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REVIEW ARTICLE

Pollution status and risk assessment of trace elements in Portuguese water, soils, sediments, and associated biota: a trend analysis from the 80s to 2021

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Abstract

Pollution of water bodies and sediments/soils by trace elements remains a global threat and a serious environmental hazard to biodiversity and human's health. Globalization and industrialization resulted in the increase and availability of these substances in the environment posing unpredictable adverse effects to living organisms. To determine pollution status and risk contamination by trace elements, data available in the literature of the last 40 years on trace elements occurrence in three environmental matrices (water bodies, sediments/soils, and biota) from Continental Portugal were collected (about 90 studies). Data were compared to water and sediment quality guidelines to assess potential ecological risks. Most environmentally relevant hazardous elements include Zn, Cu, Cd, Pb, and As. Various studies found trace elements at levels higher than those considered safe by environmental guidelines. In surface waters, Al, Zn, Se, and Ag were found above aquatic life limits in about 60% of the reviewed papers, while Cu, Zn, and As exceed those values in more than 60% of mining waters. Hg and Cd in sediments from mining areas exceeded aquatic life limits and potential ecological risk showed extremely high risk for most of the elements. The data compiled in this review is very heterogenous, varying in terms of sampling schemes, trace elements analysed, and spatiotemporal settings. This heterogenicity leads to data differences that make meaningful comparisons difficult. Nevertheless, the compilation of scattered environmental spatial and temporal trace elements data, of either natural sources or human activity as well as the ultimate effect on biological systems, is of the upmost importance to broaden its knowledge, risk assessment, and implementation of mitigation measures.

Keywords Trace elements · Risk assessment · Toxicity · Environment · Sediments · Biota

Introduction

Environmental pollution is among the main challenges of today's society and is a major source of living organism's health problems (Guerranti et al. 2019, Mandal and Kaur, 2019, Samoli et al. 2019, Taati et al. 2020, Wang and Zhou, 2021). All environmental compartments are affected by environmental pollutants though aquatic environments are perhaps the most impacted ecosystems as they are frequently the ultimate reservoir for many contaminants (Acosta-Coley et al. 2019, Ferreira da Silva et al. 2020, Liu et al. 2020). Among environmental contaminants, trace elements gained special visibility due to excessive concentrations, non/low-degradability, persistence, bio/ accumulative nature, and harmful effects on living organisms (Acosta-Coley et al. 2019, Ferreira da Silva et al. 2020, Fuentes et al. 2020, Li et al. 2018, Liu et al. 2020, Taati et al. 2020). Trace elements include naturally occurring elements present throughout

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the earth's crust and those originated from anthropogenic activities such as the industry (e.g., refineries, coal burning, petroleum combustion, nuclear power stations among others), agriculture, pharmaceutical, domestic effluents, and atmospheric sources and transport systems (e.g., wind, rain) (Fig. 1) (Fuentes et al. 2020, Liu et al. 2020, Mandal and Kaur, 2019). Most living organisms' exposure results from human activities that lead to undesirable environmental contamination. However, exposure can also be a result of natural processes such as metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals, sediment re-suspension, and metal evaporation from water resources to soil and ground water (Fig. 1) (Moiseenko et al. 2019, Zhang et al. 2014).

The presence of trace elements in the aquatic ecosystems is widely reported and both abiotic and biotic processes affect their distribution and circulation (Chon et al. 2012, Moiseenko et al. 2019, Zhang et al. 2014). Sediments play an important role in trace elements cycling (Chon et al. 2012, Martins et al. 2013). In fact, sediments can behave as both reservoir and non-point source of trace elements in the water column contributing to their persistence and recalcitrance in the aquatic environment (Chon et al. 2012, Ribeiro et al. 2018). Exposed organisms may absorb dissolved elements from surrounding water and food, and/or accumulate in various tissues in significant amounts causing harmful effects or entering the food web (Fuentes et al. 2020, Li et al. 2018). Trace element bioavailability is influenced by physical and chemical factors (e.g., temperature, phase association, adsorption, speciation at thermodynamic equilibrium, complexation kinetics, and solubility), climatic factors, and biogeochemical cycling. Therefore, an accurate ecological status of the aquatic environment should evaluate the occurrence and distribution of trace elements in different compartments such as water, sediments, and biota to have integrative data on the system.

Portugal is located along the Atlantic coast in southwestern Europe. It has more than 10 million inhabitants, and most of the Portuguese population is fixed in the coastal areas, where most industrial, agricultural, and port activities are implemented. As a result, estuaries, rivers, and coastal areas are impacted by intensive anthropogenic activities that result in the release of diverse pollutants including trace elements in these compartments. Several works stressed the ecological status regarding the occurrence of trace elements in coastal waters and estuaries, mainly Douro, Mondego, Tagus, and Sado (Alves et al. 2009, Antunes et al. 2018a, Couto et al. 2019, França et al. 2005, Ribeiro et al. 2018). Besides, mining is a relevant economic activity in Portugal; however, mining activities are responsible for trace elements pollution of the surrounding environment. In fact, several works reported the occurrence of high levels of trace elements nearby mining areas in compartments such as water, sediments, and soils and even biota (Carvalho et al. 2011, Favas et al. 2016, Ferreira da Silva et al. 2009). Therefore, trace element contamination emerged as an issue of major concern due to their high levels and consequently threat to biodiversity and humans. This review intends to (a) summarize the occurrence of trace elements in water, sediments, and aquatic biota in Portugal, (b) current gaps, (c) to assess potential risk by identifying the contaminants that represent a high concern due to their concentration and/or

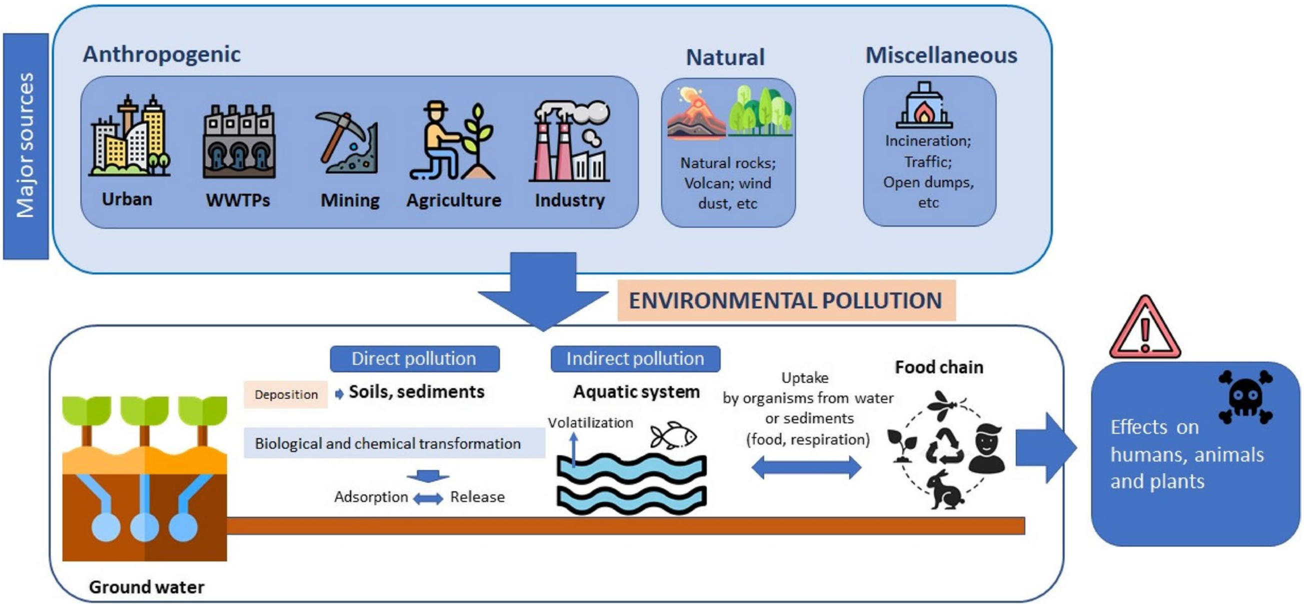


Fig. 1 Major sources of trace elements in the environment

toxicological effects, and (d) propose solutions for environmental risk management. This manuscript provides the current state of the art regarding trace elements pollution status in Portugal. Compliance with these data is important not only for researchers, local regulatory authorities, and environmental protection measures (regional, national and global) but also contributes to the global worldwide knowledge about trace elements crucial to strengthen international cooperation, to assure a more sustainable global development and support scientific policymaking.

Data collection and characterization of the study area

This search was based on ScienceDirect and ISI web of Knowledge databases considering articles published between the 1980s and 2021 that comprise waters, sediments/soil, and biota.

The area focused on this review is mainland Portugal (geographic coordinates 42°9′8" and 36°57′39"N and 6°11′10" and 9"29′45"W) corresponding to less than 1/6 of the Iberian Peninsula.

Mainland Portugal has a coast of nearly 832-km, mostly low, level, and straight, apart from several harbors located in river indentations. The northern coast is characterized by rocky bays or rias, and the southern one is rich in lagoons and sandbanks. The Portuguese Instituto Nacional de Estatística (Europa, 1985) reports 92 000 ha of rivers, streams, estuaries and bays in the territory. The Portuguese average annual runoff from rainfall is 20 000 million m^3. More 17 000 million m^3 are obtained from rivers whose springs are located in Spanish territory, causing a total annual river discharge of 37 000 million m^3 leaving the country. The entire drainage is the Atlantic Ocean, to which all the most important rivers flow in a predominantly east-west direction. There are 11 independent river systems in Portugal with the length of the main river within the country exceeding 60 km (Table 1, Fig. 2).

Ecological risk assessment

To assess ecological risk, both water and sediments reported maximum values were compared to Freshwater long-term Water Quality Guidelines for the Protection of Aquatic Life (CCME 2017) and Sediment Quality Guidelines for the Protection of Aquatic Life (CCME 2015), respectively. Furthermore, the environmental risks of trace elements in sediments were assessed by the determination of the potential ecological risk index. This index was proposed by Hakanson (1980) and indicates the degree of biological risk and can be calculated as follows: (Devanesan et al. 2017, Hakanson 1980, He et al. 2021)

$$E_r^i = \left(T_r^i\, x\, C^i\right)/C_n^i$$

where E_r^i is the potential ecological risk index of single trace element *i* in sediment samples. T_r^i is the toxicity response factor for a trace element *i*: As, Cd, Cr, Cu, Ni, Pb, Zn, and Hg are 10, 30, 2, 5, 2, 5, 1, and 40, respectively (Hakanson, 1980). C^i is the measured concentration of trace element *i* and C_n^i is the reference value of trace element *i* collected from the natural geochemical background (Ribeiro et al. 2018). Average concentrations for 90 naturally occurring elements in the Earth's crust can be found in the literature (Wedepohl 1995). The terminologies used to describe the potential ecological risk are low risk ($E_r^i \le 40$), moderate risk ($40 < E_r^i \le 80$), high risk ($80 < E_r^i \le 160$), very high risk ($160 < E_r^i \le 320$), or extremely high risk ($E_r^i > 320$).

Table 1 Hydrologic data of the principal rivers of Portugal (adapted of http://www.fao.org/3/T0798E08.htm)

River	Length (km)	Basin area (km^2)	Mean annual flow (m^3/s)	Principal tributaries
Minho	75	792	363	Coura, Mouro
Lima	65	1145	74	Laboreiro, Vez
Cávado	118	1648	94	Homem, Rabagão
Ave	85	1395	48	Este, Vizela
Douro	322	18559	527	Sabor, Tua, Corgo, Tâmega, Águeda, Coa, Tavora, Paiva
Vouga	136	3656	67	Sul, Caima, Ul, Águeda
Mondego	220	6772	117	Dão, Alva, Ceira, Arunca
Tagus	275	24913	453	Erges, Ponsul, Ocreza, Zêzere, Sever, Sorraia, Almansor
Sado	175	7628	27	Xarrama, Alcaçova, Marateca, Arcão, Avalão
Mira	130	1781	9	Torto
Guadiana	260	11541	185	Caia, Degebe, Cobro, Odeleite, Vascão

