applied sciences

MDPI

Article

Assessment and Review of Heavy Metals Pollution in Sediments of the Mediterranean Sea

Pedro Agustín Robledo Ardila [1], Rebeca Álvarez-Alonso [1], Flor Árcega-Cabrera [2], Juan José Durán Valsero [3], Raquel Morales García [3], Elizabeth Lamas-Cosío [2], Ismael Oceguera-Vargas [2] and Angel DelValls [4,5,*]

1 IGME-CSIC, NC Geological Survey of Spain, Spanish National Research Council, Balearic Island Unit, Carrer de Felicià Fuster, 7, 07006 Palma de Mallorca, Spain; pa.robledo@igme.es (P.A.R.A.); r.alvarez@igme.es (R.Á.-A.)
2 Unidad de Química en Sisal, Facultad de Química, Universidad Nacional Autónoma de México, Puerto de Abrigo S/N, Sisal 97355, Yucatán, Mexico; farcega@unam.mx (F.Á.-C.); elizabeth.lamas@enesmerida.unam.mx (E.L.-C.)
3 IGME-CSIC, NC Geological Survey of Spain, Spanish National Research Council, C/ Ríos Rosas, 23, 28003 Madrid, Spain; jj.duran@igme.es (J.J.D.V.); r.morales@igme.es (R.M.G.)
4 Environmental Science and Technology Department, University of Santa Cecilia, Santos 11045-907, Brazil
5 Water Challenge, S.L., Centro de I+D+I, C/Alamo Carolino s/n, Poligono Industrial Fuente de Rey, 41703 Dos Hermanas, Sevilla, Spain
* Correspondence: delvalls@unisanta.br

Abstract: The impact of marine sediment pollution is crucial for the health of the seas, particularly in densely populated coastal areas worldwide. This study assesses the concentration and distribution of heavy metals in the marine sediments of the main regions of the Mediterranean Sea. The results underscore high concentrations of mercury (Hg), nickel (Ni), and copper (Cu), whereas chromium (Cr), zinc (Zn), cadmium (Cd), barium (Ba), and vanadium (V) exhibit moderate values. To assess the heavy metal results, sediment quality guidelines and pollution indices (Igeo and Geochemical Signal Type-GST) were employed, revealing a consistent trend of decreasing concentrations from the coastal zone to the open sea. Principal Component Analysis (PCA) emphasizes the significant roles of Cu, Zn, Ba, and Cr in sediment chemistry. The study suggests that the distribution patterns of heavy metals are linked to wastewater discharges in coastal areas, requiring effective management strategies to ensure the health of the Mediterranean Sea.

Keywords: heavy metals; marine sediments; Mediterranean Sea; pollution; wastewater; discharge

Citation: Robledo Ardila, P.A.; Álvarez-Alonso, R.; Árcega-Cabrera, F.; Durán Valsero, J.J.; Morales García, R.; Lamas-Cosío, E.; Oceguera-Vargas, I.; DelValls, A. Assessment and Review of Heavy Metals Pollution in Sediments of the Mediterranean Sea. *Appl. Sci.* **2024**, *14*, 1435. https://doi.org/10.3390/app14041435

Academic Editor: José Carlos Magalhães Pires

Received: 8 January 2024
Revised: 2 February 2024
Accepted: 3 February 2024
Published: 9 February 2024

1. Introduction

Coastal and marine environments represent a crucial interface between human society and the natural world. Moreover, they also function as the primary sink of heavy metals, making them valuable indicators of marine sediment pollution [1,2]. These accumulated elements could be a contamination risk, releasing toxics elements through chemical and biological processes [3–5]. Additionally, due to their potential to accumulate in the food chain, they could affect human health [6–8]. Several studies have highlighted the importance of evaluating aquatic systems through marine sediments, confirming that a high level of heavy metals can become a great problem for the health of the seas [9–16]. Such contamination often can result from the discharge of wastewater into the sea (from underwater outfalls), especially in areas with high urban development, and elevate pressure of anthropogenic activities [17,18]. For instance, tourist destinations such as Mallorca Island, southern Spain, Greece, and southern Italy witness an influx of more than 50 million visitors annually, mainly during the spring and summer seasons. In these periods of high population rates, a substantial volume of poorly treated wastewater is discharged, introducing heavy metals into the sea and later into the marine sediments [2,19,20].

In this way, numerous efforts to control toxic elements in marine ecosystems have been made. Some good examples can be found in the monitoring carried out on the coasts of Greece, south of Italy, and east and southern Spain [15,21–24]. Since the 1980s, assessing marine sediment contamination has involved the use of sediment quality indices [25,26]. These indices assume that there is a threshold concentration of chemicals in sediments, below which ecosystems are considered unharmed, thus serving as essential tools for detecting contaminated areas. Furthermore, the concentration of heavy metals in marine sediments is classified from highly to slightly contaminated based on background levels [2,27,28].

In this order, the studies carried out in the Mediterranean regions mentioned above are useful to understand the pollution of marine sediments in the Mediterranean Sea and to know what the main source of heavy metals that seem to be common among the analyzed areas is. To compare the distribution and concentration of heavy metals in marine sediments, we carried out a study in the southeast of Spain, correlating the data with other regions of the Mediterranean Sea. These selected areas support strong tourism development, with a high number of visitors during the summer and spring seasons, leading to an exponential increase in water use and discharge into the sea.

In this context, the present study aimed to investigate the concentration of heavy metals found in marine sediments of the Mediterranean Sea close to the coastal areas. The objective was to identify the most contaminated areas as well as the source of contamination of the toxic elements providing a complementary benefit and/or improvement of the marine coast, such as discharge points of untreated or poorly treated water or chemical precipitation processes associated with the product of the chemical solution of each element that quickly exceeds the equilibrium situation. The study of this process and the identification of the conditions were carried out by evaluating the chemical reaction between sea water and water discharged from submarines outfalls. In addition, a study was carried out on the spatial distribution of heavy metals and metalloids and the chemical mechanisms that best describe the process.

