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Adapted methodology for comprehensive contamination assessment of bottom sediments on the content of various forms of heavy metals

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Abstract. As a result of long-term studies of bottom sediments of lakes, rivers, ponds and reservoirs of the Republic of Tatarstan, considerable factual material has been accumulated, which enabled the translation of quantitative estimates into qualitative characteristics. This necessitated a comprehensive assessment and generalization of the exceedance of the thresholds set for all metals, similarly to the specific combinatorial water pollution index (SCWPI). At the same time, the authors emphasize the features of such a comprehensive assessment of bottom sediments, and also suggest methods and algorithms for solving emerging problems. We use the method of frequency characteristics of data series of metal content (Cd, Pb, Co, Cu, Ni, Zn, Cr, Mn, Fe) in bottom sediments, score the relevant characteristics, generalize the point estimates and bring them to the appropriate classes of purity. As a result, a method for the integrated assessment of contamination of bottom sediments was developed and tested, which solves the problem of the integral assessment of the quality of bottom sediments in terms of a complex of pollutants using the example of heavy metals. The method is based on the approach of the SCWPI. Therefore, its results are comparable to combinatorial assessments of water quality, which will allow deriving a uniform assessment of the water body as a whole.

1. Introduction

Management of environmental management and environmental quality involves accounting and assessing the indicators of the state of all phase components in this environment: the atmosphere, hydrosphere, lithosphere and biota. The most important link accumulating and redistributing the flows of matter and energy is the hydrosphere formed by a complex system of water bodies [1, 2].

Bottom sediments formed due to sedimentation of inorganic and organic material suspended in water play a significant role in shaping the chemical composition of surface water bodies. Therefore, assessing the degree of contamination of water bodies involves not only determining the quality of their aquatic environment, but also a generalized characteristic of bottom sediments [2, 3].

The peculiarity of bottom sediments, as an indicator of the state of a water body, is that they are the last link in the input of substances into water bodies and watercourses, thereby integrating the geochemical features of the catchment areas, man-made discharges and water bodies [4].

2. Problem statement

In Russia, the control of the composition of bottom sediments of water systems is carried out within the framework of the Unified State System for Monitoring the Environment. Despite the fact that control of the composition of bottom sediments is provided, it can hardly be effective in the absence of clear criteria for the quality of bottom sediments, which combine the whole range of pollutants into a single indicator. The problem of qualitative assessment of bottom sediments is aggravated by the diversity of their composition, which, nevertheless, can be reduced to two main factors: the particle size distribution and the content of organic matter [5–8]. Therefore, a comprehensive integrated assessment of contamination of bottom sediments is currently relevant for a complex of pollutants, in particular, heavy metals.

3. Materials and methods

The work uses the data of long-term studies of bottom sediments of lakes, rivers, ponds and reservoirs of the Republic of Tatarstan [9, 10]. To work out the established assessment methodology, the content of metals (Cd, Pb, Co, Cu, Ni, Zn, Cr, Mn, Fe) was considered as pollutants in bottom sediments, taking into account the granulometric composition of bottom sediments and the content of organic matter in them. The analysis of the long-term data series allowed us singling out the statistical background, the actual threshold of the normal regional content of various forms (mobile and gross) of the nine scrutinized metals in bottom sediments [11].

We have generalized the exceedances of the thresholds by all metals, similarly to the specific combinatorial index of water pollution (SCWPI).

The system of formalized indicators in our proposed method uses the frequency characteristics of data series about the content of different metals in bottom sediments, scoring system for these characteristics, compiled scores and reduced figures to the appropriate purity classes, similarly to the methodological guidelines RD 52.24.643-2002 developed by the Hydrochemical Institute of the Federal Service of Russia for Hydrometeorology and Environmental Monitoring (Roshydromet).

The contamination level of bottom sediments is estimated by a relative characteristic calculated on the basis of the actual concentrations of the aggregate pollutants and the corresponding background values (standards). The estimate is based on the aggregation of information about the detection frequencies of concentrations exceeding the background values and the multiplicities of this excess. The combination of the level of contamination of bottom sediments with various metals and the frequency of detection of these cases makes it possible to obtain a complex characteristic summarizing a number of indicators in the form of a particular purity class.