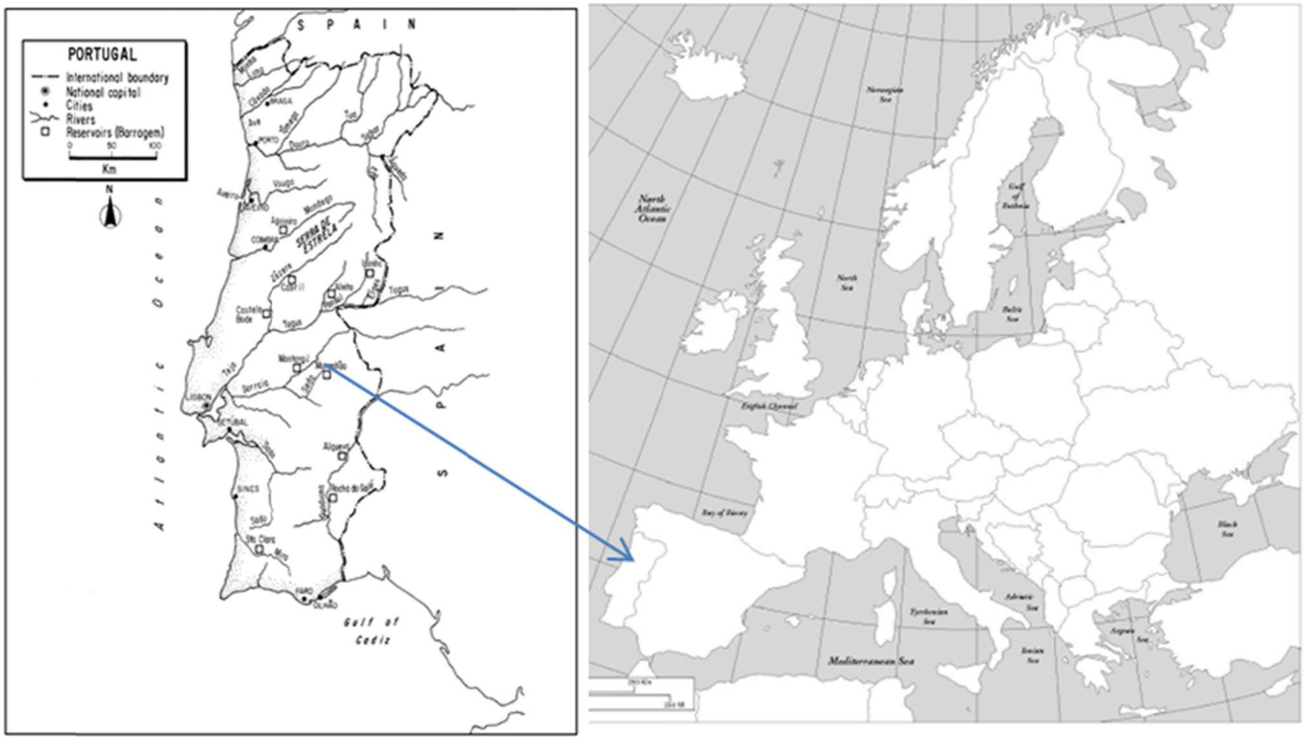


Fig. 2 Map of the main Portuguese rivers (adapted from FAO, available at http://www.fao.org/3/T0798E08.htm)

Occurrence of trace elements in water bodies, sediments/soils, and biota of Portugal

Water bodies

Trace elements occurrence in water bodies was reported in estuaries and coastal areas, lagoons, rivers, and streams and also water bodies near mining areas (streams, rivers, ground water, and irrigation waters) (Table 2). Various trace elements have been examined, though Zn, Cu, Pb, and Cd are among the most investigated (Table 2). Both Douro River and estuary are among the most studied ecosystems and various studies were conducted in order to determine a wide panel of trace elements (Li, Be, Al, V, Cr, Co, Ni, Cu, Zn, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb, and U) in surface estuarine waters in Douro estuary (Couto et al. 2014, Ribeiro et al. 2018). In the work developed by Couto and co-workers, estuarine waters were collected in 11 sampling sites in four sampling campaigns in 2007/2008. Results showed sporadic high levels for most trace elements, suggesting punctual and local sources. Significant spatial differences were also found. Most of the elements tended to increase in the inner stations to the mouth of the river. Indeed, some trace elements associated with agriculture procedures (Zn, Cu, and Ni) were higher in the middle part of the estuary, suggesting a possible common source. A comprehensive study considering different matrices such as water, sediments, and biota was also done in 2013 in the Douro River estuary. In that study, the overall concentrations were sorted as follows: Al > Zn > Li > Se > Ba > V > Cu > Mo > Pb > Ni > U > Cr > Sb > Ag > Co > Cd > Tl ~ Be. Water mean Al, Cr, Cu, Zn, Se, Ag, and Pb concentrations were above acceptable values for aquatic organisms (Ribeiro et al. 2018). A similar study was performed in Ave estuary where the trend Al > Zn > Se > Mo > Li > Ba > V > Cu > Pb > Ni > Cr > U > Be > Co ≈ Sb > Ag ≈ Cd > Tl was found (Couto et al. 2019). Al, Zn, Se, Cu, Ag, Pb, and Cd mean values were also found above aquatic life limits.

The occurrence of mercury (Hg) has also been investigated in Portuguese waters, and various works reported Hg analysis (Iglesias et al. 2020, Lillebø 2011, Ramalhosa et al. 2006). The presence of this element has been investigated in Douro River estuary, Oporto coastal area, Ria de Aveiro, Sado River estuary, and Caveira stream water with values up to 0.08 $\mu g\ L^{-1}$. In most of the published studies, Hg levels were not of environmental concern.

In a country frequently devastated by summer fires, a recent paper correlated the forest fires of October 2017 with changes in the water's chemical watercourses in the Mondego hydrological basin (showing increases in Al, Fe, Mn, As, Ba, and Zn concentrations) and biological constituents, after the beginning of rainfall due to sediments, ashes,

Table 2 Occurrence of trace elements in water bodies from Portugal based on the reported literature

Area	Source/sample collection	Trace element	Levels (μg L^{-1}) max	Main results/risk assessment	Ref
Ave river estuary	Estuarine water	Li, Be, Al, V, Cr, Co, Ni, Cu, Zn, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb, U	Al (**2384**) Zn (**55.3**) Se (**34.6**) Cu (**24.7**) Pb (**12.7**) Ag (**0.75**) Cd (**0.66**)	Al, Zn, Se, Cu, Ag, Pb, and Cd, above ALL.	(Couto et al. 2019)
Douro river	River water (dams Miranda do Douro/Régua) 17months (Jan/85-May/86)	Sr	550	Strong seasonal Sr variation in water and food chain.	(Carraça et al. 1990)
Douro river estuary	Estuarine water October 2007; January, March and July 2008	Be, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb, U	Cr(VI) (**9.0**) Se (**103**) Al (**201.1**) Zn (**39.2**) As (**25.7**) Tl (**1.23**)	Mean values in accordance to ALL (except Cr, Se) occasional high levels, reflecting occasional/local inputs. ALL exceeded for Al, Cr, Zn, As, Se and Tl.	(Couto et al. 2014)
Douro river estuary	Estuarine water May 2013	Li, Be, Al, V, Cr, Co, Ni, Cu, Zn, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb, U	Li (28.4) Be (80.1) Al (**323**) V (17) Cr (**2.1**) Co (0.7) Ni (5.9) Cu (**16**) Zn (**245**) Se (**28**) Mo (15) Ag (**0.8**) Cd (**0.1**) Sb (1.98) Ba (19) Tl (0.06) Pb (**7.3**) U (2.1)	Al, Pb, and Cu higher than acceptable, potential negative impact on living organisms.	(Ribeiro et al. 2018)
Douro river estuary	Estuarine water Campaigns from 2013-2018	Zn, Cu, Pb, Ni, Cd and Hg	n.r.	Trace elements levels below ERL and DL506/1999 and DL103/2010.	(Iglesias et al. 2020)
Oporto coast	Sea water 1994-1995	Dissolved Cd, Cu, Hg and Pb	n.r.	Mean seawater concentrations similar to polluted and industrialized European coastal areas.	(Leal et al. 1997)
Esmoriz/Paramos	Lagoon water Nov 2003 and Sep 2004	Cr, Cu, Pb and Zn	Zn (**264**) Cu (**12**) Pb (**18**) Cr nd	Trace elements equalled or exceeded limit of chronic reference values.	(Fernandes et al. 2008)
Largo Laranjo bay, Ria Aveiro	Surface water from 1997 to 2000	Hg	0.002 – 0.0074	Possible Hg source to other areas of Ria de Aveiro.	(Ramalhosa et al. 2006)
Mondego, Alva, and Ceira,Cavalos, Cerdeira, Covelo, Pomares)	Surface water October 2017-June 2018	Al, Fe, Mn, As, Ba and Zn	n.r.	Background values exceeded for Al and As in basins with extensive agricultural areas. Burnt plant material and organic matter account for increases in Al, As, Fe, and Mn content after wildfires.	(Sequeira et al. 2020a)
Sado river estuary	Estuarine water May 2006	Hg	< **0.080**	Not under environmental risk concerning Hg.	(Lillebø 2011)
Mining areas					
Murçós (Macedo, Bragança)	Surface water 2005 2008 and 2009	W, Bi, As, Al, U, Cd, Sn, Ag, Cu, Sb, Pb, Mn, Ni, Be, Zn	n.r.	Surface waters contaminated with F^{-}, Al, As, Mn and Ni and not to be used for human consumption.	(Antunes et al. 2016)

Table 2 (continued)

Area	Source/sample collection	Trace element	Levels (µg L^{-1}) max	Main results/risk assessment	Ref
Horta Vilariça, (Moncorvo, Bragança)	Ground water Year n.r.	U, As, Cu, Zn, Cr, Mn	U (**0**.61–5.56); mean values As (**4.8**) Cu (1.49) Zn (**17.2**) Cr (0.19) Mn (30.9)	U concentrations in stream water toxic to aquatic plants and invertebrates in one sampling point (n=15).	(Cordeiro et al. 2016)
Terramonte mine (Douro)	Surface water Sep 2007 and Jan, May, Aug 2008	Al, As, Co, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Zn	n.r.	Castanheira stream water not suitable for human consumption, high SO_4^{2-}, Mn, Al, Cd, Ni, and Pb.	(Carvalho et al. 2014)
Cunha Baixa, (Mangualde, Viseu)	Lagoon water Spring and autumn Year n.r.	Mn, Fe, Al, U, Sr, Zn, Cd, Be, Cu, Co, Ni, B, As, Sc, Ba, Pb	Zn (**680**) Cd (**9**) Be (43) Al (**9070**) Mn (11865) Cu (**44**) Sr (498) Co (117) U (**1842**)	High contents of Mn, Fe, Al, U, Sr. Water heavy metal (and low pH) likely to cause toxicity, sediments contaminants unavailable to the biota.	(Antunes et al. 2007)
Cunha Baixa, (Viseu)	Groundwater and private wells 1995 to 2004	F, Ca, Mg, Al, Mn, Ni, U, Zn, Ra	n.r.	High values of F, Ca, Mg, Al, Mn, Ni, U, Zn, and Ra. Health hazard due to Al, Mn, and U bioaccumulation.	(Neves and Matias, 2008)
Sevilha Mine (Coimbra)	Streams and pond water June (year n.r.)	U, Zn, Cu, Pb, Cd, Bi, Cr, Ni, As	U (**113**) Zn (**296**) Cu (**20.6**) Pb (**7**) Cd (**5.3**) Bi (13.6) Co (4.8) Cr (**29.7**) Ni (**77.4**) As (**7.5**)	U concentration 4 folds higher than guideline value for drinking water (WHO, 2011). U surface waters above threshold values to aquatic plants and invertebrates.	(Favas et al. 2016)
Alto Várzea	Water inside the mine influence area 2008 and 2009	As, Co, Cr, Sr, Th, U, W, Zn, Cu, Pb, U, Mn, Al, Li, Ni, Cd, Ba, B	Cu (**77.2**) Cr (**8.2**) Pb (**50.7**) As (**32.8**) Th (4.9) U (**57.7**)	Mn, Cu, As, Pb, and U contamination. Hazard to human consumption and agricultural.	(Antunes et al. 2018b)
S. Francisco Assis – Panasqueira	Irrigation waters Year n.r.	As, Cd, Pb	As (**7.8**) Cd (**0.36**) Pb (**23.1**)	Potential health risks through the intake of As, Cd, and Pb by food chain.	(Candeias et al. 2014)
Segura-Castelo Branco	Superficial and sub superficial waters October and December 2006	As	As (**1.190)**	High probability of water contamination. Not to be used for human consumption.	(Antunes and Albuquerque, 2013)
Miguel Vacas Alentejo	Stream water October 1998-March 2000	Cu, Zn	Cu (**1480**) Zn (**385**)	Groundwater can be used for irrigation and cattle.	(Abreu et al. 2008)

Table 2 (continued)

Area	Source/sample collection	Trace element	Levels (μg L^{-1}) max	Main results/risk assessment	Ref
Caveira - Grândola Stream	Surface water three seasonal periods Year n.r.	Al, As, Ca, Cd, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Zn	n.r.	Exceeding local and/or surface water quality standards; As, Cd, Cu, Pb, and Zn sources of potential chronic stream toxicity.	(Ferreira da Silva et al. 2015)
Corona and Lousal stream, Sado River	Drainage waters September 2000	Fe, Al, Cu, Pb, Zn, Cd, As	n.r.	Acid effluents, Fe, Al, Cu, Pb, Zn, Cd, and As exceeding ALL.	(Silva et al. 2005)

ERL, effect low range; *n.d.*, not detected; *n.r.*, not referred; *ALL*, aquatic life limit freshwater

Boldface values refer to values that exceed CCME guidelines for aquatic life limit fresh water (ALL) (CCME 2019)

debris and products of combustion runoff (Sequeira et al. 2020a, Sequeira et al. 2020b).