The study emphasizes, despite the abundance of available studies focused on the contamination of marine sediments [1,2,5,9,14–16,21,24–28] to date, that no comprehensive investigation has been found for the sources of discharges and processes in marine zones close to highly populated areas, which are considered complex. However, bibliography detailed that as the world population grows and human activities expand, it is essential to minimize anthropogenic impacts on coastal and marine ecosystems [1,2]. In addition, it indicates the need to use different types of sonar to study the seabed and the biological response of the ecosystem to the contamination of marine sediment (distribution of heavy metals related to the identification of fauna or flora or potential biomass).In the literature it has been compared the result of the concentration of heavy metals in marine sediments with international pollution indices (NOAA and EPA), and with this, obtains a range of pollution for each area and metal analyzed [2]. In addition, they use a regional index obtained from studies of different sediments in the study area and calculate the type of local geochemical signal. This methodology allows for measuring the natural concentration and the deviations produced by discharges into the sea. Some authors applied the pollutant load index or potential ecological risk, as well as other classic techniques such as Enrichment Factor or geoaccumulation index to differentiate anthropogenic pollution and that of natural origin [4,7,8]. Generally, study reviews have a strong basis of statistical analysis using methods such as Pearson Correlation, component analysis, or dendrograms to obtain groups of clusters that confirm the relationships between the variables indicated by the correlation analysis.

Due to the diversity of chemical elements that can be introduced into the sea from treatment plants and the chemical reaction that occurs when supersaturated fresh waters and marine waters come into contact, it is very important to understand the chain of processes [2]. Furthermore, no study has simultaneously focused on problematic chemical species for marine habitat and human health (e.g., As, Cu, Hg, Ni, Pb,) that produce a negative impact on the environmental sustainability of the seas or oceans and a high risk for people who are in contact with these elements.

2. Materials and Methods

The global characteristics of the Mediterranean Sea (from southern Spain to Greece) features a hot and dry climate and a closed marine environment with high seawater evaporation. The fluvial system consists of few long rivers and numerous short channels active during intense rainfall. Bathymetry indicates a regular decrease in seabed elevation from −1 to −100 m [2]. These factors intensify the impact of pollutants compared to more open seas. Wastewater discharge points, in heavily populated tourist areas along the coast, significantly contribute to the pollution in the Mediterranean Sea. Many discharge points are located between 10 and 25 m deep, extending up to 1 km offshore, leading to a substantial volume of poorly treated or untreated wastewater being discharged due to limited treatment plant capacity.

2.1. Sampling Sites and Sample Collection

To assess heavy metal contamination in the Mediterranean Sea, we collected data from various sources, including the southwest of Spain (69 samples) [15,23] Greece (53 samples) [24], South of Italy (10 and 19 = 29 samples) [21,22]. Additionally, we reviewed manuscripts presenting heavy metal analyses in the Mediterranean Sea [29,30]. The fieldwork in the southwest of Mallorca Island [2] contributed 96 samples. All examined locations shared significant anthropic pressure from tourism and urban development along the Mediterranean coast. In Mallorca, sampling conducted between 2020 and 2022 was done using dredger blades and autonomous diving equipment, supported by an oceanographic research vessel. Sampling was systematic, considering factors like distribution, bathymetry, distance to the littoral coast, and wastewater discharge points. The study focused on the areas of the coastal areas closest to the points where wastewater is discharged, while the control samples were taken on the furthest margins of the outfalls. The results showed that the highest concentrations were located near the discharge points and decreased towards the open sea. Variations could be attributed to factors such as depth, marine flow patterns, or geological substrates. The analyzed samples revealed concentrations of heavy metals that exceeded the natural values of the regional sediments.

2.2. Sediment Quality Guidelines—SQGs

The chemical parameter analyzed was made under rigorous methods and quality assurance measures for credibility and accuracy. Heavy Metals: Arsenic (As), Barium (Ba), Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb), Vanadium (V), and Zinc (Zn) were analyzed using inductively coupled plasma–mass spectrometry (ICP-MS) with Agilent 7500ce equipment (manufactured by Agilent, Santa Clara, CA, USA, EEUU), following the EPA 6020 method. Mercury (Hg) levels were determined using the EPA 7471 method for solid or semisolid waste. Main Elements of Minerals: Atomic absorption spectrophotometry, with X-ray fluorescence, was employed to assess primary mineral elements. Quality Assurance: Our X-ray laboratory participates in semi-annual intercomparison tests for ongoing quality control, ensuring precision and reliability. For ICP-MS, annual internal control tests involve sample repetitions, with achieved precision ranging from 0.1% to 2.5%, which is within the acceptable relative standard deviation range of $\leq$10%.

2.3. Contamination in Marine Sediments

The obtained results were evaluated using the Geoaccumulation Index (Igeo) [31]. The Igeo index [32] is expressed as:

$$I_{geo} = log_2\left(\frac{C_n}{1.5B_n}\right) \quad (1)$$

where C_n is the measured metal concentration, and B_n is the geochemical background concentration derived from average continental shale. Igeo index illustrate in this study six contamination levels.

In the marine sediments of Mallorca, a Geochemical Signal Type (GST) was developed based on a regional background value of heavy metals from marine sediments of Mallorca. The GST is established on local background values from unpolluted coastal areas, representing average concentrations of heavy metals in sand beach. However, in the rest of the regions, regional background levels were determined using global mean background values [33] to assess contamination extent in marine sediments. Background values are defined as heavy metal concentrations unaffected by human activities. Deviation from background levels is primarily attributed to anthropic activities [34].

2.4. Statistical Analysis and Mapping

This study conducted statistical analysis, including a correlation matrix, to compare heavy metal concentrations in five Western Mediterranean regions. The Pearson coefficient measured relationships between concentrations, and Principal Component Analysis (PCA) reduced data dimensionality, explaining variation in a new coordinate system. Both analyses utilized Statgraphics 19 software.

To plot a map of wastewater discharges, we adopted a systematic approach involving weighted considerations based on discharges and population in each region.

$$\frac{V \propto \left(r_p + f_p\right)}{200} \tag{2}$$

where V represents volume in hm^3, r_p is the resident population, f_p is the floating population, and 200 serves as the weighting factor.

Wastewater volume data, measured in $hm^3/year$, was sourced from regional public institutions, while resident and floating population figures were cross-referenced with national census data. Results from this process were utilized to generate a database and maps of heavy metals, with georeferencing done using ArcGIS 10.8.1 software. To determine pollutant distribution, the Average Nearest Neighbor (ANN) relationship [35] calculated distances between centroids and neighboring points, identifying values associated with the closest centroid.

