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# Pollution and Ecological Risk Assessment of Potentially Toxic Elements in Sediments Along the Fluvial-to-Marine Transition Zone of the Don River

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**Abstract:** The quality of sediments in the mixing zone of river freshwater and marine saline water as an important geochemical barrier for potentially toxic elements (PTEs) remains poorly understood. This study aims to analyze the current pollution with PTEs and associated ecological risks in sediments of the Don River delta and the surrounding area of the Taganrog Bay of the Sea of Azov (Russia). The PTE content was determined in fifty-four collected samples using the WDXRF and assessed using geochemical and ecotoxicological indicators. The source of Cr, Mn, Ni and Pb is mainly river runoff, and Cu, Zn and Cd are from a variety of anthropogenic sources. As shown by the assessment of the geoaccumulation index (*Igeo*), single pollution index (*PI*) and contamination factor (*CF*), these elements are the priority pollutants. According to these estimates, high and very high contamination of sediments in the estuarine zone of the Don River with Cd and Pb was detected in 72–94% and 2–57% of samples, respectively. However, environmental risks are determined almost exclusively by the level of Cd. Total contamination as assessed by the Nemerow pollution index (*NPI*), modified degree of contamination ($mC_d$) and metal pollution index (*MPI*) is of concern in 83–98% of the samples studied. The most heavily polluted sediments are in the vicinity of residential areas of the Taganrog Bay. Despite the lower average pollution levels of deltaic sediments, freshwater biota are exposed to higher potential toxic risks of adverse effects by PTE, particularly from Ni and Pb. Thus, the complex hydrological regime and uneven anthropogenic impact predetermine the geochemical state of the sediments of the estuarine zone of the Don River.

**Keywords:** heavy metals; trace elements; PTEs; surface sediments; sediment pollution; sediment contamination; pollution level; ecological risk; risk assessment; Southern Russia



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## 1. Introduction

Over the past decades, there has been growing interest among researchers in studying the state of sediments of river-to-marine transition zones of large rivers based on the content of priority pollutants. The aquatic environments of large river deltas and estuarine zones significantly moderate the continual geochemical cycles, as well as control the transport of dissolved and suspended matter from vast watersheds to seas and oceans [1–5]. Despite the high importance of fluvial–marine systems for sustainable development and pollution mitigation at both the regional and global levels, a comprehensive analysis of their current status is quite difficult to achieve [6]. The following situation is predetermined by the dynamic nature of delta and coastal landscapes, as well as constant transformation due to the natural and anthropogenic changes in natural environments [6–8].

River freshwater infilling, waves and tides, coastal abrasion and storms in the sea–river transition zone, as well as erosional processes in watersheds, strongly affect the morphology and geochemistry of large river deltas and estuarine areas [9–12]. The above processes have a significant impact on aquatic and floodplain ecosystems, paddy soils and, most dramatically, sedimentation rate and chemical composition of riverbeds and nearshore sediments [13–18]. The latter is of particular interest since the geochemistry of estuarine sediments is important both for the assessment of historic erosion and pollution within a catchment [19] and for determining the contribution of specific sources and activities [12,20,21]. Another issue related to this component of the aquatic environment is the potential ability of sediments accumulated within delta channels, as well as coastal and near-shore zones of the marine part of the system, to become a source of secondary pollution [22]. The large amounts of pollutants, accumulated within the sediments of large river deltas in highly industrialized and populated regions of the world, can be subjected to remobilization due to strong storms [23], tsunamis [24,25] or other catastrophic natural or anthropogenically induced events [26], that could occur either upstream or at sea.

Analysis of the levels and potential environmental risks of most common pollutants in river delta sediments and adjacent marine areas is important for the sustainable management of these landscapes. Many recent studies focus on emerging pollutants, particularly polycyclic aromatic hydrocarbons [27–29], polychlorinated biphenyls [30,31], microplastics [32–34], etc. due to their high toxicity [35]. At the same time «traditional» pollutants such as potentially toxic elements (PTEs) can be of high concern and significantly contribute to the total pollution; additionally, their accumulation period duration can be very long, and may correspond to the preindustrial and early industrial periods [19,36].

The assessment of sediment pollution by PTEs and the associated potential risks of their negative impact on aquatic ecosystems involves several fundamental approaches. The first approach consists of directly assessing contamination as an excess level of PTE due to anthropogenic activity relative to the natural abundance of chemical elements in sediments, or the geochemical background [1,17,20,37,38]. The global background, in particular the content of elements in the upper continental crust (UCC) [17,36,39], sedimentary rocks, soils, the regional geochemical background corresponding to threshold or baseline values in pristine sediments formed under similar conditions [17,40,41], or the preindustrial reference value, are used as the normal concentration of PTEs. Sediment contamination with an individual PTE is determined by calculating various indicators, in particular the enrichment factor (*EF*), single pollution index (*PI*), geoaccumulation index (*Igeo*), contamination factor (*CF*), etc., characterizing the excess of their contents over the background, including the use of fractional or elemental normalization. Overall pollution is defined as a sum, arithmetic mean, geometric mean, or other metric assessed on a given scale [1,37,38]. This approach does not take into account the toxicity of PTEs and their fate in landscapes, but this drawback is overcome by assessing potential ecological risks using the Hakanson scheme [42]. Direct negative effects of pollutants from sediments on aquatic biota are assessed by biotesting, but this method is expensive and time-consuming. As an alternative, current levels of PTEs in sediments are compared using sediment quality guidelines (SQGs) [2], which are empirically derived from sediment chemistry, toxicity, bioaccumulation, and community structure data [35,43]. SQGs are those levels of pollutants at which, if exceeded, significant negative biological effects occur.

Recent geochemical studies of the ecosystems of the transition zone of the Don River–Taganrog Bay system demonstrate high levels of anthropogenic PTE in floodplain and coastal soils [44–47], vegetation [47–49], waters and suspended matter [50–54], marine bottom sediments [55–57] and freshwater sediments [31,58]. At the same time, an assessment of the quality of surface and bottom sediments of the coast of the Taganrog Bay and the Don Delta in terms of the level of PTEs and possible risks to the environment has not been carried out previously. In this context, this work aims to contribute to the study of geochemistry and the quality of sediments along the fluvial to marine transition zone of the Don River. To this end, physicochemical sediment parameters, levels and sources of

PTE and related pollution status, and ecological and ecotoxicological risks were analyzed and compared in sediments of the Don River delta and adjacent coast of the Taganrog Bay.

## 2. Materials and Methods

### *2.1. Study Area*

Taganrog Bay is the largest in the shallow shelf inland Sea of Azov, located in Eastern Europe (Figure 1A). The part of the bay that juts out onto the shore contains the mouth of the largest river flowing into the Sea of Azov—the Don [4]. The modern geomorphology and sediments of the Azov region were formed in the Holocene during the last transgression of the Black Sea under conditions of uneven sea level rise with downward tectonic movements [59]. The region has a humid continental climate (Dfa according to the Köppen classification) with cold winters and dry, hot summers. North and north-eastern winds prevail during cold seasons and west to south-western during the warm season [60].

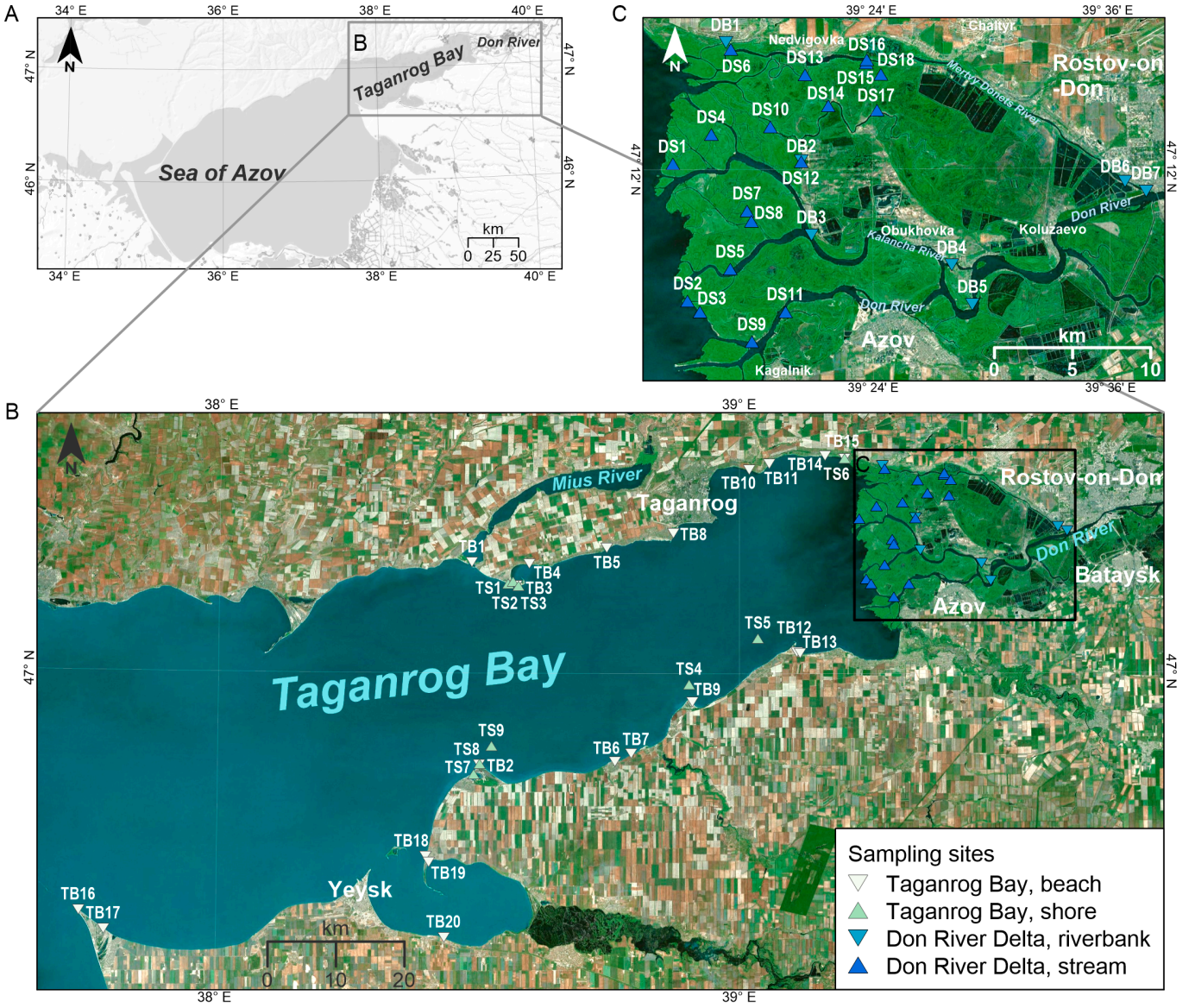


**Figure 1.** Location of sampling sites for surface and bottom sediments within the Sea of Azov basin (**A**), along the coast of the Taganrog Bay (**B**) and the Don River delta (**C**).

The study covers the Don River estuary area, including the Don River delta (Figure 1C) and the coast of the estuary from the marine edge of the delta to the marine boundary of

the estuary area on the southern coast of the Taganrog Bay and from the edge of the delta to the mouth of the Mius River on the northern coast of the bay (Figure 1B).

