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**COMPARISON OF TOXICITY OF SEDIMENTS
FROM RIVERS WITH DIFFERENT LEVELS OF ANTHROPOGENIC
LOAD (MIDDLE VOLGA REGION, RUSSIA)
BASED ON ELUTRIATE AND WHOLE SEDIMENT TESTS**

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Abstract

Description of chemical characteristics and toxicity testing of whole sediment and elutriate have been performed with 35 samples taken during the monitoring of rivers in the Middle Volga region (Tatarstan, Russia) in 2013. The locations analyzed are sites associated with agriculture, forestry, and petroleum hydrocarbons (oil) production. The toxicity tests include: (1) *Chlorella vulgaris* (algal) elutriate test, (2) *Paramecium caudatum* (ciliate) elutriate test, (3) *Daphnia magna* (cladoceran) whole sediment toxicity test, and (4) *Heterocypris incongruens* (ostracod) whole sediment toxicity test. The concentrations of metals in 43% of sediment samples have been found to exceed probable effect concentration sediment quality guidelines (SQGs). However, the concentrations of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides have turned out to be below SQGs in most sites. The correlation analysis has shown metal toxicity to daphnid reproduction and ostracod growth ($R^2 = 0.34-0.64$) and ammonia ($R^2 = 0.49-0.54$). A higher percentage of samples have shown toxicity in the whole sediment tests (86%) compared to the elutriate tests (54%). A total of 91% of samples have demonstrated toxicity for at least one species. Toxicity has been most frequently observed for daphnid reproduction (83% of samples) and ostracod growth (56% of samples) compared to daphnid (23%) survival, ostracod (11%) survival, and ciliate reproduction (54%) or algal growth (54%). The most polluted sediments have been registered in the area of oil production. The comparison of toxicity of the samples from different types of areas has indicated that 100% of samples from the oil production area, 94% of samples from the agricultural area, and 50% of samples from the forest area were toxic to at least one test organism.

Keywords: sediments, toxicity assessment, *Chlorella vulgaris*, *Paramecium caudatum*, *Daphnia magna*, *Heterocypris incongruens*, heavy metals, petroleum hydrocarbons, Middle Volga region

Introduction

Sediment quality can be influenced by contaminants released into surface waters. While concentrations of contaminants in surface waters decrease due to enhanced sewage treatment, source control, and other measures, contaminated sediments can continue to affect macroinvertebrates and organisms at higher trophic levels [1–5].

When sufficiently elevated, contaminants in the sediment can be toxic to aquatic organisms and may cause adverse ecological and economic impacts on the aquatic resources. These adversities concern declines in sport and commercial fishing, loss of recreation areas, degradation of habitats of valuable species, as well as costly remediation

and disposal actions [5]. Laboratory sediment toxicity tests allow to identify the potential effects of sediment-associated contaminants on benthic organisms [6]. Although a wide range of laboratory sediment toxicity tests are available that assess short-term effects on benthic organisms [7–9], fewer methods make it possible to assess sublethal or chronic effects of contaminants in the sediment [10–13].

Ostracod toxicity test is one of new methods of sediment toxicity assessment that has such advantages as no need to maintain a culture, short time of exposure (6 days), and small amount of sample. There are extensive literature data on the sensitivity of the test in comparison with conventional tests [14–19], but there is a lack of information about the relationship between ostracod response and sediment contamination. Water soluble contaminants move from sediment into overlying water and can affect both benthic and planktonic species. There is a lack of information about the influence of contaminated sediments at all trophic levels. Toxicity test responses with algae, primary producers, will reflect the presence of toxic substances and nutrients, while with ciliates, ostracods and daphnids, typical inhabitants of the near-benthic interface, responses will predict toxic affects to the planktonic community.

The objective of the study was to evaluate the level of contamination and toxicity of freshwater sediments from the rivers with varying levels of anthropogenic load by using a battery of toxicity tests, including whole sediment toxicity tests with the ostracod *Heterocypris incongruens* and the cladoceran *Daphnia magna*, as well as elutriate toxicity tests with the algae *Chlorella vulgaris* and with the ciliate *Paramecium caudatum* in order to reveal the relationship between contaminated sediments and toxicity to test organisms.

Materials and Methods

Sediment collection and chemical characterization. Sediment samples were collected in July and August 2013 from areas with different anthropogenic activity (agricultural sites, $n = 16$; forest sites, $n = 4$; oil production sites, $n = 15$; Fig. 1).

Three or four samples were used to collect the upper 15 cm of sediment with a Van Veen grab to obtain 2 L of sediment. The sediment samples were mixed and homogenized by stirring in a stainless steel bowl with a stainless steel spatula and then transported immediately in plastic bags to the laboratory. A portion was removed for chemical analysis and toxicity testing, then samples were stored in the dark for less than five weeks at 4 °C before toxicity testing or chemical analysis.