The presence of trace elements in water bodies has also been investigated in mining areas (Table 2). For instance, both surface and/or groundwater contamination has been observed in the vicinity of many post-mining areas, namely with an increase of As, Cd, Cu, Pb, and Zn resulting from 129 years of pyrite and Cu exploitation, spread along the Grândola stream (Ferreira da Silva et al. 2015). U mining pose, particular challenges for remediation and future land use. There are two studies in U mining areas, one in Mangualde, extensively explored until 1993, with high production of poor ore, where toxic levels of Mn, Fe, Al, U, and Sr were found. The other was in Horta da Vilariça, with U concentrations in stream water toxic to aquatic plants and invertebrates in one sampling point of the 15 sampling points selected (Antunes et al. 2007, Cordeiro et al. 2016). One study states the risk of inhabitants of a nearby village (S. Francisco de Assis) located downstream the Barroca Grande tailings deposit and impoundments, probably exposed to some potential health risks through the intake of As, Cd, and also Pb via vegetable consumption, even though waters had low metal concentrations. Zn and Mn were present in significant concentrations though below the standard parametric values. The concentrations of other elements were all legally acceptable, with values up to 7.8 μg L^{-1} for As; 0.36 μg L^{-1} for Cd, and 23.1 μg L^{-1} for Pb (Candeias et al. 2014).

Remediation processes, applied in the period of 2005–2008, using confination, tailings and debris control, and phytoremediation of the Murçós complex, contributed to a soil and water decrease of metals and arsenic; nevertheless, these procedures were not sufficient to assure a rehabilitation of the area (Antunes et al. 2016). In fact, mining activities have a considerable effect in the vicinity of the mine during its exploration. The mining places that have been abandoned or improperly closed may however continue to provoke damages to soils, water courses, and even the atmosphere. Post-mining regions represent, therefore, an important environmental issue. This topic has been a European problem of political debate and scientific concern for some 50 years (Keenan and Holcombe, 2021, Wirth et al. 2012).

Sediments and soils

Sediments are among the most studied matrices concerning the presence of trace elements and their occurrence was reported in estuaries, rivers, lagoons, and streams (Table 3). Different sediment sampling strategies (location, depth, grain size/fraction, etc.) and sediment digestion procedures (different mixtures of acids (HF, HCl, HNO_3), microwave vs conventional digestion, etc.) make inter-studies comparison of the published papers impossible. This section highlights

Table 3 Occurrence of trace elements in sediments from Portugal based on the reported literature

Area	Source/sample collection	Trace element	Levels ($\mu g\ g^{-1}$)	Main results/risk assessment	Ref
Minho	Salt marsh sediments September 2005	Al, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Al (2.3) Cr (20) Cu (22) Mn(198) Ni (22) Pb (15) Zn (92)	Probably a pristine metal area and useful as a reference for other metal-contaminated estuaries/salt marshes.	(Reis et al. 2008)
Minho	Estuarine sediments August 2009	As, Cr, Cu, Li, Pb, Sn, Zn, Hg	As (**80**) Cr (70) Cu (30) Pb (18) Sn(7) Zn (**150**) Hg (0.06)	Low metal enrichment.	(Mil-Homens et al. 2012)
Minho	Surface sediments August 2009	As, Cr, Cu, Hg, Li, Pb, Rb, tin Sn, Zn; Hg	As (**69**) Pb (18) Cu (27) Cr (**65**) Sn (6.8) Zn (**131**) Hg (0.051)	Urban and industrial contamination. Sn–W mineralizations associated with nautical sources.	(Mil-Homens et al. 2013)
Minho, Lima, Neiva, Cávado, Ave, Leça, Douro, Ria Aveiro, Mondego, Lis, Tagus, Sado, Mira, Arade, Guadiana	Estuarine sediments 2009–2010	As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn	n.r.	Anthropogenic effects identified in Ave, Leça, Tagus and Sado.	(Mil-Homens et al. 2014)
Cávado river basin	Surface river sediments 1988 and 1989	Cd, Cr, Cu, Ni, Pb, Zn	Cd (**32**) Cr (**2210**) Cu (**9440**) Ni (480) Pb (**3100**) Zn (**2700**)	Correlations -Zn/Cr, Cr/Ni and Zn/Ni – with different origins; Seasonal variations.	(Gonçalves et al. 1994)
Cávado Estuary	Estuary sediments Year n.r.	Al, As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sn, V, Zn	(mean) Al (7400) As (**6.1**) Cd (0.13) Co (3.95) Cr (20.2) Cu (**54.9**) Mn (75) Ni (9.4) Pb (30.3) Sn (2.9) V (12.8) Zn (94)	Moderate Cr and Ni enrichment. Several hotspots, no toxicological threat to living organisms.	(Gredilla et al. 2015)
Ave Basin (Ave, Selho, Pelhe, Este, Vizela)	River sediments 1986	Cd, Cr, Cu, Pb, Zn	(max) Cd (**5.8**) Cr (**1187**) Cu (**1904**) Pb (**568**) Zn (**2702**)	Leather tanning, metal plating and textile industries main sources of toxic metal contamination in these streams. Highest concentrations of all metals in the tributaries.	(Gonçalves et al. 1992)
Ave	Sediments December 1999 September 2001	Cr, Cu, Fe, Mn, Pb, Zn	n.r.	Lower Cr contamination to previous studies; moderate Cr contamination. Slight Zn pollution.	(Alves et al. 2009)
Ave	Estuarine sediments Spring, summer, autumn and winter 2013	Li, Be, Al, V, Cr, Co, Ni, Cu, Zn, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb, U	(mean) Li (57) Be (1.6) Cr (22) Co (4.6) Al (14,600) Zn (**160**) Se (0.65) Cu (29) Pb (25) Ag (0.13) Cd (0.35) U (4.2)	Igeo showed strong contamination by anthropogenic activities for Al, Mn, Ba, and Zn. EF showed high enrichment of Se, Cd, Zn, Li, Cu, Ag, Pb, and U.	(Couto et al. 2019)

Table 3 (continued)

Area	Source/sample collection	Trace element	Levels (μg g^{-1})	Main results/risk assessment	Ref
Mouths of the Ave, Douro, Lis, and Mira	Estuarine sediment May 2002	Cu, Pb, Zn, Fe, Mn	n.r.	Ave-Douro and Lis non-polluted or trace contamination. Metal enrichments in Mira area associated with drainage of mineralised areas rich in Cu, Pb, Zn, Fe, and Mn.	(Mil-Homens et al. 2006)
Transboundary Douro basin	Stream sediment 2004	As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	As (**146**) Cd (**8**) Co (22) Cr (**60**) Cu (**99**) Ni (37) Pb (**154**) Zn (**448**) Mn (5020)	Cu, Zn, and Pb higher concentrations in the most labile fractions, important anthropogenic sources. Cr and Ni lithological source.	(Reis et al. 2014)
Douro estuary	Estuarine sediments November 1998	Al, Fe, Cu, Pb, Cr, Ni, Cd, Zn, Mn	n.r.	Anthropogenic metal contamination at the north bank of the Douro estuary: deleterious effects on the macrobenthic community.	(Mucha et al. 2004a)
Douro	Sediment and rhizosediments February, May, August, and November 2004	Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	n.r.	Clear signature of anthropogenic trace metal sediment contamination (Zn, Cu, Pb, Cr, Cd, and Ni). Consequences for estuarine communities and salt marsh vegetation.	(Almeida et al. 2006)
Douro	Estuarine sediments May 1998	Zn, Cu, Pb, Cr, Ni, Cd	n.r.	Anthropogenic contamination in the north (Zn, Cu, Pb, Cr, and Ni) bank, and in the south bank (Zn, Pb, and Cd).	(Almeida et al. 2006)
Douro	Sediments May 2013	Li, Be, Al, V, Cr, Co, Ni, Cu, Zn, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb, U	Al (13,390) Zn (**164.3**) Pb (**338.4**)	Al was the trace element found at highest concentration in both sediments and water followed by Zn. Pb, Cu and Zn levels in sediments were critical in comparison to the established probable effect levels.	(Ribeiro et al. 2018)
Douro	Sediments 2014	Zn, Cu, Pb, Ni, Cd, Hg	Zn (108) Cu (22) Pb (6) Ni (14) Cd (0.3) Hg (**0.3**)	Potential biota accumulation in, consequences for the entire trophic.	(Iglesias et al. 2020)
Esmoriz–Paramos lagoon	Sediment Nov2003 and Sep2004	Cr, Cu, Pb, Zn	Zn (**545**) Cu (**232**) Pb (**299**) Cr (**255**)	High trace metal sediments and probable main source of bioaccumulation in fish tissues.	(Fernandes et al. 2008)

Table 3 (continued)

Area	Source/sample collection	Trace element	Levels (µg g^{-1})	Main results/risk assessment	Ref
Estarreja	Sediments September/November 1998	As, Hg, Pb, Zn	n.r.	High metal concentration in industrial area soil. Much higher concentrations on the water streams several Km away from the industrial complex.	(Costa and Jesus-Rydin, 2001)
Aveiro Lagoon	Sediment samples Summer 2010 February 2012 August 2012	Ca, Al, Mn, Fe, Co, Li, Cu, Cd, Zn, Ni, Pb, Ba, V, Cr	n.r.	As, Cu, Zn and Pb influenced by geochemical and geographical distance, the latter representing anthropogenic influence.	(Stoichev et al. 2020)
Ria Aveiro	Sediments and macrobenthic community Winter and summer 2006	Hg	n.r.	Anthropogenic Hg negatively affects the macrobenthic community, poor abundance, species richness, or diversity.	(Nunes et al. 2008)
Ria Aveiro	Sediments and benthic foraminifera Year n.r.	Zn, Pb, Cu, and Cr, Fe, Mn	n.r.	High Zn, Pb, and Cu in Aveiro canals; and Zn, Cr, Fe, and Mn in Murtosa; Cr and Fe in harbor areas. High As, Co and Hg in Murtosa sediments. Ílhavo not polluted.	(Martins et al. 2013)
Aveiro lagoon	Sediments July 2011	Ag, As, Cd, Cu, Fe, Mn, Ni, Pb, S, Sb, Sn, Zn	n.r.	Biogeochemical processes may play a significant role in the increase of the pollutants in the sediment.	(Martins et al. 2015)
Ria Aveiro, Mira, Tagus, Sado and Guadiana	Sediments Autumn 2009	Cd, Hg, Zn, Cr, Cu, Pb, Ni	Cd Guadiana(**1.98**) Cr Sado (**60**) Aveiro (18) Cu Sado (**52**) Aveiro and Guadiana (22) Hg Guadiana (**0.6**) Tagus (**0.4**) Ni Aveiro (6.8) Pb Tagus (**100**) Zn Aveiro (**393**)	Contamination traced to human activities and geological origin in the Mira and Guadiana estuaries. Sediments do not present acute toxicity but some particularly toxic metals and PAHs can be considered a potential risk.	(Serafim et al. 2013)
Águeda	Sediments 1995/1996	Cr, Cd, Ni, Cu, Pb, Zn	Cr (**617**) Cd(**3**) Cu (**12628**) Ni (737) Pb (**331**) Zn (**10150**)	Clear pollution by Cr, Ni, Cu, Zn, and Pb as a result from both natural and anthropogenic origins.	(Reis et al. 2005)

Table 3 (continued)

Area	Source/sample collection	Trace element	Levels ($\mu g\ g^{-1}$)	Main results/risk assessment	Ref
Mondego	Surface sediments February and August 2003	Zn, Pb, Cr, Cu, Ag, Cd, Hg	n.r.	Weak local contamination sources reflect the diffuse source of contaminants associated with rainy seasons.	(Pereira et al. 2005)
Mondego	Fluvial sediments and soils 2012	Cu, Cr, Pb, Cd, Zn, Ni	Cu (**79**) Cr (**63**) Pb (**788**) Cd (**19.5**) Zn (**1466**) Ni (43)	High levels of Pb, Cd, and Zn at some locations of the Loreto catchment, from historic traffic sources.	(Dias-Ferreira et al. 2016)
Lisboa	Urban soils November 2004-2011	Cd, Cr, Ni, Pb	Cd (0.463) Cr (**44**) Ni (46.6) Pb (5.7)	Lisbon's soils have low levels of metal pollution	(Silva et al. 2021)
Tagus salt marshes	Salt marshes sediments May 1991	Zn, Pb, Cu, Cr, Ni	(vegetated/non-vegetated) Zn (**1150/730**) Pb(**500/200**) Cu (**<70/<40**) Cr (**<60**) Ni (< 50)	Higher quantities of Zn, Pb, and Cu in sediment between roots. Plants are important vehicles for metals to be incorporated into salt marshes.	(Caçador et al. 1996)
Tagus Estuary salt marshes	Sediments Jul 1991 and Jul 1992	Zn, Pb, Cu, Cd	(vegetated/non-vegetated) Zn (**1150/730**) Pb (**500/200**)	Root-sediment systems exhibited a seasonal variation of metal concentrations.	(Caçador et al. 2000)
Tagus	Salt marshes sediments and biota January /March 2003	Cu, Cd, Pb, Zn	Cu (**89.1**) Cd (**5.9**) Pb (**199**) Zn (**427**)	Pb significant environmental contamination. Values lower than in a previous study.	(França et al. 2005)
Tagus Estuary	Sediments Jul and Dec 2004	Total Hg, MetilHg, Al, Fe, Mn	Total Hg Jul (**49**) and Dec (**67**)	Hg distribution surface sediments as the previous study; two areas with high concentrations identified in vicinity of two major ancient anthropogenic sources.	(Canário et al. 2007)
Tagus Estuary	Surface sediments Year n.r.	Cr, Ni, Pb, Cu, Zn, As, Cd	Cd (**11**) Pb and Zn Barreiro (**2858/2854**); Lisbon (**400/686**) As (**1022**) Cr (**592**) Cu (**593**)	Values comparable to 1980s, emission reduction; minor effect on contaminant distribution in surface sediments.	(Vale et al. 2008)
Tagus Estuary	Salt marsh sediments May 2007	Total Hg, MetilHg	**1.87**	Hg methylation in salt marshes due to geochemistry complexity. Stocks of Hg and MeHg in plant colonized areas.	(Canário et al. 2010)

