DETERMINATION OF THRESHOLD CONCENTRATIONS OF METALS IN THE DREDGING MATERIAL

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Abstract. The average, median, maximum and minimum concentrations of metals (Fe, Pb, Cd, Cu, Zn, Ni, Cr) in modern bottom sediments of Georgian Black Sea water area are statistically processed, geo-accumulation indices calculated, background concentrations of metals in bottom sediments aredetermined. Assessment criteria for the contamination of the dredged material are provided.

Key words: metals; dredging; threshold.
საკვანძო სიტყვები: ლითონები; დრეგირებული; ზღვრული დასაშვები.

გაფართოებული რეზიუმე

დრეგირებულ ფსკერულ ნალექებში ლითონების ზღვრული დასაშვები ნორმების განსაზღვრა. ვ. გვახარია, ნ. მაჩიტაძე, ნ. გელაშვილი, ტ. ადამია. ფსკერდაღრმავება საზღვაო-სატრანსპორტო ინფრასტრუქტურის მართვის ერთ-ერთი მნიშვნელოვანი და საპასუხისმგებლო შემადგენელი ნაწილია. ფსკერდაღრმავების სამუშაოების საშუალებით, რეგულირდება საპროექტო სიღრმეები, სატრანსპორტო დერეფნებში ხდება უსაფრთხო ნავიგაციის უზრუნველყოფა, მცირდება პორტების დასილვით გამოწვეული ნეგატიური ეფექტები და სხვ. დრეგირების შედეგად ამოღებული ფსკერული ნალექების დაბინძურების ხარისხის შეფასება მნიშვნელოვანი გარემოსდაცვითი აქტივობაა, ვინაიდან ნალექების შემდგომი მართვა (განთავსება-ხელახალი გამოყენება) სწორედ ამ კვლევის შედეგებით განისაზღვრება.

შავი ზღვის საქართველოს სექტორის აკვატორიის და სანაპიროს ფიზიკური (გეოგრაფიული, გეოლოგიური, ჰიდროლოგიური, კლიმატური) თავისებურებებიდან გამომდინარე, ფსკერის დასილვის პროცესები მეტად აქტიურია. შესაბამისად, ფსკერდაღრმავებითი სამუშაოები დიდი მოცულობისაა და პერმანენტულად სრულდება როგორც არსებული სანაოსნო ინფრასტრუქტურის საჭიროებისთვის, ასევე მათი ექსტენსიური განვითარების (ფოთი, ბათუმი, ყულევი) და ახალი პორტის (ანაკლია) მშენებლობის საერთაშორისო პროექტებისთვის.

ყოველწლიურად ამოიღება მილიონობით კუბ.მ ფსკერული ნალექი, რომლის განთავსება და უტილიზაცია არაერთ პრობლემასთან არის დაკავშირებული. ამათგან, ერთ-ერთია ამოღებული მასის (დრაგირებული მასალის) განთავსება-გამოყენების საკითხი, რაც უშუალოდაა დამოკიდებული მათ ეკოლოგიურ სისუფთავეზე, ანუ, დაბინძურების ხარისხზე. როგორც ცნობილია, დრეგირებული მასალის დაბინძურების ხარისხის შეფასების კრიტერიუმები საქართველოს ეროვნული კანონმდებლობით არ არის განსაზღვრული, რაც ართულებს მათი შემდგომი მართვის ღონისძიებების შემუშავებას. დაბინ-

ძურების ხარისხის შეფასება შესაძლებელია მხოლოდ სხვა ქვეყნების კრიტერიუმების მიხედვით, რომლებიც ამ ქვეყნების ბუნებრივი პირობების გათვალისწინებითაა შემუშავებული. აქედან გამომდინარე, ჩვენ მიერ მათი გამოყენება-შეფასებების დროს, არარელევანტური გადაწყვეტილების მიღების ალბათობა იზრდება და მძიმე ეკოლოგიური პრობლემების რისკებს უკავშირდება.

