Review

Trace Metal Contamination of Bottom Sediments: A Review of Assessment Measures and Geochemical Background Determination Methods

Nicole Nawrot [1,*] 🔾, **Ewa Wojciechowska** [1] 🔾, **Muhammad Mohsin** [2] 🔾, **Suvi Kuittinen** [2], **Ari Pappinen** [2] and **Shahabaldin Rezania** [3] 🔾

1   Faculty of Civil and Environmental Engineering, Gdańsk University of Technology, 80-233 Gdansk, Poland; esien@pg.edu.pl
2   School of Forest Sciences, University of Eastern Finland, Yliopistokatu 7, P.O. Box 111, 80100 Joensuu, Finland; muham@uef.fi (M.M.); suvi.kuittinen@uef.fi (S.K.); ari.pappinen@uef.fi (A.P.)
3   Department of Environment and Energy, Sejong University, Seoul 05006, Korea; shahab.rezania@sejong.ac.kr
*   Correspondence: nicnawro@pg.edu.pl

Abstract: This paper provides an overview of different methods of assessing the trace metal (TM) contamination status of sediments affected by anthropogenic interference. The geochemical background determination methods are also described. A total of 25 papers covering rivers, lakes, and retention tanks sediments in areas subjected to anthropogenic pressure from the last three years (2019, 2020, and 2021) were analysed to support our examination of the assessment measures. Geochemical and ecotoxicological classifications are presented that may prove useful for sediment evaluation. Among the geochemical indices, several individual pollution indices (*CF*, *Igeo*, *EF*, *Pi* (*SPI*), PT_T), complex pollution indices (*PLI*, *Cdeg*, *mCdeg*, Pi_{sum}, PI_{Avg}, PI_{aAvg}, *PIN*, PI_{Prod}, PI_{apProd}, $PI_{vectorM}$, $PI_{Nemerow}$, *IntPI*, *MPI*), and geochemical classifications are compared. The ecotoxicological assessment includes an overview of Sediment Quality Guidelines (SQG) and classifications introduced nationally (as LAWA or modified LAWA). The ecotoxicological indices presented in this review cover individual (ER^i) and complex indices (*CSI*, *SPI*, *RAC*, *PERI*, *MERMQ*). Biomonitoring of contaminated sites based on plant bioindicators is extensively explored as an indirect method for evaluating pollution sites. The most commonly used indices in the reviewed papers were *Igeo*, *EF*, and CF. Many authors referred to ecotoxicological assessment via *SQG*. Moreover, *PERI*, which includes the toxic response index, was just as popular. The most recognised bioindicators include the *Phragmites* and *Salix* species. *Phragmites* can be considered for Fe, Cu, Cd, and Ni bioindication in sites, while *Salix* hybrid cultivars such as Klara may be considered for phytostabilisation and rhizofiltration due to higher Cu, Zn, and Ni accumulation in roots. *Vetiveria zizanoides* demonstrated resistance to As stress and feasibility for the remediation of As. Moreover, bioindicators offer a feasible tool for recovering valuable elements for the development of a circular economy (e.g., rare earth elements).

Keywords: sediments; trace metals; contamination assessment; pollution indices; bioindicators; geochemical background

1. Introduction

Nowadays, the contamination of sediments with trace metals (TMs) is a salient environmental issue [1,2]. TMs delivered to the environment from anthropogenic sources are mostly represented by these elements: Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sn, V, and Zn. Supplementation from external sources also includes other potentially toxic elements (PTEs) such as metalloids (As, Sb) and non-metals (Se) [3]. PTEs are not biodegradable, persistent, and can accumulate in the environment in large amounts. TM ions cause health hazards; just to mention a few, these include emphysema (Cd), anaemia (Cd, Zn, Pb), damage to the brain (Pb), kidneys, and bones (Cd), necrosis nephritis (Cr), DNA damage

(Ni), eczema on the hands (Ni), risk of developing cancer (As), central nervous system irritation (Cu), and even death in humans [4]. Due to the toxic nature of PTEs, there is an obvious need to monitor their content. The most significant anthropogenic sources of PTEs are related to industry, urbanisation, transportation, agriculture, and mines [5–8] TMs adhered to particulate matter (PM; including PM10 and PM2.5) could be released into the surrounding environment causing contamination of soils, groundwaters, sediments, and surface waters. PTEs entering the aquatic ecosystem are associated with fine-grained fractions of suspended solids and sediments due to their large surface areas and high sorption capacities [9]. Throughout the hydrological cycle, 99% of PTEs are stored in sediments, which, therefore, act as the main sinks and carriers for contaminants in aquatic environments [10]. Contemporary studies [11–18] have revealed that stormwater run-off carried metals originating from various sources of everyday use associated with tyre wear, corrosion, roof run-off, and fuel combustion products. Zn, Pb, Cu, Cd, Ni, Ce, and As are typically observed in urban and industrial catchments [11,12].

Sediments are the ultimate repository for contaminants and provide valuable information about the environmental status of a catchment area [17]. According to USEPA [19], sediment site management and silting processes in reservoirs present a unique challenge because of the large number of difficult to control contaminant sources, dynamic phenomena influencing movement and sediment stability, dispersion of contaminants, diversified use of areas affecting the sediment environment, as well as difficulties involved in engineering cleanup works.

Sediment contamination may be evaluated in several ways. Geochemical, ecotoxicological, and bioindicator-related approaches can be distinguished. Extensive evaluation includes geochemical and ecotoxicological methods. The geochemical assessment relies on comparing TMs at particular sites to the geochemical background or baseline. The term "geochemical background" (or "natural background") has evolved. In exploration geochemistry, it refers to the non-anomalous concentration of elements in the rocks surrounding the mineral ore body. In environmental sciences, it is used to detect anthropogenic impact on the environment [20]. Establishing the geochemical background raises research concerns because it may determine the overall pollution status of an examined site. Ecotoxicological approaches are based on assessing the effects of metal toxicity on living organisms and determining certain dose limits. Bioindication is an indirect method of verifying the quality of the environment—i.e., by using aquatic plants and hydrophytes able to accumulate a large number of metals, making them suitable for environmental biomonitoring. The distribution and behaviour of aquatic plants are frequently correlated with water and sediment quality [21]. Macrophytes are able to accumulate pollutants at a higher level, irrespective of their content in the surrounding environment [22]. Moreover, the analyses of plant tissues provide time-integrated information about the quality of an examined site, even if contaminant inputs are discontinuous and quickly diluted in water [23]. One of the species widely recognised as featuring correlations between concentration of metals in sediment/soil and roots is *Phragmites australis* [15]. Hydrophytes uptake PTEs through their roots and rhizomes, stems, and leaves [24]. Plant species with a strong ability to accumulate TMs in the aboveground tissues are good candidates for phytoextraction [25].

The most simple way to evaluate TM contamination of sediments is based on total metal content. This approach reflects the geological origin and anthropogenic influence, although it is ineffective in terms of documenting mobility or bioavailability [26]. According to Ure and Davidson [27], a more accurate method taking into account these two features is to measure the "pseudo total" metal content in sediments. Pseudo total content presents the maximum potential soluble or mobile metal content, which can be identified with maximum potential hazard. Sequential extraction (or fractionation) distinguishes several factions—mobile, conditionally mobile, and immobile (depending on the applied method). Therefore, using this approach, potential metal contamination hazards can be more accurately assessed and explored. Combining fractionation with different contamination

assessment approaches (geochemical and ecotoxicological) may also offer valuable insight into sediment quality.

Sediment contamination is a well-known problem across the world; however, monitoring programs based on different PTE contamination assessment methods as well as bioindicators have to be implemented to ensure that the assessment is credible and reliable. Various studies use different approaches to evaluate the quality of sediments, which impairs the comparison of results from diverse studies. Even the definition of background values, which is a fundamental step in geochemical assessment, is often controversial. Therefore, there are four aims of this review: (1) to summarise the levels of TM content and methods used to evaluate the contamination status of bottom sediments related to surface run-off receivers from the last 3 years, (2) to assemble and critically evaluate the geochemical and ecotoxicological classifications and contamination indices used to evaluate the PTE-polluted sediment and the subsequent risk, (3) to explain the difference between geochemical background and baseline; and (4) to specify the bioindicators of TMs that have been extensively researched at different sites across the world.

2. Materials and Methods

A literature review was conducted via the Web of Science platform. In order to access a complete spectrum of data on PTEs in the bottom sediments of urban water bodies, 5 specific keywords were chosen: sediments, trace metals, contamination, pollution indices, and urban. The Web of Science Core Collection displayed a total of 519 papers, which are available in the database (starting from the year 1994). From the last 3 years (2019, 2020, 2021), there are 202 publications in total, and a further 145 results in the field of environmental science (as of May 2021). We used 25 of the latest publications from the last 3 years (2019, 2020, and 2021). To explore the last 10 years of updates regarding bioindication species, the search process was based on the following keywords: plant bioindicators, metal indicator, *Salix* or *Willow* as bioindicator, phytoextraction, and bioindicator.

3. PTEs in Bottom Sediments of Urban Water Bodies

Based on 25 of the latest publications [28–52] on the topic of bottom sediments in urban waterbodies, Table A1 in Appendix A presents (1) a list of TMs evaluated under each study, (2) their concentration ranges (in mg/kg d.w.), (3) a basic description of the site and land use, (4) indices, classifications, and an evaluation of TM bioavailability with the use of metal fractionation.

In most of the examined papers, the authors focused on five TMs: Cu, Zn, Pb, Ni, Cr, and a metalloid: As. All of the mentioned elements can be delivered by anthropogenic activities such as metalliferous mining, smelters, metallurgy, rolling, electronic, industry, the dye and paint industry, metal corrosion of materials, plastic industry, chemical industry, combustion of fossil fuels, wood industry, as well as tyre wear and lubricant oils [6]. The scope of analyses in many studies also included Fe, Mn, Co, Hg, as well as rare earth elements, i.e., La and Sc.

Most authors sampled the surface layer of sediments (0–2 cm, 0–5 cm, or 0–10 cm), where reactions occur at the water–sediment interface and where living organisms dwell. The sampling strategy is crucial for the successful collection of sediment samples with undisturbed stratification. With this aim, a grab sampler (for surface sediment extraction), hand (core extraction < 60 cm) and box corer (core extraction < 1 m) devices, or a multiple corer can be used to obtain proper samples. Sediment samples are collected to describe the condition of the sites. The specific reasons for sediment sampling include bioassays (the top 10 cm are usually collected because of biological activities), biosurvey (macroinvertebrate analyses), monitoring, examining non-point pollution, and pollutant sources. Monitoring trends and relationships in sediments requires information on current PTE burden in the uppermost sediment layer (e.g., 0–1 cm). Depending on the receiver (large/small body of water, river, stream, bay), the rate of deposition varies, which means that 1 cm of sediment builds up over different times. Therefore, the EU [53] has recommended sampling the

top layer of sediment at a depth of 1–5 cm; however, this depends on the deposition rate. This is also in line with data from the United States, which stated that more than 10% of the volume of bottom sediments (the upper 5 cm of surface sediments) are estimated to have been contaminated. The depth to which sediments are sampled should be one of the key monitoring objectives. Core sample collection is crucial for evaluating the PTE footprint. Sediments from depths greater than 15 cm below the sediment–water interface are usually collected to determine the spatial vertical properties and sedimentation history. Each sampling program requires a compromise between the number of samples, sampling frequency, measurement parameters, and cost effectiveness [54].