Table 3 (continued)

Area	Source/sample collection	Trace element	Levels ($\mu g\ g^{-1}$)	Main results/risk assessment	Ref
Tagus Estuary	Estuarine bottom sediments. Sept 2011	Zn, Pb, Cd, Ni, Cu, Cr	n.r.	Similar distributions, in the particulate form, (exception of Cr and Cu); homogenous distribution in the proximity of the discharge areas.	(Duarte et al. 2014)
Tagus Estuary	Sediments Jul 2010 and Feb 2011	Hg and metylHg	< **1** $\mu g\ g^{-1}$ and 4.4 ng g^{-1}	Locations far from historical anthropogenic Hg sources, contamination from internal estuarine water circulation.	(Cesário et al. 2016)
Tagus Estuary	Surface sediments May 2016	yttrium and rare-earth elements (REE)	Y (32) REE (210)	Major impact areas in WWTP effluents (north margin) and the heritage of industrial complex (south margin).	(Brito et al. 2018)
Portuguese-Spanish border Caia /Guadiana, Elvas, Campo Maior	Agricultural Soils Year n.r.	Cd, Cr, Cu, Ni, Pb, Zn	Cd (**0.7**) Cr (**89.0**) Cu (**45.0**) Ni (48.6) Pb (**41.9**) Zn (65.6)	Small percentage of the 630 soils sampled with high available levels of heavy metals. No evidence for extensive heavy metal contamination.	(Nunes et al. 2014)
Mira	River-estuary sediments. Year n.r.	Rare earth elements (REE)	Yttrium (1.8–17) ΣREE (9.9–182)	REE as study tool for coupling mechanisms between riverine, estuarine, and coastal areas, as a provenance tracer and as an environmental change signal.	(Cesário et al., 2018)
Sado	Estuary sediment May 2006	Cd, Cu, Pb, Cr, Hg, Al, Zn, As	Pb (**69**) Zn (**507**) Cu (**191**) Cd (**8**) Cr (**63**) Hg (**0.7**)	Low contamination level, moderate potential for adverse biological effects. 3% of SS highly contaminated, high potential for adverse biological effects, 47% have moderate contamination.	(Caeiro et al. 2005)
Sado Estuary	Estuarine surface sediments May 2006	Hg	Hg (**0.54**)	No environmental Hg risk. Classified as class 2 in degree of contamination by the national legislation, implying legal restrictive rules.	(Lillebø 2011)
Alqueva	Freshwater sediments Feb 2011 to Nov 2012	As, Cd, Cu, Cr, Pb, Zn	n.r.	Cd presented a high risk, while Pb, As and Zn showed a medium risk.	(Palma et al. 2015)

Table 3 (continued)

Area	Source/sample collection	Trace element	Levels (µg g^{-1})	Main results/risk assessment	Ref
Ria Formosa	Sediments March 2007	Cd, Pb, Ni, Cr, Cu	n.r.	Urban and industrial pollution emissions.	(Said et al. 2019)
Ria Formosa	Sediment cores and surface sediments Year n.r.	As, Cu, Pb, Sr, V, Zn, As, Cr, Ni, Co, Mo, Ag, Au, B, Bi, Cd, Ga, Hg, Sb, Sc, W	Sr (114.6) V (51.2) Zn (97) As (**70**) Cr (**79**) Ni (37) Pb (31) Cu (**37**) Co (21) Mo (24) (Ag, Au, B, Bi, Cd, Ga, Hg, Sb, Sc, W nd)	Surface sediments significant contamination, high enrichment factors for As, Cu, Pb, and Zn. Other metals have low enrichment values, suggesting natural conditions.	(Sousa et al. 2019)
Ria Formosa e Guadiana	Surface sediments Autumn 2006 and spring 2007	As, Cd, Cu, Hg, Ni, Pb, Zn	Zn (**200**) Cd (0.16) Cu (**60**) Pb (**57**) Ni (26) Hg (**0.55**) As (nd)	Enrichment Factor for Ria Formosa and River Guadiana between 1.0 for Cd and 5 for Hg.	(Blasco et al. 2010)
Guadiana estuary	Estuarine Sediments Year n.r.	Al, Fe, Mn, Co, Cr, As, Cd, Cu, Pb, Ni, Zn	n.r.	Natural origin elements (Al, Fe, Mn, Co, and Cr) distributed homogeneously along the basin, anthropic origin elements (As, Cd, Cu, Pb, Ni, Zn) punctual sources and high concentration in estuary.	(Delgado et al. 2010)
Guadiana estuary	Estuarine Sediments Year n.r.	As, Cd, Cu, Mn, Pb, Zn, Ni, Co, Cr, Hg	As (**81.8**) Cd (**1.40**) Co (22.6) Cr (**49**) Cu (**71.9**) Hg (**4.43**) Ni (41.6) Pb (**41.6**) Zn (**483**)	Moderate to considerable ecological risk associated mine drainage from Iberian Pyrite Belt. Several zones of extremely high risk, related to industrial and urban dumps and heavy traffic.	(Delgado et al. 2011)
Mining areas					
Murçós (Macedo, Bragança)	Stream sediments and soils Before remediation March and April 2005 After remediation 2008 and 2009	W, Bi, As, Al, U, Cd, Sn, Ag, Cu, Sb, Pb, Mn, Ni, Be, Zn	n.r.	Low potential ecological risk indices for As, Cr, Cu, Ni, Pb and Zn moderate for Cd and influenced by mine drainage.	(Antunes et al. 2016)
Horta da Vilariça (Bragança)	Sediment Year n.r.	U, As, Cu, Zn, Cr, Mn	U (0.124–23.9, mean value 3.92)	U sediment concentrations not toxic to benthic aquatic organisms.	(Cordeiro et al. 2016)
Vale Gatas (Vila Real)	Stream sediment Year n.r.	Ag, Pb, Bi, As, W, Cd, Zn, Ni,Cu	(mean) Cu (**114**) Pb (**312**) Zn (**143**) Ag (7.7) Ni (19) Mn (413) As (**504**) Cd (**1.2**) W (120)	Cu, Pb, Zn, Ag, As, Cd, Bi and W anomalous concentrations in many places.	(Freire Ávila et al. 2005)

Table 3 (continued)

Area	Source/sample collection	Trace element	Levels ($\mu g\ g^{-1}$)	Main results/risk assessment	Ref
Castromil (Paredes, Porto)	Soils	Ag, Al, As, Au, Ba, Bi, Ca, Co,Cr, Cu, Fe, Ga, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb,Sc, Sr, Th, Ti, U, V, Zn	As (**6909**) Pb (**6295**)	Hazardous site due to dynamic processes taking place in the abandoned tailing deposits and releasing metals to the surficial environment.	(Silva et al. 2004)
Terramonte Mine (Porto)	Stream sediments Sept 2007 and Jan, May and Aug2008	Al, As, Co, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Zn	n.r.	Low to medium risk for Al, Cu, and Zn in most tailing and stream sediments samples. Deeper sediments have high risk for Pb.	(Carvalho et al. 2014)
Valongo (Porto)	Soil samples	As, Sb, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	n.r.	Low soil toxicity close to Sb–Au and As–Au mines. If physico-chemical changes occur As and Sb will show higher potential environmental risk than Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn.	(Carvalho et al. 2011)
Fílvida stream Coval Mó (Aveiro)	Sediments October 2001	Pb, Zn, Cd, Co, Cu, Mn, Ni	Pb (3.1 %) Zn (**3331**) Ni (465) Cd (**4.3**)	High toxicity of Coval da Mó stream. Very toxic environment. Mixture and high concentrations in stream sediments near the mine too toxic to allow a stable diatom community development.	(Ferreira da Silva et al. 2009)
Cunha Baixa (Viseu)	Sediments Spring and autumn	Mn, Fe, Al, U, Sr	n.r.	Sediments were considered non-toxic, unlike the superficial water.	(Antunes et al. 2007)
Sevilha (Coimbra)	Water (streams and ponds), soil June (year n.r.)	U	U (**557**)	The average U content in the soil was considerably higher than those found in the literature.	(Favas et al. 2016)
Canto Lagar (Guarda)	Mine dumps, stream sediments, and soils Year n.r	Fe, U, As, Cu, Zn, Pb, Th	n.r.	Low/moderate contamination (except As, W, and U with high/very high contamination index). Environmental risk due to spatial mobility and dispersion or surface runoff from the dumps.	(Antunes et al. 2020)

Table 3 (continued)

Area	Source/sample collection	Trace element	Levels ($\mu g\ g^{-1}$)	Main results/risk assessment	Ref
Alto Várzea (Guarda)	Stream sediments 2008 and 2009	As, Co, Cr, Sr, Th, U, W, Zn	n.r.	Soils contaminated with As and U; not be used for any purpose.	(Antunes et al. 2018b)
S. Francisco Assis – Panasqueira (Castelo Branco)	Geogenic soil, rhizosphere samples Year n.r.	As Cd Pb	n.r.	As contents in the rhizosphere soils exceed 20 times the reference value for agricultural soils.	(Candeias et al. 2014)
Monfortinho (Erges basin (Castelo Branco)	Stream sediments	Fe, Ba, Cu, Cr, B, Zn, Pb, Sn, V, Ni, As, W, Cd	Fe (4.8%) Ba (750) Cu (**64**) Cr (**464**) B (37) Zn (**202**) Pb (**90**) Sn (25) V (313) Ni (42) As (**44**) W (8) Cd (**1**)	Moderate to high contamination, associated with old mineralizations surrounding.	(Antunes et al. 2018a)
Miguel Vacas Mine (Évora)	Soil October 1998-March 2000	Cu, Mn, Ni, Zn,	Cu (**2231**) Mn (4152) Ni (**143.4**) Zn (211.4)	Soils in the influence of drainage water contaminated with Cu, and Ni close to the maximum value by Portuguese legislation.	(Abreu et al. 2008)
Grândola Stream Caveira (Setúbal)	Stream Sediments	Al, As, Ca, Cd, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Zn	As (**420**) Ba (1591) Cu (**642**) Hg (**100**) Pb (**1000**) Sb (214) Zn (**482**)	Extreme environmental risk (waters, sediments, and soils) for biota and ecosystems surrounding the mine site.	(Ferreira da Silva et al. 2015)
Lousal (Setúbal)	Stream sediments downstream of tailing site Sep 2000	Cu, Pb, Zn, As, Cd	Cu (**1986**) Pb (**5981**) Zn (**1756**) As (**1988**) Cd (**5.7**)	All the soil samples collected in the tailings deposits exceed the permissible levels.	(Silva et al. 2005)
Aljustrel (Beja)	Soils Summer 2005 and 2006	As, Cu, Cd, Pb, Zn	As (**3936**) Cu (**5414**) Cd (**61.6**) Pb (**20000**) Zn (**20000**)	Severe contamination by As, Cd, Cu, Pb, and Zn.	(Candeias et al. 2011)
S. Domingos (Beja)	Soils April 2009	As, Cd, Cr, Cu, Ni, Pb, Zn	As (**7955**) Cd (**3.38**) Cr (24.7) Cu (**434**) Ni (14.2) Pb (**26975**) Zn (**168**)	As, Cu, and Pb severe contamination.	(Alvarenga et al. 2012)

Boldface values exceeding Interim sediment quality guidelines (ISQGs) and /or probable effect levels (PELs) ($\mu g\ g^{-1}$ dw) (CCME) or Environmental soil quality guideline (CCME) https://ccme.ca/en/resources/sediment#

some of the most relevant studies comparing, whenever possible, studies in the same geographical areas.

The Sado estuary is among the most studied ecosystems (Caeiro et al. 2005, Cortesäo and Vale, 1995). Caeiro et al. (2005) reported that from 78 sampling stations, analysed in May 2006, 3% were highly contaminated and registered a high potential for adverse biological effects, while 47% had moderate contamination by Cd, Cu, Pb, Cr, Hg, Al, Zn, and As. Nevertheless, another study, also conducted in 2006, showed that Hg was not a cause of environmental risk in this estuary (Lillebø 2011). Another study in 2009 referred that the most important anthropogenic metal sources in this estuary have been historically related to pyrite mines that discarded mining waste directly into the river without appropriate treatment (high levels of Cd and Zn), the industries on the north shore (pulp and paper mills, pesticides and fertilizers factories) and shipyards (high levels of Pb, Cu, Cr, and Ni), as well as intensive farming, mostly of rice, and fish farms around the estuary. Also, the weak residual current flow characteristic of this system enhanced the accumulation of sediment; therefore, locally introduced pollutants settled out rather than being transported away (Serafim et al. 2013).

