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Heavy Metal Content in Macroalgae as a Tool for Environmental Quality Assessment: The Eastern Gulf of Finland Case Study

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Abstract: Macroalgae are widely used for bioindication and assessment; however, in the case of pollutants of different origin, it is still unclear which contaminants in thalli can be regarded as indicative because too many factors influence the ability of algae to uptake them. The present study is a part of an international HAZLESS project and was conducted in the eastern Gulf of Finland (GoF). The main goal of our study was the application of metal concentrations in macroalgae as a tool for environmental quality assessment. To achieve this goal, we calculated the threshold metal concentrations in macroalgae (*Cladophora glomerata*) and compared our obtained values with actual concentrations. We found significant Spearman correlations in May between metals in sediments and pore water (−0.73 for Zn, −0.62 for Cd, 0.85 for Pb) and also between metals in algae and metals in pore water (1 for Cu and Cd, 0.98 for Zn and Pb). In July, Pb in algae were significantly correlated with Pb in pore water (0.88). The application of the calculated environmental quality standard (EQS_{MPC}) for macroalgae has shown moderate pollution by Cu and Pb in the coastal zone of the eastern GoF. This was confirmed by an assessment based on the comparisons of metal concentrations in water with Environmental Quality Standards for water (EQS_w). However, differences in the bioaccumulation factor and EQS_{MPC} between May and July have shown that it is necessary to compare samples taken during the same period every year for adequate results in long-term monitoring. Considering the sensitivity of accumulating processes to the surrounding environment, we believe that in the case of habitats with diverse conditions, even for the same species of algae, threshold values should be calculated and used individually for every habitat. Our results have shown that this approach can be widely used for an assessment of environmental quality via metal concentrations in opportunistic macroalgae and can be recommended for further use.

Keywords: heavy metals; *Cadophora glomerata*; bioaccumulation factor; environmental quality standard; metals in algae; metals in pore water

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1. Introduction

The rise of an anthropogenic impact on the marine environment requires the development of new water management and environmental protection approaches. In turn, it demands international cooperation and uniform actions between countries. An outstanding example of such activity is the collaboration of the Baltic Sea countries in the frame of the Convention on the Protection of the Marine Environment of the Baltic Sea Area, known as the Helsinki Convention. Another good example is the Estonia–Russia Cross Border Cooperation Programme 2014–2020 (https://www.estoniarussia.eu, accessed on 1 July 2023). The goal of our research in the HAZLESS project (https://www.estoniarussia.eu/projects/hazless/, accessed on 1 July 2023) was to adapt and implement uniform biological indicators for assessing and monitoring the state of the environment in the eastern part of the Gulf of Finland (GoF).

For the last two decades, the eastern GoF has been affected by the mass development of opportunistic algae. Nowadays, this phenomenon, known as "green tides", is widespread and well known for many water bodies around the world [1]. In turn, it raises the issue of biomonitoring in the coastal areas of seas and estuaries which opportunistic algae occupy. The high capacity of macroalgae to accumulate heavy metals [2–4], as well as the ability of algal mats to increase pollution through sediments [5], has led to the necessity of applying macroalgae in the monitoring of heavy metal pollution.

Macroalgae are primary producers, playing an initial role in the functioning of coastal ecosystems. According to the Water Framework Directive (WFD) of the European Union (Directive 2000/60/EC) [6] and the EU Marine Strategy Framework Directive (MSFD, Directive 2008/56/EC) [7], aquatic macrophytes, including macroalgae, are listed as biological quality elements (BQEs) for the environmental assessment of coastal waters. Many papers have been published regarding the use of macroalgae as indicators of pollution [8–11].

The ability of macroalgae to accumulate hazardous substances (especially heavy metals) is well known [9]. The level of accumulated pollutants in algal thalli (in mass units per g or kg of dry algal biomass) and the bioconcentration factor (BCF) (in L kg^{-1} DW) serve as a basis for environmental monitoring and water quality assessment [10]. At the same time, it is still unclear which metal content in thalli can be regarded as indicative because too many factors influence the ability of algae to uptake metals [9,12]. In spite of the fact that the BCF, together with correlation analysis, is widely used for quality assessment, the absence of standards leads to difficulties when using the BCF [13]. Also, Bilal et al. [14] found that different species of algae have various biosorption capacities, which depend on a metal's affinity to their cell walls. In addition, such factors as pH and the concentrations of Ca, Mg, K, and Na ions in the environment influence biosorption processes [9].

In the Baltic Sea, macroalgae were used for an assessment of the environmental state of the coastal area. Rinne et al. [15] proposed the use of cumulative algal cover, and the ratio of opportunistic and perennial species as an indicator of eutrophication. For the eastern GoF, the area where perennial species of macroalgae are almost absent, the authors of [16] proposed another approach involving the use of macroalgae cover area and the thickness of algal cover. In addition, the heavy metal content and the BCF have been determined in the macroalgae of the eastern GoF [5,17].

One of the problems of environmental assessment is the absence of universal criteria adequate for the evaluation of diverse aquatic habitats. Due to the physiological plasticity of algae and some difficulties in their species identification, this task becomes exigent. However, the approach that we use in this paper and describe below is promising in this respect.

Recently, Environmental Quality Standards based on macroalgae have been developed for a few areas of the Baltic Sea. This approach includes the combined use of the bioconcentration factor (or BCF) and the official quality standards for marine waters [12]. The method does not require historical data on the background concentrations of the target elements, which can be unavailable, and can be applied to many regions through the use of European as well as national water standard directives. We apply this approach, developed by Zalewska and Danowska [12], to assess the environmental quality of the coastal area of the GoF in this article, and to find out if it can be recommended as a tool for environmental assessment in the future.

2. Material and Methods

2.1. Study Area

The Gulf of Finland, situated in the eastern part of the Baltic Sea, is bordered by Sweden, Denmark, Estonia, Finland, Germany, and Russia. Its area is about 30,000 km^2. It is relatively shallow (the average depth is 38 m), with the depth decreasing from the gulf's entrance to the continent. The Neva River flows out of Lake Ladoga and discharges 76 km^3 of fresh water annually into the head of the gulf. The Neva estuary consists of the Neva Bay, and the inner and outer open estuary. The Neva Bay is the freshwater (with low mineralization (0.04–0.075 g L^{-1}) and the shallowest (depth less than 5 m) part of the Gulf. The Neva Bay is separated from the other parts by a storm-surge barrier (dam) (Figure 1). There are three large coastal bays in the eastern part of the gulf (the Luga and the Koporskaya bays and the Gulf of Vyborg).

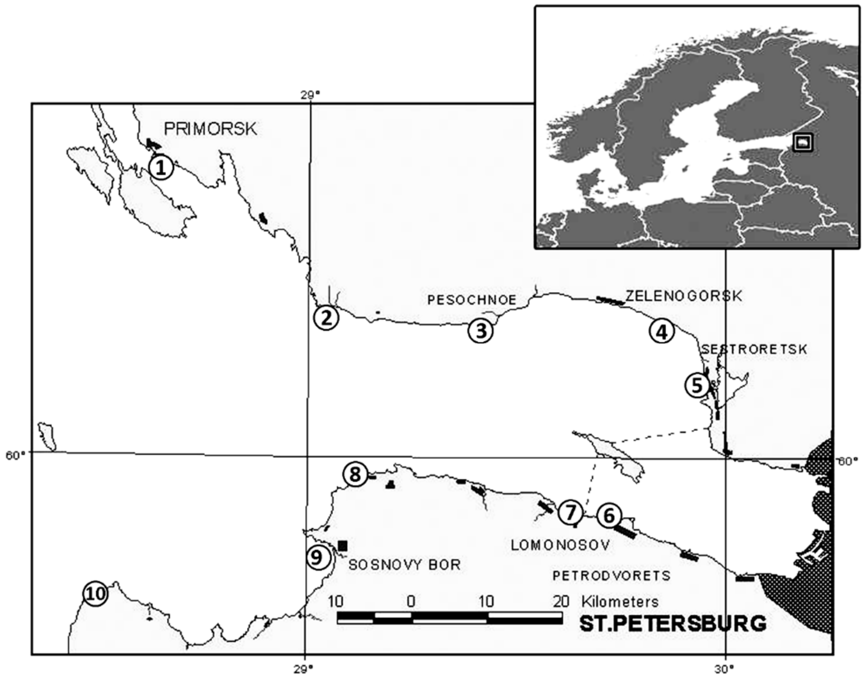

Figure 1. Schematic map of the eastern Gulf of Finland. Sampling sites are marked by numbers.