ამ შეუსაბამობის გამოსწორების მცდელობას წარმოადგენს წინამდებარე ნაშრომი, რომელშიც აღწერილია და სტატისტიკური მეთოდით დამუშავებული შავი ზღვის საქართველოს აკვატორიის თანამედროვე ფსკერულ ნალექებში მძიმე ლითონების (Fe, Pb, Cd, Cu, Zn, Ni, Cr) შემცველობის კვლევების უმდიდრესი მასალა, რომელიც 2000-2023 წლებშია მოპოვებული. ნაშრომში ნაჩვენებია ლითონების საშუალო, მედიანური, მაქსიმალური და მინიმალური კონცენტრაციები, აღწერილია მათი გენეზისის, გავრცელების და აკუმულაციის თავისებურებები, გამოთვლილია გეოაკუმულაციური ინდექსები და დადგენილია ლითონთა ფაქტობრივი ფონური კონცენტრაციები საქართველოს აკვატორიის ფსკერულ ნალექებში. მიღებული შედეგების მიხედვით, მოწოდებულია დრეგირებული მასალის დაბინძურების ხარისხის შეფასების კრიტერიუმები, რაც მოგვცემს დრეგირებული მასალის განთავსება - გამოყენების შესახებ უსაფრთხო და რაციონალური გადაწყვეტილებების მიღების საშუალებას.

დრეგირებული მასალის დაბინძურების ხარისხის კლასიფიცირების მოდელს შეიძლება რეკომენდაცია გაეწიოს განსახილველად შესაბამისი ეროვნული კანონმდებლობისთვის.

INTRODUCTION

The territory of Georgia is a strategically important transit corridor between Europe and Asia. Within the framework of the European Neighborhood Policy, together with other environmental issues, Georgia undertook the obligation to improve the ecological condition of the Black Sea and participate in the protection of the marine environment (Association Agreement 2014; Directive 2008/56/EC; 1992 Bucharest Convention 1992). The development of environmental policy and the achievement of Good Environmental Status of the marine environment significantly depend on sound environmental management based on scientific foundations.

Dredging works are one of the significant components of the management of marine-navigational infrastructure. Dredging works are conducted to achieve the design depths, serve to promote safe navigation in channels, develop port infrastructure, and reduce the adverse effect of silting. The assessment of the contamination degree of bottom sediments removed by dredging works is a significant environmental activity and determines their further management issues – disposal/reuse (Waste Management, 2008). Guideline information on the assessment of the contamination degree of dredged material is provided in a number of conventions and normative documents (OSPAR Guidelines, 1998, Dredging, 2015; Bose B.P, Dhar M., 2022). When deciding to return the dredged material to the sea (dumping), the local background condition of the environment is assessed, the physical, biological and chemical characteristics of the seabed, the sensitivity of aquatic ecosystems and other ecological factors are taken into account (Environmental, 2017; Assessment Criteria, 2011). Table 1 shows the assessment criteria for contamination with heavy metals established by the member states of the OSPAR Convention.

According to the applicable legislation of Georgia on marine activity and waste management (e Law of Georgia 1997/2024; Law of Georgia 1998/2023; Law of Georgia 2014/2024), the criteria of assessment of pollution level and ecological regulations of bottom sediments, as well as the rules for their further management are not determined. Therefore, appear certain problems when the evaluating content and pollution level of heavy metals in bottom sediments: there is a need to guide by the national norms of assessment of other countries. These assessment standards are developed with ecotoxicological approaches and taking into account the local natural background conditions of water areas of these countries that cannot be consistent with the background conditions of the marine area of our country, thus the environmental quality assessment of dredged material based on standards of any other country is not relevant.

Table 1

Assessment Criteria of contamination of the removed bottom sediments
(Assessment Criteria, 2011)