The Taganrog Bay has an area of 5600 km$^2$ and an average depth of 4.9 m. The shores of the Taganrog Bay are composed mainly of loess-like loams and Scythian clays, which, due to abrasion, are the source of material for the formation of marine sediments. Depending on the prevailing geological processes, abrasion, abrasion-landslide and accumulative shores are formed [61]. The average annual sedimentation rate is 700 g m$^{-2}$ per year [56]. The Taganrog Bay basin belongs to the Black Sea steppe province, where the zonal vegetation is represented by forb–fescue–feather grass steppes reaching the supralittoral. The sandy areas of the coast are deserts with a mosaic combination of halophyte communities, and meadows, aquatic coastal and floodplain vegetation develop in the river mouths [59]. The salinity of the waters of the bay varies from 0 to 14‰ [62]. The salinity gradient of the surface layer of water in the Taganrog Bay is on average 0.5–7‰ from the edge of the Don delta to the open part in the south [63].

The modern delta of the Don River occupies the coastal part of the flat alluvial delta plain from the branch of the main channel of the Don River, the Mertvy Donets River, to the sea edge of the land delta and occupies an area of 538 km$^2$ [64]. The delta floodplain is represented by low-lying islands (0.2–1 m a.s.l.) composed of medium- and fine-grained sands, separated by numerous branches and channels. The Don Delta has a wave-dominated regime and is subject to strong sea surges and erosion of the sea edge due to the construction of the Tsimlyansk Reservoir in 1953 (309 km from the mouth) [16]. Average annual water runoff and fluvial sediment delivery of the Don River are estimated at 20.6 km$^3$ and 0.19 Mt per year, respectively [16,60]. The Don Delta is characterized by fluctuations in water salinity depending on wind-driven phenomena [29]. Under normal conditions, fresh waters predominate (0.6–0.95‰); with strong westerly winds, water salinity can reach 5–6‰ [63]. The delta combines protected, natural, rural and urban landscapes. Most of the territory is subject to continuous overgrowth by monodominant communities of southern reed *Phragmites australis* Cav. Cattail groups of *Typha australis* Schum. and Thonn. and *Typha laxmannii* Lepech. are common on the marine edge of the delta [48,49].

Anthropogenic activity is a key factor in the deterioration of the quality of ecosystems in the transit estuarine zone of the Don River. High urbanization leads to the entry of pollutants into the waters of the Lower Don and Taganrog Bay with poorly treated wastewater and storm water from the cities of Volgodonsk, Novocherkassk, Aksay, Rostov-on-Don, Bataysk, Azov, Taganrog, Yeysk, etc. [31]. Industrial production is concentrated in the cities, including ferrous metallurgy, mechanical engineering and the chemical industry, the emissions of which contain hazardous substances [55]. Port infrastructure and maritime transportation are also an important source of water and sediment pollution [45,46,57]. The coastal areas of Taganrog Bay are occupied by agricultural lands, where erosion and surface runoff lead to the entry of fertilizers, pesticides, and manure runoff into marine ecosystems [59].

### *2.2. Sediment Sampling and Preparation*

The sampling campaign was conducted from May to July 2023. Surface and bottom sediments in the Don River delta were collected in the floodplain on the river banks at a distance of 2–3 m from the water's edge (DB; $n$ = 7) and in the channels of the Don River and its large tributaries (DS; $n$ = 18), respectively. Surface and bottom sediments on the coast of Taganrog Bay were collected from beaches in the surf zone (TB; $n$ = 20) and within the underwater coastal slope (TS; $n$ = 9), respectively (Figure 1B,C, Table A1). Surface sediments were collected to a depth of 0–20 cm from five surface subsamples using a hand auger set (Eijkelkamp Agrisearch Equipment BV, Giesbeek, The Netherlands). Bottom sediments (approximately 10–15 cm thick) were collected using Van Veen modified grab sampler (Ocean-0.025, Remstroymash, Murmansk, Russia) with a surface area of 0.025 m$^2$ in triplicate from each sampling site. All samples were placed in clean polyethylene bag using a stainless-steel spatula. Collected samples were stored at 4 °C prior to further

analysis. In the laboratory, the samples were dried in an oven at a temperature < 60 °C to prevent organic matter and chemical element loss, and were mixed, ground and passed through a 1 mm sieve [65].

### *2.3. Analytical Methods*

Measurements of pH and electrical conductivity (EC) of the sediments were made in situ using a portable multimeter (WTW, Xylem Analytics, Weilheim, Germany).

Physicochemical properties were determined in all sediment samples: total organic carbon (TOC) by the modified Tyurin method [66], the $CaCO_3$ content by Kudrin's complexometric method, with the destruction of calcium carbonate with a 0.02 mol/L HCl solution and subsequent titration of excess acid with alkali [65], and sum of exchangeable cations $Ca^{2+}$ and $Mg^{2+}$ in a 1 N KCl extract determined by the Shaimukhametov method [67]. The fine clay fraction of sediments (<1 μm) was obtained using the sedimentation method proposed by Gorbunov [68].

The total concentrations of Al, Cr, Mn, Ni, Cu, Zn, Cd and Pb were determined using wavelength dispersive X-ray fluorescence (WDXRF) (Spectroscan MAX-GV, Spectron NPO Ltd., Saint Petersburg, Russia). Prior to WDXRF analysis, air-dried bulk samples were pulverized manually with an agate mortar and pressed into a tablet on a boric acid substrate. Quantitative analysis of chemical elements was carried out using Spektr-Kvant software 4 (Spectron NPO Ltd., Saint Petersburg, Russia). Detection limits were 10 mg/kg for Cr, Mn, Ni and Pb, 5 mg/kg for Cu and Zn, and 0.1 mg/kg for Cd. All laboratory tests were performed in triplicate. For quality assurance and quality control (QA/QC), the duplicates, reagent blanks, internal standards, and certified reference material GSS 3485-86 (Vinogradov Institute of Geochemistry SB RAS, Irkutsk, Russia) were used. Accuracy and precision corresponded to the standards of the certified method [69]. All the geochemical data obtained in this study are available in Table A2.

### *2.4. Pollution and Ecological Risk Assessment*

#### 2.4.1. Enrichment Factor

The enrichment factor (*EF*) is used as a means of assessing the possible origin of elements in soils [2,45], marine and river sediments [20,21,37,38,40,70–73], and suspended matter [37], and is calculated using Equation (1):

$$EF = (C_i/C_{Al})_{Sample}/(C_i/C_{Al})_{Background}, \quad (1)$$

where $C_i$ and $C_{Al}$ are the contents of a given element and Al, respectively. The background values were referenced to upper continental crust (UCC) [39] (Table A3). *EF* values > 10 indicate anthropogenic origins of PTEs in sediments [21]. According to *EF* values, enrichment can be divided into seven classes (Table A4).

#### 2.4.2. Geoaccumulation Index

The geoaccumulation index (*Igeo*), introduced by Müller [74], is widely used to assess river and marine sediment pollution by individual inorganic pollutants [1,20,37,38,40,41,43,71,72]. *Igeo* is a measure of the level of contamination of sediments by pollutants relative to the standard, which is the geochemical background in clay rocks, taking into account the elimination of natural fluctuations in background levels [74] and is calculated according to (2):

$$Igeo = \log_2(C_i/1.5C_b), \quad (2)$$

where $C_b$ is the regional geochemical background. The average PTE content in uncultivated *Haplic Chernozems* of the Northern Azov region were used as background data [48] (Table A3). Seven pollution classes are distinguished according to *Igeo* (Table A4).

2.4.3. Single Pollution Index and Nemerow Pollution Index

The single pollution index (*PI*) is the ratio of the concentration of an element in sediments to the natural background. The calculation of *PI* is the basic method for assessing the pollution of soils and sediments by individual elements and is used to calculate many complex indicators, in particular the Nemerow pollution index (*NPI*) [41,45,70,75]. The *NPI* takes into account the combined effect of the most hazardous pollutant along with the average total contamination. Both indices are calculated as follows (3) and (4):

$$PI = C_i / C_b, \quad (3)$$

$$NPI = \sqrt{\left(PI_{avg}^2 + PI_{max}^2\right)/2}, \quad (4)$$

where $PI_{avg}$ and $PI_{max}$ are the average and maximum *PI* values for a range of PTEs under consideration, respectively. The *PI* and *NPI* define one of five classes of individual and total sediment pollution (Table A4).

2.4.4. Contamination Factor and Modified Degree of Contamination

The contamination factor (*CF*) was presented by Hakansson [42] as a measure of the level of pollution of sediments, determined by comparing pollutant contents in modern surface sediments with pre-industrial levels in deeper sediment layers. The calculation is expressed as follows (5):

$$CF = C_i / C_0, \quad (5)$$

where $C_0$ is the 'pre-industrial' background. The average contents of PTEs in the 25–45 cm layer of bottom sediment columns of the Taganrog Bay were used as the pristine reference levels [50]. Since there are no data on total Zn and Cd content in the columns, its concentrations in the bottom sediments of the Taganrog Bay from 1993 were used [57] (Table A3). Four classes of pollution are distinguished according to the *CF* (Table A4).

Total pollution was estimated by Hakanson as the sum of *CF* for 8 substances and expressed as the degree of contamination ($C_d$) [42]. Although this assessment scheme was proposed for assessing the condition of lake sediments, it has now been successfully applied to marine and river sediments as well [20,37,38,41,72]. To take into account the overall contamination of sediments regardless of the number of substances assessed, Abrahim [71] proposed the modified degree of contamination ($mC_d$) corresponding to the arithmetic mean *CF* of all substances analyzed (6):

$$mC_d = \left(\sum_{i=1}^{n} CF_i\right)/n, \quad (6)$$

where '*i*' denotes the *ith* element and '*n*' represents the number of elements analyzed. The classification of *CF* and $mC_d$ is presented in Table A4.

2.4.5. Metal Pollution Index

The metal pollution index (*MPI*) is an alternative to $mC_d$ for assessing polyelement pollution of both abiotic environments [38,40,72] and living organisms [76]. The *MPI* is the geometric mean of the *CF* values of all analyzed metals (7):

$$MPI = \left(\prod_{i=1}^{n} CF_i\right)^{\frac{1}{n}} = \sqrt[n]{(CF_1 \times CF_2 \times \ldots \times CF_n)}, \quad (7)$$

where '*i*' denotes the *ith* element and '*n*' represents the number of elements analyzed. Three pollution classes are distinguished according to *MPI* (Table A4).

2.4.6. Potential Ecological Risk Factor and Risk Index

Since PTEs have different abundances in the environment, sedimentation capacities, depending on the physicochemical conditions, and toxicities for aquatic biota, and the

potential threat of PTEs for aquatic ecosystems also varies. To take these prerequisites into account, the adverse effect of individual PTEs was assessed by calculating the potential ecological risk factor (*Er*) and their total negative impact using the potential ecological risk index (*RI*) developed by Hakanson [42], according to:

$$Er = Tr_i \times CF_i, \tag{8}$$

$$RI = \sum_{i=1}^{n} Er_i, \tag{9}$$

where $CF_i$ is the Contamination Factor and $Tr_i$ is the toxic response factor for a given element (Table A3). Table A4 shows the classification of *Er* and *RI*.