Water salinity in the Neva estuary ranges between 0.10 and 5.8 psu. The coastal zone of the eastern GoF is intensively used by various industries, including large oil terminals (near Primorsk) and for the development of new coal ports (Ust-Luga and Bronka), for recreation (the Resort District of St Petersburg), and for other purposes (Leningrad Nuclear Power Plant, sewage water discharges).

Eutrophication and chemical pollution are typical threats to the ecosystem of the Gulf of Finland. During summer, the chlorophyll *a* and the total phosphorus in the euphotic zone of the gulf averaged 10–15 and 41–75 mg m^{-3}, respectively [16]. Nowadays, the sewage waters from St. Petersburg city are purified before they are discharged into the gulf. However, secondary water pollution from sediments persists in the areas (near Petrodvorets) that were affected by highly polluted sewage water discharge in the 1970–1990s.

Macroalgae in the study area are represented by monodominant communities formed by filamentous opportunistic green algae *Cladophora glomerata* (L.) Kutz. These algae are known for their ability to form high biomass. The thick cellulose cell walls of Cladophora have a high affinity to metal ions and this allows the use of these algae as an indicator of metal pollution [18].

2.2. Sampling Design

To assess the environmental quality, we used data obtained in May and July of 2019 in frames of the state research topic of ZIN RAS and the HAZLESS Project on ten sampling sites in the coastal zone of the eastern Gulf of Finland (Figure 1). For analysis, we took samples of water at a depth of 0.5 m and pore water obtained from sediments via centrifugation at 1000 rpm.

Sediments were collected with a plastic cylinder and placed in polyethylene bags. We obtained three replicates of the samples from each site for metal detection from each site. Algae were collected for metal analysis at five sites (1, 4, 6, 9, 10) in May and at eight sites in July: at all sites of the northern shore (Sites 1–5), and at Sites 7, 9, and 10 on the southern shore. Biomasses were measured at sites 1 and 9 in May and Sites 1–3, 5, and 7 in July. The methods of biomass calculation, heavy metal identification in sediments, water, and algae have been described in detail elsewhere [5,16,17]. The metal concentrations were identified in µg L^{-1} for water, and in mg kg^{-1} for algae and sediments. In the following calculations, the metal concentrations in water were transferred to mg L^{-1}.

Water samples were analyzed within 24 h after collection. Overall, 100 mL of samples were filtered through a membrane filter; as a control sample, we used deionized water (grade 1 according to ISO 3696). Then, 2 ml of ultrapure HNO_3 and 1 ml H_2O_2 were added to the filtered samples and after were heated to avoid boiling and evaporated to a volume of 25 mL. After cooling, the analyzed samples were diluted, using deionized water, to the initial volume (100 mL).

For metal analysis in sediments and algae, all the samples were oven-dried at 30°C and sifted through a plastic sieve with pore diameter of 1 mm. The passing fraction was powdered with an agate mortar and digested using a combination of ultrapure acids HCl/HF/HNO_3 (1:1:1) in a microwave oven Mars 5 (CEM, USA). The products of digestion were transferred to the polypropylene vials, diluted to 50 ml with deionized water (grade 1 according to ISO 3696), and stored at −20°C until the analysis was carried out.

The samples were analyzed for Cu, Zn, Pb, Cd, Fe, and Mn by using inductively coupled plasma mass spectrometry (ICP-MS) with a mass spectrometer Agilent 7700x (Agilent technologies, Japan) [19]. The detection limits for metals in water were as follows: Mn—0.02 µg L^{-1}, Fe—10 µg L^{-1}, Cu—0.01 µg L^{-1}, Zn—0.01 µg L^{-1}, Cd—0.001 µg L^{-1}, and Pb—0.01 µg L^{-1}. The detection limits for metals in sediments and algae were as follows: MnO—0.0002%, Fe_2O_3—0.005%, Cu—1.0 ppm, Zn—1.0 ppm, Cd—0.01 ppm, and Pb—1 ppm. The accuracy was ensured by applying certified standards (CRM 5365-90) and providing suitable recoveries (<5%). Since a universal system of sediment quality assessment for metal concentration still does not exist, we used the low effect level (LEL), the level of sediment contamination that can be tolerated by the majority of benthic organisms without causing harm to vital functions [20]. The oxidation/reduction potential (Eh) was measured in accordance with the saturated Ag/AgCl electrode.

2.3. Data Analyses

Calculations were conducted for Cu, Zn, Cd, and Pb; these metals were defined as priority substances in the field of water policy [21]. Since the monodominant opportunistic algae *Cladophora glomerata* represents the macroalgal communities of the eastern GoF, we made calculations for this one species. High concentrations of Mn and Fe in the water are natural for the Gulf of Finland [17], and we used these two metals only in the principal component and classification analysis.

The given field-measured bioconcentration factor (BCF) was calculated using the following equation [22]:

BCF = C_a/C_w, where C_a is the metal concentration in algae (mg/kg in dry weight, DW) and C_w is the metal concentration in water collected from the site of algae sample collection (mg L^{-1}). The units of field-measured BCF were defined as L kg^{-1}.

Since the eastern GoF is a transition system, where conditions change from freshwater to brackish water, we have to use the standards for surface fresh- as well as seawater.

The Environmental Quality Standard for freshwater and seawater (EQS_W) was derived from Directive 39/2013 [21] for Cd and Pb and the standards for fishery water bodies, which were established by the Ministry of Agriculture of the Russian Federation [23] for Cu and Zn.

The Environmental Quality Standard for macroalgae (EQS_{MP}) was calculated using the following equation [12]:

$$EQS_{MP} = BCF \times EQS_W$$

where EQS_{MP} is a threshold concentration of the target substance in algal tissues, which can be accumulated in the conditions of a good environmental state.

The data were analyzed using ANOVA, Spearman rank correlation analysis, and the principal component and classification analysis. The parameters are presented as mean values and standard errors.

3. Results

3.1. Hydrochemical Parameters

The salinity, pH of water and sediments, Eh, concentrations of total phosphorus, and dissolved oxygen are presented in Table 1.

Table 1. Main hydrochemical parameters on study sites in May and July of 2019.

