.19
Channels	175.11	5.64	25.02	0.94
Lagoon	203.51	5.54	29.07	0.92
River	198.73	6.76	28.39	1.13
Landing Functional Zones				
1	107.74	6.06	15.39	1.01
2	108.82	4.98	15.55	0.83
3	122.53	5.12	3.95	1.85
4	151.52	4.34	21.65	0.72
5	203.51	5.54	29.07	0.92
6	233.02	6.79	33.29	1.13
7	186.43	6.46	26.63	1.08
8	492.69	12.21	70.39	2.04
Global[b]	184.49	5.84	26.36	0.97

[a] HEI calculated without Tl values.
[b] WPI calculated without Tl values.

displayed maximum values.

We must consider, in this case, a certain distorting effect caused by the Tl values, which are high considering their limit value for toxicity in water (0.002). However, if Tl is excluded some substantial changes are observed. The overall HEI value would become 5.84 (good quality), while the WPI value would be 0.97, indicating moderate water quality (Table 4). In the case of land uses, rice fields would have a value of 75.26 in the HEI that means a high pollution state of these waters, but for LFZs and water sources all the values would indicate a good water quality.

Regarding to WPI, the differences increased. For land uses, only rice fields would show a highly contaminated water but for the others the status is moderate. In the case of water sources, the upwellings and rivers would present values slightly higher than 1. Landing functional sectors I, III, VI, VII, and VIII would show values of WPI higher than 1 (highly contaminated, meanwhile the remainders would present a moderate pollution state (WPI 0.75–1). Comparing the real data from each sampling point for the metals with those from the indexes, the more approximate of these last can be the WPI.

4. Conclusions

The levels of the studied metals showed that Al, B, Li, Tl, and Fe appear in the area at similar or higher values than the limits established by EU legislation or EPA benchmarks. Cd, Cr, and Co were below detection limits in all samples. These samples showed

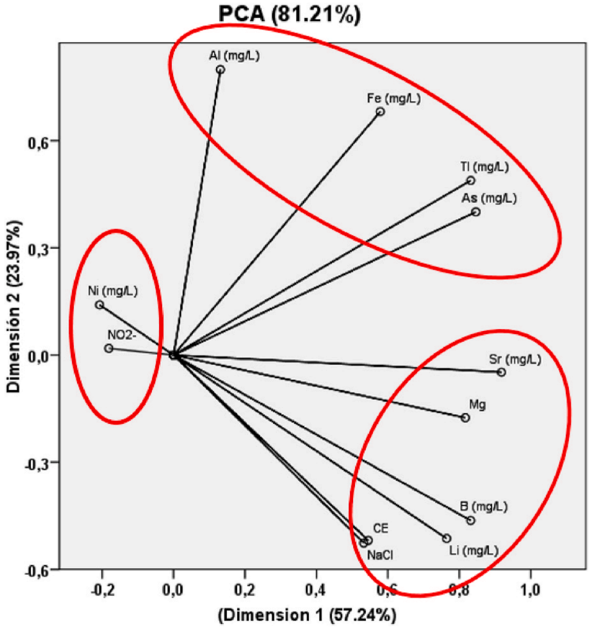

Fig. 5. PCA analysis of metals contents and water characteristics according LFSs.

values of B, Li, Sr, and Tl higher than those established by legislation.

The highest values were found in the orchard and rice farming areas. Significant statistical differences in metal concentrations were observed among landscape units for As, Li, and Tl. Compared to other water sources, irrigation channels showed significant differences in metal levels for Cd, Co, and Cr. Strong correlations were observed among Al, Sr, and Tl, as well as between Tl and Sr, and between As and Zn with Cu.

Two spatial patterns of metal distribution were observed. Al, B, Fe, Li, Sr, and Tl were more prevalent in the lagoon and its surroundings. In contrast, Cu, Ni, Pb, and Zn had higher concentrations in the western part of the study area, where orchards and rice crops dominate.

Salinity parameters (such as EC and NaCl), and the levels of Mg and Fe, significantly influence the behavior of most of the studied metals, particularly Al, As, B, Li, Sr, and Tl. Additionally, Ni was found to be strongly influenced by the NO2- content.

The two indices applied indicate pollution levels ranging from moderate to very high, with the rice fields showing the highest values in both cases, similar to the landing functional sector VIII in the south of the lagoon. The presence of high levels of Tl could distort the index values. Overall, the indices provide a reasonably accurate representation of the area's actual situation, particularly for the Water Pollution Index.

More research is needed to identify the causes of pollution in this study area, particularly the potential sources of B, Li, Sr, and Tl, and their possible impact on human health. Knowledge of these emerging elements is currently limited, especially in fragile ecosystems such as coastal wetlands. This study is valuable for the information provided and as a basis for better understanding these ecosystems and for planning conservation and restoration efforts to preserve them. We must consider that these zones will be the first affected by climate change, and their future evolution will impact human development and health.

CRediT authorship contribution statement

Vicente Andreu: Writing – review & editing, Writing – original draft, Visualization, Resources, Project administration, Methodology, Investigation, Conceptualization. **Eugenia Gimeno:** Validation, Methodology, Formal analysis, Conceptualization. **Juan Antonio Pascual:** Validation, Methodology, Investigation, Conceptualization. **Julián Campo:** Writing – review & editing, Validation, Methodology, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Vicente Andreu reports financial support was provided by Generalitat Valenciana. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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