Country	Level	As	Pb	Cd	Cr	Cu	Ni	Hg	Zn
		mg/kg							
Germany	Guidance LevRW1	40	90	1.5	120	30	70	0.7	300
	Guidance LevRW2	120	270	4.5	360	90	210	2.1	900
Netherlands	Guidance Level	29	-	-	120	60	-	-	365
	Threshold Value	-	110	4.0	-	-	45	1.2	-
Belgium	Guidance Level	20	70	2.5	60	20	70	0.3	160
	Threshold Value	100	350	7	220	100	280	1.5	500
France	Guidance Level N1	25	100	1.2	90	45	37	0.4	276
	Guidance Level N2	50	200	2.4	180	90	74	0.8	552
United kingdom	Guidance Level AL 1	20	50	0.4	40	40	20	0.3	130
	Guidance Level AL 2	70	400	4	370	300	150	1.5	800
Ireland	Guidance Level AL 1	9	60	0.7	120	40	21	0.2	160
	Guidance Level AL 2	70	218	4.2	370	110	60	0.7	410
Norway	Guidance Level C1	20	30	0.25	70	35	30	0.15	150
	Guidance Level C2	52	83	2.6	560	51	46	0.63	360
Denmark	Guidance Level AL 1	20	40	0.4	50	20	30	0.25	130
	Guidance Level AL 2	60	200	2.5	270	90	60	1.0	500
Spain	Guidance Level	80	120	1.0	200	100	100	0.6	500
	Threshold Value	200	600	5.0	1000	400	400	3	3000

The objective of the present paper is to determine the background concentrations of metals in the bottom sediments of the Georgian Black Sea water area and to develop the threshold concentrations of metals in dredged materials. Obtained results will promote the improvement of assessment criteria of contamination level of the dredged material and enhancement of the national legislation.

CHARACTERIZATION OF BOTTOM SEDIMENTS OF THE SEA AREA OF GEORGIA

The Black Sea coast of Georgia hasbasically accumulative origin, formed for a long geological period by terrigenous material transported by rivers. In terms of an energeticpoint of view, modern lithodynamic processes, namely, the distribution of sediments on the submarine slope and along the shores, are determined by the marine wave regime, currents and gravitational forces (Zenkovich V.P., 1977; Gaphrindashvili N. Et all, 2018; Gaphrindashvili N., 2019).

The chemical composition of the underwater slope bottom sediments is determined by the terrigenous material transported by rivers to the sea. In the Georgianwater area, from Gonio Cape to the Natanebi Rivermouth, bottom sediments were formed by the solid sediment load of the rivers Chorokhi, Bartskhana, Korolistskali, Kintrishi, Natanebi, Chakvistskali and Supsa. Water catchment basins of these rivers include the southwestern termination of Adjara-Trialeti (mainly the southern slope of the Meskheti Range). Terrigenous material formed due to weathering of the volcanogenic rocks and hydrothermal deposits of the Adjara-Trialeti folded system and the Anatolian plateau, transported to the seashore; therefore, the increased content of chalcophile elements (Zn, Pb, Cu) is characteristic for the sediments of the corresponding submarine slope. To the north of the Korolistskali river mouth, red soil weathering crusts developed onthe basaltic rocks are rich in iron group elements (Voitkevich G.B. et al., 1990; Turekian, K.K. and Wedepohl, 1961). The bottom sediments of adjacent to the area between the Supsa and Natanebi river mouths are characterized by increased concentrations of Fe, Cr, Ni, V and the formation of local accumulation sites.

The submarine slope adjacent to Kolkheti Lowland, from Grigoleti to the Khobi River mouth, is mainly composed with sediments of the Rioni River. In this section, the influence of the mineralogical complexes of thered soil weathering crustsisnot manifested. Manganese is a marker element of bottom sediments of this section of the submarine slopes. Chiatura deposits are the sources of manganese. Nickel is an accessory element of manganese ores, so an increase of manganese concentration is accompanied by an increase of nickel concentration (Machitadze N., Tvalchrelidze M., Gvakharia V. 2001; Machitadze N., Gvakharia V., Tvalchrelidze A. 2001; Machitadze N., Gvakharia V., Tvalchrelidze A., 2000). Gvakharia V., Machitadze N., 2008; Gvakharia V. et al., 2011; Gvakharia V. et al., 2006; Machitadze N., Gvakharia V., Tvalchrelidze M., 2004).