### 2.5. Sediment Quality Assessment

The potential adverse impacts on benthos of pollutants from sediments have been assessed indirectly using SQGs. This approach is widely used to identify priority sediment pollutants and regions of concern [2,41,43,72].

In this work, the apparent effect threshold (AET) scheme and the US National Oceanic and Atmospheric Administration (NOAA) scheme were used as SQGs. The AET scheme includes the threshold effect level (*TEL*), which corresponds to the limit value at which the likelihood of adverse effects occurring is negligible, and probable effect level (*PEL*), which indicates the toxicity of the sediment and a high likelihood of adverse biological effects occurring. The NOAA scheme includes the effect range low (*ERL*), where adverse environmental effects are rare, and the effect range median (*ERM*), where adverse environmental effects are frequent. Concentrations > *ERL* and < *ERM* show irregular environmental responses [2,43]. The number of *TEL/ERL* and *TEL/ERM* exceedances indicates potential sediment toxicity. The SQGs are established for river and marine sediments depending on the sensitivity of aquatic organisms to pollution (Table A3).

The mean *ERM* quantity (*MERMQ*) scheme was used to estimate the overall adverse environmental effects of PTEs on aquatic sediments. The *MERMQ* method requires normalizing the concentration of each chemical element to its *ERM* value, summing the resulting coefficients, and dividing by the number of PTEs under study (10) and (11):

$$ERMQ = C_i / ERM_i, \tag{10}$$

$$MERMQ = \left(\sum_{i=1}^{n} ERMQ_i\right) / n, \tag{11}$$

where *ERM* is the effect median range for a given element (Table A3) and *n* is the number of elements analyzed. *MERMQ* ranges (Table A4) have been related to the probability of toxicity (76%, 49%, 21% and 9%, respectively) in amphipod assemblages.

However, since the *MERMQ* is not applicable for assessing the potential for adverse effects at relatively low concentrations of PTEs [40], the toxic risk index (*TRI*) proposed by Zhang et al. [2] was used. The integrated *TRI* for all analyzed PTEs was obtained by summing up the individual *TRIs*, calculated as follows:

$$TRI_i = \sqrt{\left(\left[C_i / TEL\right]^2 + \left[C_i / PEL\right]^2\right) / 2}, \tag{12}$$

$$TRI = \sum_{i=1}^{n} TRI_i \tag{13}$$

where *TEL* is the threshold effect level and *PEL* is the probable effect level (Table A3). The obtained values are classified into five toxic risk classes (Table A4).

### 2.6. Data Analysis and Visualization

Statistical analysis was carried out using STATISTICA 12 (StatSoft, Tulsa, OK, USA). The normality of the data was checked by the Kolmogorov–Smirnov and Lilliefors tests. Differences in sediment characteristics were assessed using one-way analysis of variance

(ANOVA) followed by Scheffe's post hoc test for normally distributed parameters that passed Levene's test, and Kruskal–Wallis ANOVA followed by multiple comparisons of mean ranks for all groups. Principal component analysis (PCA) was used to identify significant multi-element associations and the influence of the main physicochemical parameters of sediments on their geochemistry. Only components with eigenvalues > 1 according to the Kaiser criterion were considered.

Data visualization was conducted using Grapher 17 (Golden Software, Golden, CO, USA). Violin plots and ballon plots were generated with ggpubr R in the SRplot [77]. Maps illustrating the spatial distribution of the complex pollution and risk indices were created in Surfer 15 (Golden Software, Golden, CO, USA). Data interpolation was conducted using the inverse weighted distance (IWD) method with a power of 2. The basemaps were from Rosreestr and the satellite images were from Bing Maps.

## 3. Results and Discussion

### *3.1. Physicochemical Properties of Sediments*

The main physicochemical properties of sediments of the study area that create conditions for the accumulation of PTEs were determined (Figure 2, Table A1). The distribution of pH and fine clay is close to normal, while EC and $CaCO_3$ have a pronounced right-skewed distribution, and the distribution of TOC and $\sum(Ca^{2+} + Mg^{2+})$ is multimodal. The pH values ranged between 6.5 and 9.5 (mean 7.4 ± 0.5). Most of the sediments (93%) were neutral or slightly alkaline, and only a few samples had pH values greater than 8, indicating moderate to strong alkalinity. Beach and shoreline sediments had higher pH on average (7.6 and 7.4, respectively) compared to delta sediments ($p < 0.005$). Riverbed and channel sediments within the delta were characterized by the greatest pH variability (Figure 2A). EC values ranged from 113 to 7680 µS/cm (mean 1523.5 ± 1504.9 µS/cm). A third of the samples were not saline, the majority were characterized by moderate salinity. On average, higher EC was noted in the bottom sediments of both the sea coast (2646.2 µS/cm) and the delta (1777.3 µS/cm). The content of $CaCO_3$ was from 0.4 to 27.2% (mean 6.1 ± 4.9%). Most samples were weakly to moderately carbonate, but coastal sediments had higher average $CaCO_3$ content (Figure 2B). TOC values were 0.1–0.5% (mean 1.5 ± 1.4%). Significantly lower TOC levels ($p < 0.0005$) were observed in beach sediments (0,4%), while higher TOC levels were recorded in stream sediments (2.8%). The sediments of the study area contain a fine clay fraction (<1 µm) between 1 and 36.3% (mean 13 ± 8.6%) (Figure 2C). The proportion of fine clay statistically significantly ($p < 0.005$) increases in shore sediments of the bay (18.3%) and in streamways (17.3%) in the delta. The distribution pattern of exchangeable cations is similar (Figure 2D). The content of $\sum(Ca^{2+} + Mg^{+2})$ varies from 2.2 to 46.3 cmol/kg (mean 21.0 ± 12.6 cmol/kg).

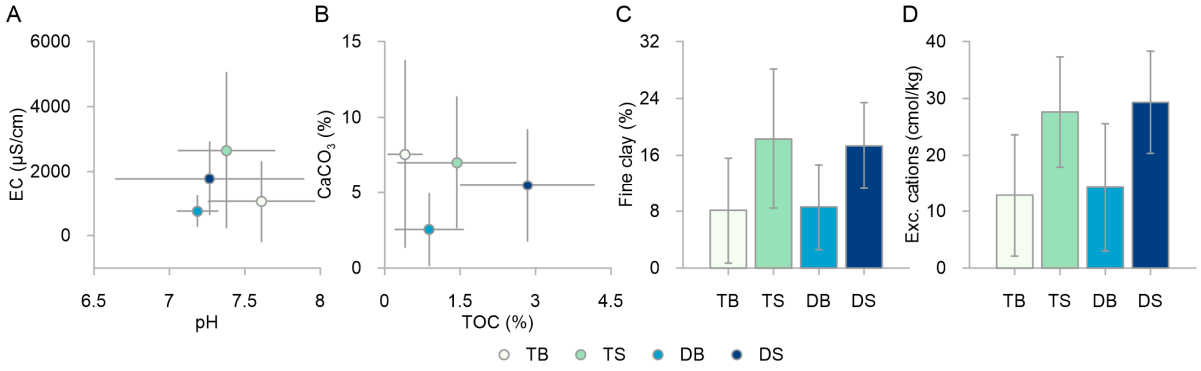


**Figure 2.** Variations in pH and electrical conductivity (EC) (**A**), total organic carbon (TOC) and $CaCO_3$ content (**B**), as well as content of fine clay (**C**) and exchangeable cations (**D**), expressed as mean values ± standard deviations, in beach and shore sediments of the Taganrog Bay (TB and TS, respectively) and in riverbank and stream sediments from the Don River delta (DB and DS, respectively).

Differences in the physicochemical properties of various types of sediments are due to hydrodynamic processes in the estuarine zone of the study region. Fine particles carried by river waters, which have the greatest sorption capacity, and organic matter with an affinity for the clay fraction are deposited in the channel facies of delta sediments [12,18,36]. Beach sand sediments on the coast of the bay are formed by the wave surf flow and gradually pass into coastal facies beyond the coastline, where the wave effect is less destructive [6,11], and the proportion of fine fractions is correspondingly higher.

### 3.2. Geochemistry of Sediments

The levels of PTE in the sediments of the study area are illustrated in Figure 3. The results showed that the distributions of Cr and Mn correspond to normal, but Cu, Zn and Cd are positively shifted, and Ni and Pb have a multimodal distribution in the sediments of the studied transition zone. The average content of PTEs in sediments of the study area decreases in the following order (in mg/kg): Mn (1272) > Cr (85.6) > Zn (85.5) > Ni (84.5) > Pb (76.3) > Cu (25.4) > Cd (2.1). Manganese, Cu, Zn and Cd reached the highest concentrations of 3516, 194, 481 and 8.5 mg/kg, respectively, in the beach sediments of the bay. The highest Pb contents (170 mg/kg) were recorded in the stream sediments of the delta, while the maximum contents of Cr (141 mg/kg) and Ni (151 mg/kg) were observed in the riverbank sediments. At the same time, the minimum contents of Mn (101 mg/kg) and Pb (18.2 mg/kg) were recorded sediments of the Don River delta, while the minimum concentrations of the remaining PTEs are characteristic of beach sediments of Taganrog Bay coast.

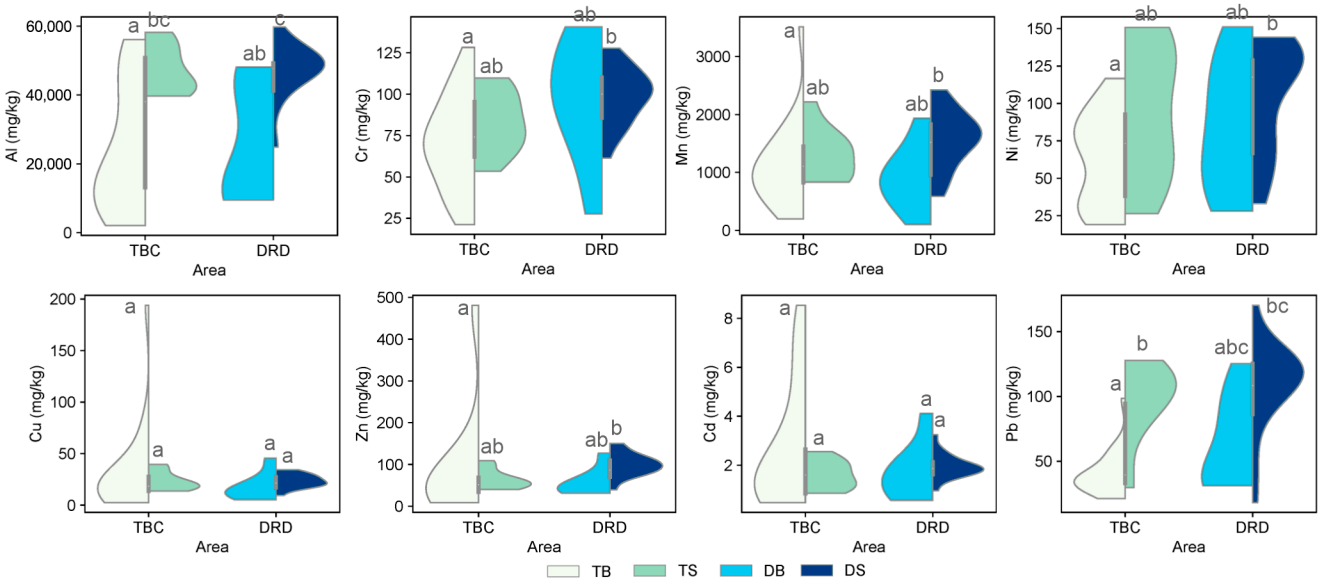


**Figure 3.** Violin plots showing PTE content in beach and shore sediments of the Taganrog Bay (TB and TS, respectively) and in riverbank and stream sediments from the Don River delta (DB and DS, respectively). Different letters indicate significant differences ($p < 0.05$) resulting from the multiple comparisons of *p*-values.