Tagus (Tejo), one of the largest estuaries on the Atlantic coast of Europe, has also been studied in several works. For instance, Caçador et al. (1996) evaluated the presence of various trace elements in two salt marshes sediments and showed that profiles of Zn, Pb, and Cu concentrations in vegetated sediments differed from those recorded in non-vegetated areas and that at subsurface layers (with higher root density) Zn, Pb, and Cu were enriched. In a monitoring study conducted by Duarte et al. (2014) in 2011, 19 sampling points were selected along Tagus estuary and concluded that with the exception of Cr and Cu, the analyzed metals (Zn, Pb, Cd, Ni, Cu, and Cr) showed similar distributions and a homogenous distribution in the proximity of discharge areas. The presence of yttrium and rare-earth elements collected in 78 sampling stations was also investigated in this estuary (Brito et al. 2018). Distribution of yttrium and rare earth elements was correlated with sediment grain size and associated with wastewater treatment plants (WWTP) located in the north margin and the legacy of an abandoned industrial complex in the south margin of the estuary (Brito et al. 2018). A study of heavy metal concentrations in sediment, benthic invertebrates, and fish in three salt marsh areas subjected to different pollution loads carried out in 2003 (França et al. 2005) obtained lower values than those obtained in previous studies for the Tagus estuary in 1993 (Caçador et al. 1993). This change could be related to a reduction in pollutant input, since the Tagus River was heavily polluted during the 1980s and the 1990s, but some industries stopped activity and several WWTP begun to operate since then.

Douro, one of the rivers with the larger hydrographic basin on the Iberian Peninsula, has also been studied in several works, from the transboundary Douro River basin to its mouth. In a study where 107 samples were collected from stream sediments in 2004 (Reis et al. 2014) higher concentrations of Cu, Zn, and, in particular, Pb, in the most labile fractions, were found. The higher values were found where the total element contents were also higher, suggesting an important contribution of anthropogenic activities to the total contents of these elements in the sediments. Cr and Ni were the main metals from a lithological source. Several other studies were focused on estuarine sediments. Water, sediments, and plants were collected in May 2013 and the possible occurrence of several trace elements as Li, Be, Al, V, Cr, Co, Ni, Cu, Zn, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb, and U were checked; Al and Zn were the trace element found at the higher concentrations at both sediments and water. Pb, Cu, and Zn levels in sediments were critical in comparison to the established probable effect levels (Ribeiro et al. 2018). Prior studies have shown an evident signature of anthropogenic trace metal contamination (Zn, Cu, Pb, Cr, Cd, and Ni) with consequences for estuarine communities and salt marsh vegetation (Almeida et al. 2006, Mucha et al. 2004b). A more recent study carried out in 2019 in 6 sampling sites showed a potential for Cd, Hg, and Pb to accumulate in organisms, with consequences for the entire trophic chain (Iglesias et al. 2020).

Ave and its tributaries have also been the focus of several research works. In 1992, a study emphasized the contribution of leather tanning, metal plating, and textile industries as the main sources of toxic metal contamination (Cd, Cr, Cu, Pb, and Zn) in these streams (Gonçalves et al. 1992). Other work, performed in1999, included more sampling stations to accomplish a better description of the basin showing similar results in Ave river and its tributary, river Este. Cd showed to be the most problematic pollutant followed by Zn, Cu, and Cr, with a strong correlation to local industry (Soares et al. 1999). Data from 2013 collected in the lower basin near the mouth of Ave river showed strong contamination by anthropogenic activities for Al, Mn, Ba, and Zn and high enrichment factors (EF)for Se, Cd, Zn, Li, Cu, Ag, Pb, and U (Couto et al. 2019).

Sediments of the biggest artificial lake of the Iberian Peninsula in the Guadiana Basin, Alqueva, that drains the western part of the Iberian Pyrite Belt, were studied and Cd was shown to contribute to the highest pollution levels followed by Pb and As. Despite the trace element contamination of the Alqueva sediments, sequential extraction studies showed that most of them were found in the oxidizable and residual fractions indicating that they were sparingly bioavailable, with exception of Cd (acid-labile fraction) and Pb (reducible fraction) (Palma et al. 2015).

Portugal is a country with a long mining tradition and still has a strong mining activity. Land pollution due to mining activities is a major issue in many European countries and Portugal is not an exception. Therefore, the presence of trace elements in mining sediments (stream sediments and soils) were reported in several works (Table 3) and at 18 different mining sites across Portugal. Environmental potential problems were found in Castromil (Au mining areas abandoned since 1940), Ag–Pb–Zn-Terramonte mines (closed in 1973), Pb-Zn Coval da Mó mines (total shutdown in 1972), Alto da Várzea radium mine (closed in 1946), tin–tungsten Panasqueira mine (still active), the tin–tungsten sector located in the Central Iberian Zone of the Iberian Massif, in the Portuguese–Spanish border - Monfortinho, Caveira (closed in de 1980s), Lousal (closed in 1988), Aljustrel (Iberian pyrite belt mining sites still active), and S. Domingos (closed in 1966) (Alvarenga et al. 2012, Antunes et al. 2018a, Antunes et al. 2018b, Candeias et al. 2011, Candeias et al. 2014, Ferreira da Silva et al. 2009, Ferreira da Silva et al. 2015, Silva et al. 2005). A recent review on the soils affected by mining activities in the Portuguese sector of the Iberian Pyrite Belt describes some of the rehabilitation actions, from constructive techniques to dig and contain the contaminated tailings and waste materials to more unconventional processes (Mourinha et al. 2022).

Biota

Trace elements have also been found in algae, plants, bivalve mollusk (e.g., mussels), and fish (Table 4). For instance, the presence of various trace elements was investigated in Ave and Douro estuaries in algae and plants located near the estuaries (Couto et al. 2019, Ribeiro et al. 2018). Estuarine plants slowly accumulate trace elements, being identified as bioindicators of estuary pollution. Those studies showed the presence of trace elements in distinct families of native estuarine flora. In the Douro estuary, high levels of Al, Zn, and Ba were determined in plants and macroalgae. No correlation was observed between flora and waters and sediments concentrations at the same sampling locations. Such differences could be related to the various parameters that affect the sorption of trace metals including plant life cycle, metal availability among others (Antunes et al., 2018a, b, Bonanno et al. 2018). Additionally, most of these plants are annual or biannual while trace elements sediments concentrations reveal chronic exposure and may explain the variations found among species and the concentrations found in sediments. In Ave estuary flora, the trace element concentrations were similar to high levels found for Al, Zn Ba, and Cu. The highest trace element levels were found in specimens of *Plantago* sp. and in macrophytes such as *Oenanthe crocata* and *Veronica anagallis-aquatica*, showing that these species may be metal accumulators and can be used as phytoindicators of local pollution. The occurrence of trace elements was also analyzed in aquatic mosses (*Fontinalis antipyretica*) in Ave (and tributaries) and Cávado rivers and a correlation was found between the elements found in selected flora and sediments (Gonçalves et al. 1992, Gonçalves et al. 1994). Data demonstrated that this species was a bioaccumulator and highlighted its importance as a metal bioindicator. Cr and Zn concentrations up to 107 and 70 times the natural concentration, respectively, were found in the plants. As mosses do not have conductive tissues, toxic metals are completely taken up from the water in accordance with their relative dissolved quantities. The increase in Hg contamination was related to the decrease of the local microbenthic community (~8400 microorganisms corresponding to 31 macrobenthic taxa) in Ria de Aveiro (Nunes et al. 2008). Invertebrates and fish trace element contamination has also been described. For instance, mussels *Mytilus* species have been wildly studied not only because they are commercially important but also because they are considered sentinels of environmental pollution making them an excellent metal biomonitoring species (Coimbra et al. 1991, Figueiredo et al. 2022, Machado et al. 1999, Santos et al. 2014). Seasonal and spatial variations of trace elements were reported in *M. galloprovincialis* (Figueiredo et al. 2022) and Santos et al. (2014) reported levels of several trace elements including Hg, Pb, Cr, and Cd below maximum allowed values.

The presence of Hg was found in green alga (*Ulva* sp.), bivalves (*Scrobicularia plana* and *Cerastoderma edule*), worms (*Hediste diversicolor*) or crabs (*Carcinus maenas*) collected from the intertidal mudflats in Sado estuary (Lillebø 2011). Nevertheless, no correlation was found among sediments and water levels and biota. In the Tagus estuary, the presence of significant levels of heavy metals was found in worms (*Nereis diversicolor*), bivalves (*S. plana*), brown shrimp (*C. crangon*), shore crab (*C. maenas*), grey mullet (*L. ramada*), sole (*Solea senegalensis*), and sand gob (*Pomatoschistus minutus*). Various studies have been showing the adverse effects of trace elements on aquatic organisms. In fact, exposure to various trace elements has been shown to induce biochemical, genotoxicity effects, and decreases survival (Gárriz and Miranda, 2020, Velma and Tchounwou, 2010).

The presence of various trace elements in diatoms and various plant species associated with mine areas was also reported (Table 4). In Fílvida stream Coval da Mó, the presence of Pb, Zn, Cd, Co, Cu, Mn, and Ni in benthic diatoms communities was shown and geochemical results showed a very toxic environment. The mixture of metals and their high concentrations in stream sediments near the mine was too toxic to allow a stable diatom community development. Further downstream, the decrease in metal concentrations to lower levels (two orders of magnitude) permitted the growth of diatoms, many of which with deformations particularly in *F. capucina var. rumpens.*

Table 4 Occurrence of trace elements in biota from Portugal based on the reported literature.

Area	Source/sample collection	Element	Levels (µg g^{-1})	Main results/ Risk assessment	Ref
Cávado river basin	Mosses 1988 and 1989	Cd, Cr, Zn, Cu, Pb, Ni	Contamination factors Cd (44) Cr (101) Cu (20) Ni (59) Pb (18) Zn (6)	High enrichment rates.	(Gonçalves et al. 1994)
Ave Basin (Ave, Selho, Pelhe, Este and Vizela)	Aquatic bryophytes (*Fontinalis antipyretica*) 1986	Cd, Cr, Cu, Pb, Zn	Max. Cd (5.2) Cr (534) Cu (1496) Pb (97) Zn (4828)	Metal pollution indexes showed a good correlation between mosses/ sediments.	(Gonçalves et al. 1992)
Ave	Local plants Spring, summer, autumn, and winter 2013	Li, Be, Al, V, Cr, Co, Ni, Cu, Zn, Se, Mo,Ag, Cd, Sb, Ba, Tl, Pb, U	(Mean) Li (57) Be (1.6) Cr (22) Co (4.6) Al (14,611) Zn (160) Se (0.65) Cu (29) Pb (25) Ag (0.13) Cd (0.35)	Igeo showed strong contamination by anthropogenic activities for Al, Mn, Ba, and Zn and EF high enrichment of Se, Cd, Zn, Li, Cu, Ag, Pb, and U.	(Couto et al. 2019)
Douro	Macrobenthic community 14 species	Zn, Cu, Pb, Cr, Cd, Ni	n.r.	Clear signature of anthropogenic trace elements. Macrobenthic community low diversity (14 species), dominated by small size opportunists controlled by natural characteristics.	(Mucha et al. 2004b)
Douro	*S. maritimus* and *J. maritimus*. 2004 winter; spring summer and autumn	Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Cd accumulated by *J. maritimus*. *S. maritimus* accumulate Cd, Fe, Mn and Pb. Cd, Fe and Pb root bioaccumulation, Mn in stems.	*S. maritimus* and *J. maritimus* potential for phytostabilization of Cd. Both plants able to bioaccumulate Cd. Pb *S. maritimus* in roots.	(Almeida et al. 2006)
Douro	Local plants and two macroalgae (*Porphyra umbilicalis* Kütz and *Enteromorpha* sp)	Li, Be, Al, V, Cr, Co, Ni, Cu, Zn, Se, Mo,Ag, Cd, Sb, Ba, Tl, Pb, U	Al *Enteromorpha* sp. (3191) *P. umbilicalis* Kütz~(1432) *Parietaria judaica* L. (5336); *P. umbilicalis* Kütz (1479)	Presence of trace elements in native local flora. Levels in plants and macroalgae not correlated to those found in waters and sediments.	(Ribeiro et al. 2018)
Oporto Coast	Mytilus edulis Dec 1979- Dec 1980	Fe, Cu, Zn, Cd	Strong annual variation.	Very high Fe values, important Zn and Cu. River water metal source.	(Coimbra et al. 1991)
Oporto coast	Algae (Enteromorpha spp. and Porphyra spp.)	Cd, Cu, Hg, Pb		*Enteromorpha* spp. and *Porphyra* spp. comparable mean concentration factors (except for Pb in *Enteromorpha* spp. and Hg in *Porphyra* spp.). *Enteromorpha* spp. used to estimate Cd, Cu and Hg mean seawater contents and *Porphyra* spp., Cd, Cu, and Pb concentration.	(Leal et al. 1997)

Table 4 (continued)