In this paper, research data of metal contents in modern bottom sediments of the shelf zone of Georgia from Sarpi to Anaklia, from 5 to 1000 isobaths have been used. A considerable part of the research results has been presented at different times in scientific reports, publications and dissertations (Tvalchrelidze M. Machitdze N., 1997, Machitadze N., Gvakharia V., Tvalchrelidze A, 2000, Tvalchrelidze M., Gvakharia V., Machitadze N., 2001; Gvakharia V., Machitadze N., Tvalchrelidze A. , 2002; Machitadze N.,etal., 2020; Oros A.et al.,2019;Gvakharia V. et al., 2010; Korshenko A. et al., 2008). Multi-year researches enable us to determine the background concentrations of metals in bottom sediments of the water area of Georgia.

MATERIALS AND METHODS

The concentration of metals (Fe, Pb, Cd, Cu, Zn, Ni, Cr) in bottom sediments was determined by the atomic absorption method (Manual, 1995). For the determination of arsenic, a spectrophotometric method with preliminary distillation was used (Method Recommendations, 1993). The accuracy of the conducted analysis was regularly checked by participation in Professional Testing sessions of QUASIMEME, ERA Water Company, Monaco Marine Laboratory. Analysis was conducted in the accredited laboratory of the scientific research firm "Gamma".

Average, median, maximum and minimum concentrations of metals were obtained using the statistical processing of the research results concerning the metal content in the bottom sediments of the Georgian sea area. The geoaccumulation index I_{geo} (Müller, 1969; Abrahim G.M.S. & Parker R.J. 2008, Nowrouzi M. & Pourkhabbaz A. 2014; Looi L.J. et al., 2019) to assess the contamination level of bottom sediments with studiedmetals is used.

Geoaccumulation index I_{geo} was calculated by the following formula:

$I_{geo} = \log(2) (Cn/1.5Bn)$

Cn - actual metal concentration; Bn - the geochemical background concentration of the metal (Turekian, Wedepohl, 1961; Lentz, D.R., 2003). The assessment criteria of contamination degree are given in Table 2.

Table 2

The assessment criteria of contamination degree

Geoaccumulation IndexI_{geo}		
Class	I_{geo} Value	Sediment Quality
0	<0	Uncontaminated
1	0–1	Uncontaminatedto Moderately contaminated
2	1–2	Moderately contaminated
3	2–3	Moderately to heavily contaminated
4	3–4	Heavily contaminated
5	4–5	Heavily to extremely contaminated
6	>5	Extremely contaminated

DISCUSSION OF RESULTS

When dredging works, such sediments, the placement of which in the sea will not cause changes in the local background concentration of metals, may be subject to dumping. This purpose is served by the criteria for assessing the quality of the dredged material, which should be based on the determination of the local natural background concentrations of metals and the subsequent calculation of the threshold concentrations.

DETERMINATION OF BACKGROUND CONCENTRATIONS OF METALS

The average, median, maximum and minimum concentrations of heavy metals were obtained as a result of systematization and statistical processing of our research data (Table 3). The table also provides background concentrations of metals for shales (Turekian K.K. and Wedepohl, K.H. 1961; Lentz, D.R., 2003).

Table 3

Content of heavy metals in the bottom sediments of the Black Sea Sector of Georgia

Element	Fe,%	Cu, mg/kg	Zn, mg/kg	Cr, mg/kg	Pb, mg/kg	Mn, %	As, mg/kg	Ni, mg/kg	V, mg/kg	Mo, mg/kg
Average	5.37	107.5	124.4	175.7	18.7	0.17	14.3	67.5	170.4	1.8
Median	4.80	75	110	79.9	17	0.14	12	68.1	140	1.8
Minimal	2.44	20	56	30	6	0.06	5.2	18	520	4.1
Maximal	15.04	600	575	1300	48	0.65	69	170	34	0.5
n,sample number	290	248	336	336	273	335	148	262	185	188
Background (Turekian K.K. and Wedepohl, K.H. 1961; Lentz, D.R., 2003)	4.72	45	95	90	20	0.085	13	68	130	2.6

According to the Table 3, the greatest difference between the mean and median concentrations of the studied metals was observed for copper and chromium.

By comparing the average concentrations of metals with the geochemical background, we can see the biggest difference in the case of copper, chromium and manganese, while the average content of the rest of the elements is practically within the limits of the geochemical background.