Site	pH Water		pH Sediments		Eh, mv (sat. Ag/AgCl Electrode)		Salinity	Ptot mg/L	Oxygen ml/L
	May	July	May	July	May	July	July	July	July
1	8.3 ± 0.05	7.23 ± 0.07	7.23 ± 0.06	6.77 ± 0.09	−252	−178	2.2	125	7.2
2	7.5 ± 0.05	7.43 ± 0.6	6.8 ± 0.06	6.67 ± 0.07	−19	−200	1.5	60	7.08
2 under algae	7.5 ± 0.06	7.6 ± 0.05	n.d.	6.7 ± 0.06	n.d.	−210	n.d.	n.d.	n.d.
3	n.d.	7.3 ± 0.06	n.d.	7.27 ± 0.07	n.d.	−189	1	50	7.2
4	7.4 ± 0.05	8.4 ± 0.07	6.77 ± 0.03	7.17 ± 0.03	−256	−142	0.45	102	7.2
5	8.03 ± 0.03	7.53 ± 0.05	6.63 ± 0.03	6.77 ± 0.03	−196	−154	0.08	98	7
6	7.47 ± 0.03	8.13 ± 0.04	7.13 ± 0.03	6.97 ± 0.03	−226	−231	0.108	88	7.2
7	7.03 ± 0.03	7.13 ± 0.03	6.10 ± 0.06	6.9 ± 0.06	−216	−33	1.6	45	7.3
8	6.7 ± 0.2	6.7 ± 0.3	6.27 ± 0.3	6.8 ± 0.02	−301	−240	2.16	148	7.3
8 under algae	6.6 ± 0.05	6.7 ± 0.05	6.8 ± 0.3	6.43 ± 0.03	−290	−225	n.d.	n.d.	n.d.
9	7.47 ± 0,03	7.07 ± 0.03	7.3 ± 0.06	7.33 ± 0.03	−287	−315	2.2	50	7.3
9 under algae	7.57 ± 0.03	7.13 ± 0.03	6.73 ± 0.03	6.77 ± 0.03	−292	−225	n.d.	n.d.	n.d.
10	7.27 ± 0.03	7.37 ± 0.03	6.8 ± 0.06	6.87 ± 0.03	−121	−133	3.2	42	7.3

n.d.—no data; pH values are given as an arithmetic mean ± standard error.

In the previous studies [5], it was detected that algal mats can create specific conditions in the coastal zone, affecting the metal distribution in the bottom sediments; we also measured the parameters under the algal layer on the sites with algal mats.

Eh and pH are very important for the water bodies because they reflect oxidation–reduction reactions. In our study, most sites were characterized by the alkaline reaction of water. The exception was site 8, where the water had an acid reaction (Table 1). Unlike the water, the sediments from most sites were characterized by an acid reaction. The Eh potential had very low and negative values on all study sites, which shows the prevalence of reduction reactions on the border water sediments [24].

The salinity increased from east to west, with a decrease under the influence of the Neva river.

3.2. Metal Concentrations in the Water and Sediments

The metal concentration in the water in May on the majority of sites was distributed in the following order:

$$Zn > Cu > Pb > Cd$$

The distribution of metals on the different study sites in May is shown in Figure 2.

As seen from Figure 2, on the northern shore (Sites 1–5), the highest concentrations of all four metals were observed at Site 4. It is remarkable that at this site, the concentration of cadmium exceeded that of lead and was significantly higher than that on other sites. The concentrations of Zn were higher at Sites 1–4 and significantly lower at Site 5, which is the closest point to the Neva Bay (Figure 2). The concentrations of copper increased in the direction from Site 1 (the most distant site) to Sites 4 and 5, where they were significantly higher.

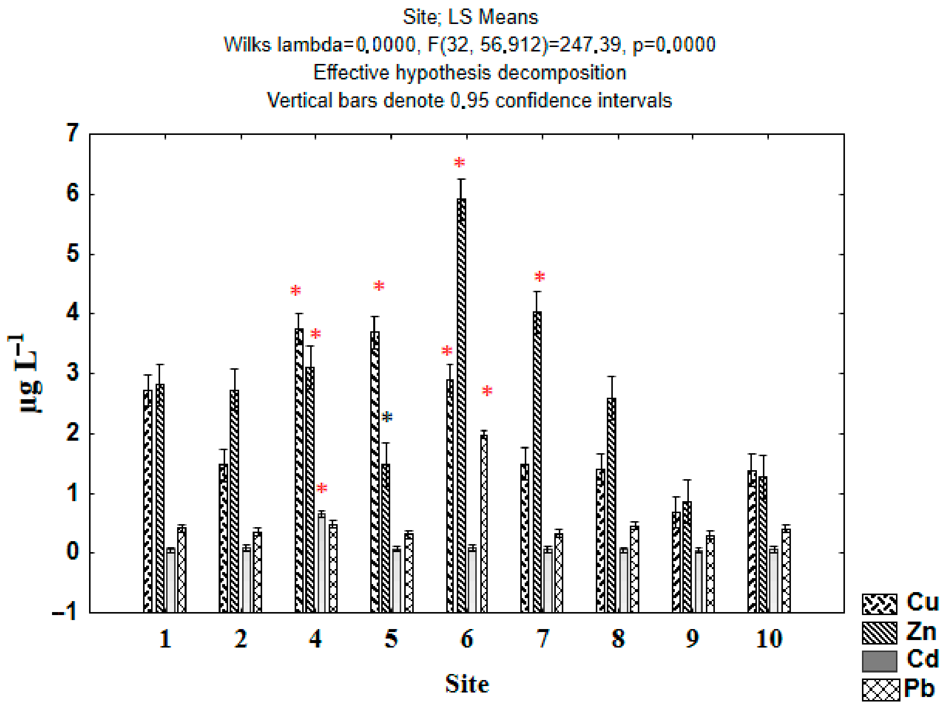

Figure 2. Metal distribution in the water on study sites of the EGoF in May 2019. *—significantly higher; *—significantly lower.

On the southern shore (Sites 6–10), the maximum metal concentration was observed at Site 6, which is situated in Neva Bay. The concentrations of all metals (Zn, Cu, Pb), excluding cadmium, were significantly higher at this site. In the direction to the west, from Neva Bay to Koporskaya Bay, the concentrations of metals decreased. In Luga Bay, we observed some non-significant rises in concentrations, which could be caused by the proximity of the Ust' Luga port. The maximum Zn concentration was found in Neva Bay (Site 6) and reached 5.91 $\pm$ 0.33 µg L^{-1}. The highest concentrations of copper were on the northern shore at Sites 4 and 5 (3.75 $\pm$ 0.02 and 3.69 $\pm$ 0.16 µ L^{-1}, respectively). The maximum concentration of Pb was found in Neva Bay, reaching 1.98 $\pm$ 0.07 µg L^{-1}.

The concentrations of cadmium were at the same level on the majority of sites, excluding Site 4, where Cd concentrations exceeded lead concentrations and reached a value of 0.66 $\pm$ 0.06 µg L^{-1}.

In July, the metal distribution differed from that in June (Figure 3). Significantly higher concentrations of Zn were found at Sites 5 and 8. The maximum Zn concentration was found at Site 8 and reached 4.09 $\pm$ 0.12 µg L^{-1}. Copper particularly repeated the pattern of Zn with significantly higher concentrations at Sites 5, 6 and the maximum concentration at Site 10 (1.92 $\pm$ 0.06 µg L^{-1}). The lead concentration did not change significantly across the sites, excluding Site 8, where the Pb concentration was significantly higher and reached 1.67 $\pm$ 0.04 µg L^{-1}.