3. Results and Discussion

3.1. Mediterranean Sea: A Good Sink for the Sequestration of Pollutants

The seabed of areas of the Mediterranean Sea studied is mainly composed of sand (<80%) and small amounts of fine sediments, silt, or clay <20%. Gravel-sized sediments there are not abundant and, like clays, are generally deposited in the zones closest to the littoral coasts [2]. These factors, as well as bathymetry, intensify the impact of pollutants compared to more open seas. Wastewater discharge points in heavily populated tourist areas along the coast significantly contribute to the pollution in the Mediterranean Sea. Many discharge points are located between 10 and 25 m deep, extending up to 1 km offshore, leading to a substantial volume of poorly treated or untreated wastewater being discharged due to limited treatment plant capacity (Figure 1). The evaluation and review of marine sediment contamination was based on the regional background level inferred from uncontaminated sands and was compared with global contamination indices [2,36–38]. Statistical methods and spatial distribution analysis were applied to each area.

Figure 1. Wastewater discharge volumes in the north-central Mediterranean Sea. Estimates have been calculated with data provided by the Public Institutions from different countries. Subsequently, a weighting has been carried out between the volume of water (hm^3/year) and the resident and floating population ($\alpha\, r_p + f_p$).

3.2. Suitable Sea to Detect Relationship Pollution between Mediterranean Regions

The correlation matrices (Figure 2) reveal predominantly positive relationships among heavy metals, with specific exceptions like As-Cr in the M-A limit (southeast of Spain) and Hg-Zn in the south of Italy (Gulf of Taranto). However, Mallorca (southwest of Spain) exhibits a unique pattern with positive correlations among As and V but negative correlations with other heavy metals. The enrichment of As and V may be linked to nitrogenous fertilizer discharges and coastal aquifer pumping systems. Matrices compare study areas, excluding anomalous values from punctual discharges in northern Greece and southern Italy.

The Igeo index distribution, shown in Figure 3, varies significantly between heavy metals but reveals similar contamination patterns in marine sediments. The percentage distribution of Igeo index classes indicates contamination levels for each heavy metal in different regions.

Mallorca stands out for Ba, Cr, Pb, and Zn; Greece for Cr, Ni, Pb, and Zn; M-A limit for Cu, Ni, Pb, and Zn; southern Italy for Cr, Cu, Ni, Pb, and Zn. The pollution ranking, based on Igeo classes, is as follows:

SE Spain (Mallorca): Cu > Zn > Pb > Ni > Hg > Ba > Cr > As > Cd > V
SW Spain (M-A limit): Hg > Ni > Cd > Cu > Pb > Zn > As
SW Italy (Gulf of Taranto): Hg > Cr > Zn > Cu > Pb > Ni
S Italy (Sicily) (north (a) and south (b)): (a) Hg > Ba, and (b) Cu > Zn > Pb > Cr > Hg
Greece: Ni > Cu > Cr > Zn > Pb > As

The contamination levels of heavy metals, assessed by the Igeo index, show similarities across regions, which are directly related to their discharge sources. In Sicily (a), the index is influenced by industrial lixiviate discharge, while in Sicily (b), it is associated with diverse anthropic activities linked to tourism.

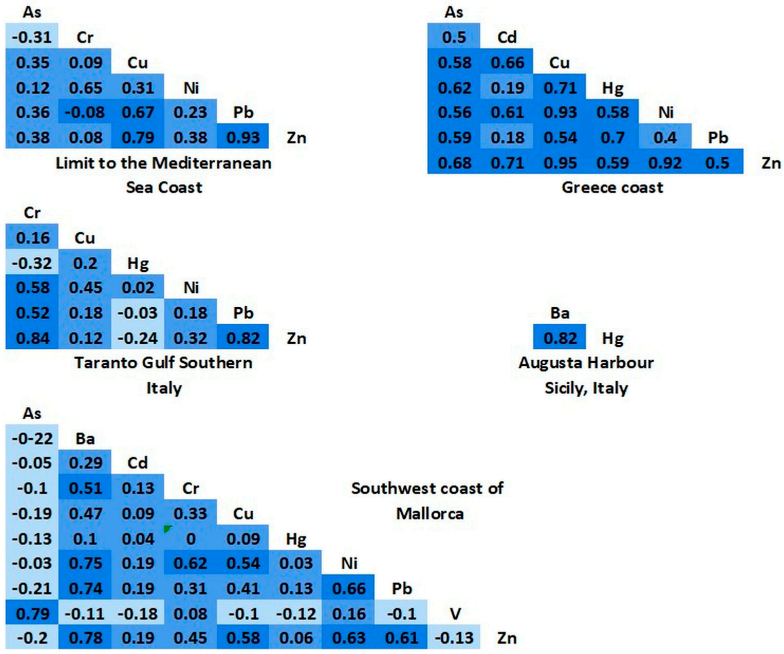
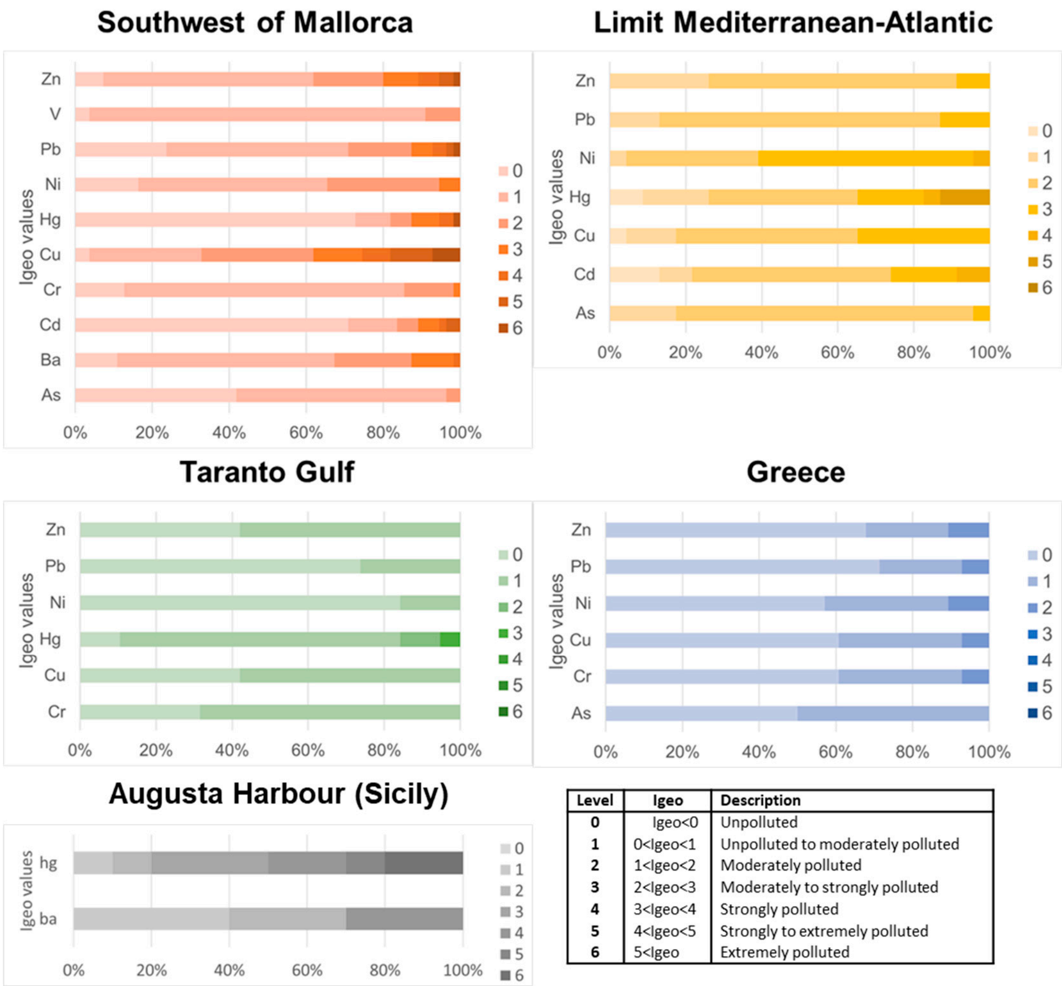