Hydrological regime and landscape conditions form the features of sedimentation in different environments [10,13,64,70]. Sediment characteristics such as pH, redox potential, texture and TOC influence the bioavailability of metals [2,26,36,38]. Thus, the sediments of riverbeds and channels of the Don River delta and shore sediments of the coast of the Taganrog Bay are characterized by a comparatively higher salinity, content of organic matter and exchangeable carbonates and heavier textures (Figure 2), which contribute to the absorption and accumulation of PTEs [44,78]. The levels of Cr, Mn, Ni and Zn in riverbed sediments are 1.1–1.7 times higher than in other types of sediments in the study area, and the average Pb content is up to 2.7 times higher (Figure 3).

The contents of Mn, Cd, Ni and Pb in the sediments of the estuarine zone of the Don River are 1.5–2 times higher than in the soils of the Lower Don floodplain and the coast of the Taganrog Bay, while the levels of Cr, Zn and Cu, on the contrary, are 1.1–1.7 times lower [45,46]. At the same time, a dilution effect is observed in the marine bottom sediments of the Taganrog Bay, which is manifested in a decrease of 2–5 times in the average contents of Mn, Ni, Pb and Cu compared to coastal sediments [55]. Thus, soils act as sources of elements of the first group, which are then intensively accumulated by coastal sediments.

The PTE levels in the Don River estuarine sediments are comparable to other sea–river transition zones in the world. In modern sediments of the Yellow River Delta, China, the Cu and Zn contents are 28.5 and 77.8 mg/kg, respectively [6], which is comparable to the Don River Delta. In sediments of the Ogun River Estuary, Nigeria, the average contents of Ni, Cd and Pb (22.2, 0.7 and 20.4 mg/kg, respectively) are 3–4 times lower than in the Don Estuary [5], which is due to lower urbanization and industrialization of the region. Lee et al. found lower levels of all PTEs in the 0–20 cm sediment layer of the Nakdong River Estuary, South Korea [15], than in the sediments of the study region. The coast of South Andaman Island, India, is characterized by higher average contents of Cr and Cu (390 and 48 mg/kg, respectively), comparable Ni and Zn (108 and 70 mg/kg, respectively), and lower levels of Mn and Pb (538 and 19 mg/kg, respectively) in sediments compared to the coast of Taganrog Bay [21]. The enrichment in Cr and Cu is probably due to the volcanic origin of the island's sediments. On the Mediterranean coast near Alexandria, Egypt, the average Zn content (160.4 mg/kg) is twice as high as in the Taganrog Bay, while the levels of other PTEs are 2–5 times lower. Mostafa et al. attribute Zn input to untreated municipal wastewater and oil refinery effluents, as well as transport emissions [17]. Thus, differences in the geochemistry of sea–river transition zone sediments are due to both natural and anthropogenic factors.

### *3.3. Potential Sources of PTEs*

Environmental factors determine differences in the geochemistry of sediments along the fluvial-to-marine transition zone of the Don River. Factor 1 versus Factor 2 of PCA, using sediment characteristics and PTE concentrations, explains most of the data variability (61.2%). The distribution areas of different types of sediments of the study area overlap in the PCA space (Figure 4A). Seashore and floodplain sediments gravitate toward the centroid of the PCA space. At the same time, the stream sediments of the delta mainly occupy the space of positive values of Factor 1 and negative values of Factor 2; additionally, the coastal sediments of the bay are concentrated in the space of positive values of Factor 2. High and moderate positive correlations with Factor 1 are demonstrated by Cr (0.566), Mn (0.735), Ni (0.818), Pb (0.79). These PTEs are associated with TOC, fine clay, and exchangeable cations, which have moderate correlations with Factor 1 (0.658, 0.624 and 0.661, respectively). The remaining metals, namely Cu, Zn and Cd, are positively correlated with Factor 2 (0.637, 0.526 and 0.811, respectively). It is also worth noting that no significant correlations were found between pH, EC and carbonate content with any of the identified factors (Figure 4B).

The PCA results showed that Cr, Mn, Ni and Pb may originate from a common source and their behavior in sediments is controlled by the same conditions, whereas Cu, Zn and Cd may originate from a different source [2]. The accumulation of the Cr–Mn–Ni–Pb association in sediments is facilitated by an increase in the organic matter content and a heavier texture, most pronounced in the delta stream sediments as shown above (Figures 2 and 3). The flow of the Don River, which drains agriculturally developed plowed watersheds in its lower reaches [45,46], makes a significant contribution to the input of PTEs of this group into the sediments of the estuarine zone of the Don River [31,50,54]. Beach sediments of Taganrog Bay act as a geochemical barrier for Cu, Zn and Cd coming from surrounding terrestrial landscapes [45,59]. The origin of the Cu–Zn–Cd association in sediments is most likely associated local anthropogenic sources in the coastal area of the study region, along which urban and rural settlements are located [45]. Potential sources of PTEs include

municipal and industrial wastewater, and transport and industrial emissions [56,57]. The significant contribution of anthropogenic sources for Cu, Zn and Cd in marine and deltaic sediments is also noted by other researchers [1,36,38].

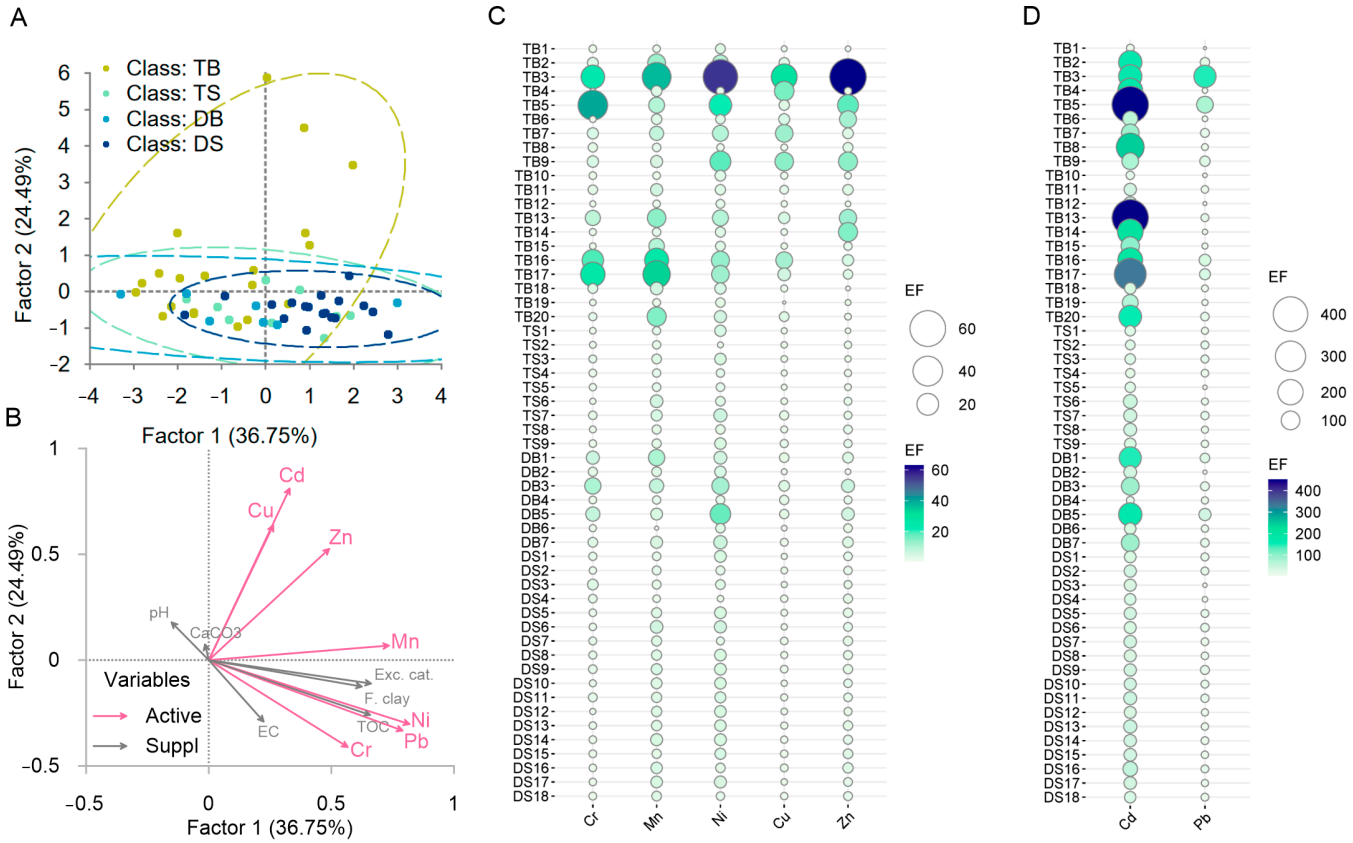


**Figure 4.** Biplots of the first two PCAs illustrating the sample points (**A**) and main physicochemical parameters and PTEs (**B**), as well as bubble plots of enrichment factors (*EF*) of PTE (**C**,**D**) in beach and shore sediments of the Taganrog Bay (TB and TS, respectively) and in riverbank and stream sediments from the Don River delta (DB and DS, respectively). Confidence ellipses ($\alpha = 0.05$) of the positions of group centroids are superimposed by dashed lines.

The contribution of anthropogenic sources to the accumulation of PTEs by sediments in the study area was assessed based on the *EF* values, which represent the excess of PTE contents in sediments over the UCC, normalized to the reference element. Extremely high enrichment was noted in beach sediments of the Taganrog Bay (Figure 4C,D). *EF* values up to 50 were found for Cu (29), Mn (37) and Cr (40); *EF* was > 50 for Ni (56), Zn (63), Pb (149) and Cd (453). Values $1 < EF < 3$ were found for Cr (2.2), Zn (2.3) and Cu (2.6); $5 < EF < 10$ for Mn (5.6) and Ni (6.1); $10 < EF < 25$ for Pb (13) and $25 < EF < 50$ for Cd (48) in shore sediments. The maximum *EF* values of riverbank and streamway sediments increase in the series Cu (3.7 and 1.8), Zn (6.1 and 3.5), Cr (10.2 and 3.8), Mn (10.3 and 5.6), Ni (18 and 5.1), Pb (36 and 17), Cd (167 and 56). In general, beach and floodplain sediments are more enriched in metals compared to bottom marine and river sediments of the study area.