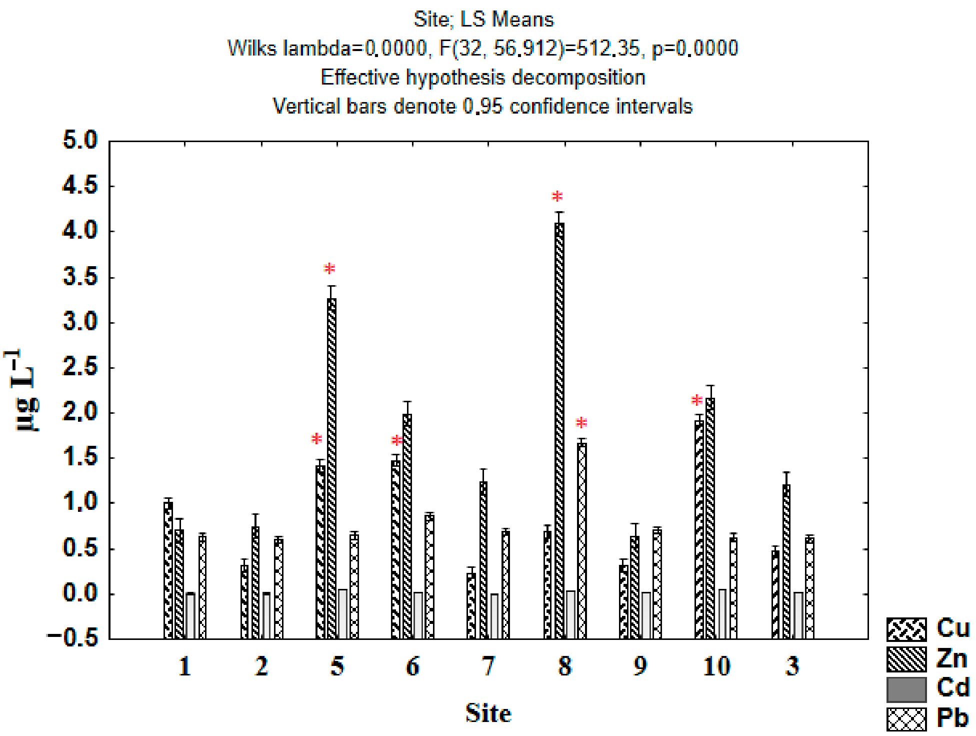

Figure 3. Metal distribution in the water on study sites of the EGoF in July 2019. *—significantly higher.

The cadmium concentration did not change significantly over the study sites.

The concentration of metals differed significantly during the study period. The copper concentration in July decreased at all study sites, except at Site 10, where its concentration increased but non-significantly (ANOVA, F (14;30) = 303.73, $p = 0.000$).

The dynamics of Zn concentration varied widely; in July, Zn concentrations decreased significantly at Sites 1, 2, 6, 7 and rose at Sites 5, 8, 10 (F (14;30) = 234.33; $p = 0.000$).

The lead concentrations in July increased significantly at all sites, except for Site 6, where the lead concentration was halved in comparison with June (F (14;30) = 463.22; $p = 0.000$).

A significant decrease in Cd concentration was observed at all study sites (F (14;30) = 53.389; $p = 0.000$).

The metal concentrations in the pore water are presented in Table 2. The concentrations of metals in the pore water were several times higher than those in the water column. Only Pb was an exception; its concentration in the pore water exceeded that in the water layer, but not by more than twice.

Judging by the concentrations, the metals in the sediments are primarily distributed in the order Zn > Pb > Cu > Cd. Significantly, the highest concentrations of all metals were found at Site 1 (Figure 4). The highest concentrations of Zn were registered in sediments at Sites 1 and 5 (36.22 ± 2.01 and 35.13 ± 2.26 mg kg^{-1}, respectively). The highest concentrations of lead, copper, and cadmium were recorded at Site 1 near port Primorsk, reaching 23.9 ± 1.40; 10.33 ± 0.53 and 0.30 ± 0.02 mg kg^{-1}, respectively.

Table 2. Total metal content in the pore water (μg L^{-1}) in May and July 2019.

Site	Pore Water				
	Month	**Cu**	**Zn**	**Cd**	**Pb**
1	May	3.61 ± 0.14	8.11 ± 0.3	0.07 ± 0.004	2.67 ± 0.16
	July	5.8 ± 0.15	1.96 ± 0.06	0.082 ± 0.005	1.18 ± 0.05
2	May	n.d.	n.d.	n.d.	n.d.
	July	2.45 ± 0.07	2.41 ± 0.08	0.048 ± 0.0014	0.94 ± 0.04
3	May	n.d.	n.d.	0.049 ± 0.001	n.d.
	July	2.99 ± 0.09	0.84 ± 0.03	0.014 ± 0.0003	0.77 ± 0.03
4	May	n.d.	n.d.	n.d.	n.d.
	July	n.d.	n.d.	n.d.	n.d.
5	May	n.d.	n.d.	n.d.	n.d.
	July	3.54 ± 0.12	0.87 ± 0.04	0.018 ± 0.001	0.79 ± 0.03
6	May	18.2 ± 0.65	15.1 ± 0.53	0.17 ± 0.009	2.29 ± 0.13
	July	5.55 ± 0.15	1.97 ± 0.06	0.022 ± 0.001	1.59 ± 0.07
7	May	4.98 ± 0.18	21.93 ± 0.82	0.18 ± 0.009	1.37 ± 0.08
	July	1.83 ± 0.03	10.4 ± 0.29	0.58 ± 0.02	1.67 ± 0.08
8	May	6.13 ± 0.24	8.49 ± 0.35	0.12 ± 0.006	2.15 ± 0.12
	July	3.25 ± 0.09	2.34 ± 0.07	0.029 ± 0.001	0.77 ± 0.03
9	May	4.41 ± 0.17	9.21 ± 0.33	0.01 ± 0.006	1.25 ± 0.07
	July	10.49 ± 0.3	2.59 ± 0.07	0.049 ± 0.003	1.3 ± 0.05
10	May	n.d.	n.d.	n.d.	n.d.
	July	n.d.	n.d.	n.d.	n.d.

n.d.—no data.

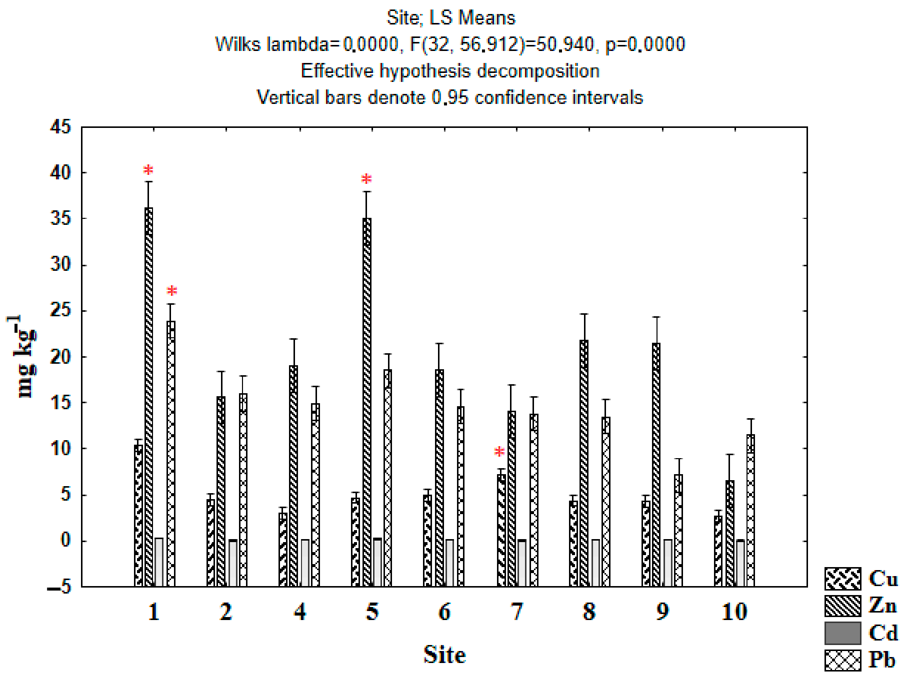

Figure 4. Metal distribution in sediments on study sites of the EGoF in May 2019. *—significantly higher.

3.3. Macroalgae Biomass and Metal Accumulation

Figures 5 and 6 present the measured metal concentrations in the macroalgae at the study sites in May and July, respectively. The biomass of macroalgae was measured in May, but only for Sites 1 and 9. At Site 1, it reached 409.27 ± 263.73 $gDWm^{-2}$, or 2 kg of fresh biomass per square meter. At Site 9, the biomass of the macroalgae was 346.36 ± 101.21 $gDWm^{-2}$ (or 1.7 kg of fresh biomass per square meter).