The most frequently used indices were Geoaccumulation Index (*Igeo*) (17 studies), Enrichment Factor (*EF*) (13 studies), Contamination Factor (*CF*) (10 studies), Pollution Load Index (*PLI*) (6 studies), Metallic Pollution Index (*MPI*) and Modified Contamination Degree (*mCd*) (each used in 3 studies), Nemerow Pollution Index (*PI$_{Nemerow}$*) (2 studies), *MRI* and Pollution Index (*PI*) (each used in 1 study). Two studies undertook a sediment assessment using the German classification LAWA, while one study refers to Romanian legislation. Reference to the ecotoxicological assessment via Sediment Quality Guidelines (SQG) was carried out in eight studies, while Ecological Risk Index (*Er^i*), Risk Index (*RI*), and Potential Ecological Risk Index (*PERI*) (which account for metal toxicity) were used in 17 studies. Moreover, only two studies assessed health risk. Three papers considered the use of chemical sequential extraction for element analyses, which is important to assess the bioavailability and mobility of TMs. Only one study included a Risk Assessment Code (*RAC*) analysis, which takes into account the risk determination based on the metal binding to the exchangeable and carbonate fraction. Health risk—as Hazard Index (*HI*) and Hazard Quotient (*HQ*)—was calculated in two papers. The common use of indices enables the results to be compared between various studies. However, calculations of geochemical indices are strongly dependent on the adopted reference value (geochemical background).

Another important issue, addressed in three studies, is the fractionation analysis of TMs. Fractionation allows the environmental behaviour of trace elements to be assessed [55]. However, the procedure itself is highly labor-intensive and cost-prohibitive. Most works are based on assessing the total metal content of the samples; nevertheless, fractionation is an indispensable method when it comes to exploring the actual metal bioavailability and mobility.

The above characteristic offers an overview of the most often used indices for geochemical and ecotoxicological evaluation of sediments. The next part of this review presents a "conventional" division of tools for assessment of sediment quality, taking into account geochemical and ecotoxicological approaches.

4. Assessment Techniques for Sediments Contaminated with HMs

The most effective approach in assessing sediment contamination with PTEs relies on the use of several assessment tools that can be grouped according to geochemical and ecotoxicological evaluation, as shown in Figure 1. Another method for indirect assessment of TM sediment contamination is the use of bioindicators.

Geochemical evaluation is usually based on pollution indices (PIs), while geochemical classifications are usually implemented by national governments. Both approaches rely on the establishment of a geochemical background. Among ecotoxicological methods, descriptive classifications (usually based on the ecotoxicological effect on benthic organisms—Sediment Quality Guidelines (SQG) as well as those based on toxicological, chemical, and ecological tests) and ecotoxicological indices (EIs) are used. Since the preference for adopting a sediment assessment method is usually on the side of the lawmakers, many classification and indices have been introduced since 1980.
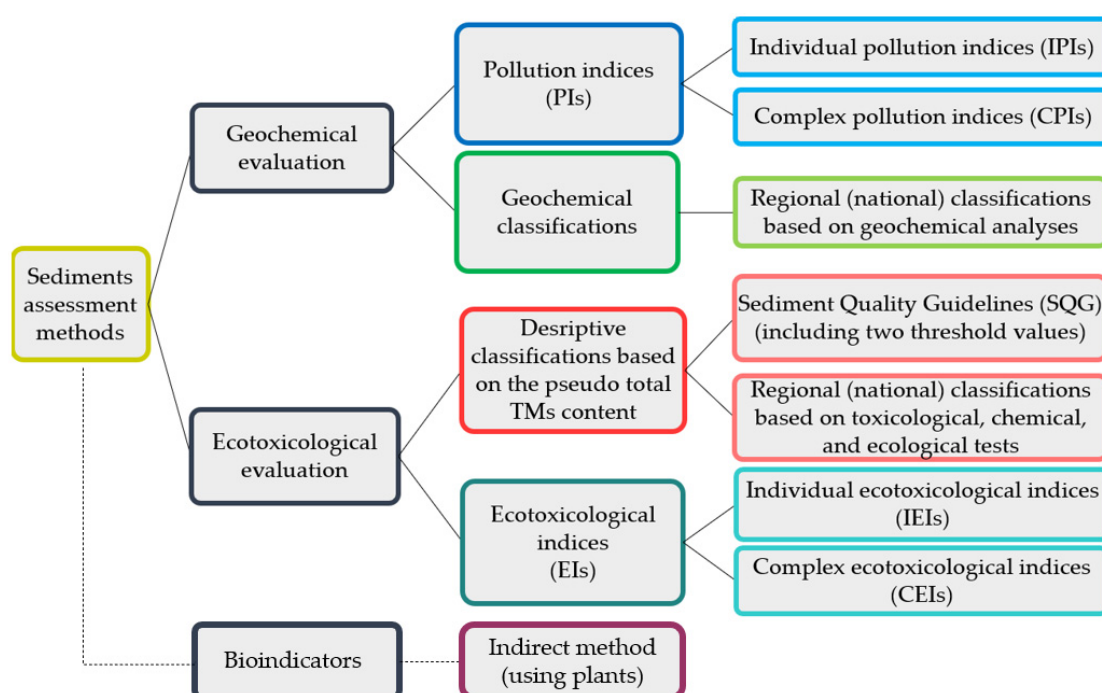
Figure 1. Division of the methods of assessment of sediment contamination with PTEs.

4.1. Geochemical Evaluation

4.1.1. Geochemical Background and Geochemical Baseline

There are two controversial issues within contemporary geochemistry and environmental biochemistry: the geochemical background and the geochemical baseline of an element or chemical compound. The geochemical baseline is easier to determine—it is commonly used for assessing the environmental status before embarking on a specific investment (e.g., constructing a power plants). In exploratory geochemistry, geochemical background means the natural concentration of an element in the environment, i.e., a non-anomalous concentration of elements that corresponds to Clarke's characteristic for their geochemical environment [20]. There are several methods to determine the accurate geochemical background. Once this value is determined, the pollution status can more precisely be assessed. These methods rely on statistical (indirect, theoretical) and empirical (direct, geochemical) determinations. An integrated approach combining both methods is also in use. Geochemical methods involve analysing samples unaffected by anthropogenic activities, which are also referred to as preindustrial samples. Usually, deep core samples and/or samples collected at a certain distance from pollution sources are used to establish geochemical background values. Statistical methods involve a determination and elimination of outliers, which are identified by standard deviation, regression analysis, or by using the Tukey boxplot method [56].

The geochemical background is not a constant value over time due to natural processes taking place at the interface of water and sediment. Additionally, the geochemical background value is local or regional rather than global. The adopted geochemical background affects the overall assessment environment quality. Sometimes, the reference level follows the shale standard (from 1961), i.e., the average content of elements in the earth's crust [57], although this approach is incorrect.

4.1.2. Pollution Indices

According to Weissmannová and Pavlovský [6], pollution indices (PIs) can be divided into two categories including Individual (single) PIs (IPIs) and Complex (total) PIs (CPIs). In such a division, IPIs are calculated based on the contents of each metal separately in particular sediments. IPIs can be used to classify sediments into several classes according

to the degree of pollution presented by a single metal. CPIs are calculated as multielement indices based on IPIs. Moreover, CPIs can be composed of IPIs separately. PIs are of most use when they meet several criteria: (1) they are easy to calculate, (2) they make reference to the geochemical background, and (3) they are widely used, which makes it possible to compare sediments from different sites.

Individual Pollution Indices (IPIs)

The IPIs used for sediment assessment are presented in Table A2 in Appendix B. In this group, five indices were identified: Contamination Factor (*CF*) [58], Geoaccumulation Index (*I_{geo}*) [59], Enrichment Factor (*EF*) [60], Pollution Index (*P_i*) [15,54], and Threshold Pollution Index (*PI_T*) [28]. Each of these indices compares the concentration of a given metal in a sample (*$C_{mSample}$*) to its comparative concentration—represented by *C_{mPre}* (preindustrial concentration of TM) or *$C_{mBackground}$* (geochemical background concentration of TM) [40,58,61–64].

CF is originally defined as a ratio of mean TM content averaged from at least five samples (*$C_{mSample}$*) and metal concentration in preindustrial sediments [58,61,62]. According to Dung et al. [20] the ratio can also refer to background TM content. This approach is included in *P_i*. However, usually both indices (*CF* and *P_i*) are treated by authors interchangeably. The difference lies in the classification of the contamination levels; it also depends on whether the values of *C_{mPre}* and *$C_{mBackground}$* are consistent with each other. *CF* and *P_i* are easy to calculate, although both omit natural variability, grain-size, and reference elements ratios. Moreover, they do not take into account metal fractionation even though the formulas of the equations themselves make it possible.

I_{geo} proposed by Müller [59] is a commonly used index, which uses a completely different approach from other IPIs, since it defines seven classes of TM sediment contamination. The TM content in a sample is referred to as *$C_{mBackground}$*. The formula includes a constant value of 1.5, which is used to offset the natural TM fluctuations in the environment and detect minor anthropogenic impact [6].

EF is an effective tool for TM content comparison [13]. In comparison to other IPIs, *EF* requires the most extensive data input, such as geochemical background concentration of TM (*$C_{mBackground}$*) and reference element concentration in a sample (*C_{ref}*) as well as in the reference environment (*B_{ref}*). The reference element has a low occurrence variability. The reference element—and this could be Sc, Mn, Ti, Al, Fe, and Ca—has a low occurrence variability. Frequently used reference metals are Mn, Al, and Fe [12]. Usually, Fe has a relatively high natural concentration in comparison to other metals and is therefore not expected to be enriched from anthropogenic sources [64]. The use of *EF* seeks to reduce the metal variability associated with the granulometric composition (mud/sand ratios). The *EF* could be also expressed as a percentage.

PI_T is based on the single Pollution Index (*P_i*), which refers the TM content in a sample to the tolerance levels of metal concentration (*C_{TL}*). *C_{TL}* could be established by national guidelines or criteria regarding health-threatening TM content [63]. The determination of the threshold parameter (*C_{TL}*) is freeform and can be adjusted to the state of the environment and defined individually by national regulations. Therefore, this index may be an effective tool in the hands of environmental managers.

All of the described IPIs omit the metal fractionation and mobility/bioavailability. IPIs are usually calculated in accordance with total metal content; however, they can be easily applied in calculations that include fractionation (as described in Section 4.3).

Complex Pollution Indices (CPIs)

A list of CPIs is presented in Appendix C. CPIs mostly rely on *CF* or *P_i* values for TMs under analysis. Thus, the starting point for a comprehensive metal contamination assessment is IPI analysis. Table A3 in Appendix C presents calculation formulas with classifications and descriptions (pros and cons considered by the authors) for the following CPIs: Pollution Load Index (*PLI*) [62], Contamination Degree (*C_{Deg}*) [58], Modified Con-

tamination Degree (mC_{Deg}) [64], Sum of Pollution index (PI_{sum}) [63], Average of Pollution Index (PI_{Avg}) [63], Weighted average of Pollution Index (PI_{wAvg}) [58,59,63], Background Enrichment Factor = New Pollution Index (PIN) [65], Product of Pollution Index (PI_{Prod}) [63], Weighted power product of Pollution Index (PI_{wpProd}) [63], Vector modulus of Pollution Index ($PI_{vectorM}$) [63], Nemerow Pollution Index ($PI_{Nemerow}$) [66], Integrated Pollution Index ($IntPI$) [67], and Metallic Pollution Index (MPI) [68,69].

PLI is a very easy-to-use index based on CF values specified for a selected number of metals. Moreover, the deterioration of site quality could be straightforwardly specified because the unity value of PLI (PLI = 1) is the boundary differentiating the adverse impact on the quality of sediments from non-polluted sites [62]. The overarching merit is a comprehensive assessment of sediments, while the disadvantages are related to the shortcomings of the CF index.

C_{Deg} and mC_{Deg} are also based on CF values for analysed TMs. The difference lies in the classification of sediment contamination status. C_{Deg} defines sediment contamination referring to four categories, while mC_{Deg} distinguishes seven ranges of sediment quality [58,64].

The equations for calculating PI_{sum} and PI_{Avg} are similar to those for C_{Deg} and mC_{Deg}. The difference lies in the use of individual Pi ($Pi = SPI = PI$) factors related to $C_{mBackground}$ (not to C_{mPre}) [63]. In order to evaluate the sediments with PI_{sum}, it is necessary to specify the classification scale for each individual case. The defined scale should refer to the number of selected TMs used to assess contamination. The pollution evaluation with PI_{Avg} is easy to apply due to the reference to unity (1). PI_{wAvg} application when the TM weight is equal to unity ($w_i = 1$) is a special form of PI_{sum}.