Figure 2. Correlation matrix in each area considered. Relationship between west and east of the Mediterranean Sea.



Level	Igeo	Description
0	Igeo<0	Unpolluted
1	0<Igeo<1	Unpolluted to moderately polluted
2	1<Igeo<2	Moderately polluted
3	2<Igeo<3	Moderately to strongly polluted
4	3<Igeo<4	Strongly polluted
5	4<Igeo<5	Strongly to extremely polluted
6	5<Igeo	Extremely polluted

Figure 3. Results of the Igeo index in sites from central-north of Mediterranean Sea. Dates are show in class of percentage of pollution in relation to the Igeo method.

Figure 4 shows the analysis using PCA principal components corresponding to the heavy metal concentration of the analyzed samples. As can be seen, the PCA does not separate different families of concentrations between the regions studied. The PCA suggests randomness in the presence of metals analyzed because the origin of the wide variability of percentage concentrations is related to the discharge of untreated wastewater. This masks certain concentrations that may be significant if studied in isolation. However, what the global PCA analysis shows is that the concentration and type of heavy metals in discharged wastewater is so broad that it is not possible to classify it.

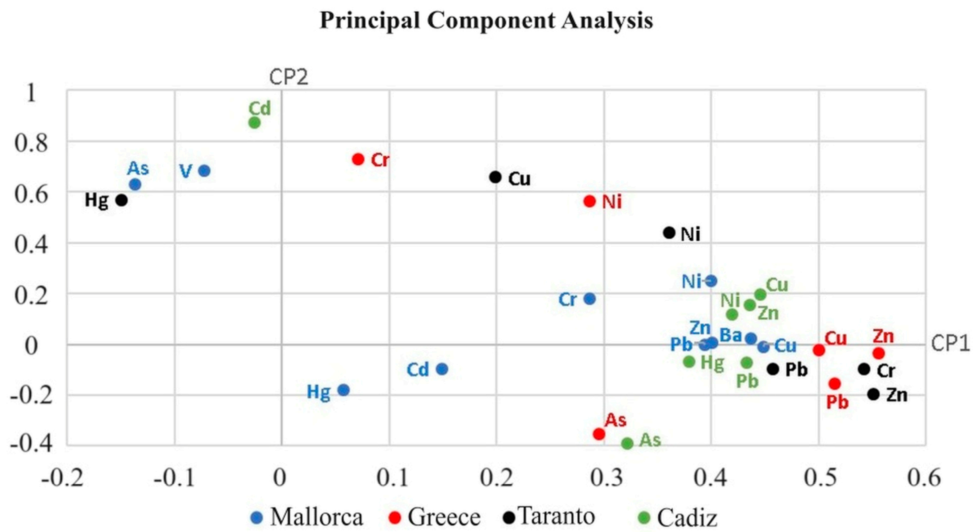


Figure 4. PCA loading plot for the studied heavy metals in the southwest of Mallorca. PC1 and PC2 account for 3.76% and 19.72% of the variance, respectively.

3.3. Comparing Major Heavy Metals Trap Regions: Connections Evidence

In the studied Mediterranean regions, slight variations exist in the distribution of heavy metal concentrations. The general trend indicates elevated pollution near discharge points (outfalls or spillways), decreasing towards the open sea. While some samples exhibit lower contaminant concentrations, they remain significantly higher than background values from regional indices. As, Ni, and V show a moderately homogeneous spatial pattern with moderate values, while Cu, Hg, and Pb concentrations are exceptionally high around wastewater discharge points, surpassing background values by several orders of magnitude.

The distribution of pollution in the Mediterranean Sea demonstrates high agreement (Figures 5 and 6). This clear correlation is because zones near the coast in densely populated areas are points where poorly purified waters with high concentrations of heavy metals are discharged into the sea. Moreover, because the cause of most pollution appears to be common, some heavy metals seen in higher concentrations are common between these areas. Occasionally, certain regions in southern Italy and northern Greece show anomalously high concentrations in some heavy metals, which are attributed to discharges from the metallurgical or mining industry [24]. Most areas with significant pollution values are linked to poorly treated wastewater discharges near the coast, particularly in regions experiencing seasonal overpopulation during Mediterranean summers. Increased tourist pressure in these areas renders it challenging to treat the water consumed by visitors. As depicted in Figure 5, the distribution and concentration of Cu, Pb, Hg, and Zn in the central-northern Mediterranean reveal a similar spatial pattern, with the highest values near coastal areas where wastewater discharges occur.