All sediment samples from the studied region are extremely highly enriched in Cd (Figure 4D), with the proportion of extreme samples in above-water marine and river sediments reaching 75% and 57%, respectively. Several studies show that high Cd enrichment in marine sediments is typical for urbanized regions [5,17,21]. Also, bottom marine and river sediments are highly enriched in Pb (56% and 57%, respectively). Cd and Pb are definitely of anthropogenic origin [21], with average *EF* values in different types of sediments being 31–154 and 10–22, respectively. Enrichment of beach sediments of the Taganrog Bay from high to extreme was noted in 20–30% of samples by Cr, Mn, Ni, Cu and Zn, in 50% of

samples by Pb. High enrichment of Cr, Mn, Ni (14–29% of samples) and high to extreme enrichment of Pb (72% of samples) are observed in floodplain sediments.

### *3.4. PTE Contamination of Sediments and Associated Ecological Risks*

The maximum *Igeo* values for Cr did not exceed 0 in the sediments of the study area (Figure 5A). The highest *Igeo*, up to 4.8, was achieved for Cd in the beach sediments of the Taganrog Bay. Also in this area, *Igeo* maxima were noted for Mn (1.7), Cu (1.5) and Zn (2.2). The highest *Igeo* for Ni (1.5) and Pb (2.1) were recorded in the shore sediments of the bay and the stream sediments of the delta, respectively. Among all the elements, Cd turned out to be the most dangerous: contamination of the sediments of the study area (% of samples) varied from weak (6%) and moderate (22% and 48%) to high (17%) and very high (7%) (Figure 5E). Pollution according to *Igeo* for Mn, Ni and Cu reached a moderate level in 1.9–35% of samples, for Zn and Pb moderate and considerable (from moderate to high according to Müller [74]) in 3.7% and 50% of samples, respectively.

Higher pollution estimates are obtained by *PI* values (Figure 5B) than from *Igeo*, since *PI* does not allow for the natural variability of elements to be taken into account [74]. The elements form the following series by decreasing maximum *PI* values: Cd (43) > Zn (6.8) > Pb (6.6) > Mn (4.9)> Ni = Cu (4.3) > Cr (1.5). Relatively higher *PI* values are noted for marine sediments compared to river sediments. High and very high sediment pollution by *PI* was obtained in 1.9–9.3% of samples for Mn, Cu and Zn, in 35% of samples for Ni, 50% of samples for Pb and 94% of samples for Cd (Figure 5F). The sediments of the estuarine zone of the Don River are more contaminated with Cr, Mn, Ni and Cu than the soils of the Lower Don floodplain and the coast of the Taganrog Bay [45]. Thus, marine and deltaic sediments of the estuarine zone of the Don River act as the final depot of elements in cascade coastal ecosystems [50].

The total pollution of sediments with PTE relative to the regional geochemical background was estimated by the *NPI* (Figure 6A). In the sediments of the study area, the *NPI* values varied within a range of 1.8–31, with an average of 7.8. The average *NPI* values in the beach and shore sediments of the Taganrog Bay were 9.7 and 6.0, and in the floodplain and channel sediments of the Don Delta they were 6.4 and 7.3, respectively. Pollution hotspots have been identified along the northern coast of Taganrog Bay. The majority of samples in the study area were assessed as highly contaminated (87%), while moderately and slightly contaminated accounted for 11% and 2%, respectively.

The elements in decreasing order of maximum *CF* values form the following series: Cd (36) > Zn (13) > Mn (10) > Pb (9.5) > Cu (6.5) > Ni (6.1) > Cr (3.4). The maximum *CFs* in beach sediments of the Taganrog Bay were recorded for Mn, Cu, Zn and Cd, in floodplain sediments for Cr and Ni and in delta beds for Pb (Figure 5C). River stream sediments were characterized by higher average *CF* values of all elements, except Cu and Cd, compared to other sediment types. Modern levels of Cr and Zn in sediments of the bottom estuarine zone exceed pre-industrial levels by two times, while Mn, Ni, Pb exceed them by three–four times and Cd by nine times. This fact indicates the anthropogenic nature of these changes [15,71]. The results obtained are consistent with the results of studies of the bottom sediments of the Azov Sea and Taganrog Bay, where an increase in the content of PTE has been noted over the past 30 years [50,51,57], which is a consequence of economic development, urbanization and industrialization of the Azov basin. According to the *CF*, the pollution varied from low to considerable for Cr, from low to very high for Mn, Ni, Cu and Zn and from moderate to very high for Cd and Pb (Figure 5G). It should be noted that the proportions of highly contaminated Cd and Pb samples were 67% and 33%, respectively.

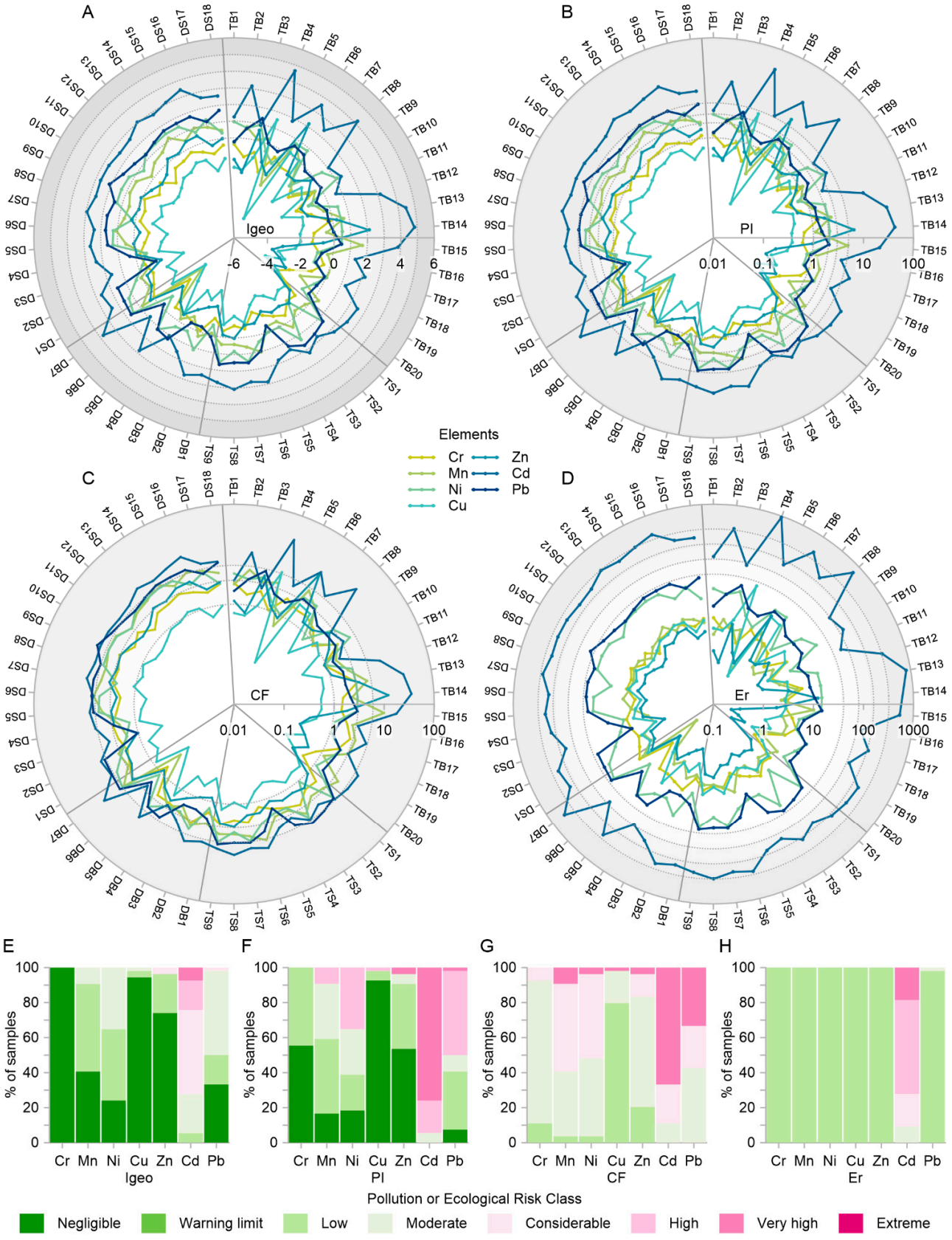


**Figure 5.** Values of geoaccumulation indices (*Igeo*) (**A**), single pollution indices (*PI*) (**B**), contamination factors (*CF*) (**C**) and potential ecological risk factors (*Er*) (**D**) in sediments of the study area and the corresponding distribution of samples by pollution (**E**–**G**) and ecological risk classes (**H**).

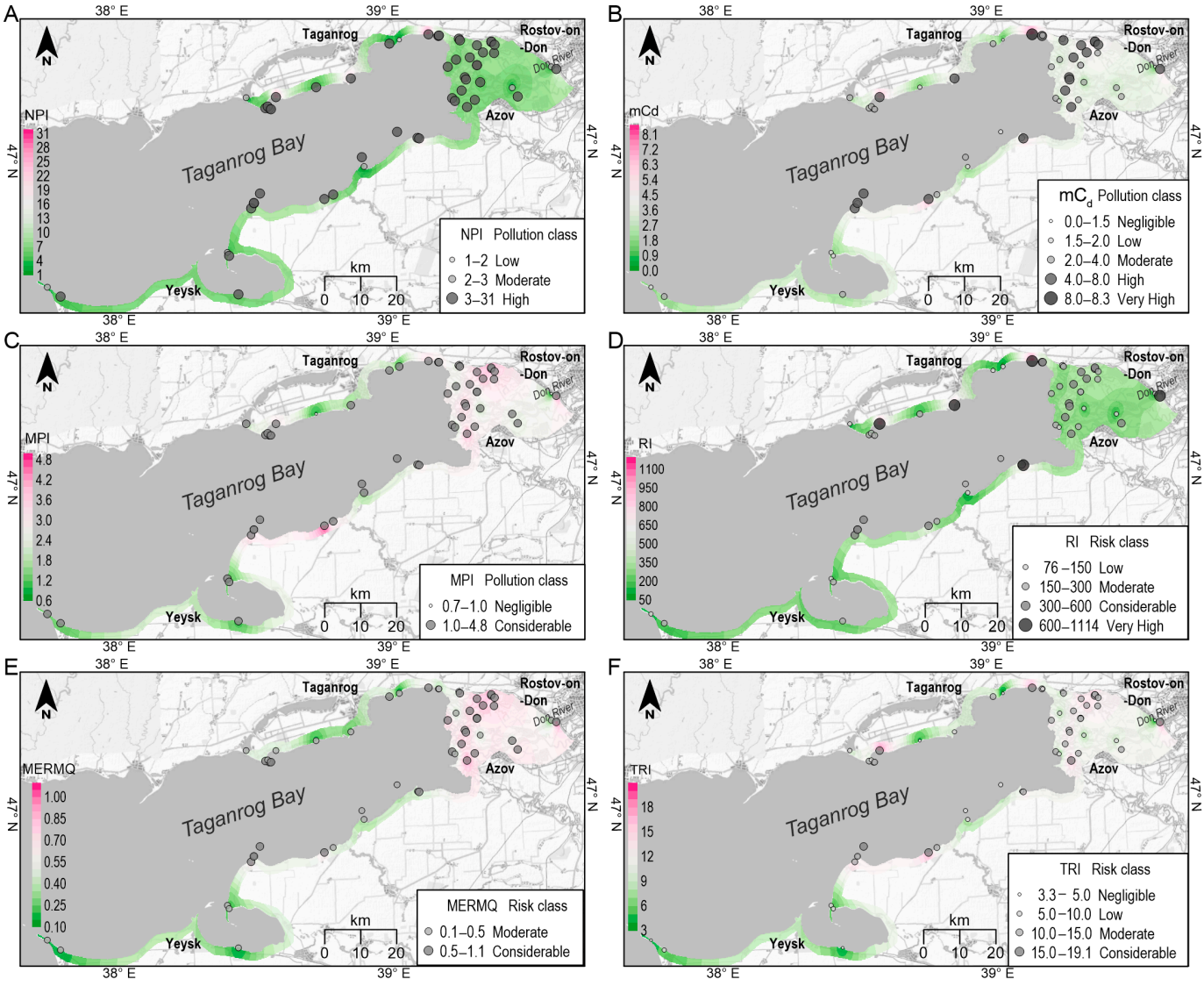


**Figure 6.** Spatial distribution of the Nemerow pollution index (*NPI*) (**A**), modified pollution degree ($mC_d$) (**B**), metal pollution index (*MPI*) (**C**), potential ecological risk index (*RI*) (**D**), mean effect range median quantity (*MERMQ*) (**E**) and integrated toxic risk index (*TRI*) (**F**) in sediments of the study area, as well as classification of samples by total PTE pollution (**A**–**C**) and ecological risk classes (**D**–**F**).