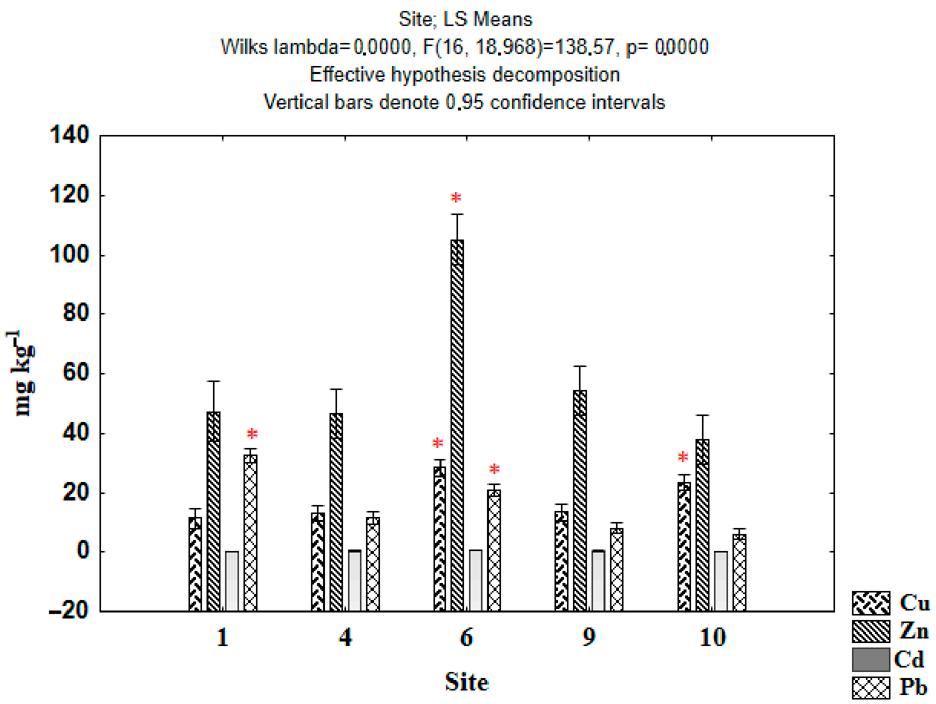

Figure 5. Metal content in biomass of *Cladophora glomerata* in May 2019. *—significantly higher.

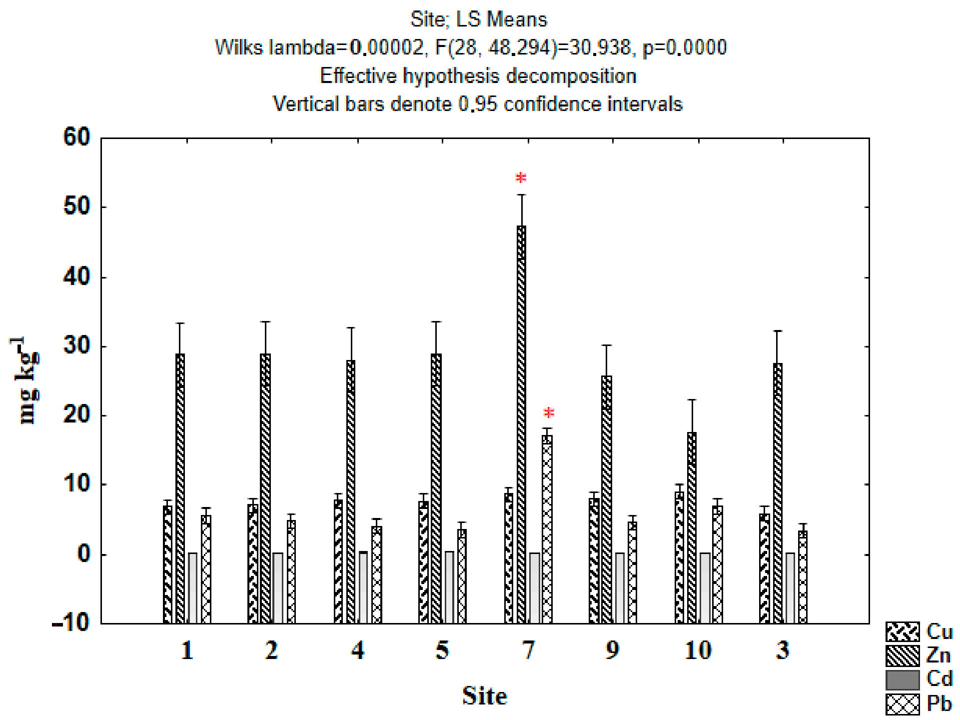

Figure 6. Metal content in algal biomass in July 2019. *—significantly higher.

The highest macroalgae biomass in July was at Sites 1 (326.17 ± 191.86 gDWm^{-2} or 1.6 kg of fresh biomass per square meter) and 2 (696.5 ± 143.14 gDWm^{-2}, or 3.5 kg of fresh biomass per square meter). The algae biomass on Sites 3, 5, and 7 was 34.75 ± 18.34, 46.56 ± 15.57 and 19.17 ± 10.62 gDWm^{-2}, respectively. At Sites 8 and 9, besides particular thalli of fresh algae, we observed decaying biomass with a thickness up to 30 cm (Site 8).

In May, the Zn, Cu, and Cd concentrations in the macroalgal biomass repeated the same concentration pattern in the water (Figure 5).

The maximum metal concentrations were recorded in the algae from Site 6. The Zn content at this site reached 105.20 ± 6.30 mg kg^{-1} of dry weight, and was significantly higher than that on the other sites. The concentration of copper at Site 6 reached 28.35 ± 1.70 mg kg^{-1} and was also significantly higher in comparison with the other sites. Cadmium also had the highest concentration in macroalgae at Site 6 (0.56 ± 0.04 mg kg^{-1}). Lead had the highest concentration in macroalgae at Site 1 (31.06 ± 1.77 mg kg^{-1}). At Site 6, the Pb content in macroalgae was 20.70 ± 1.24 mg kg^{-1}. The lead content in macroalgae at Sites 1 and 6 was significantly higher than that at Sites 4, 9, and 10.

In May, the Spearman rank correlations were significant for Cd content in algae and in the water (R = 0.66, $p < 0.05$), also for Pb content in algae and in the sediments (R = 0.84, $p < 0.05$), and Pb content in algae and in the water (R = 0.51, $p < 0.05$).

In July, none of the analyzed metal concentrations in the algal biomass showed a significant difference at Sites 1–5 (on the northern shore) (Figure 6). A significant sharp rise in Zn and Pb concentrations was recorded in *Cladophora glomerata* from Site 7 (southern shore). Even though the concentrations of Zn at most sites, on average, did not exceed 28 mg kg^{-1}, at Site 7, the concentration reached 47.30 ± 3.70 mg kg^{-1}. Lead concentrations at the majority of the studied sites did not exceed 7.00 mg kg^{-1}, but, at Site 7, the concentration was 17.00 ± 1.20 mg kg^{-1}.

In July, significant Spearman rank correlations were found for Zn in the algae and Zn in the water (R = −0.53).

The ANOVA showed that the Cu concentration in macroalgae in July significantly decreased at all study sites (F (6,14) = 21.566; $p = 0.000$) compared to that in May. The same pattern was found for Zn (F (6,12) = 5.6357; $p = 0.005$). The Cd concentration in macroalgal biomass in July was significantly lower at Sites 4 and 9 (F (6,14) = 48.544; $p = 0.000$), and also the Pb concentration in July was significantly lower at all sites, except Site 10 (F(6,14) = 65.057; $p = 0.000$), than in May.