For analysis of whole sediment samples, grain size, as well as the concentrations of total organic carbon (TOC), metals, organochlorine pesticides, polycyclic aromatic hydrocarbons (PAHs), and total petroleum hydrocarbons (TPHs) were measured [20–23].

Elutriate tests were performed with *Ch. vulgaris* [24], and *P. caudatum* [25] (Table 1). Elutriate samples were prepared by passing sediments through a 1-mm sieve to remove detritus and stones, then the mixed sediment and water (reconstituted water with hardness of about 100 mg CaCO₃/L [1]) in the ratio 1:4 were put on a shaker (100 rpm) for one hour. Using reconstituted water instead of site water is acceptable for testing sediments and aimed at increasing test repeatability. After one hour of settling, the supernatant was siphoned off and centrifuged at 2500 rpm for 15 min to remove particles prior to toxicity testing or chemical analysis, i.e., measurement of pH, conductivity, hardness, dissolved oxygen, metals and ammonia content [6, 26].

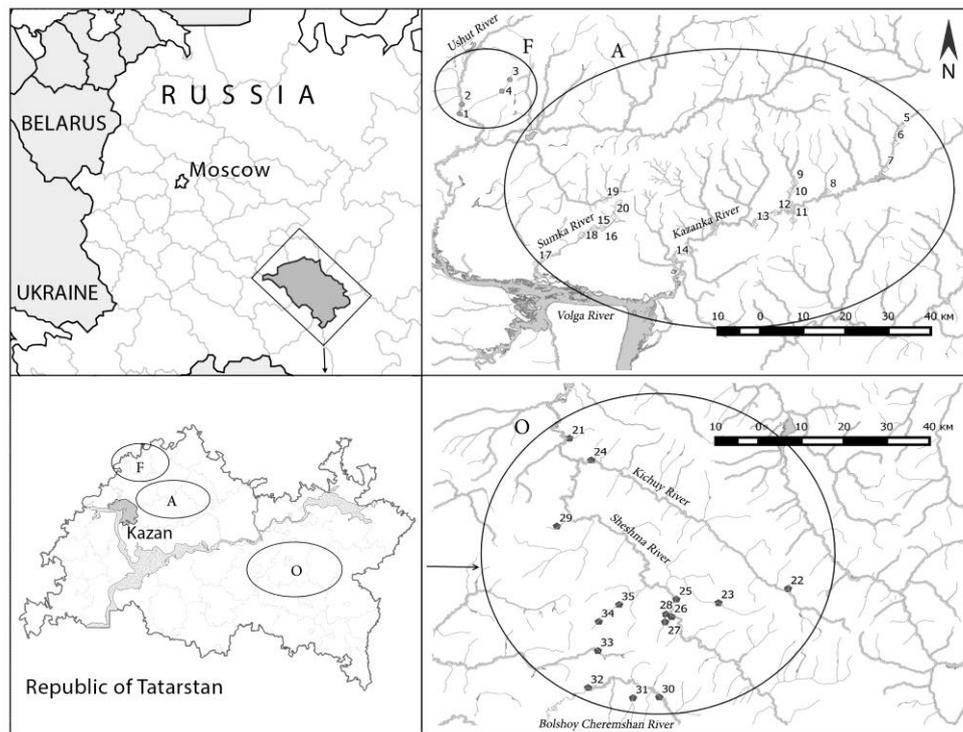


Fig. 1. Location of the sediment sampling sites: A – Agricultural area; F – Forest area; O – Oil production area

***P. caudatum* elutriate toxicity tests.** The elutriate toxicity tests with *P. caudatum* were carried out according to the methods described by Temporal Handbook for Development Freshwater Sediment Quality Guidance [25] with modifications according to the test conditions described in Table 1. One drop of the yeast suspension (125 mg dry yeast dissolved in 25 mL of deionized water) was added to 10 mL of the elutriate. After shaking thoroughly, 0.3 mL was added to the 6-well plate (6 replicates) with 0.5 mL volume in the cell. One ciliate was put into every cell (Table 1). Reproduction (R) was determined after a 24-h exposure and was calculated as:

$$R = \frac{\bar{n}_s}{\bar{n}_c} \cdot 100\%.$$

Where \bar{n}_c is the average number of organisms in control at the end of testing,

$$\bar{n}_c = \frac{\sum n_{\text{end}}}{\sum n_{\text{start}}};$$

\bar{n}_s is the average number of organisms in the sample at the end of testing,

$$\bar{n}_s = \frac{\sum n_{\text{end}}}{\sum n_{\text{start}}}.$$

Table 1. Test conditions for carrying out toxicity tests with algae (*Chlorella vulgaris*), ciliates (*Paramecium caudatum*), daphnids (*Daphnia magna*), and ostracods (*Heterocypris incongruens*)