The current results and the statistical treatment revealed that the marine sediments studied in different areas of the Mediterranean Sea present high concentrations of common metals such as Cu, Pb, Zn or Cd. The analogous enrichment of these heavy metals in southern Italy, eastern and southern Italy, Spain, and Greece indicated the existence of a common and main anthropogenic source of these elements. Other areas of Mediterranean

Sea, or even in other parts the world such as southern China or southwestern Turkey [4,38], show a similar pattern, with high values of heavy metals in coastal areas of highly populated cities. Although the values of these metals may vary between the areas studied, the sequence, from highest to lowest presence, is usually similar between them. For example, the order in southeast China is Cu, Pb, and Zn. In Turkey, Cu and Pb are among the four most enriched metals. The statistical analyses of different regions confirm results that support the thesis of this article, showing that spatial patterns of concentration and sequences of heavy metals is similar to those mentioned.

These aspects show how specifically the high concentrations of metals and metalloids are close to the submarine outfalls. Thus, is important in the possible application of active methods to reduce concentration, since the actions can be carried out in more areas that are limited. On the other hand, it is useful for opening new lines of research into chemical vectors that break the balance of the solution and give rise to the chain precipitation of heavy metals in waters that become supersaturated upon contact with the sea water. The chemical relationship between certain elements is crucial to understanding the wide variety of metals deposited in marine sediments, specifically in sand grain fraction. In addition, it will be very useful to carry out simulations that determine the constant of the solubility product of different substances working in a virtual laboratory that models marine waters in contact with poorly treated purified waters.