The additivity of the action of various metals with their simultaneous presence is realized by summing individual indicators that evaluate the contribution of each of them separately.

In addition to the system of formalization of the estimated parameters of the SCWPI, for the compatibility of both assessments, a similar final gradation of purity classes was used, implemented in the form of five basic and three complementary gradations.

At the same time, instead of linear interpolation for scoring, we used nonlinear one (polynomial and logarithmic), as it more truly encompasses the breakdown of ranges. For example, Fig. 1 shows the dependence of S_α scores (in the terminology of [12]) on the exceedance occurrence frequency of. At the same time, we used a 5-point scale of ranks similar to SCWPI: <1, 1-10, 10-30, 30-50,> 50, with a ranking from 0 to 4.

Another important difference from the classical method of calculation is the difference in the scale evaluating the multiplicity of exceedances (Appendix G [12]). The scale of scores that take into account the multiplicity of exceedances in relation to bottom sediments, in our opinion, is too stretched. At the same time, the authors of the technique of the SCWPI suggest researchers, in some cases, to set the gradations themselves, depending on the nature and toxicity classes of the substances under consideration. Explicitly, such an amendment to the RD [12] is present only for oxygen, and it is emphasized that the proposed scale is calculated for substances of the 2-class of hazardousness.

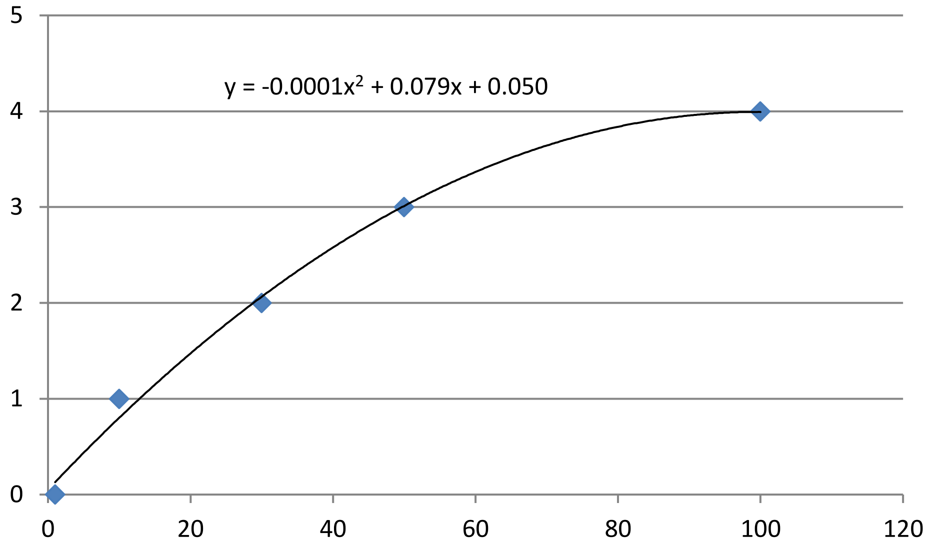

Figure 1. Polynomial dependence of the scoring S_α on the exceedance frequency

Due to the fact that we assess the quality of bottom sediments relative to background concentrations of pollutants, it was decided to estimate the scale (similar to Appendix G [12]), taking into account not only the hazard classes of various metals, but also the actually observed ranges of their concentrations in bottom sediments. As a result of analyzing the frequency characteristics of variational series of our own observations, the boundaries of the scale were the averaged frequency characteristics of the variational series of metal contents in bottom sediments, reduced to their median. For example, the rounded values of the ratios of the maximum values of the 95% confidence interval observed over all the variation ranges of concentrations to their medians form the limiting (most extreme) range of the scale, starting from 20.