Area	Source/sample collection	Element	Levels (µg g^{-1})	Main results/ Risk assessment	Ref
Ria Aveiro	Macrobenthic community Winter 2006 and summer Approx. 8400 organisms representing 31 macrobenthic taxa	Hg	n.r.	Increase of Hg contamination associated with reduced total abundance, lower species diversity, and dominance of taxa tolerant to Hg.	(Nunes et al. 2008)
Ria Aveiro	61 living benthic foraminiferal species Year nr	Zn, Pb, Cu, Cr	Max Pb(153) Zn(128) Cu(95) Cd(75) Cr(22) dominant species *H. germanica* (<74%), *A. sepida and Q. seminulum*	Extremely high concentrations of Zn, Cu, Fe, and Cd in the digestive gland of *S. officinalis* from two coastal lagoons in Portugal.	(Martins et al. 2013)
Tagus estuary salt marshes	*Spartina maritima, Arthrocnemum fruticosum, Halimione portulacoides* every 2 months, Jul1991 – Jul 1992	Zn, Pb, Cu, Ni, Cr	*H. portulacoides* (leaves, stems and roots Zn (963) Pb (840) Cu (274) Ni (13) Cr (6)	Greatest concentrations in roots. *H. portulacoides* more effective accumulator of metals than S. *maritima*, and both root-sediment systems exhibited a seasonal variation of metal concentrations.	(Caçador et al. 2000)
Tagus	*Nereis diversicolor*, *S. plana*, *C. crangon*, *C. maenas*, *L.ramada*, *Solea senegalensis*, *Pomatochistus minutus*	Cu, Cd, Pb, Zn	n.r.	Some species contain significant levels of heavy metals.	(França et al. 2005)
Tagus	*S. fruticosa, H. portulacoides and S. maritima* May 2007	Hg and methylHg	Max *H. portulacoides* leaves (0.056)	Concentrations in belowground biomass exceeded up to 3 (Hg) and 15 (MeHg) times the levels in sediments.	(Canário et al. 2010)
Tagus Estuary	Phytoplankton May -July 2010 January /February 2011	Cr, Ni, Cu, Cd, Hg, Pb	n.r.	A shift towards species less susceptible to trace elements was observed, disclosing some individual taxa as potential indicators.	(Cabrita 2014)
Tagus Estuary	Edible tissues of *Mytilus galloprovincialis*	S, K, Ca, Fe, Cu, Zn, As, Br, Sr, Cr, Cd, Hg, Se, Pb	Max Cr (0.93) Pb (1.1) Cd (0.96) Hg (0.12)	Highest levels found in two areas close to the city for Pb and Cd, but below the maximum allowed values. Comparing with previous work with various species of bivalve molluscs, Cd, Pb, Hg and Cr were the lowest in this study.	(Santos et al. 2014)

Table 4 (continued)

Area	Source/sample collection	Element	Levels (μg g^{-1})	Main results/ Risk assessment	Ref
Portuguese Coast	Rare earth elements *Mytilus galloprovincialis*			$\sum$REE concentration was greater in the spring. A negative Ce and Eu anomaly was observed.	(Figueiredo et al. 2022)
Sado Estuary	*Ulva* sp., *Scrobicularia plana* and *Cerastoderma edule*, *Hediste diversicolor*, *Carcinus maenas* in intertidal mudflats	Hg	*Ulva sp.* (0.050) *H. diversicolor* (0.073) *S. plana* and *C. edule* (0.041) *C. maenas* (0.17)	No significant relations found between Hg concentrations in biota (*Ulva sp, H. diversicolor, S. plana, C. edule and C. maenas*) and abiotic matrices (sediment and water column).	(Lillebø 2011)
Ria Formosa	*Sarcocornia fruticosa* March 2007	Cd, Pb, Ni, Cr, Cu	n.r.	Remediation strategies.	(Said et al. 2019)
Douro, Ria de Aveiro, Mondego, Tagus, Sado, Mira, Ria Formosa and Guadiana	Juvenile *S. solea, S. senegalensis (Senegalese sole), P. flesus*, *D. vulgaris D. labrax* July 2005	Cu, Zn, Cd, Pb	Muscle dry weight Cu (2.1) Zn (59)	Juveniles of five fish species showed detectable contamination levels of Cu and Zn in the muscle, and Zn had the highest mean concentrations.	(Vasconcelos et al. 2011)
Aveiro lagoon and Formosa Lagoon	Digestive gland and mantle of female *Sepia officinalis*	Fe, Cu, Zn, Cd, Hg, Pb	n.r.	Extremely high concentrations of Zn, Cu, Fe, and Cd in the digestive gland of *S. officinalis* from the two coastal lagoons	(Pereira et al. 2009)
Algarve coast	*Mytilus galloprovincialis*	Cd, Cu, Fe, Mn, Ni, Zn	Max Cd (3.1) Cu (7.0) Fe (294) Mn (15.5) Ni (0.77) Zn (398)	Increased concentration near urban centers and industrial effluents. Metal concentrations higher in west compared to east coast. Cd and Cu concentrations increased over the last 10 years.	(Machado et al. 1999)
Mining areas					
Horta Vilariça (Bragança)	25 plant species culminating 233 samples	U	*Scorpiurium deflexifolium* (49.6) *Fontinalis antipyretica* (35.7) shoots of *Rorippa sylvestris* (33.8), roots of *Oenanthe crocata* (17.8) *Nasturtium officinale* (10.9)	*Rorippa sylvestris* maximum translocation factor being a promising candidate as bioindicator species.	(Cordeiro et al. 2016)

Table 4 (continued)

Area	Source/sample collection	Element	Levels (µg g^{-1})	Main results/ Risk assessment	Ref
Fílvida stream Coval Mó (Aveiro)	Benthic diatom communities. *Fragilaria capucina var. rumpens, Fragilaria cf. crotonensis and Achnanthidium minutissimum*	Pb, Zn, Cd, Co, Cu, Mn, Ni	n.r.	Geochemical show very toxic environment. Metal mixture and high concentrations in stream sediments near the mine too toxic to allow stable diatom community development. Downstream, metal decrease (two orders of magnitude) permitted diatoms growth, though with deformations particularly in *F. capucina var. rumpens.*	(Ferreira da Silva et al. 2009)
Sevilha (Coimbra)	53 plant species belonging to 22 families were collected from 24 study places	U	roots *Juncus squarrosus* (450) *Carlina corymbose* (181) *Juncus bufonius* (39.9) *Callitriche stagnalis* (55.6) *Lemna minor* (53.0) *Riccia fluitans* (50.6)	The accumulation pattern in the studied aquatic plants (*L. minor, R. fluitans, C. stagnalis and Lythrum portula*) dominated over most of the terrestrial counterpart.	(Favas et al. 2016)
S. Francisco de Assis – Panasqueira (Castelo Branco)	14 edible vegetables (VEG), *Solanum tubersum sava* and *Brassica olerácea L.*	As, Cd, Pb, Cu, Zn, Mn	As (0.8–14.4); Cd (0.1–0.1); Cu (3.7–19.6); Mn (21–270.2), Pb (0.2–4.2); Zn (35–176.6). Highest concentrations of As, Pb, Zn and Mn in cabbages, potatoes concentrate more Cd and Cu.	As, Cd and Pb contents above the maximum for vegetables; Cu, Zn and Mn below maximum allowed in vegetables. All vegetables contaminated by As, Cd and Pb and toxic if continually consumed.	(Candeias et al. 2014)
Miguel Vacas (Vila Viçosa, Évora)	*Prunus domestica L.,* *O. europaea L. spp.* *Quercus ilex L.* 1998-2000	Cu, Mn, Ni, Zn	Cu (21) Mn (4000) Ni (16) Zn (57)	No significant correlations between total and available soil fraction content and plant concentrations. Trace element content in all trees, except holm oak. This species is able to accumulate Mn and to some extent Ni.	(Abreu et al. 2008)
Iberian Pyrite Belt (Lousal, Aljustrel and São Domingos)	*Cistus ladanifer L.,* *Erica andevalensis C.-R.,* *Juncus effusus L.,* *Scirpus holoschoenus L.,* *Thypha latifolia L.*	Mn, Fe, Cu, Zn, Pb	n.r.	Aquatic plants with high capacity for Zn bioaccumulation and translocation; metal mobility sequence: Zn > Cu > Pb.	(Durães et al. 2015)

Global assessment of trace elements in Portugal

Our literature survey revealed that currently available data is heterogenous, varying in terms of study design, selected trace elements, and spatiotemporal locations. This heterogenicity leads to data differences that make meaningful comparisons difficult. Furthermore, comprehensive studies are scarce in what concerns spatiotemporal monitoring studies using different matrices (e.g., water, sediments, and biota) as they require multidisciplinary teams to obtain, integrate and correlate different data. Transboundary cooperative monitoring programs should also be promoted as many hydrographic basins are shared between Portugal and Spain. Additionally, the establishment of environmental geochemical background levels of trace elements is highly needed as they have strong regional characteristics and are crucial for accurate risk assessment. The overall spatial distribution of studies is represented in Fig. 3. The coastline and particularly in the north of Portugal had coverage for multiple environmental matrices types, whereas a notable number of interior districts had no sample coverage for any matrix type (Fig. 3). The spatial register of sample locations may indicate that there is enhanced research interest in those regions. Most papers published are focused on coastal areas and estuaries, mainly along the Atlantic coastline. Even in the main rivers, most studies analyze their mouths, where the biggest Portuguese cities are located. In fact, coastal transition ecosystems as estuaries and coastal lagoons are among the most productive in terms of biological importance and therefore of high environmental relevance. However, they are also amongst the most modified due to anthropogenic activities and vulnerable to contamination by diverse classes of pollutants including trace elements.

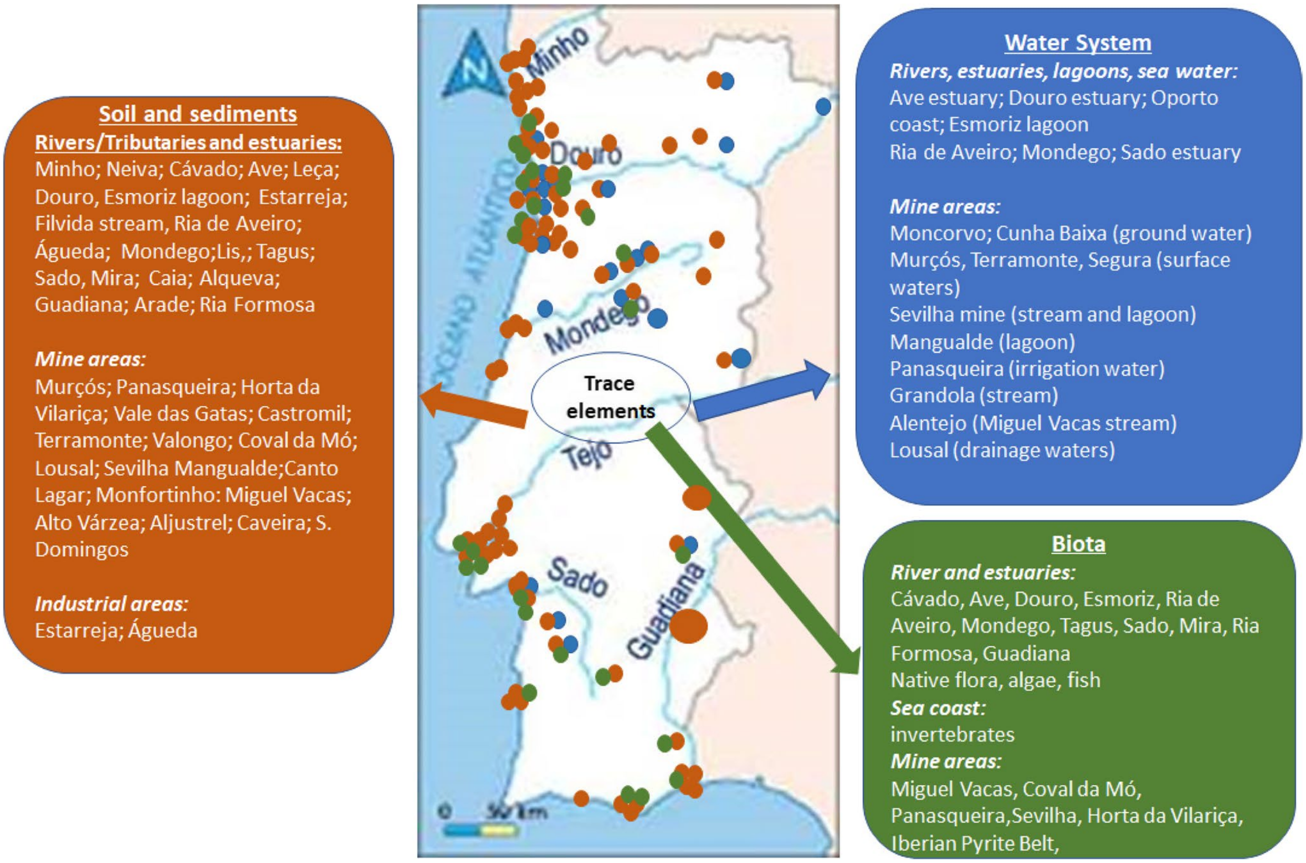
The total number of research regarding matrix type may also represent the scientific priority for environmental trace metals research. For example, there is a larger number of papers reporting trace metals in sediments/soil in contrast to water. This can indicate a shift away from this historically important exposure pathway. In fact, since the launch of the Water Framework Directive, significant efforts were made regarding the release of pollutants in addition to the implementation of WWTPs that contributed to the reduction of water trace element concentrations. Also, water trace elements reflet recent or occasional discharges while sediments and soils are major reservoirs and frequently act as sources of their presence in water bodies (Chon et al. 2012). Therefore, the majority of papers (59%) published in this period focus on sediments while a similar percentage focus either on waters or biota (~20%) (Fig. 4). There are only 8% of the papers with an integrated approach with determinations on water, sediments, and biota. The distribution of trace elements in each type of matrix (water, sediments/soils, and biota) as can be seen in Fig. 5.