The comparison of median and geochemical background concentrations of metals is especially significant for us. Calculations show that the median concentrations of copper and manganese are the most increased compared to the geochemical background. As we mentioned, copper and chromium in oursea area have specific sources of origin, they are characterized by uneven distribution and the presence of accumulation sites. In accumulation sites, the maximum concentration of copper reaches 600 mg/kg, and chromium - 1300 mg/kg (Table 3); as for manganese, it is distributed relatively evenly throughout the water area, at the same time, the average concentration is almost twice as high as the geochemical background.

Based on the peculiarities of the distribution of elements in the studied area, it is more reasonable to use the median concentration to estimate the background concentration, since it excludes the influence of extreme concentrations on the calculations.

The geoaccumulation indices I_{geo} of average and median concentrations of metals calculated using the above-given method are given in Table 4.

According to the contamination assessment criteria by the geoaccumulation index (Table 2), the average concentrations of zinc, lead, arsenic, nickel, vanadium and molybdenum meet the category “Uncontaminated” ($I_{geo}<0$); the average contents of copper, chromium and manganese are classified as “Uncontaminatedto Moderately” category (I_{geo} from 0 to 1).

Table 4

Geoaccumulation indices

Element	Fe	Cu	Zn	Cr	Pb	Mn	As	Ni	V	Mo
I_{geo} *Average*	-0.40	0.67	-0.20	0.38	-0.68	0.40	-0.44	-0.60	-0.19	-1.10
I_{geo} *Median*	-0.56	0.15	-0.37	-0.76	-0.82	0.13	-0.70	-0.58	-0.48	-1.12

As for the median concentration, Zn,Cr, Pb, As, Ni, V, Mo meets the category “ Uncontaminated”, while CuandMn fall within the category “Uncontaminated to Moderately”.

The concentration, whose $I_{geo}<0$, we consider as the background. In the bottom sediments of the study area, this criterion does not meet the median concentrations of only 2 elements: copper ($I_{geo}=0.15$) and manganese ($I_{geo}=0.13$), i.e. the local background of these two elements is higher than the geochemical background. These elements, as mentioned above, are distinguished by a different character of distribution. In this view, the median concentration is considered to be the local background concentration.

DETERMINATION OF THRESHOLD CONCENTRATIONS OF METALS IN DREDGED SEDIMENTS

The analysis of threshold concentrations in dredged material established by the member states of OSPAR Convention (Table 1) show that the ratio between the threshold and background concentrations is within 2-4. The most commonly used ratio is 3. We use the differentiated approach to determine the threshold concentrations taking into account the hazard classes of metals (Method Recommendations 2.1.7.003-02). For elements of hazard class I, the ratio of the threshold and background concentration was determined by 2, for elements of class II - by 2.5, and for elements of class III - by 3. Background concentrations were multiplied by appropriate coefficients to obtain threshold concentrations of elements and calculate the geoaccumulative indices of the obtained concentrations. The results along with hazard classes are given in Table 5.

Table 5

Threshold concentrations of elements and geoaccumulative indices

Element	As, mg/kg	Pb, mg/kg	Zn, mg/kg	Cr, mg/kg	Mo, mg/kg	Cu, mg/kg	Ni, mg/kg	V, mg/kg	Mn,%	Fe,%
Hazard Class	I	I	I	II	II	II	II	III	III	-
Threshold Concentration	24	34	220	200	4.5	188	170	420	0.4	14.4
I_{geo}	0.3	0.2	0.6	0.6	0.2	1.5	0.7	1.1	1.6	1.0

According to the geoaccumulation index, concentrations of elements of hazard class I and II fell into the contamination category "Uncontaminated to Moderately" ($I_{geo}$from 0 to 1). In this case, copper is also an exceptiondue to the high background concentration (the maximum threshold concentration was 188, I_{geo}=1.5). Therefore, the reduction of threshold concentration to 100 mg/kg was considered expedient, accordingly, its index I_{geo} equaled 0.6 and the threshold concentration of copper fell into the category "Uncontaminated to Moderately".