3.4. Comparison of Spearman Rank Correlations between Metals in the Pore Water, the Water Column, and Algae

The correlations in May and July are presented in Tables 3 and 4, respectively.

Table 3. Spearman rank correlations between metal concentrations in the pore water (Me pore), sediments (Me sed), the water column (Me w), and algal biomass (Me alg) in May 2019.

Metal	Cu Pore	Zn Pore	Cd Pore	Pb Pore
Cu sed	n.s	n.s	n.s	n.s
Zn sed	n.s	−0.73	n.s	n.s
Cd sed	n.s	n.s	−0.62	n.s
Pb sed	n.s	n.s	n.s	0.85
Cu w	n.s	n.s	n.s	n.s
Zn w	n.s	0.62	n.s	n.s
Cd w	n.s	n.s	0.62	n.s
Pb w	n.s	n.s	n.s	0.79
Cu alg	1.00	0.98	1.00	n.s
Zn alg	1.00	0.98	1.00	n.s
Cd alg	1.00	0.98	1.00	n.s
Pb alg	n.s	n.s	n.s	0.98

n.s.—not significant.

Table 4. Spearman rank correlations between metal concentrations in pore water (Me pore), water column (Me w), and algal biomass (Me alg) in July 2019.

Metal	Cu Pore	Zn Pore	Cd Pore	Pb Pore
Cu w	0.52	n.s	n.s	n.s
Zn w	−0.66	n.s	−0.57	n.s
Cd w	−0.51	−0.45	−0.83	n.s
Pb w	n.s	n.s	−0.67	n.s
Cu alg	n.s	0.74	0.63	0.73
Zn alg	−0.47	n.s	0.54	n.s
Cd alg	0.51	n.s	n.s	n.s
Pb alg	n.s	0.80	0.95	0.88

n.s.—not significant.

In May, Cu and Cd in the pore water showed the highest correlation with the concentration of these metals in the algal biomass (R = 1). The Zn concentration also showed a very high correlation with the metal concentration in algal biomass (R = 0.98). Also, all of these metals in algal tissues correlated with each other (Table 3). Zn and Cd in the pore water were negatively correlated with the concentrations of these metals in the sediment. Pb in the pore water was positively correlated with Pb in the sediments, the water, and the algae. Cd and Pb in the water were significantly correlated with Cd and Pb in algal tissues. The Spearman rank correlation was 0.66 for Cd in the water and algae and 0.51 for Pb in the water and algae.

In July, we observed other correlations (Table 4).

In July, Cu in the pore water was positively correlated with Cu in the water column and with Cd in the water column and algae. However, there was no correlation between Cu concentrations in the pore water and in algae (Table 4). Zinc in the pore water did not correlate with Zn in the water and algae but had a negative correlation with Cd in the water. A strong positive correlation was observed for Zn in the pore water and copper and lead in the algae. Cadmium in the pore water was strongly negatively correlated with Zn, Cd, and Pb in the water and positively correlated with Cu, Zn, and Pb concentrations in algae (Table 4). Lead in the pore water had a strong positive correlation with Cu and Pb in algae (Table 4).

3.5. Results of Principal Component and Classification Analysis

PCCA extracted two main factors that influenced the distribution of metals in the eastern GoF in May (Figure 7). Factor 1 was positively correlated with Eh and had a negative correlation with salinity. The majority of metals from the water, the pore water, and algae, which are usually regarded as anthropogenic pollution, were positively correlated with Factor 1 and grouped with Eh potential.

Factor 2 is highly positively correlated with Cu, Cd, Zn, and Pb in sediments; this allows us to connect it with the anthropogenic sources of their loading.

In July, the influence of the factor, related to conditions at the water–sediment interface, on metal distribution in the studied environments decreased (Figure 8, Factor 2) and contributed 25.21% to the total dispersion. However, there were still high correlations with metals in the pore water and metals in the macroalgae. Copper in the pore water had a strong negative correlation with Factor 2. Factor 1 contributed 47.18%; it was positively correlated with oxygen and strongly negatively correlated with water temperature and pH.

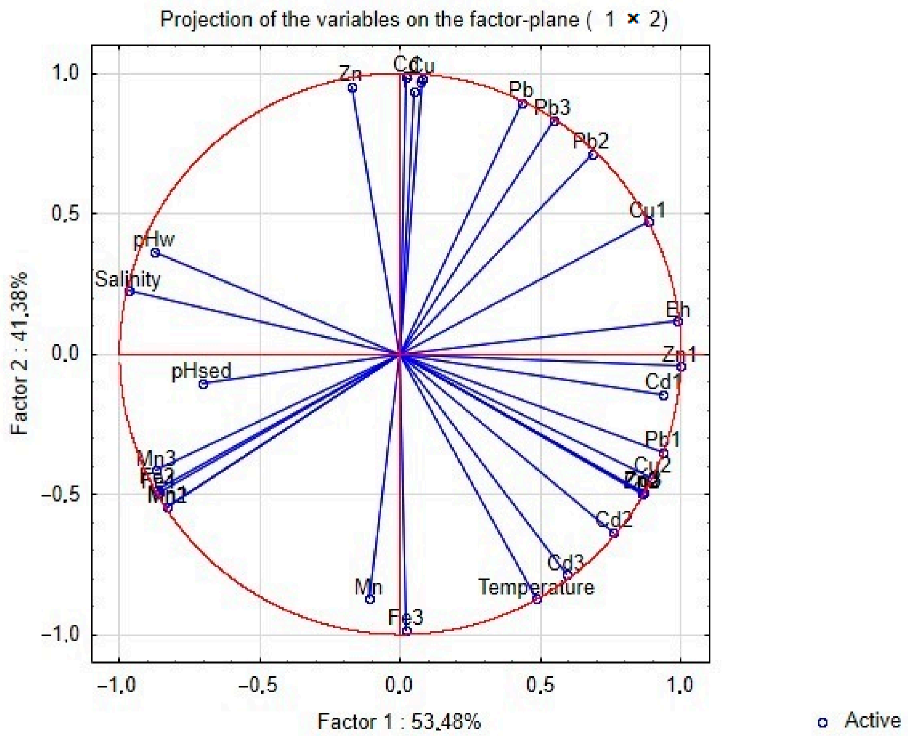

Figure 7. Principal component and classification analysis for main hydrochemical parameters (Eh, Temperature, pH in sediments (pHsed), water pH (pHw), salinity) and metal distribution in sediments (Me), water (Me1), pore water (Me2), and algae (Me3) in May 2019.