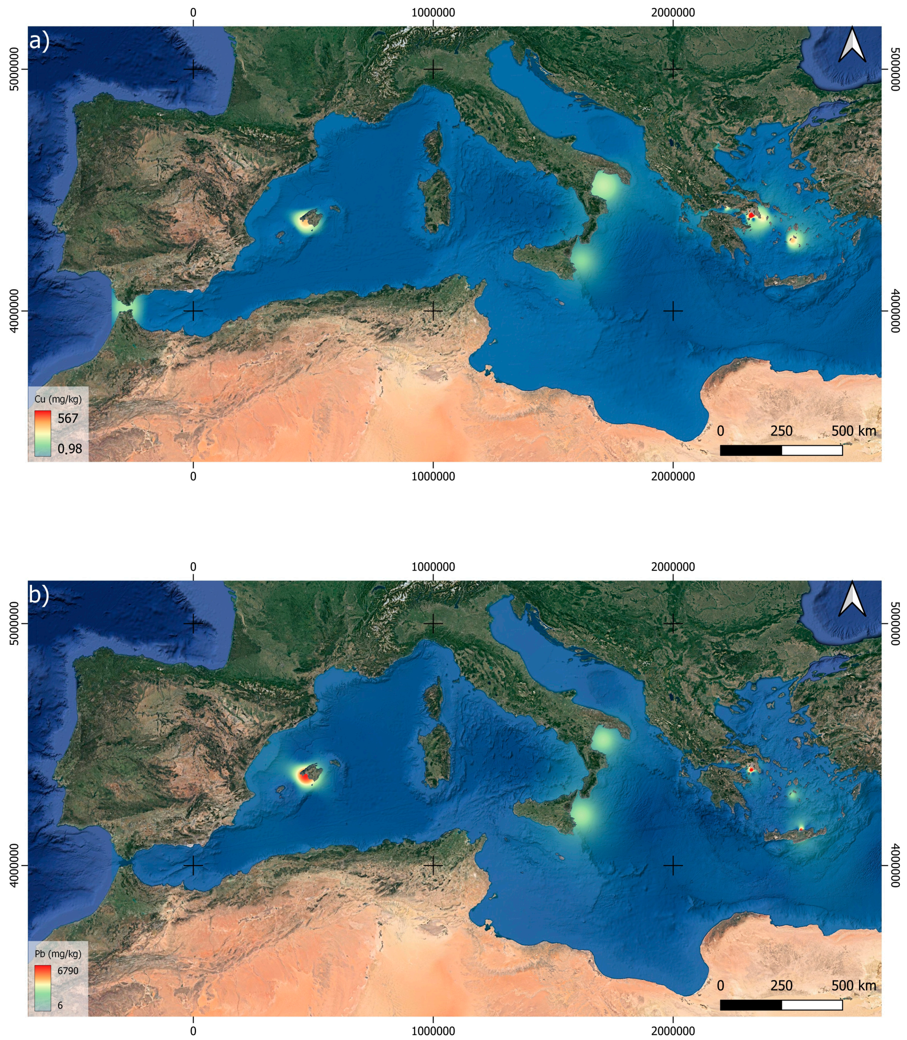


Figure 5. *Cont.*

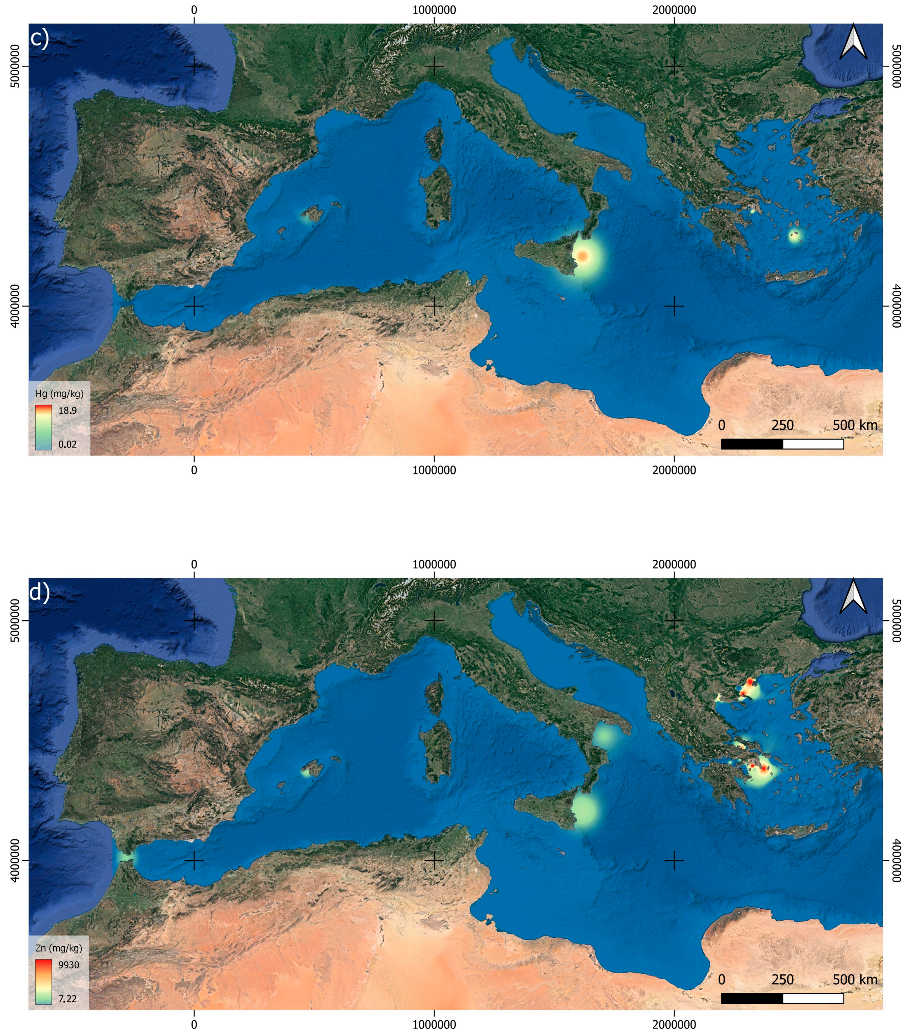


Figure 5. Maps of pattern of (**a**) Cu, (**b**) Pb, (**c**) Hg, and (**d**) Zn distribution in the Mediterranean according to the database of the analyzed regions.

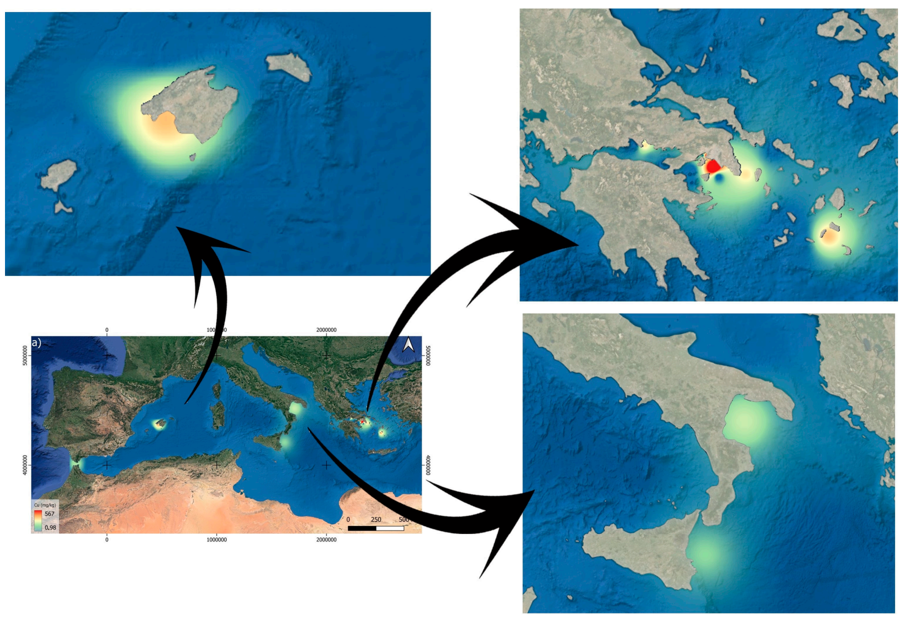


Figure 6. Example of Cu distribution in marine sediments from different study areas in the Mediterranean Sea. The enlarged images are aligned with the Figure 5a in the text.

4. Conclusions

In this study, the high concentration and great variety of heavy metals in the Mediterranean Sea has been confirmed, with its consequent environmental implications. The most abundant heavy metals in the studied areas are Cu, Hg, Pb, Zn, and Ni. The high concentrations of As, Cr, Cd, Ba, and V also stand out. However, the most relevant aspect is the relationship between the specific distribution and diversity of metals and metalloids and the distribution of wastewater discharges on the Mediterranean coast (very rich in these toxic elements). In this sense, only significant volumes of discharged and poorly treated wastewater could explain the data obtained. These volumes of wastewater must necessarily be associated with areas that have undergone very rapid urban development in the last decade and significant seasonal tourist pressure. All metals in some area exceed global and regional background levels. Although correlations were observed between the concentration of some metals (Cu or Pb, for example), the general pattern shows randomness between all metals and areas studied. This means that the seabed near the coast of urban areas acts as a potential sink for toxic substances that are subsequently released into the environment. Even considering that the Igeo index moderates the values obtained, it continues to demonstrate that the contamination of marine sediments is very high. Therefore, it can be seen how some heavy metals have given percentage results between classes 4 and 6 of the Igeo index. For example, Cd, Cu, or Hg in the SW of Spain. In the case of SE Spain, Hg and Cd, or in Southern Italy, Hg reaches class 6. Furthermore, although Greece presents more moderate values in class percentage, the amplitude range of concentrations is very high.

These results have allowed us to understand that the most important geochemical process is the chain chemical precipitation when wastewater meets seawater. The supersaturation of chemical elements in dilution causes them to precipitate on or between marine sediments. This fact allows the use of heavy metals in marine sediments as a reliable indicator of anthropogenic impact. Furthermore, the geochemical signature in marine areas that is highly pressured by anthropogenic activities tends to deviate extremely from natural background values. Therefore, there is a high possibility of risk to the environment, the ecosystem, and human health, which is already a fact in the deterioration of coastal–coastal habitats. Furthermore, the toxic elements analyzed could be incorporated into the food chain in these areas that are visited by more than 50 million people a year. In the context of acidification of the Mediterranean Sea and increases in average annual temperature, which is a consequence of climate change, marine health is in danger. Consequently, it is essential that administrations make decisions at a critical time for the health of the seas and that legislation specifically regulates the protection and conservation of these exceptional marine environments. It is important to note that the health of the seas is regulated by European directives and included in the 2030 agenda, adopted by the United Nations, as one of the Sustainable Development Goals (SDG, Goal 14-Target 14.1).