4. Discussion

As a result of the study, the following base scale was determined, which is adjusted by a coefficient that takes into account the hazard class of a particular metal being evaluated:

- <1 (0 points)
- 1-3 (1 point)
- 3-9 (2 points)
- 9-20 (3 points)
- > 20 (4 points)

The formed scale is also logarithmic, which is clearly shown in Fig. 2.

Hazard class adjusts the scale as follows:

Scale rank multiplicity = Rank multiplicity × (0.5 × Hazard class).

That is, the current gradation of the exceedance multiplicity scale is calculated for hazard class 2. For the first class, the ranges of its gradations will be, respectively, 2 times (× 0.5) lower, and for grade 3 1.5 times higher.

Among the metals we considered, the first class (highly hazardous) substances include Cd, Pb, and Zn; the second class (moderately hazardous) includes Co, Ni, Cu, Cr; the third class (little dangerous) makes up Mn. When calculating the gradations of the scale of Fe exceedances, we also refer to the third class, although this metal is not considered dangerous.

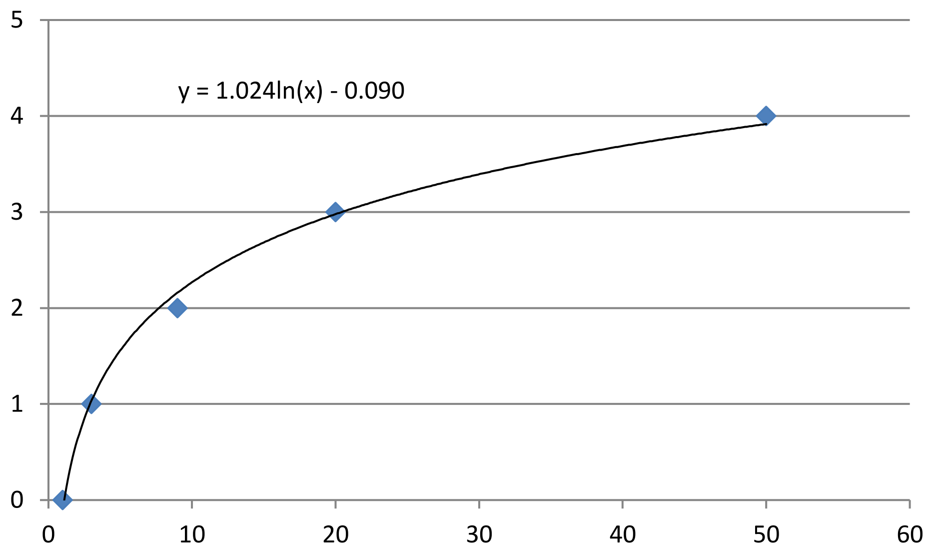

Figure 2. Logarithmic dependence of the scoring S_α on the exceedance frequency

Since most of the heavy metals in water bodies are bound with organic or inorganic ligands, the bottom sediments of water bodies can theoretically adsorb both metal ions and their complex compounds with dissolved organic and inorganic substances. A special role in the binding of metal ions into a durable chelate complex is played by humic substances, widely represented in pelitic fractions (particles less than 0.01 mm). Thus, active sorption by bottom sediments of metals depends on the share of pelitic fractions in them. Respectively, the content in bottom sediments of the fraction of pelitic fractions above 30 % forms their special capacity, theoretically capable of accumulating metal concentration 2–3 times higher than bottom sediments with a low content this fraction.

At the same time, when summarizing estimates considering a series of observations as a whole, the total proportion of samples with a high content of fine particles is important rather than the absolute content of pelitic fractions in a particular sample. For such an assessment, we have introduced another factor correcting the background indicator itself against which frequencies and multiplicities are calculated. The correction is a linear relationship: $K_{pelit} = 0.48 \times D + 0.52$; where D is the proportion of observations with a particle content of <0.01 mm more than 30 % expressed as fraction of 1. The dependence is established as a result of analyzing the frequency characteristics of concentration series of various metals in bottom sediments with different particle size distribution. In addition, the calculated background values also rely on an indicator such as a pelitic fraction content of more than 30 %, suggesting higher background concentrations for such bottom sediments.