Relative to the pre-industrial level, the overall pollution was assessed using $mC_d$ and *MPI*. The $mC_d$ values varied within 1–8 (mean 3.6), and *MPI* ranged within 0.8–4.7 (mean 2.7). According to both $mC_d$ and *MPI*, only 3.7% of sediment samples from the study area are classified as unpolluted (Figure 6B,C). The $mC_d$ analysis allowed us to obtain a more detailed assessment of the overall pollution level. Thus, the shares of slightly and moderately polluted sediments were 13.0% and 44.4%, respectively, while those of highly and very highly polluted sediments were 37.0% and 1.9%, respectively. An increased level of overall pollution with metals was noted in sediments of the Don River delta (Figure 6B).

Analysis of potential ecological risks of individual elements showed that *Er* values for Cr, Mn, Ni, Cu and Zn did not exceed 40; *Er* for Pb reached 47 in only one sample (Figure 5D). Accordingly, most of the studied PTEs pose a low individual potential ecological risk and make a minimal contribution to the overall risk (Figure 5H). *Er* values for Cd varied within 59–1068, with an average value of 21.2, reaching a maximum in the beach sediments of the bay. In general, Cd levels in two thirds of the samples of different types in the study area pose a high and very high potential ecological risk. Similar assessments of

the ecological risk of all elements except Cd were obtained for the soils of the Lower Don and the coast of the Taganrog Bay [46].

*RI* values varied significantly from 76 to 1114 in the sediments of the study area. An extremely high overall risk was noted in the coastal sediments of the Taganrog Bay near residential areas (Figure 6D). The total pollution of sediments of the study area by PTE presents a low ecological risk in 20.4% of samples, moderate and considerable risk in 37.0% and 33.3% of samples, respectively, and high risk in 9.3% of samples.

According to individual pollution indices of *Igeo*, *PI* and *CF*, the priority pollutants of sediments in the study area were Cd, Pb and Zn. Moreover, high levels of these elements also pose the greatest ecological risk (Figure 5). The leading role of Cd in sediment contamination and contribution to ecological risk has also been noted near the mouths of the Guarda River and Ita Channel, Brazil [38], in the wetlands of the Yellow River delta, China [2], along the coast of East Java, Indonesia [72], and on the Egyptian Mediterranean Sea coast [22].

### 3.5. Ecotoxicology of Sediments

The sediment samples from Taganrog Bay do not exceed the *ERMs* for Cr, Cu, Cd and Pb (Table 1). Most of the Cr, Cu and Pb contents are also below the *ERL* values, while Cd is mainly in the range from *ERL* to *ERM*. Although most Zn values are below the *ERL*, in individual samples the contents exceed the *ERM*. Only Cr does not exceed the *PEL* in all sediments on the coast of the bay. Most of the sediment samples are below the *TEL* for Cu and Zn, and in the range from *TEL* to *PEL* for Cd and Pb. Ni deserves priority attention, the levels of which in most samples exceeded the *ERM* and *PEL*. Thus, Cr and Cu pose a relatively low ecotoxic risk in the sediments of the Taganrog Bay, while Zn, Cd and Pb pose a moderate risk, and Ni poses a high risk. The importance of Ni as a pollutant of particular interest has also been noted in coastal marine sediments of the Mediterranean Sea [22]. The sediment samples from the Don River delta do not exceed the *ERM/PEL* for Cu and Zn; in most samples, their levels are below the *ERL/TEL* (Table 1). Thus, these elements pose a minimal risk of adverse effects. The contents of Cr and Cd in most samples are below the *ERM*, but above the *TEL*, indicating moderate risks. The main high-risk sources are Ni and Pb, the levels of which in most delta sediment samples exceed the *ERM/PEL*. These results are consistent with previous studies showing that the bottom sediments of the Lower Don were moderately contaminated with Ni [31].

**Table 1.** Relative percentage of samples amongst ranges of Sediment Quality Guidelines.

| Area | Elements | Effects Range | | | Effects Level | | |
|---|---|---|---|---|---|---|---|
| | | *<ERL* | *ERL–ERM* | *≥ERM* | *<TEL* | *TEL–PEL* | *≥PEL* |
| Taganrog Bay | Cr | 62.1 | 37.9 | 0 | 17.2 | 82.8 | 0 |
| | Ni | 3.4 | 27.6 | 69 | 0 | 31 | 69 |
| | Cu | 79.3 | 20.7 | 0 | 51.7 | 44.8 | 3.4 |
| | Zn | 89.7 | 3.4 | 6.9 | 86.2 | 6.9 | 6.9 |
| | Cd | 37.9 | 62.1 | 0 | 10.3 | 72.4 | 17.2 |
| | Pb | 55.2 | 44.8 | 0 | 17.2 | 72.4 | 10.3 |
| Don River Delta | Cr | 20 | 80 | 0 | 4 | 24 | 72 |
| | Ni | 4 | 12 | 84 | 0 | 12 | 88 |
| | Cu | 100 | 0 | 0 | 96 | 4 | 0 |
| | Zn | 80 | 20 | 0 | 84 | 16 | 0 |
| | Cd | 100 | 0 | 0 | 4 | 92 | 4 |
| | Pb | 16 | 36 | 48 | 16 | 16 | 68 |

In descending order of maximum *ERMQ* values, the elements formed the following series: Ni (3) > Pb (1.5) > Zn (1.2) > Cr (1.0) > Cd (0.9) > Cu (0.7). *ERMQ* analysis showed that, on average, the risks of most elements, except Cu and Cd, were higher in the Don River Delta sediments compared to the Taganrog Bay coast (Figure 7A). According to

*ERMQ*, Cr, Cu, Zn and Cd demonstrated low to significant risks, while the proportions of samples with moderate and significant risks were 96%, 17%, 82% and 100%, respectively. High risk of Ni and Pb was found in 50% and 1.9% of sediment samples in the study area (Figure 7B). *MERMQ* values ranged from 0.14 to 1.02, with an average of 0.5. Moderate weighted average risk was characteristic of 55.6% of marine and river sediment samples from the estuarine region of the Don River, mainly in its delta (Figure 6E).

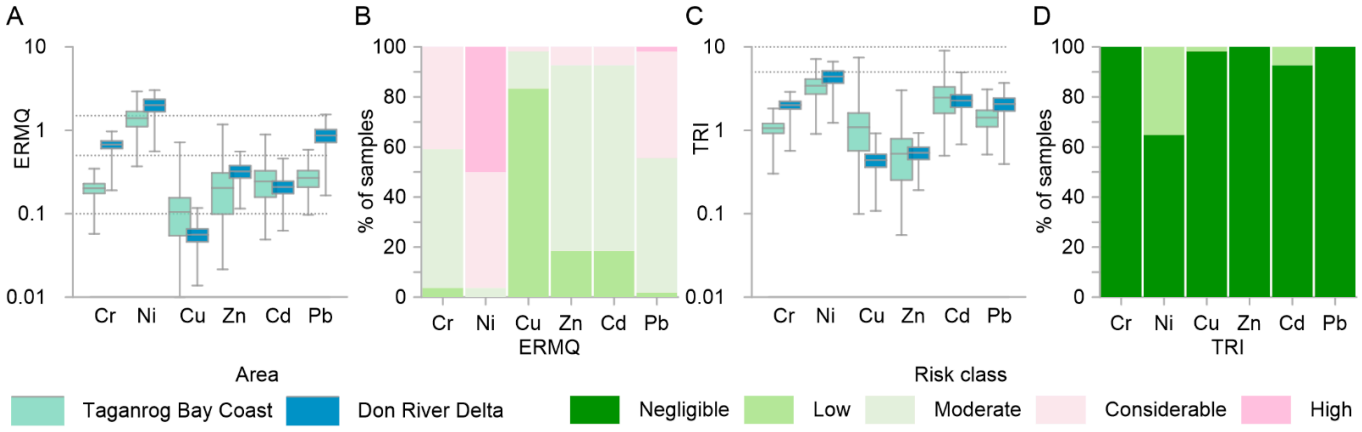


**Figure 7.** Variability of effect range median quantity (*ERMQ*) (**A**) and toxic risk indices (*TRI*) (**C**) in sediments of the study area presented as a box (mean ± 95% CI) and whisker (minimum–maximum) plot, as well as the percentage of distribution of individual ecological risks (**B**,**D**).

In all sediment samples, the *TRI* values were less than five for Cr, Zn and Pb (Figure 7C). The maximum *TRI* values for Ni, Cu and Cd were 7.2, 7.4 and 9, respectively. According to the *TRI*, a low risk of potential impact of these elements was found in 35%, 2% and 7% of the samples, respectively (Figure 7D). The values of the total toxic risk varied within the range of 3.3–19.1, with an average of 10.8. The total risk was classified from negligible and low to moderate and considerable (9.3%, 31.5%, 46.3% and 13%, respectively). In two thirds of the samples, it was above the acceptable low level. In general, the area of increased total toxic risks of sediment pollution by PTEs was observed in the Don River Delta (Figure 6F).

## 4. Conclusions

In the present study, we investigated the geochemistry, controlling factors, possible sources, pollution hazards and potential ecological and ecotoxicological risks of exposure to seven toxic elements (i.e., Cr, Mn, Ni, Cu, Zn, Cd and Pb) in sediments of the Don River estuarine region.

The average PTE content showed a decreasing order of Mn > Cr > Zn > Ni > Pb > Cu > Cd and was consistent with PTE levels in sediments of highly urbanized and industrialized river-sea transition zones. The results showed that the hydrological regime, landscape–geochemical conditions and anthropogenic impact determine the intensity of PTE accumulation by sediments of the study area. In particular, stream sediments of the Don River delta are characterized by higher levels of Cr, Mn, Ni, Zn and Pb on average than other types of sediments.