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app14041435/s1.

Author Contributions: P.A.R.A.: conceptualization, methodology, investigation, validation, writing—original draft preparation; R.Á.-A.: conceptualization, methodology, investigation, validation, writing—original draft preparation; F.Á.-C.: manuscript review, data analysis, methodology, discussion and significant conclusions from the data collected; J.J.D.V.: data analysis, methodology, discussion and significant conclusions from the data collected; R.M.G.: methodology and data processing; E.L.-C.: methodology and data processing; I.O.-V.: methodology and data processing; A.D.: manuscript review, data analysis, methodology, discussion and significant conclusions from the data collected. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Geological and Mining Institute of Spain (IGME-CSIC) from the project (23-PI89) "Research in technical projects". It was developed within the framework of the Spanish National Research Council (CSIC) and in collaboration to the Nature Protection Service, of the Guardia Civil (Police of Spain_Ref: 28745).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in the study are included in the article and Supplementary Material, further inquiries can be directed to the corresponding author. Data is available upon request from P.A. Robledo Ardila pa.robledo@igme.es.

Acknowledgments: We appreciate the help of the Territorial Unit of Geological Survey from Spain in Balearic Islands (IGME-CSIC). We also appreciate the work of the Spanish Institute of Oceanography (IEO)and the Coordinator of the Peripheral Administration of the State in the Balearic Islands. We would like to thank the research team of the Alcalá University (UH), Madrid for their support to this work.

Conflicts of Interest: The authors declare no conflicts of interest and the funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Rangel-Buitrago, N.; Rizzo, A.; Neal, W.J.; Mastronuzzi, G. Sediment pollution in coastal and marine environments. *Mar. Pollut. Bull.* **2023**, *192*, 115023. [CrossRef]
2. Robledo, P.A.; Álvarez, R.; Durán Valsero, J.J.; Árcega-Cabrera, F.; Lamas-Cosio, E.; Morales, R.; Durán, S. Assessment of heavy metal pollution in marine sediments from southwest of Mallorca Island, Spain. *Environ. Sci. Pollut. Res.* **2023**, *30*, 16852–16866. [CrossRef]
3. Murray, K.S. Statistical comparisons of heavy-metal concentrations in river sediments. *Environ. Geol.* **1996**, *27*, 54–58. [CrossRef]
4. Bastami, K.D.; Bagheri, H.; Kheirabadi, V.; Zaferani, G.G.; Teymori, M.B.; Hamzehpoor, A.; Soltani, F.; Haghparast, S.; Harami, S.R.M.; Ghorghani, N.F.; et al. Distribution and ecological risk assessment of heavy metals in surface sediments along southeast coast of the Caspian Sea. *Mar. Pollut. Bull.* **2014**, *81*, 262–267. [CrossRef]
5. Valdés, I.J.; Vargas, G.; Sifeddine, L.; Guiñez, M. Distribution and enrichment evaluation of heavy metals in Mejillones Bay (23°S), northern Chile: Geochemical and statistical approach. *Mar. Pollut. Bull.* **2005**, *50*, 1558–1568. [CrossRef] [PubMed]
6. Octavio-Aguilar, P.; Olmos-Palma, D. Efectos sobre la salud por agua contaminada con metales pesados. *Publicación Semest. Herreriana* **2022**, *4*, 43–47. [CrossRef]
7. Suresh, G.; Ramasamy, V.; Sundarrajan, M.; Paramasivam, K. Spatial and vertical distributions of heavy metals and their potential toxicity levels in various beach sediments from high-background-radiation area, Kerala, India. *Mar. Pollut. Bull.* **2014**, *91*, 389–400. [CrossRef] [PubMed]
8. Xu, F.; Qiu, L.; Cao, Y.; Huang, J.; Liu, Z.; Tian, X.; Li, A.; Yin, X. Trace metals in the surface sediments of the intertidal Jiaozhou Bay, China: Sources and contamination assessment. *Mar. Pollut. Bull.* **2016**, *104*, 371–378. [CrossRef] [PubMed]
9. Calmano, W.; Ahlf, W.; Förstner, U. Sediments and Toxic Substances Chp Sediment quality assessment: Chemical and biological approaches. In *Environmental Science*; Springer: Berlin/Heidelberg, Germany, 1996. [CrossRef]
10. Paneer, S.A.; Laxmi, P.S.; Kakolee, B.; Hariharan, G.; Purvaja, R.; Ramesh, R. Heavy metal assessment using geochemical and statistical tools in the surface sediments of Vembanad Lake, southwest coast of India. *Environ. Monit. Assess.* **2012**, *184*, 5899–5915. [CrossRef]
11. Perumal, K.; Antony, J.; Muthuramalingam, S. Heavy metal pollutants and their spatial distribution in surface sediments from Thondi coast, Palk Bay, South India. *Environ. Sci. Eur.* **2021**, *33*, 63. [CrossRef]
12. Luo, M.; Zhang, Y.; Li, H.; Hu, W.; Xiao, K.; Yu, S.; Zheng, C.; Wang, X. Pollution assessment and sources of dissolved heavy metals in coastal water of a highly urbanized coastal area: The role of groundwater discharge. *Sci. Total Environ.* **2022**, *807*, 151070. [CrossRef]
13. Sakan, S.; Devic, G.; Relic, D.; Andelkovic, I.; Sakan, N.; Dordevic, D. Evaluation of sediment contamination with heavy metals: The importance of determining appropriate background content and suitable element for normalization. *Environ. Geochem. Health* **2014**, *37*, 97–113. [CrossRef]
14. Moukhchan, F.; March, J.; Cerdà, V. Distribution of trace metals in marine sediments of the Bay of Palma de Mallorca (Mallorca Island, Spain). *Environ. Monit. Assess.* **2012**, *185*, 695–706. [CrossRef]
15. Rodríguez-Barroso, M.R.; García-Morales, J.L.; Coello, M.D.; Quiroga, J.M. An assessment of heavy metal contamination in surface sediment using statistical analysis. *Environ. Monit. Assess.* **2009**, *163*, 489–501. [CrossRef]
16. Ramachandra, T.V.; Sudarshan, P.B.; Mahesh, M.K.; Vinay, S. Spatial patterns of heavy metal accumulation in sediments and macrophytes of Bellandur wetland, Bangalore. *J. Environ. Manag.* **2018**, *206*, 1204–1210. [CrossRef]
17. Crain, C.M.; Halpern, B.S.; Beck, M.W.; Kappel, C.V. Understanding and managing human threats to the coastal marine environment. *Ann. N. Y. Acad. Sci.* **2009**, *1162*, 39–62. [CrossRef] [PubMed]
18. Violintzis, C.; Arditsoglou, A.; Voutsa, D. Elemental composition of suspended particulate matter and sediments in the coastal environment of Thermaikos Bay, Greece: Delineating the impact of inland waters and wastewaters. *J. Hazard. Mater.* **2009**, *166*, 1250–1260. [CrossRef] [PubMed]