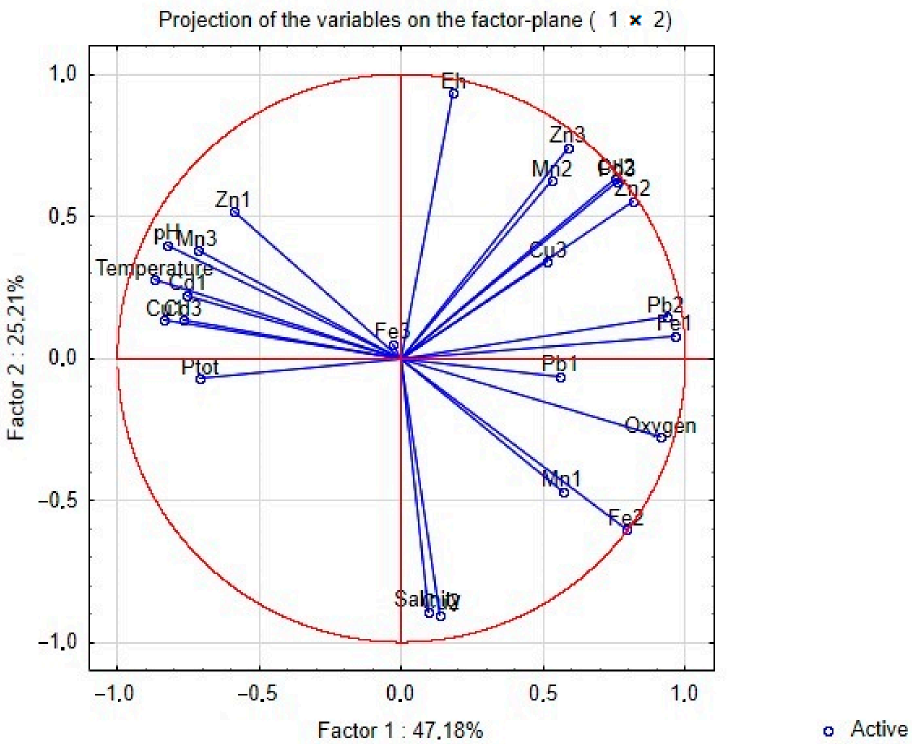

Figure 8. Principal component and classification analysis for main hydrochemical parameters (Eh, Temperature, water pH (pH), salinity) and metal distribution in water (Me1), pore water (Me2), and algae (Me3) in July 2019.

3.6. Calculated Bioconcentration Factor (BCF) and Environmental Quality Standard (EQS) for Macroalgae Cladophora Glomerata in the Eastern Gulf of Finland

The calculated BCF and EQS values for macroalgae from the eastern GoF (EQS_{MPC}) are presented in Table 5.

Table 5. Calculated bioconcentration factor for *C. glomerata* (BCF, L kg^{-1}), Environmental Quality Standard for water (EQS_W), mg L^{-1}, for *C. glomerata* (EQS_{MPC}), mg kg^{-1} DW, and concentrations of metals in tissues of *C. glomerata* (C_{clad}), (min-max, mg kg^{-1} DW).

Metal	Cu	Zn	Cd	Pb
EQS_W	0.001	0.01	0.00008	0.00012
BCF, May	9.4×10^3	2.9×10^4	4.8×10^3	3.5×10^4
BCF, July	1.6×10^4	2.8×10^4	3.2×10^4	1×10^4
EQS_{MPC} May	9.41	285.97	0.39	4.1
EQS_{MPC} July	16.29	282.3	2.58	1.2
C_{clad} May	10.8–28.3	38–105.17	0.15–0.56	6.02–31.07
C_{clad} July	5.87–9.02	17.67–47.3	0.14–0.32	3.41–17.01

From May to July, BCF values increased for Cu and Cd; however, ANOVA did not show any significant difference in BCF values between these periods (Table 5). BCF for Zn and Pb remained at the same level seasonally.

4. Discussion

The studies on metal pollution during the last decades have highlighted a problem with finding indicators that can correctly reflect the environmental state of water ecosystems. Due to their well-known ability to absorb trace elements, macroalgae have become an important object for a number of studies around the world. It was found that they can play a buffer role in coastal ecosystems, decreasing metal pollution [25]. Many recent studies have proposed using algae in water treatment systems and also for the production of biosorption materials [26]. This study provided evidence that opportunistic macroalgae *C. glomerata* may be used as a good indicator in the biomonitoring of metal pollution in an estuarine brackish ecosystem, such as in the eastern GoF. Previously, the use of macroalgae as a bioindicator in such estuaries was problematic, and, due to low salinity and specific geochemical processes in sediments (low oxygen), the perennial species of algae are rare.

4.1. Hydrochemical Parameters

One of the most critical factors which influences many processes in water bodies is pH [27]. Usually, water pH in coastal areas and surface waters fluctuates during the day, which is caused by the intense photosynthetic activity of algae and seagrasses [28]. On the majority of study sites, the pH was alkaline, which is usual for coastal areas with a high productivity [27]. However, the pH at Site 8 showed acidic conditions. In previous years, at this site, we recorded an extremely high biomass of macroalgae, which could reach a few kilos of wet weight per square meter [29]. Across more than ten years of observations, Site 8 was annually affected by the formation of thick algal mats that caused massive hypoxia with strong hydrogen sulfide release [5,17]. However, recently, we have observed a sharp decrease in native algal biomass at this site, which can be a clear sign of a decrease in productivity and changes in the state from a hypereutrophic to a dystrophic phase [30]. The latest data on water pH, presented in this paper, confirm the shift to dystrophic conditions at Site 8. At the same time, the pH of sediments was acidic at all study sites.

The negative Eh values and acidic pH in sediments are evidence of reduction reactions and hypoxic conditions on the water–sediment interface [30]. Hypoxia may form due to the decomposition of large amounts of organic matter (algal detritus). At the same time, the main water column remains oxygenated (Table 1). Similar conditions had previously been spotted in some Mediterranean lagoons [30]. In coastal eutrophication and macroalgal blooms, decaying organics, covering the bottom and buried in sediments, create hypoxic conditions and intensify reduction reactions with the intense release of hydrogen sulfide. In turn, this decreases the pH of the water–sediment interface. During midsummer, when massive algal mats accumulate in shallow coastal areas, hypoxic conditions can spread to the whole water column. However, in the case of the eastern GoF, even in the absence of algal mats, conditions in coastal areas can be characterized by reduction reactions in the sediment with the oxygenated water layer above. Despite the low pH at the water–sediment interface, the buffer capacity of water is usually enough to maintain alkaline conditions in the main water column [27], but, in the case of the eastern GoF, we have found at least one site with intense dystrophic processes.

4.2. Metals in Water and Sediments

Sediments accumulate pollutants, and the distribution of metals in coastal sediments reflects the anthropogenic impact and accumulation of organic matter in sediments. The highest metal concentrations were found at Site 1, near port Primorsk and the oil terminal Vysotsk. In addition, higher metal concentrations were registered at Sites 5, 8, and 9. Site 5 is affected by its proximity to the river Sestra and a large city square with high recreational activity. For many years, Sites 8 and 9 have been affected by massive macroalgal blooms with oxygen deficiency that promoted organic matter accumulation in sediments [5].

Comparing the data obtained in 2019 with our previous data, it can be noted that the level of contamination in sediments decreased in 2019 (Table 6). The dynamics of metal content in sediments varied from year to year and were different for different metals. The copper content decreased from 2012 to 2019; Zn concentration varied from year to year and reached its lowest concentrations in 2019; contamination by cadmium rose from 2012 to 2017, and then decreased in 2019; and lead concentration sharply decreased in 2019, following a rise between 2012 and 2017. According to our observations, 2019 was the first year when the concentration of metals in sediments did not exceed the LEL values. It is likely to be related to engineering construction works in Neva Bay.

Table 6. Heavy metal content (min-max, mg kg^{-1} DW) in the coastal sediments of the eastern Gulf of Finland in different years.

Year	Cu	Zn	Cd	Pb
2012 [17]	1.46–67.37	10.29–83.83	<0.05–0.20	2.45–31.6
2014 [16]	1.90–55.7	7.13–66.12	0.04–0.29	6.22–32.67
2017 [5]	1.63–22.91	7.81–77.61	0.03–0.53	8.05–240
2019	2.66–10.33	6.61–36.22	0.05–0.3	7.12–23.9
Low Effect Level [20]	16	120	0.6	31

The distribution of metals in water changed during the season. In May, a peak of Zn and Pb concentrations was observed at Site 6 in Neva Bay in close proximity to a lighthouse. According to the water quality standards for fishery water bodies [23], in May 2019, the concentration of copper and lead exceeded the approved concentrations at almost all study sites. The concentration of cadmium exceeded the approved concentrations at Site 2 and was almost equal to it at S6. In July, the concentrations decreased, but still exceeded the approved level at Sites 1, 4, 5, 6, and 10 for copper and at all study sites for lead. The concentrations of other metals were lower than the highest approved level.