PIN is based on Pi ($Pi = SPI = PI$) and requires the TM class to be determined (from 1 to 5 in reference to Pi). This very precise scale classifies sediments into five categories [68].

PI_{Prod} is a Cartesian product of Pi applied for a selected number of metals. The classification should be powered by n (count of TMs) to determine the contamination of sediments [63]. PI_{wpProd} uses the weight of Pi in an equation, which is similar to those used for calculating PI_{Prod} [63]. $PI_{vectorM}$ was introduced by Gong et al. [63] and depends on Pi and the number of TMs selected for investigation. $PI_{Nemerow}$ determination emphasises the maximum value of a single Pollution Index (Pi) for all TMs; however, it does not include the weight of Pi [66]. $IntPI$ is an easy-to-calculate index based on the Pi mean value. The classification based on $IntPI$ divides sediment contamination into low, moderate, and strong [67,70].

MPI is equal to PLI. The general difference lies in $C_{mBackground}$ used in the equation for the Pi calculations [71].

In relation to CPIs, one major advantage is the possibility to comprehensibly evaluate the effects of several metals simultaneously. The authors of this review believe that the the Pi weight, which represents the impact of an individual metal on the overall sediment pollution rating, plays a significant role in the calculations. This approach is used by PI_{wAvg} and PI_{wpProd}. Moreover, it would seem to be more accurate to include the maximum Pi as a reference in the calculations of $PI_{Nemerow}$. Despite the mentioned advantages of PI_{wAvg}, PI_{wpProd}, and $PI_{Nemerow}$, it is still desirable to use simpler calculations, which are included by PLI, C_{Deg}, mC_{Deg}, PI_{sum}, etc.—due to their simplicity and frequent use in different studies.

4.1.3. Geochemical Classifications Referring to the Geochemical Background

Extensive environmental monitoring is required to develop geochemical classification and a database. Often, such studies end by mapping a given area to present geochemical data as accurately as possible [72]. Since determining the geochemical background is usually a fundamental step while assessing the environmental status of a given site, such classifications have a temporary value [20].

In Poland, the first attempts to classify lake and river sediments contaminated with TMs were made by Bojakowska and Sokołowska [73]. This so-called "geochemical classification of aquatic sediments" approach involves standardising samples, taking into account

a grain size smaller than 0.2 mm. Moreover, this classification applies to samples digested with hydrochloric acid, nitric acid, or aqua regia. The geochemical criteria distinguish four geochemical quality classes presented and described in Table 1. This classification was developed in 1998, so the geochemical background could have changed since then. However, it is still used in Poland in the absence of other regulations. In Table 1, the geochemical quality classes are collated with geochemical background values established using different approaches. Depending on the goals, TM contents in analysed sediments can be compared with preindustrial concentrations [58], trace metal content in world soils [74], or shale standard [57].

Table 1. The concentration of various trace metals (TMs) in mg/kg d.w. for each class of sediments—geochemical classification of aquatic sediments [57,58,73–75].

Trace Metal	Geochemical Background [in mg/kg d.w.]					Geochemical Quality Classes			
	Preindustrial	World Soils	Shale Standard	Gdansk Region Sediments (Poland)	Sediments (Poland)	I	II	III	IV
	[58]	[74]	[57]	[75]	[73]	[73]	[73]	[73]	[73]
As	-	1.5	13	-	**<5**	**<10**	**<20**	**<50**	**≥50**
Cd	1.0	0.62	0.3	0.5	**1**	**<1**	**<3.5**	**<6**	**≥6**
Cr	90	84	90	7	**5**	**<50**	**<100**	**<400**	**≥400**
Cu	50	25.8	45	5	**6**	**<40**	**<100**	**<200**	**≥200**
Pb	70	29.2	20	11	**10**	**<50**	**<200**	**<500**	**≥500**
Hg	0.25	-	0.4	-	**≤0.05**	**<0.1**	**<0.5**	**<1.0**	**≥1.0**
Ni	-	33.7	68	4	**5**	**<30**	**<50**	**<100**	**≥100**
Zn	175	59.8	95	41	**48**	**<200**	**<1000**	**<2000**	**≥2000**

Bold—geochemical quality classes description according to Bojakowska and Sokołowska: Class I—uncontaminated sediments (boundary value of elements concentration determined as from 5 to 10 times higher than the geochemical background); Class II—moderately contaminated sediments (TMs content from 10 to 20 times higher than the geochemical background); Class III—contaminated sediments (TMs content from 20 to 100 times higher than the geochemical background); Class IV—highly contaminated sediments [73].

4.2. Ecotoxicological Evaluation

In order to assess the level of contamination that is still safe for living organisms, it is necessary to apply ecotoxicological criteria or use indicators that take into account the level of metal toxicity.

4.2.1. Descriptive Classifications Based on Total TM Content

Internationally, a range of sediment quality guidelines (SQGs) have been proposed for contaminants. Originally, they provided the information on SQGs compared with a reference or background concentration of analysed substances [76]. After the 1980s, SQGs were developed to evaluate sediment quality where harm to aquatic organisms and the environment was observed [77]. In general, SQG approaches that use different criteria and factors are divided into two main categories [76]:

- Empirically based SQGs—relying on the empirical relationships needed to determine the sediment contamination level at which a toxic response occurs; these are frequently used for TMs and As.
- Theoretically based SQGs—relying on the parameters that describe the bioavailability of contaminants (equilibrium partitioning, EqP); these are mainly used for organic compounds (less often for TMs).

Both types of SQG predict adverse ecological effects caused by sediment contamination by the response of benthic organisms. SQGs feature two concentration thresholds: the first below which adverse effects are not expected to occur (threshold effect concentration—TEC) and the second above which adverse effects are expected to occur more often than not (probable effect concentration—PEC). The limitation of this approach is that it leaves significant uncertainty in the "grey" area of contaminant concentrations that lie between TEC and PEC. Therefore, it may be necessary to perform a site-specific analysis. Another relevant issue in the case of SQGs is that these descriptions apply to only one type of

contaminant, which may lead to inaccurate conclusions in the contamination description, as the sediments are a sink for various type of contaminants that can contribute to their overall toxicity. Table 2 outlines the most popular empirical SQGs used in practice. All of them are based on differently described terms of TEC and PEC (e.g., TEL/PEL, ERL/ERM, or LEL/SEL) [78–80]. Moreover, we presented the average TEC and PEC values calculated based on the literature (TEC$_{lit}$ and PEC$_{lit}$).

Table 2. Sediment quality guidelines (SEQs) for TMs and metalloid in mg/kg d.w. that reflect threshold effect concentration (TEC) and probable effect concentration (PEC) [77–82].

Element	Empirical SQGs with TEC and PEC in mg/kg·d.w.											
	Smith et al. [78]		Long and Morgan [79]		Persaud et al. [80]		MENVIQ [81]		ANZECC/ARMCANZ [82]		Average Values Based on the Literature	
	TEL	PEL	ERL	ERM	LEL	SEL	MET	TET	SQGV	SQGV-High	TEC$_{lit}$	PEC$_{lit}$
As	5.9	17	33	85	6	33	7	17	20	70	14	44
Cd	0.596	3.53	5	9	0.6	10	0.9	3	1.5	10	1.72	7
Cr	37.3	90	80	145	26	110	55	100	80	370	56	163
Cu	35.7	197	70	390	16	110	28	86	65	270	43	211
Pb	35	91.3	35	110	31	250	42	170	50	220	39	168
Hg	0.174	0.486	0.15	1.3	0.2	2	0.2	1	0.15	1.0	0.17	1
Ni	18	36	30	50	16	75	35	61	21	52	24	55
Zn	123	315	120	270	120	820	150	540	200	410	143	471
Limitations for empirical SQGs:												
Advantages	(1) Allows for thresholds prediction at which a toxic response of benthic organisms is probable (2) A useful tool that allows making the first guess on the sediment contamination problem (3) Quite simple to use with a large database of lab and field tests											
Disadvantages	(1) The assessment of risk and possible negative outcomes associated with toxic concentration levels, which require a separate risk evaluation (2) "Grey" area between thresholds test errors (3) Difficult to apply in a context of contaminant mixtures (4) Relatively expensive research and development of new SQGs (5) The availability of SQGs guidelines criteria and documentation is limited											

TEC—Threshold-Effects Concentration; PEC—Probable-Effects Concentration; TEL—Threshold-Effects Level; PEL—Probable-Effects Level; ERL—Effects Range: Low; ERM—Effects Range: Median; MET—Minimal Effect Threshold; TET—Toxic Effect Threshold; SQGV—Sediment Quality Guideline Value; ANZECC/ARMCANZ [82]—currently used classification in Australia and New Zealand.

In parallel with the intense work undertaken on SQGs in North America and Australia, several approaches and descriptive classifications and recommendations were also developed in Europe. It is worth noting that the authorities and legislators usually consider water quality as a priority, paying less attention to the state of sediments. It should be emphasised that contaminants accumulated for decades in the bottom sediments of water bodies could be released into the water column and cause its recontamination, thereby directly affecting water quality. Despite the large-scale processes that can affect the stability of sediments, there are different inceptors of secondary water recontamination, such as pH fluctuation, or the disturbance of sediment structure during dredging operations or boat movement.

In Germany, the Länder-Arbeitsgemeinschaft Wasser classification (LAWA) [83] is used to assess Hg, Cd, Zn, Pb, Cu, Cr, and Ni content in water, suspended solids, and sediments. The LAWA classification is constrained to the methodology of digestion with the use of aqua regia. This approach does not allow silicates to dissolve; therefore, the term "pseudo total" concentration of TMs is used in the literature. However, in terms of the actual contamination status of sediments and their impact on the aquatic environment, the mobile and unstable forms of TMs are most relevant [75]. In the light of this, digestion by using aqua regia or diluted acids (e.g., hydrochloric acid, nitric acid) may determine the bioavailable fraction of TMs that take part in environmental processes, while it remains impossible to determine the content of TMs bound in minerals resistant to weathering processes. LAWA classification divides sediments into seven classes of contamination, depending on the TM contents in aquatic ecosystems. The boundary values for each class are presented in Table 3.

Table 3. The concentration of various trace metals (TMs) in mg/kg d.w. for each class of sediments—classification LAWA and modified LAWA [83,84].

Classification	Trace Metal [in mg/kg d.w.]	Contamination Class						
		I	I–II	II *	II–III	III	III–IV	IV
LAWA [83]	Cd	≤0.3	≤0.6	≤1.2	≤2.4	≤4.8	≤9.6	>9.6
	Cr	≤80	≤90	≤100	≤200	≤400	≤800	>800
	Cu	≤20	≤40	≤60	≤120	≤240	≤480	>480
	Pb	≤25	≤50	≤100	≤200	≤400	≤800	>800
	Hg	≤0.2	≤0.4	≤0.8	≤1.6	≤3.2	≤6.4	>6.4
	Ni	≤30	≤40	≤50	≤100	≤200	≤400	>400
	Zn	≤100	≤150	≤200	≤400	≤800	≤1600	>1600
Modified LAWA [84]	As	3–5	<10	<20	<40	< 70	<100	>100
	Cd	0.2–0.4	<0.5	<1.2	<5	< 10	<25	>25
	Cr	60–80	<90	<100	<150	< 250	<500	>500
	Cu	20–30	<40	<60	<150	<250	<500	>500
	Pb	25–30	<50	<100	<150	<250	<500	>500
	Hg	0.2–0.4	<0.5	<0.8	<5	<10	<25	>25
	Ni	10–30	<40	<50	<150	<250	<500	>500
	Zn	90–110	<150	<200	<500	<1000	<2000	>2000

* Quality goal—Class II. Class I refers to uncontaminated sediment; Class I–II—sediments unpolluted or with very small anthropogenic interference; Class II corresponds to moderately polluted sediments, and it is a reference for the other levels of pollution; Class II–III—twice as much as Class II—defines moderate to significant contamination of sediments; Class III—four times more than Class II—defines significant pollution; Class III–IV—eight times more than Class II—refers to very strong pollution; Class IV—means more than eight times exceeding Class II—ultimate pollution. Comparative value is the average contents of TM expressed in mg/kg [83,84].