The origin of all the studied PTE is due to human activity, as shown by the PCA and *EF*. At the same time, it should be emphasized that Cr, Mn, Ni and Pb enter mainly with river runoff, and their behavior is controlled by the texture of sediments and the content of organic matter, while Cu, Zn and Cd are associated with local anthropogenic sources.

Based on the results of the analysis of *Igeo*, *PI* and *CF*, it was revealed that the priority pollutants of the sediments of the Don Delta and the coast of the Taganrog Bay are Cd and Pb. These elements make the greatest contribution to pollution and increased ecological risks. An increased level of total pollution of sediments in the Don River delta and along the coast of the Taganrog Bay, identified using the *NPI*, *MPI* and $mC_d$, was found locally near residential areas. A holistic approach to assessing the state of sediments in the study area

included an analysis of ecotoxicological risks of potential impact of inorganic pollutants. It has been established that although the average level of PTE pollution of sediments in the Don River delta is lower than that of the surrounding coast, it poses a more significant risk of negative effects on freshwater organisms.

The study has a number of limitations, primarily due to the need for a detailed examination of the mechanisms of geochemical transformation and migration of elements in accessible forms between the biota and abiotic components of aquatic landscapes. Nevertheless, the preliminary results of the comprehensive assessment of sediment pollution, potential ecological and ecotoxicological risks of PTEs may be useful for improving environmental monitoring of the transit zone of the Don River–Sea of Azov system and achieving sustainable development goals.

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**Data Availability Statement:** Data are openly available within this article in Appendix A.

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## Appendix A

**Table A1.** Location and physicochemical properties of sediment samples from the study area.

| Area | | Site | Coordinates | | pH | EC | TOC | $CaCO_3$ | Fine Clay | $\Sigma(Ca^{2+} + Mg^{2+})$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | µS/cm | | % | | cmol/kg |
| Taganrog Bay coast | Beach | TB1 | N47°08′43.26″ | E38°29′02.69″ | 8.0 | 895 | 0.5 | 1.3 | 22.1 | 27.8 |
| | | TB2 | N46°52′48.04″ | E38°30′00.47″ | 7.5 | 184 | 1.1 | 5.7 | 11.0 | 17.3 |
| | | TB3 | N47°06′54.36″ | E38°34′08.69″ | 7.8 | 417 | 0.1 | 5.5 | 1.5 | 3.1 |
| | | TB4 | N47°08′37.10″ | E38°35′37.10″ | 8.1 | 142 | 0.5 | 1.4 | 13.3 | 21.8 |
| | | TB5 | N47°09′53.32″ | E38°44′34.04″ | 7.2 | 336 | 0.3 | 6.1 | 4.7 | 6.1 |
| | | TB6 | N46°53′02.08″ | E38°45′34.99″ | 7.8 | 113 | 0.2 | 12.7 | 16.4 | 22.8 |
| | | TB7 | N46°53′41.78″ | E38°47′29.00″ | 7.4 | 173 | 0.3 | 6.1 | 4.6 | 5.5 |
| | | TB8 | N47°11′02.98″ | E38°52′17.58″ | 7.5 | 237 | 0.2 | 1.8 | 2.9 | 4.2 |
| | | TB9 | N46°57′45.83″ | E38°54′31.32″ | 7.7 | 167 | 0.1 | 2.3 | 2.9 | 7.9 |
| | | TB10 | N47°16′03.11″ | E39°01′04.04″ | 7.8 | 318 | 0.7 | 4.1 | 20.5 | 26.0 |
| | | TB11 | N47°16′33.64″ | E39°03′20.70″ | 7.3 | 668 | 0.4 | 2.9 | 6.1 | 7.1 |
| | | TB12 | N47°01′43.39″ | E39°06′33.84″ | 8.4 | 116 | 0.1 | 5.0 | 24.0 | 41.5 |
| | | TB13 | N47°01′36.91″ | E39°06′54.43″ | 7.6 | 354 | 0.6 | 2.2 | 6.7 | 10.9 |
| | | TB14 | N47°17′11.18″ | E39°09′50.18″ | 7.0 | 856 | 0.3 | 11.0 | 11.0 | 19.6 |
| | | TB15 | N47°16′56.50″ | E39°12′03.67″ | 7.1 | 805 | 1.4 | 9.1 | 7.0 | 15.5 |
| | | TB16 | N46°41′01.21″ | E37°44′11.15″ | 7.6 | 3880 | 0.1 | 11.2 | 1.5 | 4.5 |
| | | TB17 | N46°39′32.98″ | E37°47′05.68″ | 7.9 | 3248 | 0.4 | 12.3 | 1.1 | 4.1 |
| | | TB18 | N46°45′32.40″ | E38°23′54.78″ | 7.3 | 3080 | 0.2 | 27.2 | 1.0 | 2.7 |
| | | TB19 | N46°45′02.84″ | E38°24′16.49″ | 7.4 | 2884 | 0.4 | 14.2 | 3.4 | 5.5 |
| | | TB20 | N46°39′08.10″ | E38°26′03.44″ | 7.8 | 2312 | 0.2 | 9.3 | 1.3 | 3.1 |

**Table A1.** *Cont.*

| Area | Site | Coordinates | | pH | EC | TOC | $CaCO_3$ | Fine Clay | $\Sigma(Ca^{2+} + Mg^{2+})$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | µS/cm | | % | | cmol/kg |
| | | TS1 | N47°07′02.50″ | E38°33′15.05″ | 7.5 | 1258 | 0.4 | 3.8 | 15.1 | 22.1 |
| | | TS2 | N47°07′13.66″ | E38°33′45.47″ | 7.2 | 2750 | 1.3 | 17.1 | 14.4 | 17.8 |
| | | TS3 | N47°06′51.84″ | E38°34′24.85″ | 7.9 | 1740 | 1.5 | 7.1 | 19.3 | 26.6 |
| | | TS4 | N46°59′08.77″ | E38°54′06.95″ | 7.2 | 1193 | 0.9 | 5.2 | 9.2 | 21.8 |
| | Shore | TS5 | N47°02′46.79″ | E39°02′02.87″ | 7.3 | 888 | 1.1 | 5.2 | 8.0 | 19.7 |
| | | TS6 | N47°16′57.43″ | E39°12′06.77″ | 7.1 | 1166 | 1.5 | 7.2 | 8.9 | 22.6 |
| | | TS7 | N46°52′01.81″ | E38°29′22.45″ | 7.6 | 5700 | 1.6 | 9.5 | 36.3 | 42.4 |
| | | TS8 | N46°52′48.83″ | E38°30′03.46″ | 7.7 | 1441 | 0.3 | 6.0 | 25.2 | 31.5 |
| | | TS9 | N46°54′14.80″ | E38°31′23.52″ | 6.9 | 7680 | 4.3 | 2.0 | 28.3 | 44.0 |
| | | DB1 | N47°16′22.77″ | E39°16′29.42″ | 7.3 | 650 | 0.6 | 7.0 | 4.7 | 9.5 |
| | | DB2 | N47°12′17.93″ | E39°20′17.59″ | 7.4 | 1381 | 0.7 | 2.5 | 13.2 | 19.7 |
| | | DB3 | N47°09′43.85″ | E39°20′48.05″ | 7.1 | 321 | 0.4 | 0.5 | 2.0 | 3.3 |
| | Riverbank | DB4 | N47°08′40.88″ | E39°27′53.71″ | 7.0 | 876 | 1.7 | 2.2 | 14.2 | 28.4 |
| | | DB5 | N47°07′18.26″ | E39°28′55.45″ | 7.2 | 487 | 0.3 | 0.4 | 3.5 | 2.2 |
| | | DB6 | N47°11′30.59″ | E39°36′42.52″ | 7.2 | 206 | 0.5 | 1.0 | 5.6 | 8.1 |
| | | DB7 | N47°11′10.72″ | E39°37′46.02″ | 7.1 | 1356 | 2.0 | 4.2 | 17.1 | 28.7 |
| | | DS1 | N47°12′11.34″ | E39°13′46.96″ | 6.5 | 3100 | 3.5 | 4.1 | 13.6 | 20.6 |
| | | DS2 | N47°07′27.73″ | E39°14′31.20″ | 7.5 | 1527 | 1.7 | 8.1 | 20.2 | 31.1 |
| | | DS3 | N47°07′04.91″ | E39°15′08.06″ | 7.0 | 1298 | 0.9 | 1.9 | 13.0 | 27.8 |
| | | DS4 | N47°13′12.00″ | E39°15′44.35″ | 7.2 | 145 | 0.4 | 0.4 | 5.8 | 4.4 |
| Don River Delta | | DS5 | N47°08′33.36″ | E39°16′40.40″ | 7.3 | 1467 | 1.4 | 4.0 | 20.2 | 29.4 |
| | | DS6 | N47°16′08.15″ | E39°16′45.01″ | 7.5 | 1882 | 2.8 | 6.3 | 14.6 | 27.8 |
| | | DS7 | N47°10′33.78″ | E39°17′32.39″ | 7.4 | 2570 | 3.8 | 5.3 | 31.5 | 46.3 |
| | | DS8 | N47°10′12.14″ | E39°17′44.66″ | 7.0 | 2170 | 2.4 | 3.1 | 23.0 | 32.1 |
| | | DS9 | N47°06′02.77″ | E39°17′45.42″ | 6.6 | 2590 | 2.4 | 8.0 | 13.4 | 27.2 |
| | Stream | DS10 | N47°13′27.59″ | E39°18′44.82″ | 7.5 | 1110 | 2.8 | 7.9 | 17.3 | 29.1 |
| | | DS11 | N47°07′04.87″ | E39°19′27.80″ | 7.2 | 234 | 2.4 | 2.7 | 14.1 | 26.1 |
| | | DS12 | N47°12′14.80″ | E39°20′17.16″ | 7.0 | 1456 | 2.2 | 3.9 | 15.3 | 27.3 |
| | | DS13 | N47°15′14.94″ | E39°20′30.70″ | 7.3 | 1357 | 4.4 | 8.3 | 15.1 | 26.0 |
| | | DS14 | N47°14′10.86″ | E39°21′41.51″ | 7.0 | 1431 | 4.5 | 5.5 | 13.8 | 26.6 |
| | | DS15 | N47°15′39.17″ | E39°23′36.78″ | 7.1 | 1130 | 4.2 | 6.8 | 29.5 | 43.6 |
| | | DS16 | N47°15′45.97″ | E39°23′38.58″ | 7.0 | 2010 | 4.3 | 16.9 | 18.2 | 38.4 |
| | | DS17 | N47°14′00.89″ | E39°24′08.57″ | 7.2 | 1324 | 2.0 | 2.6 | 14.6 | 28.1 |
| | | DS18 | N47°15′14.72″ | E39°24′21.85″ | 9.5 | 5190 | 5.0 | 3.0 | 18.9 | 36.0 |