Test organisms	<i>Chlorella vulgaris</i> (derived from algal culture in the exponential phase)	<i>Paramecium caudatum</i> (derived from culture in the exponential phase)	<i>Daphnia magna</i> (48-h old neonates)	<i>Heterocypris incongruens</i> (52-h old neonates)
Amount of test media	50 mL of elutriate in a flask	0.3 mL of elutriate in a cell of microplate with volume 0.5 mL	10 mL sediments and 40 mL of overlying standard water (hardness of about 100 mg/L)	1 mL sediments and 4 mL of overlying standard water (hardness of about 100 mg/L)
Aeration	None	None	None	None
Duration and temperature	72 h at 23 °C	24 h at 25 °C in the dark	28 days at 20 °C	6 days at 25 °C in the dark
Number of organisms at the start of the test	1·10 ⁴ cells/mL	1	1	10
Lighting	8000 lux (continuous)	Dark	1000 lux (photoperiod 16:8 light/dark)	Dark
Number of replicates	3	6	10	6
Renewal of overlying water	None	None	3 times a week (Monday, Wednesday, Friday)	None
Feeding	None	Yeast suspension before testing	Algae, three times a week	Algae on day 0
Endpoints	The size of the population after 72 h	Survival, reproduction	Survival, reproduction	Survival, length
Test acceptability	The cell density in the control cultures must have increased by a minimum of a factor of 16, pH variation after 72h ± 1.5 units	Survival in control 80%. The number of organisms must have increased by a minimum of a factor of 2	Survival of 80% in control and > 60 offspring per adult replication day in control	80% survival and 1.5x increase in length in control

***Ch. vulgaris* elutriate toxicity tests.** The elutriate toxicity tests with algae were conducted in basic accordance with [24, 27] (Table 1). The medium with all nutrient salts was added to 50 mL conical flasks with control (sterile deionized water) and test samples. Before adding algal culture, the pH value was adjusted (pH 7.5 ± 0.1). After 72 h of incubation in a chamber with constant 8000 lux illumination and temperature 23 °C, the optical density of algal culture was measured.

The percent of growth (G) for algae was calculated as:

$$G = \frac{\bar{D}_s}{\bar{D}_c} \cdot 100\%,$$

where: \bar{D}_c is the mean optical density in control (from 3 replicates), $\bar{D}_c = \bar{D}_{\text{end}} - \bar{D}_{\text{start}}$; \bar{D}_s is the mean optical density in sample (from 3 replicates), $\bar{D}_s = \bar{D}_{\text{end}} - \bar{D}_{\text{start}}$.

***D. magna* whole sediment toxicity test.** The whole sediment toxicity tests with daphnids were performed in a water-sediment system in basic accordance with [28] and [29] using toxicity endpoints of survival and reproduction (see test conditions for

measuring the sediment toxicity (Table 1)). The overlying water was renewed three times a week (Monday, Wednesday, Friday), feeding at each water renewal with $1.0 \cdot 10^8$ algae *Ch. vulgaris* cells/L. The number of organisms at the beginning of the test was 1, number of replicates – 10, duration of testing – 28 days. Survival and reproduction was recorded with each water renewal and the neonates were counted and discarded.

Survival was calculated as:

$$S = \frac{n_{\text{end}}}{n_{\text{start}}} \cdot 100\%$$

where: n_{end} is the number of daphnids at the end, n_{start} is the number of daphnids at the beginning.

Reproduction (R) was calculated as:

$$R = \frac{\bar{n}_s}{\bar{n}_c} \cdot 100\%$$

where: \bar{n}_c is the mean offspring per female in control (from 10 replicates),

$$\bar{n}_c = \frac{\sum n_{\text{offspring}}}{\sum n_{\text{females}}};$$

\bar{n}_s is the mean offspring per female in sample (from 10 replicates),

$$\bar{n}_s = \frac{\sum n_{\text{offspring}}}{\sum n_{\text{females}}}.$$

***H. incongruens* whole sediment toxicity test.** The whole sediment toxicity tests with ostracods were conducted according to [30] (Table 1). Organisms at the beginning of the exposures were collected 52 h after the onset of the incubation of cysts, in the standard freshwater at 25 °C, under continuous illumination. Neonates were pre-fed with *Spirulina* micro-algae for 4 h prior to their transfer to the testing cups. The number of organisms at the beginning of the test was 10, six replicates. Exposures were conducted for six days without water renewal and without additional feeding.

Survival (S) was calculated as:

$$S = \frac{n_{\text{end}}}{n_{\text{start}}} \cdot 100\%$$

where: n_{end} is the number of ostracods at the end; n_{start} is the number of ostracods at the beginning.