Following the LAWA classification, Ahlf et al. [84] introduced guidelines for evaluating sediment quality based on integrated toxicological, chemical, and ecological approaches (hereafter referred to as modified LAWA). This approach is based on a series of three different tests that should be performed step-by-step, starting from an ecotoxicological assessment. If the ecotoxicological test confirms sediment contamination, the second step is introduced, which focuses on chemical analyses. The final assessment stage involves an additional and thorough analysis of factors that may harm the environment. The classification of TM sediment contamination applied by Ahlf et al. [84] (Table 3) combines temporary valuation standards of river mud and ATV standards concerning sewage and garbage. The final evaluation is based on the concentration limits for class II, which constitutes a point of reference.

In accordance with the Water Framework Directive, water and sediment quality assessment considers the extent of deviation from reference conditions with no or with very minor anthropogenic influence. The general conclusion from analyses of sediments guidelines is that they have advantages as well as limitations for their application in sediment quality assessment [85].

4.2.2. Ecotoxicological Indices (EIs)

EIs as indicators of ecotoxicology comprise numerous indices, such as Ecological Risk Factor (*ER*= *Er^i* = Risk Index (*RI*)) [58]—the only IEI, Contamination Severity Index (*CSI*) [86], Sediment Pollution Index (*SPI*) [58,64], Risk Assessment Code (*RAC*) [35], Risk Index (*PERI*) [87,88], and the probability of Toxicity Index (*MERMQ*) [86]. The list of IEIs and CEIs are presented in Table A4 Appendix D with classification and a summary of strengths and weaknesses.

ER describes the ecological risk caused by TM. T_r^i in the *ER* formula represents the toxic-response factor for a given metal, and so this index ties the risk assessment with the metal content in a sample [6]. *SPI* also refers to T_r^i of TMs and additionally takes into account the average shale concentration of TMs. Moreover, *SPI* is tailored for the comprehensive evaluation of several elements at the same time. Another difference between *ER* and *SPI* lies in diverse points of reference—*ER* classification refers to ecological risk, and *SPI* refers to the sediment pollution level. *PERI* is a complex index based on a single

ER. The toxic response factors for TMs according to Håkanson [58] are as follows: Hg—40, Cd—30, As—10, Cu—5, Pb—5, Cr—2, and Zn—1. T_r^i in the limnic system was discussed and established by Håkanson according to the "abundance principle" of elements in different matrixes. The element with the highest mean concentration must be ranked as 1.0; according to this assumption, analysed elements were marked with the following abundance number: Zn = 1 < Cu = 3.4 < Pb = 13 < Cr = 110 < As = 140 < Cd = 230 < Hg = 1160. Note that the abundance number is not equal to the toxic factor. Håkanson corrected the abundance number to reflect the "sink-effect". This effect is related to different footprints caused by substances (e.g., Cr has the lowest sink-factor = 2, which implies that this element leaves the heaviest footprint in the sediment, while Hg has the highest sink-factor =320, which means that much more Hg can be found in water compared to sediments). Taking into account the dimension problem, Håkanson corrected the abundance numbers that correspond to T_r^i. Moreover, according to Kabata-Pendias and Pendias [58], the highest T_r^i corresponds to strong chemical and biological activity in the case of Hg and high solubility in acidic environments and mobility for Cd. Quite low T_r^i for Pb is related to its low mobility. $T_r^i = 2$ for Cr is related to the principle that only Cr(VI) is toxic; at the same time, Cr(VI) is easily reduced to poorly soluble Cr(III), which is generally difficult for plants and benthic organisms to absorb [58].

CSI requires the use of computed weight of each TM according to Pejman et al. [86]: (Cu—0.075, Zn—0.075, Cr—0.134, Ni—0.215, Pb—0.251, Cd—0.25). The weight of TMs may result from statistical analyses (e.g., Principal Component Analyses—PCAs and/or Factor Analyses—FAs). Moreover, *CSI* requires the application of ERL and ERM, and at the same time, it is highly accurate and could provide a precise evaluation of sediments.

RAC depends on exchangeable and carbonate fractions determination (determined with CH_3COOH 0.11 M solution) [35]. The classification refers to the percentage of mobile fractions in relation to the total concentration of bound TMs in all fractions together. It is worth noting that *RAC* is the sole index that combines the speciation analyses of TMs. Therefore, it is very valuable for evaluating the mobility and bioavailability of metals.

MERMQ is also referred to in the literature as a combined effect of Toxic Metals (*mPECQ*). This complex EI is based on TM content in the sample and the second threshold level of effects (e.g., ERM for *MERMQ* and PEC for *mPECQ*) [86].

4.3. Extended Sediments Quality Ranking

4.3.1. Integrated Geoaccumulation Index—*Igeo$_{integrated}$*

The approach described by Von Tümpling et al. in 2013 [89] relies on *Igeo* introduced by Müller [59], and this index is combined with metal speciation analysis based on BCR (Community Bureau of Reference) three-stage sequential extraction—this approach is referred to as "extended use of *Igeo* in combination with BCR fractionation". To compare the results obtained with *Igeo$_{integrated}$* between fractions, an integrated *Igeo* was introduced ($\Sigma Igeo_{integrated}$). The sum of *Igeo$_{integrated}$* offers a general overview of the contamination degree of the considered elements in one fraction in comparison to $\Sigma Igeo_{integrated}$ of other fractions. The $\Sigma Igeo_{integrated}$ equation is as follows:

$$\sum Igeo_{integrated} = \sum_{j=1}^{m} \sum_{k=1}^{n} m_{j,k}$$

where *m* is the quality class, *j* is the sampling point (SP), and *k* is the element. The geoaccumulation classes (described in Table A2 Appendix B) of all the examined TMs are added for each fraction. If there is no contamination or no accumulation of an investigated element, the resulting sum is 0. The maximum class is 6.

The *Igeo$_{integrated}$* approach can completely change the result of the sediment assessment based on the total TM content performed by *Igeo*. The results reported by Von Tümpling et al. [89] for Klinke River in Germany indicated that F3, F2, and F1 had the greatest $\Sigma Igeo_{integrated}$. At the same time, the "good chemical status" classification in accor-

dance with total TM content was overturned by the sequential extraction method, which demonstrated that changes in element speciation can lead to higher TM mobility, which may increase the hazardous potential of sediments.

4.3.2. Fractionation of TMs

In order to establish how TMs behave in the sediment–water or soil–water environments, the presence of physical and chemical forms of metals—i.e., fractionation, also called speciation—must be determined. Therefore, speciation is an identification of various physicochemical forms of elements in the analysed material and/or mutual proportions of these forms. This approach helps to understand the mobility of metals in the environment, although the sample processing is time consuming [90].

The analytical methods for the chemical section of TMs in the solid phase involve single reagent leaching, sequential extractions, and ion exchange resins [55]. In general, the processes involving the separation of different species are based on selective chemical reactions and/or extraction procedures (e.g., liquid–liquid, solid-phase extraction). The final result of element contents is presented in mg/kg and or mg/L (ppm—parts per million) or ng/kg and/or ng/L (ppb—parts per billion). Therefore, the overall process is complex, arduous, and susceptible to critical errors that are sometimes neglected. In the field of geochemistry, sequential extraction has proven its value. Nevertheless, accuracy at every stage of sample processing and analysis is crucial to guarantee an acceptable level for detecting (LOD—limit of detection) and quantifying the analytes [91]. TMs may be determined by commonly used instruments such as flame (FAAS), hydride generation (HGAAS), and electrometry (ETAAS) atomic absorption spectrometry, as well as inductively coupled plasma mass spectrometry (ICP-MS) and emission spectrometry (ICP-OES). In comparison with procedures in which total TM contents are determined in a direct manner, the extraction methods generate more uncertainties. This inconvenience is caused by difficulties in isolating compounds from substrates, upsetting the equilibrium between different chemical species, insufficient analytical sensitivity, or a lack of certified reference materials [92].

Many selective extraction methods have been developed, among others, by Tessier et al. [93], Boszke [94], Miller et al. [95], and Fiedler et al. [21]. One method that seeks to minimise errors during sample processing and analysis was proposed by the European Community Bureau of Reference—the BCR method [96].

The BCR three-step extraction procedure is similar to those proposed by Tessier et al. [90]. The key difference involves combining the first fraction of the procedure (instead of evaluating the exchangeable and carbonate fractions separately, the BCR procedure combines both); therefore, BCR distinguishes four factions (F1—exchangeable, F2—reducible, F3—oxidisable, and F4—residual). The description of subsequent steps of the BCR extraction procedure is presented in Table 4.

Table 4. The BCR three-steps sequential extraction scheme [90].

Extraction Step	Fraction	Operational Definition	Chemical Reagents/Conditions
1	F1	Acid extractable (water and acid soluble)	Acetic acid: CH_3COOH (0.11 mol/L); pH 2.85
2	F2	Reducible (Fe/Mn oxides)	Hydroxyloammonium chloride: $NH_2OH \cdot HCl$ (0.1 mol/L), pH 2.0
3	F3	Oxidisable (organic substance and sulphides)	Hydrogen peroxide: H_2O_2 (8.8 mol/L) followed by ammonium acetate: CH_3COONH_4 (1.0 mol/L), pH 2.0
4	F4	Residual (remaining, non-silicate bound metals)	Acid digestion (e.g., Aqua regia: 3 HCl + HNO_3 or HF + HNO_3)

4.4. Bioindicators

In recent decades, the interest in using bioindicators as monitoring tools to examine environmental pollution caused by TMs has been growing steadily. Numerous plants are used as bioindicators to construct assumptions regarding environmental conditions. In this context, plants including macrophytes can be used as bioindicators for TM-related environmental pollution due to their ability to absorb metals from air, water, sediment, soil, and the food chain [97]. In general, bioindicators are characterised by the following abilities: they are easy to grow and cultivate, can withstand polluted environments, and can accumulate high pollutant concentration in their biomass; they are ecologically and economically important for society, and they should be abundant and widespread. In addition, bioindicators not only provide sediment, soil, and water remediation but are also a feasible tool for the recovery of valuable elements to develop a circular economy [98]. In practice, aquatic and related fauna, microbial systems, fungi, animals, and plants are popular targets of TM monitoring programs used as bioindicators to formulate conclusions regarding the environmental contamination status. Biological indicators provide information on the long-term impact of TM contamination [97]. There are many reasons to use a given species as bioindicators, while the key issue lies in the correlation of analysed toxic compounds/elements between species and contaminated matrix (as waters, sediments, or soils) [99].

In this review, different bioindicator plant species were identified from different studies based on their survival, highest metal accumulation, and biomass production in different polluted environments (soil and water) (Table 5). Moreover, metals such as Zn, Cd, Cu, and Ni were predominantly investigated in most regions. For instance, Salinitro et al. [100] depicted the linear relation of Ni in soils and in *Poa annua* shoots ($R^2 = 0.78$) and *Senecio vulgaris* ($R^2 = 0.88$). Therefore, these species have been demonstrated to be reliable indicators of both total and bioavailable Ni fractions in an anthropogenic environment. Extensive research on bioindicators in an estuarine and coastal environment was performed by Farias et al. [98]. In this study, *Ulva australis*, *Zostera muelleri,* and *Ruppia megacarpa* were selected for bioindicator identification due to their great abundance and the highest content of TMs inside their tissues. These species were verified as potential bioindicators of TM (As, Cu, Pb, and Zn) pollution in estuary sediments.

Some authors also focused on highly toxic elements such as Hg and As. These non-essential elements are uptaken passively by plants [24]. Many plant species presented tolerance to As contamination, as presented by Singh et al. [101] based on the example of *Vetiveria zizanoides*, which demonstrated resistance to As stress and feasibility for revegetation/remediation of As-contaminated soils. Although Hg in plants has no metabolic function, it could be easily translocated from roots and rhizomes to shoots [102].

High resistance to changes in salinity, fertility, textures, and pH is presented by an extensively distributed species Phragmites australis [103]. Ganjali et al. [104] demonstrated that Phragmites roots can be used as bioindicators of Fe, Cu, Cd, and Ni.