Maximum values found and the percentage of papers with values above Aquatic Life limits are summarized in Table 5.

In waters, Zn, Cu, Pb, Cd, and As are among the trace elements most determined and various works reported trace element maximum levels higher than those established by CCME guidelines for aquatic life for Al, Zn, Se, Cu, Pb, Ag Cd, Cr, U, Ni, and As suggesting that adverse biological effects are expected to occur (Table 5, Fig. 5). In sediments, the pattern is similar, Pb, Cu, Zn, Cr, and Cd, and various works reported maximum levels surpassing the corresponding Interim sediment quality guidelines (ISQGs). Among them, As, Cd, Cr, Pb, and Hg rank among the priority metals that are of public health significance ranging from extremely high risk to high risk (Table 5, Fig. 5) (Tchounwou et al. 2012). Thus, adverse biological effects are likely to occur namely due to the presence of high levels of As, Cd, and Pb. The mean concentration of trace elements in surface water sediments is lower than that from mining areas (Table 5), nevertheless, both sediments/soils from surface waters and mining areas indicate that the degree of pollution by these trace elements is severe and deserves attention.

These metallic elements are considered systemic toxicants recognized as multiple organ damage inducers, even at reduced exposure concentrations. They are also classified as human carcinogens (known or probable) according to the US Environmental Protection Agency, and the International Agency for Research on Cancer. Pb, Cr, Zn, As, and Cu exceeded water quality guidelines in some studies (Abreu et al. 2008). A worse scenario is found for sediments with Zn, Cu, As, Pb, and Cr exceeding acceptable values in the majority of the studies (Table 3) (Abreu et al. 2008, Couto et al. 2019, Gonçalves et al. 1992, Ribeiro et al. 2018). Though Al is not among the most studied element, Al values also exceed acceptable values for both water and sediments in some studies.

Hg contamination is also a serious environmental health problem and its complexity in the environment has been systematically examined (Eagles-Smith et al. 2018). Even if Hg is not among the most analyzed elements, its occurrence was investigated in all matrices (Tables 1, 2, and 3). Hg is an element of natural occurrence found in trace amounts in air, water, and soil. Inorganic Hg appears naturally in surface water because of rocks and soil erosion and weathering processes. Hg in surface waters remains inorganic, but in certain environmental conditions, such as acidic pH, high organic matter and low dissolved oxygen, a fraction of it may be in a more toxic organic form, methylHg. MethylHg has a tendency to bioaccumulate, entering the food chain, therefore becoming a human health threat (Eagles-Smith et al. 2018). Hg is one of the most harmful environmental contaminants and therefore mentioned in the high-priority environmental



Soil and sediments

Rivers/Tributaries and estuaries:
Minho; Neiva; Cávado; Ave; Leça; Douro, Esmoriz lagoon; Estarreja; Filvida stream, Ria de Aveiro; Águeda; Mondego;Lis,; Tagus; Sado, Mira; Caia; Alqueva; Guadiana; Arade; Ria Formosa

Mine areas:
Murçós; Panasqueira; Horta da Vilariça; Vale das Gatas; Castromil; Terramonte; Valongo; Coval da Mó; Lousal; Sevilha Mangualde;Canto Lagar; Monfortinho: Miguel Vacas; Alto Várzea; Aljustrel; Caveira; S. Domingos

Industrial areas:
Estarreja; Águeda

Water System

Rivers, estuaries, lagoons, sea water:
Ave estuary; Douro estuary; Oporto coast; Esmoriz lagoon
Ria de Aveiro; Mondego; Sado estuary

Mine areas:
Moncorvo; Cunha Baixa (ground water)
Murçós, Terramonte, Segura (surface waters)
Sevilha mine (stream and lagoon)
Mangualde (lagoon)
Panasqueira (irrigation water)
Grandola (stream)
Alentejo (Miguel Vacas stream)
Lousal (drainage waters)

Biota

River and estuaries:
Cávado, Ave, Douro, Esmoriz, Ria de Aveiro, Mondego, Tagus, Sado, Mira, Ria Formosa, Guadiana
Native flora, algae, fish
Sea coast:
invertebrates
Mine areas:
Miguel Vacas, Coval da Mó, Panasqueira,Sevilha, Horta da Vilariça, Iberian Pyrite Belt,

Fig. 3 Distribution of published works concerning the presence of trace elements on water, sediments/soils, and biota in Portugal, ball marks in blue represent water bodies; in brown sediments/soil samples and green refers to biota

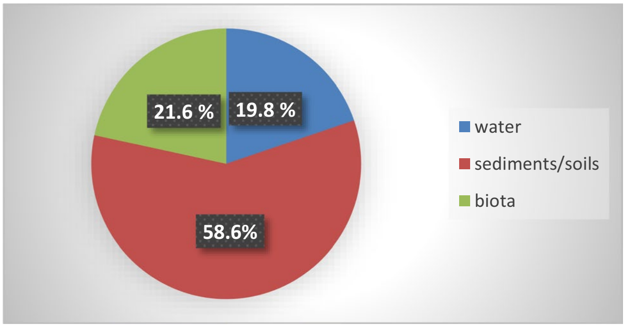


Fig. 4 Distribution percentage of published works regarding the occurrence of trace elements in water, sediments/soils, and biota

pollutants directory within the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Commission 2009), the European Union Water Framework Directive (EU-Directive 2000), and the United States Environmental Protection Agency (U.S. EPA). Hydrodynamic flow patterns have been related to Hg dispersion and pathways in coastal areas, causing harmful effects on biota (Iglesias et al. 2020). Several estuaries show problematic and deep-concerning levels (see boldface levels in Table 3).

Arsenic, usually detected at low concentrations, has a wide distribution in practically all environmental matrices in both inorganic (trivalent arsenite and pentavalent arsenate) and organic forms (methylated metabolites). Environmental As pollution occurs because of natural phenomena such as volcanic eruptions and soil erosion, but also by anthropogenic activities (Mandal 2017, Tchounwou et al. 2012). As water concentration is usually less than 10 µg L^{-1}, although higher levels have been reported near natural mineral deposits or mining sites. Higher values were reported in two Portuguese mining sites, and at Segura, the As water content in December 2006 (1.190 mg L^{-1}) was even higher than in October 2006 (0.636 mg L^{-1}) and was related to the As released from Fe oxy-hydroxide (Antunes and Albuquerque, 2013, Antunes et al. 2018b). Natural levels of As in soil usually range from 1 to 40 µg g^{-1} (Tchounwou et al. 2012) and CCME report values of probable effect levels (PELs) (CCME 2006) of up to 41.6 µg g^{-1} in marine/estuarine sediments and a guideline value of 12 µg g^{-1} in soils. Higher values were reported in several estuarine or stream sediments

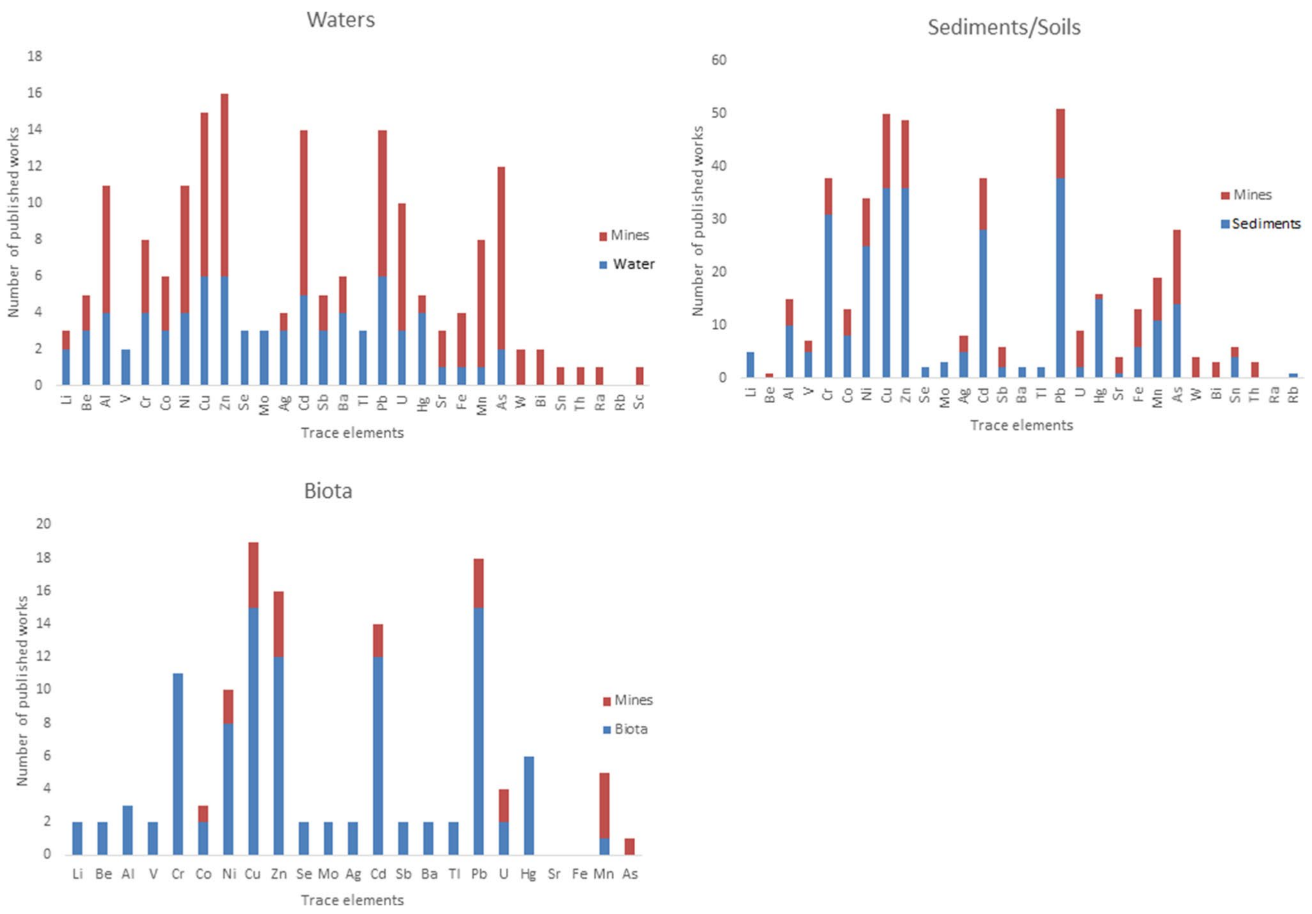


Fig. 5 Distribution of trace elements in each matrix (water, sediments/soils, and biota)

(see boldface values Table 3) in Minho (Mil-Homens et al. 2013), transboundary Douro (Reis et al. 2014), Tagus (Vale et al. 2008), Ria Formosa (Sousa et al. 2019), and Guadiana (Delgado et al. 2011). In mining areas, values of 2000 µg g^{-1} or higher were found in Castromil (values up to 6909 µg g^{-1}) (Silva et al. 2004), Aljustrel (maximum value of 3936 µg g^{-1}) (Candeias et al. 2011) and S. Domingos (Alvarenga et al. 2012), where a value of 7955 µg g^{-1} was reported and As presented high mobilizable contents in all sampled soils, even though its effective bioavailable fraction represented less than 10% of the pseudo-total content.

Cd is broadly disseminated in the earth's crust with a mean concentration of about 0.1 mg kg^{-1}. Cd is commonly used in industry in activities such as the production of alloys, pigments, and batteries (Tchounwou et al. 2012). Cd compounds are considered human carcinogens by various regulatory agencies such as The International Agency for Research on Cancer (IARC) (IARC 1993, 2009) and the US National Toxicology Program; it has also been extensively investigated by United Nations Environment Programs and the International Commission on Occupational Health. US Poison and Disease Registry (ATSDR 1997) rated Cd as the sixth most toxic substance. World Health Organization (Lata and Mishra, 2019) placed cadmium in a priority position in the study of food contaminants. Plants act as a Cd carrier, in different salt chemical water-soluble forms, into the food chain, so Cd polluted vegetable consumption or living close to highly-industrialized places enhance toxicity potential (Lata and Mishra, 2019).

CCME reports values of 0.1 µg L^{-1} for long-term exposure in freshwaters and 4.2 µg g^{-1} of PEL in marine/estuarine soils and a guideline value of 1.4 µg g^{-1} in agricultural soils (CCME 2006). Values superior to 19.5 µg g^{-1} were reported in Cávado (Gonçalves et al. 1994) and in Mondego (Dias-Ferreira et al. 2016) estuarine sediments. Waters in mining areas with values above CCME guideline were reported in three of the mines studied (Antunes et al. 2007, Candeias et al. 2014, Favas et al. 2016) and in Ave estuary, where 80% of the samples collected exceeded this limit (Couto et al. 2019).