Threshold concentrations of elements of class III fell into the "Moderately contaminated" category (I_{geo}>1). The elements of this hazard class are characterized by low toxicity, in addition, these metals are present in rocks and bottom sediments as oxide compounds that have low reactivity, they do not change valency in the marine environment and hardly transit from the solid phase to the soluble phase, due to this, their compounds are chemically inert. Iron is not assigned a hazard class at all.

Finally, we obtained the following background and threshold concentrations of dredged material (Table 6).

Table 6

Background and threshold concentrations of dredged material

Element	As, mg/kg	Pb, mg/kg	Zn, mg/kg	Cr, mg/kg	Mo, mg/kg	Cu, mg/kg	Ni, mg/kg	V, mg/kg	Mn, %	Fe, %
Background Concentration	12	17	110	80	1.8	75	68	140	0.14	4.8
Threshold Concentration	24	34	220	200	4.5	100	170	420	0.40	14.5

The ratio between the threshold and background concentrations of copper has decreased.
We believe that such restriction will ensure to avoid the introduction of highly copper-contaminated material into the marine environment, due to which, the risks of increment the background concentration in bottom sediments will increase.

COMPARATIVE ANALYSIS OF THRESHOLD CONCENTRATIONS

According to Table 1, in the states of the OSPAR Convention, the threshold concentrations of metals for dredged material are different; the threshold concentration is determined by the multiplicity of the background concentration, the value of which depends on specific objective conditions, and varies from 2 to 10, the strictest threshold concentrations for dredged material are obtained by doubling the background concentration. Compared to these concentrations, our threshold concentrations are stricter for arsenic and lead, and lighter for copper, nickel and chromium.

Compared to the values obtained bymultiplying the background concentration by 3, our threshold values are relatively strict.

According to the comparison results, it is clear that using threshold concentrations of other countries for the assessment of the contamination levelof the dredged material from our harbours is not appropriate and it is important to develop our normativevalues. In the case of using the loyal threshold values within thequality assessment of dredged material, there are risks of contamination of the bottom sediments in the environment of dumping areas, which will entailan adverse ecological impact.

We consider that in case of our proposed threshold values, the dumping of dredged material in any section of our sea areawill not significantly affect the local natural background.

The calculation of background concentrations of highlytoxic metals -cadmium and mercury in the bottom sediments of our waters was not possible, since the insufficient material related to the distribution of these elements did not allow us to obtain high-precision results. In such case, the threshold concentration can be calculated according to the rule we use: since these two elements belong to hazard class I, the geochemical background will be multiplied by 2. If we take the relatively strict criteria-the geoaccumulation index $I_{geo}<0.5$, the threshold concentration of mercury will be about 0.8 mg/kg, and cadmium - about 0.6 mg/kg. By using a relatively loyal criteria - $I_{geo}>1$, the threshold concentration of mercury will be 1.3 mg/kg, and cadmium - 1 mg/kg. In this case, the threshold concentration will be equal tothe triple background. If we look at the threshold values (Assesment Criteria, 2011), we will see that our threshold concentrations for mercury are of the same order, and for cadmium - relatively strict.

CONCLUSIONS

- Average, median, maximum and minimum concentrations of metals (Fe, Pb, Cd, Cu, Zn, Ni, Cr, V, Mo) in the bottom sediments of the water area of Georgia have been estimated based on the multi-year research data;
- According to the average and median concentration values, the geoaccumulation indices of the studied metals are calculated; described - features of the distribution of metals, criteria and categories of contamination level; it is shown that in terms of ecological protection point of view, the median concentrations of metals should meet the requirements of the "Uncontaminated" and "Uncontaminated to Moderately" categories;
- Background concentrations of metals are determined in bottom sediments of the territorial waters of Georgia - median concentrations of metals are considered as local background concentrations;
- Threshold concentrations of metals are established to assess the dredged material. Threshold concentrations are established based on the local natural background and geoaccumulation index I_{geo}, taking into account the hazard classes of metals;
- The developed threshold values are compared with the ones of OSPAR Convention countries; as a result of the data analysis, the need to create a national normative base for assessment is substantiated; we hope that the information provided in this paper will contribute to the more comprehensive management of the control and quality assessment of the ecological condition of the marine and general environment.

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