Phragmites and *Salix* species were studied widely for the phytoremediation of TMs in temperate and boreal climates. *Salix schwerinii* and *S. myrsinifolia* are known as bioindicators in boreal climates. In addition, hybrid cultivars of *Salix*, such as Klara (*Salix viminalis* × *S. schwerinii* × *S. dasyclados*) and/or Karin (*S. viminalis* × *S. schwerinii*) are in use in bioindication. Salam et al. [105] proved that Klara (*Salix viminalis* × *S. schwerinii* × *S. dasyclados*) accumulated high concentrations of Cu, Zn, and Ni in leaves, shoots, and roots from soils. At the same time, Klara may be considered for phytostabilisation and rhizofiltration due to the highest TM accumulation in the roots. *Phragmites* is an emergent plant worldwide that has demonstrated high TMs phytostabilisation properties [106,107]. In three reviewed papers, the authors focused on rare earth elements (lanthanide) such as Pr, Nd, Tb, Sm, Dy, and Er. Mikołajczyk et al. [108] have thoroughly documented the potential of *Artemisia vulgaris*, *Papaver rhoeas*, and *Taraxacum officinale* for phytoextraction of rare earth elements whose occurrence is increasing due to the development of modern technologies.

Table 5. A list of plant species tested as candidates for bioindication across the world.

Plant Species/Cultivars	Climate/Region	Analysed Pollutants	Trial	Source	Reference
Phragmites australis	Temperate/China	Zn and Cd	Pot experiment	Hydroponic	[109]
Atraclytis seratuloides, Lygeum spartum, and *Gymnocarpos decander*	Mediterranean/Tunisia	Cr, Co, Zn, Pb	Field	Soil, cement site	[110]
Phragmites australis	Temperate/Poland	Cr, Ni, Cu, Zn, Cd, Pb	Pot experiment	Sediment	[107]
Vetiveria zizanoides	Tropical/India	As	Field	Soil	[101]
Alopecurus pratensis, Elytrigia repens, Poa angustifolia, Holcus lanatus, Arrhenatherum elatius, Bromus inermis Leyss, Artemisia vulgaris, Urtica dioica, Achillea millefolium, Galium mollugo, Stellaria holostea, and *Silene vulgaris*	Temperate/Germany	Cr, Ni, Cu, Zn, Cd, Pb, As	Pot experiment (cold-house)	Soil	[3]
Boehmeria nivea		Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu	Growth chamber	Hydroponic	[111]
Morus alba, Acacia nilotica, Acacia ampliceps, and *Azadirachta indica*	Tropical/Pakistan	Pb	Greenhouse	Municipal and industrial wastewater	[112]
Salix schwerinii	Boreal/Finland	Ni, Cu, and Zn	Growth chamber	Soil	[113]
Senecio vulgaris, Polygonum aviculare, and *Poa annua*	Mediterranean/Italy	Cr, Cu, Zn, Cd, and Pb	Field	Soil	[100]
Klara (*S. viminalis* × *S. schwerinii* × *S. dasyclados*)	Boreal/Finland	Ni, Cu, and Zn	Pot experiment (greenhouse)	Soil	[105]
Artemisia vulgaris Phalaris arundinacea Heracleum sphondylium Bistorta officinalis	Temperate/UK	Mn, Zn, and As Mn and Ni Cr and Zn Mn and Zn	Field	Soil	[114]
Conocarpus lancifolius	Temperate/Pakistan	Zn, Cd, and Pb	Pot experiment (greenhouse)	Soil	[115]
Salix subfragilis	Temperate/Korea	Mn, Cu, Zn, Cd, and Pb	Field trial	Sediment (wetland)	[116]
Ruppia megacarpa, Zostera muelleri, and *Ulva australis*	Temperate-desert/Australia	Cu, Zn, Cd, Pb, As, and Se	Field trial	Estuary site	[98]
Achillea millefolium, Artemisia vulgaris, Papaver rhoeas, Tripleurospermum inodorum, and *Taraxacum officinale*	Temperate/Poland	Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Lu	Field trial	Soil	[108]
Salix schwerinii	Boreal/Finland	Cr, Ni, Cu, and Zn	Pot experiment (greenhouse)	Soil (landfill)	[117]
Amaranthus viridis, Bassia indica, Conyza bonariensis Cronquist, Portulaca oleracea, Rumex dentatus, Solanum nigrum, Lycopersicon esculentum, Phragmites australis, and *Pluchea dioscoridis*	Semi-desert/Egypt	Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Fe	Field trial	Soil (sewage sludge dump site)	[118]
Salix schwerinii, Klara, Karin and *Salix myrsinifolia*	Boreal/Finland	Cu and Zn	Pot experiment (greenhouse)	Soil	[119]
Phalaris arundinacea	Temperate/Czech Republic	Cr, Cd, and Hg	Field trial	Constructed wetland	[120]
Asclepias syriaca, Desmodium canadense, Panicum virgatum, Raphanus sativus, and *Solanum lycopersicum*	Boreal/Canada	Pr, Nd, Sm, Tb, Dy, and Er	Growth chamber	Soil	[121]
Oenanthe sp., *Juncus* sp., *Typha* sp., *Callitriche* sp.1, and *Callitriche* sp.2	Temperate/France	Cr, Ni, Cu, Zn, Cd, Pb, and As	Field trial	Urban stormwater	[122]
Phragmites australis	Tropical/Iran	Fe, Ni, Cu, and Cd	Field trial	Sediments	[104]

Bioindicator use in biomonitoring programs may be an effective approach, although each time, it requires extended research to recognise how metals in a potential bioindicator correlate with the evaluated matrix (water, sediments, or soils). Species properties regarding metal uptake, the antagonistic and synergistic properties between the elements as well as whether the metal is essential or non-essential play a key role in evaluating bioindication technology [23]. Nevertheless, this is a useful assessment tool, offering the additional potential for recovering valuable elements, and so it is expected to develop relatively soon.

5. Conclusions

By applying geochemical and ecotoxicological assessment and classification indices, a numeric evaluation may be obtained regarding the extent of sediment contamination. An analysis of the results yielded by recent studies using the Web of Science Core Collection (based on five keywords: sediments, trace metals, contamination, pollution indices, urban) shows that the following occur most often: (1) the researchers studied metal concentration in the surface layer of sediments (0–2 cm, 0–5 cm, 0–10 cm); (2) the most frequently used geochemical indices were *Igeo*, *EF*, and *CF*; (3) ecotoxicological evaluation was mainly performed by using *SQG* and *PERI*, which includes the toxic response index. The above-presented indices and classifications summarise the geochemical and ecotoxicological approaches of sediment assessment. The geoaccumulation indices help to determine whether the accumulation of TMs is due to natural processes or anthropogenic interference. Ecotoxicological assessment supports the overall contamination assessment of sediments and its harm for living organisms. The final results can be calculated for individual elements (*CF*, *Igeo*, *EF*, *Pi* (*SPI*), PT_T) and by using complex pollution indices (*PLI*, *Cdeg*, *mCdeg*, Pi_{sum}, PI_{Avg}, PI_{aAvg}, *PIN*, PI_{Prod}, PI_{apProd}, $PI_{vectorM}$, $PI_{Nemerow}$, *IntPI*, and *MPI*) for a larger set of TMs. Similar approaches can be applied for ecotoxicological indices (individual: ER^i and complex: *CSI*, *SPI*, *RAC*, *PERI*, and *MERMQ*).

Geochemical indicators largely refer to the total metal content in the sample, although the inclusion of mobile and bioavailable fractions would appear to be indispensable for geochemical and ecotoxicological assessment. The use of $Igeo_{integrated}$ may help comprehensively verify the sediment quality. This approach includes contamination analysis, taking into account metal fractionation. A "good quality assessment" of sediments via *Igeo* may turn out to be worse after checking TM fractionation and referring to $Igeo_{integrated}$ (especially when a large proportion of TMs are bound in mobile or water-soluble fractions). Conversely, when TMs are mainly bound to an immobile and/or residual fraction, the *Igeo* assessment may be mendacious, resulting in an overestimation of the pollution level.

Bioindication is an indirect method of environmental assessment, which can support environmental quality assessment monitoring programs. Nowadays, the simultaneous use of different classifications and indices reflects a more accurate assessment of TM pollution. The most recognised bioindicators include *Phragmites* and *Salix* for TM phytoremediation, particularly Zn, Cd, Cu, and Ni in a boreal and temperate climate. Hybrid cultivars of *Salix* such as Klara (*Salix viminalis* × *S. schwerinii* × *S. dasyclados*) and Karin (*S. viminalis* × *S. schwerinii*) are also applied in biomonitoring and considered for phytostabilisation and rhizofiltration. *Vetiveria zizanoides* demonstrated resistance to As. Rare earth elements (lanthanides) such as Pr, Nd, Tb, Sm, Dy, and Er constitute a separate group of analysed metals investigated in plant research. This issue is of serious concern for the recovery of valuable elements in the development of a circular economy. *Artemisia vulgaris*, *Papaver rhoeas*, and *Taraxacum officinale* present lanthanide phytoextraction potential.

In order to be properly managed or remediated, sediments must be comprehensively evaluated. Monitoring programs for sediments in urban retention systems are crucial in this regard. A promising evaluation method is the use of bioindicators, which also have the potential to recover valuable elements. Therefore, future research should focus on developing this tool while evaluating the quality of sediments.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Comparison of trace elements investigated in bottom sediments of diverse urban water bodies (river, lakes, receivers, retention tanks, etc.) with concentration ranges in mg/kg d.w., indication of indices used for pollution evaluation, classifications, and verification of health risks and an indication of the use of metal fractionation.

Authors	Location	Use	Analysed HMs	TMs Ranges [mg/kg d.w.]	Sampling	Indices	SQG	Heath Risk	Chemical Speciation Analysis
Sun et al., 2018 [28]	Songhua River, Jilin City (China)	Urban area with petrochemical industries	Five elements: Cr, Ni, Cu, Zn, Pb	Total HMs content: 123.98–346.34	Surface sediment (0–5 cm)	*Igeo, PERI, RAC*			+
Vieira et al., 2019 [29]	Arthur Thomas Lake, Londrina (Brazil)	Urban lake; strongly agroindustrial economy (with coffee production)	27 elements: Na, K, Mg, Ca, Sr, Ba, Sc, La, Th, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Ag, Au, Al, Ga, P, As, Sb, Bi, S, Se	Na (1–3), K (10–30), Mg (50–290), Ca (90–570), Sr (5.00–32.0), Ba (37–180), Sc (19.4–57.1), La (14.0–35.0), Th (3.20–5.90), Ti (220–950), V (323–1331), Cr (74.0–185), Mo (0.30–1.00), Mn (640–174.-3), Fe (8940–16830), Co (19.70–62.30), Ni (18.5–63.6), Ag (0.01–3.20), Au (0.50–247.1), Ga (17.0–28.0), P (50–170), As (1.30–3.50), Sb (0.10–0.70), Bi (0.00–0.60), S (10–180), Se (0.01–1.40)	Sediment cores (0–90 cm)	*EF, Igeo*	+		
Kumar et al., 2020 [30]	Yamuna River, Chambal River, Gulf of Mannar, Ganges River, Betwa River, Ken River, Beas River, Gomti River, and Gangotri River (India)	Review of different TMs from sediment samples from Indian rivers'	10 elements: Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, As	Cr (0.075–2628.3), Mn (0.097–2436.5), Fe (4.23–2312.44), Co (1.10–624), Ni (0.01–1813), Cu (0.019–5214), Zn (0.13–2759), Cd (0.015–272), Pb (0.17–1297), As (0.12–197)	No data	*CF, EF, Igeo, PERI (=MRI), RI*		*HI, HQ*	
Cui et al., 2019 [31]	Harbin City, Song (China)	Urban and rural rivers:Majiagou River (urban section, industrial zone) Yunliang River (rural section)	Six elements: Cr, Ni, Cu, Zn, Cd, Pb	Urban river: Cr (75.12–203.15), Ni (7.91–30.38), Cu (4.00–82.54), Zn (128.17–1416.71), Cd (0.08–4.08), Pb (8.86–57.49) Rural river: Cr (53.65–81.92), Ni (BDL *–13.11), Cu (15.75–22.29), Zn (113.23–2474.05), Cd (BDL–4.29), Pb (9.31–114.42)	Surface sediment	*CF (=Pi), PI_{Nemerow}, RI*			
Liu et al., 2020 [32]	Pearl River Estuary, Xixiang River, Gongle Chung, Gushu Chung, Nanchang Chung, Tiegang reservoir flood discharge river, and Southern Airport drainage river (China)	Urban area	Six elements: Cr, Ni, Cu, Zn, Hg, Pb	Cr (35–510), Ni (15.0–194), Cu (38,0–1600), Zn (105–2600), Hg (0.009–0.85), Pb (22.9–160)	Surface sediment	*Igeo, RI*			