Accounting for critical indicators of pollution, in relation to bottom sediments, is also somewhat modified and does not come from $S_\alpha \geq 9$, accounting for 56.3 % of the maximum possible value (9 out of 16), but from $S_\alpha \geq 12$ (75 %), which we think is more justified if we consider that we are talking about critical pollution.

Since the value of the specific combinatorial index is the weighted average of all quotients of S_α, it is convenient to present this indicator in a normalized (reduced to fractions 1) form, simply dividing it by 16 (the maximum possible value of S_α). Thus, the analyst more clearly determines the proportion of current pollution relative to the maximum possible value.

The final grades of grade points, adapted to the assessment of sediments, are as follows:

With the values of the specific combinatorial index (not normalized, that is, not reduced to 16):

- <1 (Clean bottom sediments, class 1 cleanliness)
- 1-3 (Slightly polluted, class 2)
- 3-5 (Moderately Polluted, class 3a)
- 5-6 (Heavily polluted, class 3b)

- 6-8 (Dirty, class 4a)
- 8-9 (Dirty, class 4b)
- 9-10 (Very dirty, class 4c)
- 10-11 (Very dirty, class 4d)
- > 11 (Extremely Dirty, class 5).

In this gradation, there are two points between classes, and one subclass each.

The system of calculating the specific combinatorial pollution index of bottom sediments (SCWPI-BS), adapted by us, was tested on three groups of water bodies with different anthropogenic load: 1) Forest lakes and lakes of the Raifsky area of the Volga-Kama State Biosphere Reserve; 2) Lakes in rural areas of various regions of the Republic of Tatarstan; 3) Water bodies of Kazan located directly within the city.

The content of mobile forms of 9 metals in surface (up to 20 cm) layers of bottom sediments was assessed, the upper limits of regional standards were taken as threshold levels [11] (Table 1). The upper limits were accepted due to the fact that the classical method for calculating SCWPI does not operate with background values, but with maximum permissible concentrations, the excess of which uniquely determines the toxic effect.

Table 1. Summary table of concentrations of gross and movable forms of metals recommended for use in calculating SCWPI-BS

Metal	**Rivers and water reservoirs**	**Lakes**
	Gross forms	
Cd	0.92	0.62
Pb	18.8	25.2
Co	15.5	13.8
Cu	31.1	37.4
Ni	63.9	45.7
Zn	74.9	103.2
Cr	44.7	39.8
Mn	925.0	773.5
Fe	26227.0	26746.7
	Movable forms	
Cd	0.42	0.38
Pb	3.70	7.34
Co	0.68	0.81
Cu	1.45	3.27
Ni	2.14	3.31
Zn	7.49	19.4
Cr	1.22	1.04
Mn	318.3	350.6
Fe	351.5	252.5

The calculation of SCWPI-BS for three groups of reservoirs showed the adequacy of the results obtained to expert assessments carried out by experts. The results of the calculation are presented in Table 2.

Recall that the indicated indices S are normalized and reduced to fractions 1, therefore, when compared with ULAIR, they can be multiplied by 16. Kaverage is calculated similarly to the SCWPI method.

Table 2. The result of SCWPI-BS calculation for three groups of reservoirs with different anthropogenic load

Group	$S_{combinatorial}$	$S_{specific}$ (SCWPI-BS)	$K_{average}$	Purity class
1	0.55	0.06	2.47	Clean 1
2	1.84	0.20	11.3	Moderately polluted 3a
3	4.15	0.46	21.0	Dirty 4b

5. Conclusions

Thus, the accepted and widely used methodology for assessing combinatorial water pollution can be adapted for assessing the quality of bottom sediments.

The system of formalized indicators of the adapted method uses the same frequency characteristics of the data series: scoring system for these characteristics, compilation of the scores and bringing them to the appropriate purity classes as the original guidelines of RD 52.24.643-2002. However, the heterogeneity of the composition of bottom sediments should be taken into account, as well as the distribution of metals in different layers, their hazard class, and the calculations should be adjusted using appropriate coefficients.

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