Cr is naturally present in the earth's crust, with oxidation states (II) to (VI). Cr compounds are stable in the trivalent form and occur in nature in this state in minerals. Cr reaches different environmental matrices (air, water, and soil) from various natural and anthropogenic sources with the greatest contribution coming from industries (Tchounwou et al.

Table 5 Maximum trace element values and respective Aquatic Life limits (water and sediments)

Element	Higher water values found (nature/mine) (µg L^{-1})	Freshwater long-term Water Quality Guidelines for the Protection of Aquatic Life (CCME 2021) (µg L^{-1})	% papers above limits	Higher sediments found (nature/mine) (µg g^{-1})	Sediment Quality Guidelines for the Protection of Aquatic Life (CCME 2021) ISQG/ PEL (µg g^{-1})	% papers above limits	Potential ecological risk
Al	2384 (Ave) 9070 (Cunha Baixa Mine)	100	75% (3/4) 14% (2/7)				
Hg	0.08 (Sado) --	0.026	25% (1/4) 0% (0/1)	67 (Tagus) 100 (Grândola)	0.170–0.486	56% (9/16) 100% (1/1)	Extremely high risk Extremely high risk
Cr	3.1 (Douro) 29.7 (Sevilha Mine)	1**	50% (2/4) 50% (2/4)	2210 (Cávado) 464 (Monfortinho)	37.3–90 (total)	50% (16/32) 14% (1/7)	High risk Low risk
Ni	--- 77.4 (Sevilha Mine)	25*	0% (0/4) 14% (1/7)				
Cu	24.7 (Ave) 1480 (Miguel Vacas Mine)	2*	50% (3/6) 63% (5/8)	12628 (Águeda) 5414 (Aljustrel)	35.7–197	46% (17/37) 50% (7/14)	Extremely high risk Extremely high risk
Zn	264 (Esmoriz) 680 (Cunha Baixa Mine)	7*	67% (4/6) 67% (6/9)	10150 (Águeda) 20000 (Aljustrel)	123–315	46% (17/37) 50% (7/14)	Very high risk Extremely high risk
As	25.7 (Douro) 1190 (Segura Mine)	5	50% (1/2) 70% (7/10)	1022 (Tagus) 7955 (S.Domingos)	5.9–17	54% (7/13) 57% (8/14)	Extremely high risk Extremely high risk
Se	34.6 (Ave) --	1	100% (3/3) ----				
Mo		73	0% (0/3) ---				
Ag	0.8 (Douro)	0.25	100% (3/3) 0% (0/1)				
Cd	0.66 (Ave) 9 (Cunha Baixa Mine)	0.10*	40% (2/5) 43% (3/7)	32 (Cávado) 61.6 (Aljustrel)	0.6–3.5	37% (11/30) 60% (6/10)	Extremely high risk Extremely high risk
Tl	1.23 (Douro) ---	0.8	33% (1/3) ----				
Pb	18 (Esmoriz) 50.7 (Alto Varzea Mine)	1*	50% (3/6) 50% (4/8)	3100 (Cávado) 26975 (S.Domingos)	35–91.3	41% (16/39) 54% (7/13)	Extremely high risk Extremely high risk
U	-- 1842 (Cunha Baixa Mine)	15	--- (0/3) 33% (2/6)				

*Assuming water hardness<60 mg/L and DOC 0.5 ppm; Cr (VI)

2012). Hexavalent Cr, a powerful oxidizing agent, is a toxic industrial pollutant classified as a human carcinogen by several regulatory and non-regulatory agencies such as ATSDR, IARC, and EPA (ATSDR 2012, EPA 1992, IARC 1990). CCME reports a guideline value for the protection of aquatic life of 1 µg L^{-1} for freshwater and ISQGs and PELs of 52.3 and 160 µg g^{-1}. A very high value (1187 µg g^{-1}) in the Selho river (Ave tributary) was reported and reflected the wastewater discharged from the leather tanning industries located in Guimarães city (Gonçalves et al. 1992). This

Ave tributary presented very high metallic levels related to industrial activities and probably illegal industrial wastewater discharges without prior treatment.

Pb is present in trace amounts in the earth's crust. Pb is the second most toxic metal after As because of its toxic effects on living organisms (ATSDR 2016). Although Pb occurs naturally in the environment, anthropogenic activities such as fossil fuel burning, mining, and manufacturing contribute to its release in elevated concentrations. Pb has many different industrial (batteries, ammunition, metal products), agricultural and domestic applications (Tchounwou et al. 2012). It is considered by the IARC as a probable human carcinogen. CCME ISQGs and PELs for Pb are 30.2 and 112 μg g^{-1} respectively; these values were exceeded in several places in the literature cited in this review (boldface in Table 3).

Remediation and risk management

Human activities such as agricultural production, urban expansion, industrial activities, and mining have been pointed out as the main contributors of trace elements input into the environment in the last years. Trace elements pollution remediation is difficult mostly because of their persistence and non-biodegradability in the environment. Additionally, as a sink and source, soils and sediments represent a repository of bioavailable heavy metals/trace elements and take part in the returning of contaminants into circulation in the aquatic environment depending on favorable situations. Therefore, sediment chemistry provides valuable information essential to assessing sediment quality in contaminated sites and potentially harmful effects (Sarkar et al. 2014). Hence, the improvement/implementation of tools for their successful and effective environmental removal and well as protection policies are needed to diminish their contamination potential and production, respectively.

There are several techniques that can be used, depending on the concentration and nature of the contaminant, the soil and site characteristics, the contaminant's availability, and the existence of specific regulations. The remediation can be performed by the containment/isolation of the contaminated matrices or soils, by using constructive techniques/physical treatments; the immobilization/stabilization of the contaminants in the contaminated material (soils or tailings); or by extraction/removal of the contaminants from the soil (Liu et al. 2018, Song et al. 2021, Wang et al. 2021). The technique used is always site-specific, and, often, it combines different strategies. *In* or *ex situ* remediation techniques for contaminated sites targeting specifically the contaminants can be used (Liu et al. 2018). The techniques can be further classified as physical (e.g., soil washing, electrokinetic), chemical (e.g., chemical addition to the soil to react and immobilize the contaminants), or biological (e.g., plants and/or microorganisms to degrade, immobilize or extract the contaminant). In mining areas (Lousal, Aljustrel, and S.Domingos) constructive techniques were widely applied in the rehabilitation of soil (excavation, storage, and capping) (Mourinha et al. 2022). In Aljustrel, for instance, the dispersed slag deposits, mining residues, and contaminated soils were removed and confined, and the deposits were sealed with limestone and clay and covered with clean clay soil and vegetation. Channels were constructed on the perimeter to collect drainage waters, conducted to evaporation-concentration ponds, and processed in artificial wetlands to protect the hydrological environment (Mourinha et al. 2022).

In contrast to the conventional physical and chemical techniques for soil remediation, phytoremediation is a plant-based and cost-effective technology that has been pointed out as an alternative or complementary strategy to constructive techniques. The main phytoremediation mechanisms are based on phytostabilization (immobilization of pollutants in the rhizosphere by the action of roots, bacteria, and soil amendments); phytoextraction (plant aerial part uptake and accumulation); phytostimulation (degradation in the rhizosphere by microorganisms, stimulated by the plant's exudates); phytodegradation (plant enzymes degradation within the plant tissues); phytovolatilization (conversion to volatile forms and atmospheric release), phytodesalinization (salt removal in saline soils with halophytes), and rhizofiltration (removal of contaminants from polluted aquatic environments).

In the cited data phytoremediation is the most used approach and various species have been used including native plants. In fact, phytoremediation was developed as a sustainable alternative to chemical and physical pollution remediation approaches but is less expensive and environmentally friendly. One study carried out in Ria Formosa showed that *Spartina maritima* and *S. fruticosa* acted as Ag, Cd, Mo, Cu, Pb, and Zn remediators, altering the sediment metal distribution in depth and accumulating them, mostly in roots (and in rhizomes for *S. maritima*). Metal translocation to aerial organs was found residual. *S. maritima* proved to be a more effective metal stabilizer than *S. fruticosa* (Moreira da Silva et al. 2015). Another study compared *Scirpus maritimus* and *Juncus maritimus* from Douro salt marshes in the bioaccumulation of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. Both plants affected the sediment composition and revealed the potential for Cd phytostabilization. *S. maritimus* could also concentrate Pb in its roots (Almeida et al. 2006). Various studies showed *Brassica juncea*, *Medicago sativa*, *Echinophora platyloba*, *Chara aculeolata* to be Pb hyperaccumulators (Zulfiqar et al. 2019). Durães et al. (2015) compared the capability to uptake, translocate and tolerate Cu, Zn, and Pb by macrophytes (*Juncus effusus L., Scirpus holoschoenus L., Thypha latifolia L.*, and *Juncus* sp.) and land plants (*Cistus ladanifer L., Erica andevalensis C.-R., Nerium oleander L., Isatis tinctoria L., Rosmarinus officinalis L., Cynodon dactylon L.* and *Hordeum murinum L.*) from Aljustrel, Lousal and São Domingos mining sites and Morocco (Tighza and Zeida) and concluded that the aquatic plants showed a higher capacity for Zn bioaccumulation and translocation with the metal mobility sequence Zn>Cu>Pb. Another study highlighted the uranium concentrations in water–soil–plant matrices and the efficiency, taking into account a heterogeneous assemblage of terrestrial and aquatic native plant species to act as biomonitor and phytoremediator for environmental U-contamination in the Sevilha mine (Favas et al. 2016). In that study, a total of 53 plant species belonging to 22 families were collected from 24 sampling sites. The maximum potential of U accumulation was recorded in roots of *Juncus squarrosus* (450 mg kg^{-1}), *Carlina corymbosa* (181 mg kg^{-1}), *Juncus bufonius* (39.9 mg kg^{-1}), *Callitriche stagnalis* (55.6 mg kg^{-1}), *Lemna minor* (53.0 mg kg^{-1}), and *Riccia fluitans* (50.6 mg kg^{-1}) confirming the unique efficiency of roots in accumulating this element from soil or sediments (phytostabilization) (Favas et al. 2016). U accumulation by *Scorpiurium deflexifolium*, *Fontinalis antipyretica*, *Nasturtium officinale* (roots), *Oenanthe crocata* (rhizomes/ roots), and *Rorippa sylvestris* (aerial parts) was also demonstrated and showed a consistent higher trend of its concentration in the majority of the plants in comparison to water (Cordeiro et al. 2016). The perennial herb *Rorippa sylvestris* (creeping yellowcress) had significantly higher U concentration in the shoots compared to roots, with translocation factor (TF) 700 times higher than unity, acting as a possible phytoextractor. The process of natural attenuation of contamination by phytostabilization of U in the rhizosphere, with the contribution of the native plant community offered an cost-effective and technical benefit, and this study could contribute to improve U-contaminated areas using the studied plant species in future environmental projects (Cordeiro et al. 2016). However, phytoremediation as also some drawbacks (Farraji et al. 2016) The extensive treatment period makes it only suited for remote areas, and the trace elements accumulated in biomass may lead to secondary pollution. Also, this process does not degrade the trace elements, but decreases the compound's ability to migrate to soil and water. It is also possible that if flora is consumed by wildlife, these pollutants could enter the food chain. However, various complementary processes and methods can be used to enhance phytoremediation efficiency and overcome its present disadvantages. Phytoremediation can also be operated at large scales and contribute to the conservation of soil and ecosystem structure, prevention of erosion and leaching of metal. Furthermore, phytoremediation in degraded areas can offer more habitats for wildlife.

Nevertheless, the overexploitation of natural resources leads to their depletion and negative ecological impact affecting not only all living organisms' health but also economic growth. Therefore, governments and policymakers should implement measures for better management and sustainable production as well as strategies for the reduction and release of these contaminants to the environment, promoting sustainable use and consumption.

Conclusions

Trace elements are ubiquitous environmental pollutants in aquatic and terrestrial ecosystems and have been considered a severe environmental problem. The potential hazard of an environmental chemical is a function of various factors including its persistence, toxicity, and bio/accumulative potential. Due to these three main characteristics trace elements are considered hazardous. Most hazardous trace elements environmentally relevant include Cr, Zn, Cd, Pb, Hg, and As. The trophic transfer of these elements in aquatic and terrestrial food chains/webs has important implications for both wildlife and human health. Reviewed data on surface waters showed that Al, Zn, Se, and Ag were above aquatic life limits in 60% of the published works. Cu, Zn, and As exceed aquatic life limits in more than 60% of mining waters. Hg and Cd in sediments from mining areas exceeded aquatic life limits and potential ecological risk showed extremely high risk for most of the elements. According to a potential ecological risk assessment, an extremely high risk was detected for Hg, Cu, As, Cd, and Pb. Therefore, it is crucial to continue to monitor the concentrations of trace elements in different environmental matrices for environmental protection works, management and mitigation measures. Furthermore, the establishment of environmental background concentrations of trace elements should be documented in the different environmental matrices and specific research area for later use as reference and to allow an accurate environmental risk assessment.

Data availability Applicable

Author contribution All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Cristina Couto and Cláudia Ribeiro. The first draft of the manuscript was written by Cristina Couto and Cláudia Ribeiro and both authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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