Table A1. *Cont.*

Authors	Location	Use	Analysed HMs	TMs Ranges [mg/kg d.w.]	Sampling	Indices	SQG	Heath Risk	Chemical Speciation Analysis
Chassiot et al., 2019 [33]	Saint-Charles River, Lake St. Charles (Canada)	Upstream an urban reservoir; urban area with diverse industries	14 samples: V, Cr, Mo, Mn, Co, Ni, Cu, Ag, Zn, Cd, Hg, Sn, Pb, As	No data of ranges	Sediment cores and surface sediment	*EF, Igeo, MPI*			
Hanfi et al., 2020 [34]	Sediment samples around the world: Europe ([Europe]), Asia ([Asia]), Africa ([Africa]), North America ([North America])	Review of different TMs from sediment samples around the world (including 41 research paper reported between 1980 and 2018)	Six elements: Cr, Ni, Cu, Zn, Cd, Pb	Cr (29–196[Europe]; 0.85–144[Asia]; 1.4–85.7[Africa]; 17.1–125[North America]), Ni (35–128.45[Europe]; 12–126[Asia]; 1.9–67[Africa]; 18.1–26.5[North America]), Cu (73–466.9[Europe]; 10.99–269[Asia]; 11.3–243[Africa]; 15–356[North America]), Zn (125–1166[Europe]; 50.6–2377[Asia]; 13.1–1840[Africa]; 59–1811[North America]), Cd (0.2–4.6[Europe]; 0.12–72[Asia]; 0.33–6.9[Africa]; 0.1–8[North America]), Pb (48–1880[Europe]; 13.3–2582.5[Asia]; 11.2–737[Africa]; 10.9–2583[North America])	Surface sediment	*CF (=Pi), Igeo*			
Xia et al., 2020 [35]	Caohai Wetland (China)	The natural area of black-necked crane habitats in the Caohai wetland	Nine elements: Be, V, Cr, Ni, Cu, Zn, Cd, Hg, Pb	Be (0.83–2.19), V (49.1–103.1), Cr (83.5–145.9), Ni (40.3–65.7), Cu (13.5–30.9), Zn (108.9–365.4), Cd (0.5–7.34), Hg (0.30–1.34), Pb (37.3–76)	Surface sediment (0–10 cm)	*EF, Igeo, PERI, RAC*			
Dhamodharan et at., 2019 [36]	Cooum River, Chennai, (India)	Urban area	10 elements: Cr, Mn, Fe, Ni, Cu, Zn, Cd, Hg, Pb, As	Cr (7.12–155), Mn (139–2167), Fe (17,389–49,568), Ni (3.54–53.1), Cu (12.3–59.39), Zn (19.7–438), Cd (0.7–24.4), Hg (0.01–0.79), Pb (0–30.6), As (45–497)	Surface sediment	*Igeo, EF, CF, PLI, PERI*			
Siddiqui and Pandey, 2019 [37]	Ganga River (China)	Urban area	Eight elements: Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb	Cr (7.12–155), Mn (139–2167), Fe (17,389–49,568), Ni (3.54–53.1), Cu (2.1–73.98), Zn (6.3–104.3), Cd (0.21–3.6), Pb (2.1–36.5)	Surface sediment (0–10 cm)	*CF, EF, Er^i, Igeo, mCd, MPI, PERI, PI*	+		
Hafijur Rahaman Khan et al., 2020 [38]	Ganges-Brahmaputra-Meghna (Bangladesh)	Bengal Basin river system	19 elements: Sc, Th, U, Hf, Nb, Ta, W, Cr, Mo, Co, Ni, Cu, Cd, Ga, In, Tl, Ge, Pb, Bi	Sc (7.93–16.79), Th (13.28–29.51), U (2.5–4.71), Hf (3.31– 12.50), Nb (11.75– 17.68), Ta (1.08–1.58), W (1.46–2.90), Cr (43.48–120.61), Mo (0.12–0.72), Co (9.99–19.81), Ni (19.20–85.80), Cu (11.70–48.96), Cd (0.02–0.17), Ga (13.48–23.48), In (0.01–0.09), Tl (0.12–1.04), Ge (1.33–1.63), Pb (19.63–28.78), Bi (0.14–0.88)	Surface sediment	*CF, EF, Igeo, PLI*			

Table A1. *Cont.*

Authors	Location	Use	Analysed HMs	TMs Ranges [mg/kg d.w.]	Sampling	Indices	SQG	Heath Risk	Chemical Speciation Analysis
Dević et al., 2020 [39]	Belgrade (Serbia)	Urban area of New Belgrade; Sava River and reservoirs for diesel fuel and mazut; high traffic zone	10 elements: V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb	V (49.9–299.9), Cr (37–150.9), Mn (395–925), Fe (17,400–32,400), Co (15.99–36.99), Ni (50–139.9), Cu (5.5–30.9), Zn (1–615), Cd (1–4), Pb (20–190)	Sediment cores and surface sediment	$Igeo$, PERI, PLI, $PI_{Nemerow}$			
Wang et al., 2019 [40]	Mid-channel of the Wen-Rui Tang River and its tributaries (China)	Rural–urban area	Five elements: Cr, Cu, Zn, Cd, Pb	Average: Cr (248 ± 131), Cu (995 ± 2011), Zn (2345 ± 2901), Cd (62 ± 125), Pb (217 ± 226)	Surface sediment (0–10 cm)	$E_r{}^i$, PERI, RAC	+		
Cui et al., 2020 [41]	Dongfenggou River, Miaotaigou River, Huaijiagou River, Harbin (China)	Suburban rivers	Six elements: Cr, Ni, Cu, Zn, Cd, Pb	Cr (64.0–180.6), Ni (11.8–106.4), Cu (14.6–182.5), Zn (175.8–1198.8), Cd (0.3–3.8), Pb (16.8–150.6)	Surface sediments	PLI, RI			
Barhoumi et al., 2019 [42]	Someşu Mic River (Romania)	Different human activities around, e.g., industries, urban, and agriculture	Eight elements: Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb	Cr (9.39–43.15), Mn (159.90–4707.21), Fe (11,359–35,661.28), Ni (14.73–47.69), Cu (7.22–65.56), Zn (42.12–236.82), Cd (0.04–0.35), Pb (12.27–131.39)	Surface sediment (0–20 cm)	EF, $Igeo$, Romanian legislation	+		
Nodefarahani et al., 2020 [43]	Namak Lake (Iran)	Seasonal lake nourished by surface run-off and groundwater resources	Nine elements: V, Cr, Mn, Fe, Ni, Cu, Zn, Al., Pb	V (0.55–3.19), Cr (0.507–1.83), Mn (5.1–34.1), Fe (195.6–1117), Ni (0.239–1.209), Cu (0.57–1.3), Zn (0.346–1.225), Al (1.140–1.903), Pb (0.15–1.16)	Surface sediment	$Igeo$, EF, mPECQ	+		
Nargis et al., 2018 [44]	River Buriganga (Bangladesh)	Most of the industries and/or factories, such as tanneries, metal goods manufacturing, electroplating, batteries, shipyard, are located on the banks of the river	15 elements: Ba, U, V, Cr, Mo, Mn, Ni, Cu, Zn, Cd, Hg, As, Bi, Se, Pb	Ba (20.80 ± 2.21^M **; 23.09 ± 2.63^W ***), U (0.45 ± 0.09^M; 0.50 ± 0.11^W), V (7.51 ± 2.25^M; 8.66 ± 2.77^W), Cr (39.70 ± 18.84^M; 41.45 ± 15.88^W), Mo (0.40 ± 0.09^M; 0.44 ± 0.11^W), Mn (37.58 ± 3.13^M; 39.06 ± 2.72^W), Ni (6.39 ± 0.96^M; 7.14 ± 1.11^W), Cu (14.07 ± 15.93^M; 15.93 ± 18.38^W), Zn (36.73 ± 34.38^M; 40.71 ± 37.33^W), Cd (0.21 ± 0.02^M; 0.23 ± 0.03^W), Hg (0.016 ± 0.001^M; 0.018 ± 0.001^W), As (0.18 ± 0.12^M; 0.21 ± 0.13^W), Bi (0.33 ± 0.02^M; 0.36 ± 0.02^W), Se (1.07 ± 0.05^M; 1.19 ± 0.05^W), Pb (10.41 ± 13.61^M; 11.40 ± 15.09^W)	Surface sediment (0–5 cm)	C_{deg}, CF, $E_r{}^i$, PLI, PERI			

Table A1. *Cont.*

Authors	Location	Use	Analysed HMs	TMs Ranges [mg/kg d.w.]	Sampling	Indices	SQG	Heath Risk	Chemical Speciation Analysis
Xia et al., 2020 [45]	Wuhan (China)	20 lakes along a rural to the urban gradient in central China	11 elements: Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Al, As	Cr (111.35 ± 43.93[RRG] ****; 95.50 ± 4.89[RCFG] *****; 111.29 ± 36.18[UPG] ******; 99.78 ± 8.47[UCFG] *******), Mn (970 ± 640[RRG]; 420 ± 140[RCFG]; 590 ± 100[UPG]; 710 ± 160 [UCFG]), Fe (37,570 ± 12,660[RRG]; 38,640 ± 3110[RCFG]; 38,260 ± 3010[UPG]; 39,900 ± 3080 [UCFG]), Co (19.81 ± 7.54[RRG]; 15.93 ± 1.40[RCFG]; 14.12 ± 1.37[UPG]; 16.63 ± 1.09 [UCFG]), Ni (32.10 ± 9.24[RRG]; 43.67 ± 4.25[RCFG]; 40.47 ± 3.30[UPG]; 44.61 ± 3.50 [UCFG]), Cu (105.45 ± 113.98[RRG]; 37.37 ± 5.47[RCFG]; 93.72 ± 74.94[UPG]; 62.65 ± 35.21 [UCFG]), Zn (105.75 ± 43.16[RRG]; 95.97 ± 13.15[RCFG]; 166.71 ± 4.71[UPG]; 134.41 ± 37.27 [UCFG]), Cd (0.50 ± 0.16[RRG]; 0.32 ± 0.06[RCFG]; 0.61 ± 0.16[UPG]; 0.45 ± 0.11 [UCFG]), Pb (32.59 ± 6.55[RRG]; 29.51 ± 2.15[RCFG]; 62.87 ± 27.83[UPG]; 39.06 ± 11.88 [UCFG]), Al (25,770 ± 15,580[RRG]; 23,600 ± 9400[RCFG]; 45,500 ± 3290[UPG]; 33,760 ± 16,500 [UCFG]), As (6.53 ± 1.89[RRG]; 10.04 ± 1.05[RCFG]; 10.69 ± 0.85[UPG]; 11.15 ± 1.49 [UCFG])	Surface sediment (0–5 cm)	*EF, RI*			
Wojciechowska et al., 2019 [46]	Gdansk (Poland)	Bottom sediments of urban retention tanks	Six elements: Cr, Ni, Cu, Zn, Cd, Pb	Cr (2.43–25.8), Ni (3.76–11.03), Cu (3.04–1133), Zn (17.9–362), Cd (0.088–0.60), Pb (5.77–162)	Surface sediment (0–5 cm)	*CF, Igeo, LAWA, PLI, RI,*		HQ	
Nawrot et al., 2020 [47]	Gdansk (Poland)	Bottom sediments of urban retention tanks	Six elements: Cr, Fe, Ni, Cu, Zn, Cd, Pb	Cr (2.45–74.5), Fe (3993–63,817), Ni (1.57–25.8), Cu (3.24–119), Zn (12.5–584), Cd (0.003–0.716), Pb (4.91–309)	Sediment cores	*AF, EF, mC_{deg}*			+