4.3. Correlations between Metals in the Sediments, the Pore Water, the Water Column, and Algae

Our study found some correlations between metals in pore water, sediments, water, and algae. During the season, these correlations were not the same. In agreement with the literature data [31], in May, we found very high significant correlations between Cu, Zn, and Cd in the pore water and algal biomass. It is evident that in May, these metals had very high bioavailability [31]. This suggestion can also be confirmed by ANOVA, which showed that the concentrations of metals in algae in May were significantly higher than those in July. Similar results were obtained by [31], who observed highly significant correlations of Zn in pore water and in the tissues of Polychaeta *Nereis virens*. In agreement with the literature data [31], in May, we found negative correlations between Cd in sediments and Cd in pore water, as well as Zn in sediments and Zn in pore water.

Positive correlations between the lead content in sediments, pore water, water, and algal tissues are evidence of the high bioavailability of this metal in the conditions of the Gulf of Finland during all studied periods. At the same time, the positive correlation of the metals in pore water and algal tissues (Pb in pore water highly correlated with Cu in algae, Cd in pore water highly correlated with Cu, Zn and Pb in algae) provides some evidence that conditions at the water–sediment interface are favorable for the release of all these metals, but, further, other processes, e.g., competition between ions, play an important role in the accumulation of metals in algal thalli [9]. Similarly to our study, the pair of metals Cd and Pb has also shown high significant correlation in other investigations [32].

PCCA has indicated the main factors influencing the distribution of metals in the eastern Gulf of Finland. Considering the correlations with Eh and oxygen, we can suppose that they are related to the conditions at the water–sediment interface. All of the correlations between metals in the water and sediments indicate that the influence of Factor 1 on the distribution of metals in the eastern GoF is related to oxidation–reduction conditions in water-sediment interface (Figure 7). These deductions can also be supported by the negative correlations of Factor 1 with Mn and Fe because ferromanganese complexes are sensitive to the processes on the water–sediment interface [33]. In May, the factor related to the sources of anthropogenic loading (Factor 2) was distinguished. Also in May, metals such as Mn and Fe were grouped separately from other metals (Cu, Zn, Cd, Pb), which can reflect the differences in their original source: anthropogenic or natural. It was shown that the sediments of the Gulf of Finland are naturally rich in Mn and Fe and form ferro-manganese concretions [34]. Precipitation and rivers are considered to be the main sources of metal loading to the Baltic Sea [35]. The main source of the metal loading in the eastern Gulf of Finland is the runoff from the Neva River [36]. In our previous paper [17], we discuss in detail the dependence of Fe, Mn, and other metal concentrations on natural as well as human-induced conditions in the eastern Gulf of Finland.

Oxidation–reduction potential, and changes in the Eh, pH, and oxygen regime are very important for biogeochemical processes at the water–sediment interface. The results of PCCA for July (Figure 8) allow us to suppose that the main factor, which significantly influences the distribution and accumulation of metals in the GoF in midsummer, can be related to an oxygen regime. Our previous studies have demonstrated that hypoxic conditions lead to increased heavy metal pollution in surface sediments [5]. In other papers, it was also recorded that oxygen conditions, Eh, and pH are strongly connected, i.e., oxygen deficiency leads to an intense release of Fe and other metals from sediments [37], as well as oxygen enrichment leads to an increase in oxidation–reduction potential and metal absorption [38].

4.4. Bioconcentration Factor and Environmental Quality Standard

The BCF values obtained for *Cladophora* correspond to those of the previous studies on heavy metal contents in Baltic macroalgae [9,11]. In our study, BCF was higher in July than in May, but the metal content in algae was higher in May, which reflects higher metal concentrations in water during the May sampling.

The eastern GoF is a complex system with freshwater and brackish water parts. The salinity did not exceed 3.2 (maximum at Site 10) at any of the study sites, and thus cannot be regarded as marine level. Thus, we used values calculated with EQSW for the freshwater.

Despite an insignificant difference for BCF in May and July, the EQSMPC values for Cu, Cd, and Pb differed several times between months. In May, the Cu content in algae exceeded EQSMPC at all study sites (Sites 1, 4, 6, 7, 9, and 10). This result corresponds to the Cu concentration in water, which exceeded EQSW at all sites. Although copper concentrations in algae in July were lower than the EQSMPC values and did not show exceeded levels, the analysis of the copper content in water showed that copper contamination was present at Sites 1, 4, 5, 6, and 10.

The zinc content in algae was the highest among all other metals, but at all sites it was below EQSMPC values. As other studies have shown, high Zn content is usual for algae and it has been suggested to use some species of algae as possible sorbents for Zn removal in the Baltic Sea [39]. The cadmium content in algae was higher than EQSMPC at Sites 4 and 6; however, the Cd concentration in water showed a contamination level only at Site 4. In July, Cd in algae as well as in water did not show any contamination. The Pb content in algae across both months showed contamination at all study sites, which was also confirmed by studying the water samples.

Applying the calculated Environmental Quality Standard (EQS_{MPC}) for macroalgae, we have tracked the moderate pollution by Cu and Pb in the eastern GoF [21,40]. These findings correspond to those of our early studies on the metal concentrations in sediments [5,16,17], which also showed an increasing level of pollution by Pb and Cu. Moreover, after the construction of new ports, a rise in the level of Zn and Cd in sediments was registered [5]. This makes the monitoring of these two metals in the GoF environment very important. In the eastern GoF, the use of EQS_{MPC} as a threshold concentration of metals in algae, which can indicate metal contamination, was justified. This was confirmed by the assessment based on the comparison of metal concentrations in the water with Environmental Quality Standards for water. However, the difference in BCF and EQS_{MPC} between May and July showed that it is necessary to compare samples that are taken during the same period every year in order to have adequate results for long-term monitoring. The calculated EQS_{MPC} values for cadmium and lead were much lower than those that were calculated for a complex of macroalgal species from the southern Baltic Sea by Zalewska and Danowska [12]. The EQS_{MP} values for *Cladophora spp.* were 24 mg kg^{-1} DW for lead and 7 mg kg^{-1} DW for cadmium [12]. We analyzed only *C. glomerata*, which is a dominating species in the eastern GoF, and obtained EQS_{MPC} maximal values which were 4.1 mg kg^{-1} DW for lead and 2.58 mg kg^{-1} DW for cadmium. Lower values can be explained by the fact that the ability of algae to accumulate metals highly depends on the environmental conditions: temperature, pH, and the ions Ca^{2+}, Na^{+}, and K^{+} [9].

Compared with the southern Baltic Sea, the conditions in the GoF are characterized by lower temperature and salinity and a high influence of the Neva River inflow. The mixture of fresh and saline waters creates specific conditions which greatly influence the hydrology and chemical processes [36]. Considering the sensitivity of accumulation processes to the surrounding environment, we believe that in the case of habitats with diverse conditions, even if we deal with the same species of algae, threshold values should be calculated and used individually for every habitat.

5. Conclusions

In our study, we used threshold metal concentrations in macroalgae as a tool for environmental quality assessment and showed that this approach allows the use of macroalgae as an indicator of environmental state in water ecosystems. The level of pollution, which was shown by the calculated threshold values of metals in macroalgae, has been confirmed by the metal contents in water samples. We found that during the season, the bioaccumulation ability of macroalgae can vary. This shows the need for careful selection of the season and data for adequate monitoring. Our results have shown that this approach, initially developed by Zalewska and Danowska [12], can be widely used and recommended for environmental quality assessment with opportunistic species of macroalgae.

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