**Table A2.** Concentration of PTEs (mg/kg) in sediment samples from the study area.

| Site | Al | Cr | Mn | Ni | Cu | Zn | Cd | Pb |
|---|---|---|---|---|---|---|---|---|
| TB1 | 56,074 | 109.6 | 871.2 | 102.5 | 19.9 | 43.5 | 0.7 | 33.1 |
| TB2 | 14,812 | 66.2 | 1761.6 | 81.9 | 18.3 | 25.9 | 2.7 | 59.1 |
| TB3 | 3174 | 85.9 | 1123.9 | 102.3 | 32.2 | 164.2 | 0.6 | 98.5 |
| TB4 | 35,972 | 40.9 | 1327.4 | 38.0 | 194.0 | 47.2 | 7.6 | 39.9 |
| TB5 | 2116 | 95.3 | 194.6 | 26.3 | 2.6 | 31.5 | 1.1 | 33.8 |
| TB6 | 52,371 | 74.3 | 1826.0 | 88.7 | 73.7 | 481.4 | 3.5 | 59.2 |
| TB7 | 16,399 | 77.5 | 1127.0 | 92.2 | 68.9 | 51.7 | 1.6 | 55.3 |

**Table A2.** *Cont.*

| Site | Al | Cr | Mn | Ni | Cu | Zn | Cd | Pb |
|---|---|---|---|---|---|---|---|---|
| TB8 | 20,116 | 62.4 | 417.6 | 19.1 | 9.4 | 53.3 | 5.5 | 34.9 |
| TB9 | 7406 | 37.1 | 353.6 | 77.3 | 35.0 | 88.7 | 0.6 | 36.8 |
| TB10 | 51,313 | 101.0 | 826.3 | 116.7 | 27.0 | 57.7 | 0.8 | 39.4 |
| TB11 | 11,638 | 37.5 | 573.3 | 23.9 | 9.2 | 34.4 | 0.5 | 25.3 |
| TB12 | 51,842 | 62.7 | 827.1 | 73.2 | 20.4 | 40.2 | 2.6 | 33.7 |
| TB13 | 13,225 | 128.3 | 1731.9 | 74.8 | 19.7 | 127.4 | 6.5 | 32.9 |
| TB14 | 38,088 | 62.3 | 801.1 | 74.1 | 16.5 | 461.9 | 8.5 | 38.7 |
| TB15 | 40,204 | 58.1 | 3515.9 | 72.3 | 16.9 | 68.1 | 4.3 | 53.2 |
| TB16 | 3703 | 81.2 | 881.1 | 27.8 | 14.0 | 13.1 | 0.8 | 24.9 |
| TB17 | 3703 | 108.3 | 1171.4 | 26.4 | 7.3 | 8.8 | 1.4 | 21.2 |
| TB18 | 21,160 | 74.2 | 1107.6 | 53.0 | 10.3 | 13.0 | 0.7 | 36.9 |
| TB19 | 23,276 | 31.9 | 401.2 | 38.1 | 4.8 | 19.5 | 1.7 | 32.2 |
| TB20 | 9522 | 21.3 | 1347.7 | 28.3 | 10.0 | 10.5 | 1.6 | 29.4 |
| TS1 | 51,842 | 73.2 | 967.7 | 129.1 | 19.2 | 39.8 | 1.4 | 97.5 |
| TS2 | 44,436 | 67.9 | 869.1 | 26.4 | 18.2 | 57.4 | 1.0 | 111.9 |
| TS3 | 50,784 | 105.3 | 1447.3 | 130.9 | 22.4 | 49.6 | 1.4 | 127.8 |
| TS4 | 42,320 | 84.9 | 833.3 | 52.6 | 15.7 | 53.2 | 0.8 | 94.4 |
| TS5 | 39,675 | 69.0 | 857.5 | 52.8 | 13.8 | 43.3 | 1.1 | 29.7 |
| TS6 | 41,791 | 53.4 | 2220.0 | 70.2 | 18.5 | 64.2 | 2.2 | 76.2 |
| TS7 | 41,262 | 100.3 | 1626.4 | 145.3 | 36.9 | 64.6 | 2.0 | 113.6 |
| TS8 | 57,132 | 87.0 | 1425.3 | 92.7 | 27.6 | 109.0 | 2.6 | 109.3 |
| TS9 | 58,190 | 109.8 | 1469.8 | 150.8 | 39.7 | 96.3 | 2.0 | 121.6 |
| DB1 | 10,051 | 69.1 | 986.5 | 33.9 | 10.0 | 31.2 | 1.6 | 41.3 |
| DB2 | 45,494 | 136.0 | 1303.9 | 115.9 | 16.3 | 35.9 | 2.0 | 31.1 |
| DB3 | 9522 | 110.1 | 667.1 | 63.2 | 12.3 | 47.4 | 0.9 | 32.0 |
| DB4 | 48,139 | 94.5 | 945.3 | 68.6 | 45.7 | 75.6 | 0.6 | 92.7 |
| DB5 | 11,638 | 97.2 | 529.6 | 117.6 | 10.9 | 53.7 | 2.1 | 86.2 |
| DB6 | 16,399 | 27.6 | 101.0 | 28.0 | 5.4 | 31.1 | 0.6 | 33.4 |
| DB7 | 41,262 | 140.8 | 1936.1 | 151.3 | 25.7 | 127.0 | 4.1 | 125.4 |
| DS1 | 46,023 | 104.3 | 957.9 | 126.8 | 17.2 | 86.6 | 1.6 | 118.2 |
| DS2 | 47,610 | 85.7 | 1124.0 | 69.0 | 21.6 | 84.8 | 1.9 | 117.3 |
| DS3 | 24,863 | 105.5 | 587.6 | 43.7 | 9.5 | 39.4 | 1.0 | 18.2 |
| DS4 | 46,552 | 118.9 | 738.0 | 33.0 | 25.1 | 100.6 | 1.6 | 49.8 |
| DS5 | 47,610 | 91.4 | 1508.2 | 128.4 | 21.6 | 108.4 | 1.9 | 117.0 |
| DS6 | 42,320 | 77.0 | 2245.2 | 124.8 | 17.1 | 83.4 | 1.6 | 127.9 |
| DS7 | 55,545 | 117.2 | 1734.1 | 60.1 | 32.4 | 126.6 | 2.3 | 127.6 |
| DS8 | 49,197 | 106.1 | 1591.1 | 132.5 | 24.2 | 103.8 | 1.9 | 108.4 |
| DS9 | 49,197 | 127.8 | 1869.9 | 134.0 | 28.6 | 110.5 | 2.0 | 170.4 |
| DS10 | 49,197 | 79.9 | 1830.2 | 126.9 | 19.6 | 87.7 | 1.9 | 122.9 |
| DS11 | 37,559 | 102.2 | 1217.0 | 88.6 | 18.6 | 70.0 | 1.7 | 105.2 |
| DS12 | 48,139 | 61.4 | 1597.3 | 128.9 | 21.3 | 77.1 | 1.8 | 94.1 |
| DS13 | 51,842 | 98.4 | 1739.3 | 134.5 | 27.1 | 120.9 | 2.5 | 107.1 |
| DS14 | 51,842 | 100.1 | 2423.3 | 144.3 | 27.4 | 109.9 | 2.1 | 125.1 |
| DS15 | 59,777 | 119.1 | 1533.6 | 142.2 | 34.4 | 145.7 | 2.6 | 125.3 |
| DS16 | 52,371 | 98.7 | 2178.7 | 87.3 | 32.7 | 150.5 | 3.2 | 128.9 |
| DS17 | 43,907 | 80.7 | 1907.0 | 126.7 | 18.5 | 85.3 | 1.9 | 86.6 |
| DS18 | 52,900 | 107.9 | 1520.0 | 66.7 | 29.0 | 107.0 | 1.8 | 126.7 |

**Table A3.** Parameters used to assess sediment pollution and ecological risk of PTEs.

| Parameter | | Unit | Cr | Mn | Ni | Cu | Zn | Cd | Pb | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Geochemical background | UCC | mg kg$^{-1}$ | 92 | 774 | 47 | 28 | 67 | 0.09 | 17 | [39] |
| | $C_b$ | | 95 | 720 | 35 | 45 | 71 | 0.2 | 26 | [78] |
| | $C_0$ | | 41 | 347 | 25 | 30 | 37.4 | 0.24 | 18 | [50,57] |
| Toxic response factor | $Tr$ | unitless | 2 | 1 | 5 | 5 | 1 | 30 | 5 | [38,42] |
| Sediment quality guidelines * | $TEL_f$ | mg kg$^{-1}$ | 37.3 | – | 18 | 35.7 | 123 | 0.596 | 35 | [79,80] |
| | $ERL_f$ | | 80 | – | 30 | 70 | 120 | 5 | 35 | [79] |
| | $PEL_f$ | | 90 | – | 36 | 197 | 315 | 3.53 | 91.3 | [79,80] |
| | $ERM_f$ | | 145 | – | 50 | 390 | 270 | 9 | 110 | [79] |
| | $TEL_s$ | | 52.3 | – | 15.9 | 18.7 | 124 | 0.68 | 30.24 | [35,80] |
| | $ERL_s$ | | 81.8 | – | 20.9 | 34 | 150 | 1.2 | 46.7 | [80,81] |
| | $PEL_s$ | | 160 | – | 42.8 | 108 | 271 | 4.21 | 112 | [35,80] |
| | $ERM_s$ | | 370 | – | 51.6 | 270 | 410 | 9.6 | 218 | [80,81] |

Note(s): * The subscripts *f* and *s* denote the effect levels for freshwater and marine sediments, respectively.

**Table A4.** Criteria for classifying metal sediment enrichment, pollution and ecological risks.

| Index | | Class | | | | | | | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Negligible | Warning Limit | Low | Moderate | Considerable | High | Very High | Extreme | |
| Enrichment | *EF* | ≤1 | – | 1–3 | 3–5 | 5–10 | 10–25 | 25–50 | >50 | [40] |
| Pollution | *Igeo* * | ≤0 (0) | – | 0–1 (1) | 1–2 (2) | 2–3 (3) | 3–4 (4) | 4–5 (5) | >5 (6) | [74] |
| | *PI* | ≤1 | – | 1–2 | 2–3 | – | 3–5 | >5 | – | [70] |
| | *NPI* | ≤0.7 | 0.7–1 | 1–2 | 2–3 | – | >3 | – | – | [75] |
| | *CF* | – | – | <1 | 1–3 | 3–6 | – | ≥6 | – | [42] |
| | $mC_d$ | <1.5 | – | 1.5–2 | 2–4 | – | 4–8 | 8–16 | 16–32 | [71] |
| | *MPI* | <1 | 1 | – | – | >1 | – | – | – | [76] |
| Ecological Risk | *Er* | – | – | <40 | 40–80 | 80–160 | 160–320 | ≥320 | – | [42] |
| | *RI* | – | – | <150 | 150–300 | 300–600 | – | ≥600 | – | [42] |
| | *ERMQ* | – | – | <0.1 | 0.1–0.5 | 0.5–1.5 | ≥1.5 | – | – | [43] |
| | *MERMQ* | – | – | <0.1 | 0.1–0.5 | 0.5–1.5 | ≥1.5 | – | – | [43] |
| | *TRI* | ≤5 | – | 5–10 | 10–15 | 15–20 | – | >20 | – | [2] |

Note(s): * *Igeo* classes according to Müller [74] are indicated in brackets.

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