Table A1. *Cont.*

Authors	Location	Use	Analysed HMs	TMs Ranges [mg/kg d.w.]	Sampling	Indices	SQG	Heath Risk	Chemical Speciation Analysis
Jaskuła et al., 2021 [48]	Warta River (Poland)	Bottom sediments of the third longest river in Poland	Six elements: Cr, Ni, Cu, Zn, Cd, Pb	Cr (0.78–193), Ni (0.56–36.7), Cu (0.40–116), Zn (0.50–519), Cd (0.03–14.5), Pb (1.0–144)	Surface sediment (0–5 cm)	*EF, Igeo, MPI, PLI*	+		
Kostka and Leśniak, 2021 [49]	Wigry Lake (Poland) * WL	Bottom sediments	Seven elements: Cr, Mn, Fe, Cu, Zn, Cd, Pb	Cr (0.20–22.61), Mn (18–1698), Fe (80–32,857), Cu (0.02–59.7), Zn (3.1–632.1), Cd (0.003–3.060), Pb (7.0–107.5)	Surface sediment (0–5 cm)	SQG	+		
Ribbe et al., 2021 [50]	Lake Victoria, Ugandan part (Uganda)	Bottom sediments of the largest tropical lake in the world	Seven elements: Cr, Ni, Cu, Zn, Cd, Pb, As	Cr (29–100), Ni (19–56), Cu (21–121), Zn (49–103), Cd (0.06–0.26), Pb (10–25), As (2.9–6.6)	Surface sediment (the upper 15 cm)	*Igeo,* LAWA			+
Xiao et al., 2021 [51]	Lijiang River, Guilin City (China)	Analysis of a 160 km section of the river	10 elements: Cr, Mn, Co, Ni, Cu, Zn, Cd, Hg, Pb, As	Cr (24.38–95.38), Mn (176.25–1572.50), Co (4.50–15.38), Ni (11.63–37.13), Cu (9.38–102.75), Zn (53.63–258.0), Cd (0.16–4.41), Hg (0.08–2.13), Pb (17.88–171.75), As (9.97–36.44)	Surface sediment (0–5 cm)	*Igeo, mC$_{deg}$, RI*			
Castro et al., 2021 [52]	San Luis River (Argentina)	Bottom sediments	Nine elements: Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb, As	Cr (0.5–32), Mn (10–420), Co (0.5–14), Ni (1–19), Cu (0.5–70), Zn (0–600), Cd (0–1,5), Pb (0–45), As (0.5–18)	Surface sediment (0–2 cm)	*CF, EF, Igeo*	+		

Explanations: * BDL—below detection limit; ** M—in monsoon; *** W—in winter; **** RCFG—rural commercial fishing group; ***** RRG—rural reservoir group; ****** UPG—urban park group; ******* UCFG—urban commercial fishing group * WL Wigry Lake in Poland is located in Wigry National Park (non urban area)—just to comparison with other studies.

Appendix B

Table A2. A list of Individual (single) Pollution Indices (IPIs) given in the literature with classification and a basic description of strengths and weaknesses.

Index	Formula	Classification	Description (Pros "+" and Cons "–")	References
Contamination Factor (*CF*)	$CF = \frac{C_{mSample}}{C_{mPre}}$ $C_{mSample}$—TM content $* C_{mPre}$—preindustrial concentration of TM	CF < 1—low, $1 \leq CF < 3$—moderate, $3 \leq CF < 6$—considerable, $CF \geq 6$—very high	+ dedicated to individual metal + simple in use (easy to calculate) + comparing the sample to the reference contamination status of analysed element (pre-industrial) − omits the TM availability and mobility in the environment − omits the natural variability process, grain-size, and reference elements ratios	[58]

Table A2. *Cont.*

Index	Formula	Classification	Description (Pros "+" and Cons "−")	References
Geoaccumulation Index (I_{geo})	$I_{geo} = \log_2\left[\dfrac{C_{mSample}}{1.5 \times C_{mBackground}}\right]$ $C_{mSample}$—TM content $C_{mBackground}$—geochemical background concentration of TM	Class 0: Igeo ≤ 0—uncontaminated, Class 1: 0 < Igeo ≤ 1—uncontaminated to moderately contaminated, Class 2: 1 < Igeo ≤ 2—moderately contaminated, Class 3: 2 < Igeo ≤ 3—moderately to strongly contaminated, Class 4: 3 < Igeo ≤ 4—strongly contaminated, Class 5: 4 < Igeo ≤ 5—strongly to extremely contaminated, Class 6: Igeo > 5—extremely contaminated	+ dedicated to individual metal + simple in use (easy to calculate) + comparing the sample to the background contamination status of analysed element + 1.5 multiplication factor reduces the possible variation of lithogenic effects + precise scale + widely used − omits the TM availability and mobility in the environment − omits the natural variability process, grain-size, and reference elements − incorrect selection of *Background* leads to mistaken results	[59]
Enrichment Factor (*EF*)	$EF = \dfrac{\frac{C_{mSample}}{C_{ref}}}{\frac{C_{mBackground}}{B_{ref}}}$ $C_{mSample}$—TM content $C_{mBackground}$—geochemical background concentration of TM C_{ref}—concentration of the reference TM in analysed sample B_{ref}—reference TM concentration in the reference environment	EF < 1—no enrichment, 1 ≤ EF < 3—minor enrichment, 3 ≤ EF < 5—moderate enrichment, 5 ≤ EF < 10—moderately severe enrichment, 10 ≤ EF < 25—severe enrichment, 25 ≤ EF < 50—very severe enrichment, EF ≥ 50—ultra-high enrichment	+ dedicated to individual metal + simple in use (easy to calculate) + comparing the sample to the reference contamination status of analysed element and to the normalise element (e.g., Al or Fe) as well as to reference content of analysed TM and normalise element + estimate the anthropogenic impact at all the possibility of contamination assessment of several TMs in reference to normalise element + precise scale + widely used − omits the TM availability and mobility in the environment − omits the natural variability process, grain-size − incorrect selection of *reference* value leads to mistaken results	[60]
Pollution Index (P_i) = Single Pollution Index (*SPI*)	$P_i = SPI = PI = \dfrac{C_{mSample}}{C_{mBackground}}$ $C_{mSample}$—TM content $C_{mBackground}$—geochemical background concentration of TM	P_i < 1—unpolluted, low level of pollution 1 ≤ P_i ≤ 3—moderate polluted 3 > P_i—strong polluted	+ dedicated to individual metal + simple in use (easy to calculate) + comparing the sample to the background contamination status of analysed element +/− similar to CF − omits the TM availability and mobility in the environment − omits the natural variability process, grain size, and reference elements ratios	[15,54]

Table A2. *Cont.*

Index	Formula	Classification	Description (Pros "+" and Cons "–")	References
Threshold Pollution Index (PI_T)	$PI_T = \dfrac{C_{mSample}}{C_{TL}}$ $C_{mSample}$TM content C_{TL}—tolerance levels of metal concentration;	PI_T < 1—unpolluted $1 \leq PI_T \leq 2$—low polluted $2 \leq PI_T \leq 3$—moderate polluted $3 \leq PI_T \leq 5$—strong polluted $5 \leq PI_T$—very strong polluted	+ dedicated to individual metal + simple in use (easy to calculate) + comparing the sample to the tolerance level of metal concentration (which could be assumed as a comparative value before assessment) +/− freedom in determining the threshold parameter (C_{TL}) (which can be matched with stringent pollution determination regulations) +/− similar to CF − omits the TM availability and mobility in the environment − omits the natural variability process, grain size, and reference elements ratios	[28]

* Preindustrial concentration of TM according to Håkanson [58] [mg/kg]: Hg—0.25, Cd—1.0, As—15, Cu—50, Pb—70, Cr—90, Zn—175.

Appendix C

Table A3. A list of Complex Pollution Indices (CPIs) given in the literature with classification and basic description of strengths and weaknesses.

Index	Formula	Classification	Description (Pros "+" and Cons "–")	References
Pollution Load Index (*PLI*)	$PLI = \sqrt[n]{CF_1 \cdot CF_2 \cdot CF_3 \cdot \ldots \cdot CF_i}$ CF_i—Contamination Factor of i element n—the number of analysed TMs	PLI < 1—not polluted PLI = 1—baseline levels of pollution PLI > 1—polluted	+ allows for identifying the contamination in relation to several trace metals + easy to apply (easy to calculate) + widely used + gives the comprehensive screen of sediment sample + allows comparing samples taken from different locations + used *CF* (includes C_{mPre})* − omits the TM availability and mobility in the environment − omits the natural variability process, grain size, and reference elements ratios − incorrect selection of C_{mPre} value could lead to mistaken results	[62]

<div align="center">Table A3. *Cont.*</div>

Index	Formula	Classification	Description (Pros "+" and Cons "−")		References
Degree of contamination (C_{deg})	$C_{deg} = \sum\limits_{i=1}^{n} CF_i$ CF_i—Contamination Factor of i element n—the number of analysed TMs	$C_{deg} < 8$—low degree of contamination $8 \leq C_{deg} < 16$—moderate degree of contamination $16 \leq C_{deg} < 32$—considerable degree of contamination $C_{deg} \geq 32$—very high degree of contamination	+ + + + + − − − − −	allows for identifying the contamination in relation to several trace metals easy to apply (easy to calculate) precise scale assesses a sum of contamination factors used CF (includes C_{mPre}) * not widely used does not include geochemical background the preindustrial reference value is necessary omits the TMs availability and mobility in the environment omits the natural variability process, grain size, and reference elements ratios	[58]
Modified contamination factor (mC_{deg})	$mC_{deg} = \frac{1}{n} \cdot \sum\limits_{i=1}^{n} CF_i$ CF_i—Contamination Factor of i element n—the number of analysed TMs	$mC_{deg} < 1.5$—very low $1.5 \leq mC_{deg} < 2$—low $2 \leq mC_{deg} < 4$—moderate $4 \leq mC_{deg} < 8$—high $8 \leq mC_{deg} < 16$—very high $16 \leq mC_{deg} < 32$—extremely high $mC_{deg} \geq 32$—ultra-high	+ + + + + + − − − −	allows for identifying the contamination in relation to several trace metals easy to apply (easy to calculate) precise scale assesses a sum of contamination factors used CF (includes C_{mPre}) * widely used does not include geochemical background the preindustrial reference value is necessary omits the TMs availability and mobility in the environment omits the natural variability process, grain size, and reference elements ratios	[64]
Sum of Pollution Index (PI_{sum})	$PI_{sum} = \sum\limits_{i=1}^{n} P_i$ P_i—calculated value for Pollution Index n—the number of analysed TMs	The classification for Pi can be used in PI_{sum}. The values in PI_{sum} should be multiplied by n (count of TMs): $PI_{sum} < 1n$—unpolluted, low level of pollution $1n \leq PI_{sum} \leq 3n$—moderately polluted $3n < PI_{sum}$—heavily polluted	+ + + − − − −	defined as the sum of all determined contents of TMs, expressed as Pi dedicated to combining all analysed TMs based on Pi (includes $C_{mBackground}$) does not require the variation of natural processes omits the TMs availability and mobility in the environment the key is the choice of appropriate $C_{mBackground}$ value does not include precise scale	[63]