19. Reynoldson, T. The role of environmental factors in the ecology of tubificid oligochaetes—An experimental study. *Ecography* **1987**, *10*, 241–248. [CrossRef]
20. Cabaço, S.; Machás, R.; Vieira, V.; Santos, R. Impacts of urban wastewater discharge on seagrass meadows (*Zostera noltii*). *Estuar. Coast. Shelf Sci.* **2008**, *78*, 1–13. [CrossRef]
21. Romano, E.; Bergamin, L.; Croudace, I.W.; Pierfranceschi, G.; Sesta, G.; Ausili, A. Measuring anthropogenic impacts on an industrialised coastal marine area using chemical and textural signatures in sediments: A case study of Augusta Harbour (Sicily, Italy). *Sci. Total Environ.* **2021**, *755*, 142683. [CrossRef] [PubMed]
22. Buccolieri, A.; Buccolieri, G.; Cardellicchio, N.; Dell'Atti, A.; Di Leo, A.; Maci, A. Heavy metals in marine sediments of Taranto Gulf (Ionian Sea, Southern Italy). *Mar. Chem.* **2006**, *99*, 227–235. [CrossRef]
23. Bhuiyan, M.K.A.; Qureshi, S.; Billah, M.M.; Kammella, S.V.; Alam, M.R.; Ray, S.; Monwar, M.M.; Kamal, A.H.M. Distribution of Trace Metals in Channel Sediment: A Case Study in South Atlantic Coast of Spain. *Water Air Soil Pollut.* **2017**, *229*, 14. Available online: https://link.springer.com/article/10.1007/s11270-017-3653-5 (accessed on 1 March 2023). [CrossRef]
24. Kanellopoulos, T.D.; Kapetanaki, N.; Karaouzas, I.; Botsou, F.; Mentzafou, A.; Kaberi, H.; Kapsimalis, V.; Karageorgis, A.P. Trace element contamination status of surface marine sediments of Greece: An assessment based on two decades (2001–2021) of data. *Environ. Sci. Pollut. Res. Int.* **2022**, *29*, 45171–45189. [CrossRef] [PubMed]
25. Tunca, E.; Aydın, M.; Şahin, Ü.A. An ecological risk investigation of marine sediment from the northern Mediterranean coasts (Aegean Sea) using multiple methods of pollution determination. *Environ. Sci. Pollut. Res. Int.* **2018**, *25*, 7487–7503. [CrossRef] [PubMed]
26. Kwok, K.W.H.; Batley, G.E.; Wenning, R.J.; Zhu, L.; Vangheluwe, M.; Lee, S. Sediment quality guidelines: Challenges and opportunities for improving sediment management. *Environ. Sci. Pollut. Res. Int.* **2014**, *21*, 17–27. [CrossRef] [PubMed]
27. Radomirović, M.; Tanaskovski, B.; Pezo, L.; Ceccotto, F.; Cantaluppi, C.; Onjia, A.; Stanković, S. Spatial and temporal distribution of pollution indices in marine surface sediments—A chemometric approach. *Environ. Sci. Pollut. Res.* **2021**, *28*, 42496–42515. [CrossRef]
28. Sanz-Prada, L.; Garcia-Ordiales, E.; Flor-Blanco, G.; Roqueñí, N.; Álvarez, R. Determination of heavy metal baseline levels and threshold values on marine sediments in the Bay of Biscay. *J. Environ. Manag.* **2022**, *303*, 114250. [CrossRef] [PubMed]
29. Acosta, J.A.; Faz, A.; Martínez-Martínez, S.; Arocena, J.M. Enrichment of metals in soils subjected to different land uses in a typical Mediterranean environment (Murcia City, southeast Spain). *Appl. Geochem.* **2011**, *26*, 405–414. [CrossRef]
30. Christophoridis, C.; Dedepsidis, D.; Fytianos, K. Occurrence distribution of selected heavy metals in the surface sediments of Thermaikos Gulf, N. Greece. Assessment using pollution indicators. *J. Hazard. Mater.* **2009**, *168*, 1082–1091. [CrossRef]
31. Shin, P.K.; Lam, W.K. Development of a marine sediment pollution index. *Environ. Pollut.* **2001**, *113*, 281–291. [CrossRef]
32. Muller, G. Index of geoaccumulation in sediments of the Rhine River. *GeoJournal* **1969**, *2*, 108–118.
33. Wedepohl, K.H. The composition of the continental crust. *Geochem. Cosmochim. Acta* **1995**, *59*, 1217–1232. [CrossRef]
34. Birch, G.F. Determination of sediment metal background concentrations and enrichment in marine environments—A critical review. *Sci. Total Environ.* **2017**, *580*, 813–831. [CrossRef]
35. Oncina, J. Algoritmos de Búsqueda de Vecinos Más Próximos en Espacios Métricos. Ph.D. Thesis, Universidad Politécnica de Valencia, Valencia, Spain, 1996.
36. EPA. *An Overview of Sediment Quality in the United States*; Environmental Protection Agency: Washington, DC, USA, 1987.
37. Buchman, M.F. NOAA Screening Quick Reference Tables (SQuiRTs). National Oceanic and Atmospheric Administration 08-1. 1999. Available online: https://repository.library.noaa.gov/view/noaa/9327 (accessed on 1 January 2023).
38. Pekey, H. Heavy Metal Pollution Assessment in Sediments of the Izmit Bay, Turkey. *Environ. Monit. Assess.* **2006**, *123*, 219–231. [CrossRef] [PubMed]