Table A3. *Cont.*

Index	Formula	Classification	Description (Pros "+" and Cons "−")	References
Average of Pollution Index (PI_{Avg})	$PI_{Avg} = \frac{1}{n} \cdot \sum_{i=1}^{n} P_i$ P_i—calculated value for Pollution Index n—the number of analysed TMs	PI_{Avg} values in excess of 1.0 show a lower quality of the sediments, which is conditioned by high contamination and low quality	+ allows for identifying the contamination in relation to several trace metals + based on Pi (includes $C_{mBackground}$) + easy to apply (easy to calculate) + lack of threshold for maximum values − does not require the variation of natural processes − omits the TMs availability and mobility in the environment − the key is the choice of appropriate $C_{mBackground}$ value − does not include precise scale	[63]
Weighted Average of Pollution Index (PI_{wAvg})	$PI_{wAvg} = \sum_{i=1}^{n} w_i \cdot P_i$ P_i—calculated value for Pollution Index w_i weight of P_i n—the number of analysed TMs	When PI_{wAvg} is used with the $\Sigma w_i = 1$ condition, terminologies can also be used as single indices (the classification for Pi can be applied)	+ dedicated to combining all analysed TMs + based on Pi (includes $C_{mBackground}$) − does not include precise scale − require to establish the weight of P_i values for each TM − the condition $\Sigma w_i = 1$ is not necessary, so the "average" is just for the sake of meaning in terminology	[58,59,63]
Background enrichment factor = New Pollution Index (PIN)	$PIN = \sum_{i=1}^{n} W_i^2 \cdot P_i$ P_i—calculated value for Pollution Index W_i class of TM considering degree of contamination (from 1 to 5 basing on P_i) n—the number of analysed TMs	$0 \leq PIN < 7$—clean $7 \leq PIN < 95.1$—trace contaminant $95.1 \leq PIN < 518.1$—lightly contaminant $518.1 \leq PIN < 2548.5$—contaminant $PIN \geq 2548.8$—high contaminant	+ dedicated to integrating contamination into a single value + based on Pi (includes $C_{mBackground}$) + precise scale − not widely used − omits the TMs availability and mobility in the environment − requires the computation of W_i	[65]
Product of Pollution Index (PI_{Prod})	$PI_{Prod} = \prod_{i=1}^{n} P_i$ P_i—calculated value for Pollution Index n—the number of analysed TMs	The classification for Pi can be used in PI_{Prod}. The values in PI_{Prod} should be powered by n (count of TMs): $PI_{Prod} < 1^n$—unpolluted, low level of pollution $1^n \leq PI_{Prod} \leq 3^n$—moderately polluted $3^n < PI_{Prod}$—heavily polluted	+ defined as the product of all determining contents of TMs, expressed as Pi + dedicated to combining all analysed TMs + based on Pi (includes $C_{mBackground}$) − does not require the variation of natural processes − omits the TMs availability and mobility in the environment − the key is choice of appropriate $C_{mBackground}$ value − does not include precise scale − not widely used	[63]

Table A3. *Cont.*

Index	Formula	Classification	Description (Pros "+" and Cons "−")	References
Weighted power product of Pollution Index (PI_{wpProd})	$PI_{wpProd} = \prod\limits_{i=1}^{n} P_i^{w_i}$ P_i—calculated value for Pollution Index w_i weight of P_i n—the number of analysed TMs	When PI_{wpProd} is used with the $\Sigma w_i = 1$ condition, terminologies can also be used as single indices (the classification for Pi can be applied)	+ dedicated to combine all analysed TMs + based on Pi (includes $C_{mBackground}$) − does not include precise scale − require to establish the weight of P_i values for each TM − the condition $\Sigma w_i = 1$ is not necessary	[63]
Vector modulus of Pollution Index ($PI_{vectorM}$)	$PI_{vectorM} = \sqrt{\frac{1}{n} \cdot \sum\limits_{i=1}^{n} P_i^2}$ P_i—calculated value for Pollution Index n—the number of analysed TMs	Not specified	+ easy to apply (easy to calculate) + application of $C_{mBackground}$ + based on Pi + dedicated to combine all contaminations in one index − not specified scale − not widely used (not much described in the literature) − does not require the variation of natural processes	[63]
Nemerow Pollution Index ($PI_{Nemerow}$)	$PI_{Nemerow} = \sqrt{\frac{\left(\frac{1}{n} \cdot \sum_{i=1}^{n} P_i\right)^2 + P_{imax}^2}{2}}$ P_i—calculated value for Pollution Index P_{imax}—the maximum value of the single pollution indices of all TMs n—the number of analysed TMs	$PI_{Nem} < 0.7$—safety domain $0.7 \le PI_{Nem} < 1$—precaution domain $1 \le PI_{Nem}$ w< 2—slightly polluted domain $2 \le PI_{Nem} < 3$—moderately polluted domain $PI_{Nem} > 3$—seriously polluted	+ reflects the sediment environmental pollution + emphasize the maximum value of the single P_i of all TMs + precise scale + dedicated to combine all analysed TMs with reference to the maximum value of the single P_i − does not include weight of P_i values − needs to rank elements	[66]
Integrated Pollution Index ($IntPI$)	$IntPI = mean(P_{ii})$ P_i—calculated value for Pollution Index	$IPI < 1$—low contaminated $1 \le IPI \le 2$—moderately contaminated $IPI < 2$—heavily contaminated	+ easy to apply (easy to calculate) + application of $C_{mBackground}$ + based on Pi − not widely used − does not require the variation of natural processes	[67]
Metallic Pollution Index (MPI)	$MPI = (Pi_1 \cdot Pi_2 \cdot \ldots \cdot Pi_n)^{1/n}$ P_i—calculated value for Pollution Index n—the number of analysed TMs	$MPI > 1$—indicate pollution $MPI < 1$—indicate no pollution	+ similar to PLI + basing on Pi values + gives the comprehensive screen of sediment sample + allows to compare samples taken from different locations − omits the TM availability and mobility in the environment − omits the natural variability process, grain size, and reference elements ratios	[68,69]

* (includes C_{mPre})—with reference to the literature, the CPIs are related to the IPI, but it should be noted that in the IPI C_{mPre} and $C_{mBackground}$ are two different concepts that are often confused/or taken interchangeably.

Appendix D

Table A4. A list of ecotoxicological indices (EIs) given in the literature with classification and basic description of strengths and weaknesses.

Index	Formula	Classification	Description (Pros "+" and Cons "–")	References
Individual Ecotoxicological Index (IEI)				
Ecological Risk Factor (*ER*, E_r^i) Risk Index (*RI*)	$ER^i = T_r^i \cdot CF^i$ ∗ T_r^i – toxic-response factor for a given element "i" CF^i—contamination factor for a given element "i";	$ER^i < 40$—low potential ecological risk; $40 \leq ER^i < 80$—moderate potential ecological risk; $80 \leq ER^i < 160$—considerable potential ecological risk; $160 \leq ER^i < 320$—high potential ecological risk; $ER^i \geq 320$—very high ecological risk	+ dedicated to the toxicity of individual metals + simple in use (easy to calculate) + uses *CF* values − omits the TM availability and mobility in the environment − omits the natural variability process, grain size, and reference elements ratios	[58]
Complex Ecotoxicological Index (CEI)				
Contamination Severity Index (*CSI*)	$CSI = \sum_{i=1}^{n} w \cdot \left(\left(\frac{C_{mSample}}{ERL} \right)^{\frac{1}{2}} + \left(\frac{C_{mSample}}{ERM} \right)^2 \right)$ *w*—the computed weight of each TM according to Pejman et al. [86] ** $C_{mSample}$ TM content *ERL*—Effects Range-Low according to Table 2 *ERM*—Effects Range-Median according to Table 2 $w = \frac{(loading\ value_i \cdot eigen\ value)}{\sum_{i=1}^{n}(loading\ value_i \cdot eigen\ value)}$ *loading value_i* and *eigen value*—determined with the use of PCA/FA	$CSI < 0.5$—uncontaminated $0.5 \leq CSI < 1$—very low severity of contamination $1 \leq CSI < 1.5$—low severity of contamination $1.5 \leq CSI < 2$—low to moderate severity of contamination $2 \leq CSI < 2.5$—moderate severity of contamination $2.5 \leq CSI < 3$—moderate to high severity of contamination $3 \leq CSI < 4$—high severity of contamination $4 \leq CSI < 5$—very high severity of contamination $5 \leq CSI$—ultra-high severity of contamination	+ helpful in determining the limit of toxicity above which adverse impacts on the sediment environment are observed + precise scale + dedicated to combining all contaminations in one index + includes adverse biological effects − not widely used − needs the *ERL* and *ERM* values − requires the *w* values of each TM, which should be calculated using PCA/FA with considered the factors attributed to anthropogenic sources	[86]
Sediment Pollution Index (*SPI*)	$SPI = \frac{\sum_{i=1}^{n} \frac{C_{mSample}^i}{C_{mAverage}^i} \cdot T_r^i}{\sum_{i=1}^{n} T_r^i}$ $C_{mSample}$ TM content in a sample $C_{mAverage}$—average shale concentration of TM ∗ T_r^i —toxic-response factor for a given element "i" *n*—the number of analysed TMs	$0 \leq SPI < 2$—natural sediments $2 \leq SPI < 5$— low polluted $5 \leq SPI < 10$—moderately polluted $10 \leq SPI < 20$—highly polluted $SPI > 20$—dangerous sediments	+ includes the toxicity of individual metal + simple in use (easy to calculate) + combined index + delivers the information of diverse sites contamination − omits the TM availability and mobility in the environment − omits the natural variability process, grain size, and reference elements ratios − neglecting the changes of TM/reference element ratios based on natural processes − TM toxicity weights are available for Hg, Cd, As, Cu, Pb, Cr, and Zn	[58,64]

Table A4. *Cont.*

Index	Formula	Classification	Description (Pros "+" and Cons "−")	References
Risk Assessment Code (*RAC*)	The exchangeable and carbonate fractions are determined by a single extraction with a CH_3COOH 0.11 M solution	Percentage extracted by CH_3COOH 0.11 M solution is compared to the following scale: $RAC \leq 1$—no risk $1 < RAC \leq 10$—low risk $11 < RAC \leq 30$—medium risk; $31 < RAC \leq 50$: very high risk	+ indicates the potential risk to the ecosystem caused by TMs bounded in fractions weakly associated in the sediments + Delivers real risk information − the extraction procedure is needed (time-consuming procedure)	[35]
Risk Index (*PERI*)	$PERI = \sum_{i=1}^{n} ER^i$ n—the number of analysed TMs ER^i—calculated value for Ecological Risk Factor	$PERI < 90$—low $9 \leq PERI < 180$—moderate $180 \leq PERI < 360$—strong $360 \leq PERI < 720$—very strong $PERI \geq 720$—highly strong	+ comprehensive ecological risk and contamination assessment + includes the toxicity of analysed metals (basing on ER^i) + simple in use (easy to calculate) − disadvantages similar to ER^i	[87,88]
The probability of toxicity (*MERMQ*)	$MERMQ = \dfrac{\sum_{i=1}^{n} \frac{C_{mSample}{}^i}{ERM^i}}{n}$ $C_{mSample}$ TM content n—the number of analysed TMs ERM—Effects Range-Median according to Table 2 This index is also found as combined effect of Toxic Metals, means (*mPECQ*): $mPECQ = \sum_{i=1}^{n} \dfrac{\frac{C_{mSample}{}^i}{PEC^i}}{n}$ $C_{mSample}$ TM content n—the number of analysed TMs PEC—probable effect concentration according to Table 2	$MERMQ < 0.1$—low-risk level (probability of toxicity—9%) $0.1 \leq MERMQ < 0.5$—medium risk level (probability of toxicity—21%) $0.5 \leq MERMQ < 1.5$—high risk level (probability of toxicity—49%) $MERMQ > 1.5$—very high-risk level (probability of toxicity—76%)	+ dedicated to combining all contaminations in one index + precise scale + helpful in determining the biological effects + identification of risk areas − not widely used − needs the ERM/PEC values + does not require the variation of natural processes	[86]

* Toxic response factor for subsequent trace metals according to Håkanson [58]: Hg—40, Cd—30, As—10, Cu—5, Pb—5, Cr—2, Zn—1. ** Weight of each heavy metal according to Pejman et al. [86]: Cu—0.075, Zn—0.075, Cr—0.134, Ni—0.215, Pb—0.251, Cd—0.25.

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