Growth (G) was calculated as:

$$G = \left(1 - \frac{\bar{L}_c - \bar{L}_s}{\bar{L}_c} \right) \cdot 100\%$$

where: \bar{L}_c is the mean length increment of ostracods in control after 6 days from 6 replicates (i.e., increase in length, μm); \bar{L}_s is the mean length increment of ostracods in sample after 6 days from 6 replicates (i.e., increase in length, μm).

The length measurement was performed by a micrometer slip after ostracod fixation using Lugol's solution. The length was not measured if mortality was more than 30% (only 1 sample).

Table 2. Sediment grain size, TOC, PEC (probable effect concentrations) quotients for metals, polycyclic aromatic hydrocarbons [32] and for total petroleum hydrocarbons [33]

Sample	> 0.25 mm	0.1–0.25 mm	0.05–0.1 mm	0.01–0.05 mm	0.001–0.01 mm	< 0.001 mm	TOC. %	Sum PEC metals quotient	Total petroleum hydrocarbons quotient	Sum PEC PAHs quotient
Forest area										
Control	70.5	29.5	< 0.001	< 0.001	< 0.001	< 0.001	0.1	0.10	0.25	ND
1	71.6	28.5	< 0.001	< 0.001	< 0.001	< 0.001	0.1	1.05	0.28	ND
2	49.1	50.9	< 0.001	< 0.001	< 0.001	< 0.001	0.8	0.98	0.25	ND
3	74.9	24.7	0.4	< 0.001	< 0.001	< 0.001	< 0.1	0.30	0.43	ND
4	34.7	64.9	0.4	< 0.001	< 0.001	< 0.001	0.4	0.10	0.32	ND
Agricultural area										
1	9.1	24.9	20.7	29.7	15.0	0.6	0.8	1.90	0.41	ND
2	25.7	18.3	12.3	23.7	18.6	1.4	4.6	2.26	0.54	ND
3	51.4	24.6	5.3	11.9	6.8	0.0	1.3	0.66	0.60	ND
4	0.0	3.0	14.8	49.0	31.7	1.5	3.4	1.87	1.86	9.55
5	13.8	10.4	8.1	31.6	33.0	3.1	1.0	1.50	0.47	ND
6	61.0	8.9	4.8	14.9	10.4	< 0.001	1.7	1.46	0.53	ND
7	8.4	7.4	14.0	44.2	24.6	1.4	1.2	1.67	2.36	2.63
8	1.4	3.3	6.9	50.2	35.9	< 0.001	1.9	0.86	2.43	ND
9	36.5	17.0	7.8	24.0	14.7	0.1	1.1	1.55	0.51	ND
10	14.9	50.0	9.7	15.6	9.8	< 0.001	0.8	1.36	0.51	ND
11	28.1	42.3	12.2	14.3	3.2	< 0.001	0.2	0.33	0.52	ND
12	73.7	7.6	3.7	10.7	4.4	< 0.001	1.7	0.39	0.52	ND
13	55.1	28.9	4.5	7.3	4.2	< 0.001	0.9	1.56	2.32	ND
14	0.0	2.7	8.1	51.5	34.9	2.8	0.8	1.66	3.44	ND
15	1.2	12.0	15.6	42.5	27.7	1.0	1.2	2.11	1.79	ND
16	56.2	36.4	2.9	3.6	0.9	< 0.001	0.5	0.97	1.10	ND
Oil production area										
1	< 0.1	1.9	9.3	37.9	46.8	4.2	< 0.1	3.78	2.20	ND
2	23.6	25.3	11.4	22.6	16.6	0.5	23.6	2.98	1.23	0.10
3	12.6	17.7	14.5	30.0	23.2	2.0	12.6	2.46	1.68	ND
4	11.1	33.9	11.3	19.0	22.4	2.4	11.1	2.80	4.83	0.25
5	28.0	13.7	6.9	20.3	28.4	2.7	28.0	2.86	4.56	ND
6	2.2	3.0	7.8	51.0	33.2	2.7	2.2	3.32	2.21	ND
7	5.8	10.4	10.5	37.1	33.4	2.8	5.8	3.87	1.83	ND
8	17.6	1.9	5.5	30.6	40.6	3.8	17.6	3.57	1.47	ND
9	6.2	22.0	11.3	28.4	29.5	2.7	6.2	3.16	0.59	ND
10	2.8	6.9	11.0	34.8	40.2	4.2	2.8	3.12	0.83	ND
11	0.0	2.9	8.2	51.4	35.1	2.4	0.0	3.58	0.59	ND
12	3.4	24.6	12.5	33.3	24.8	1.5	3.4	2.58	0.71	14.29
13	0.7	5.5	14.8	51.3	26.6	1.1	0.7	2.89	0.54	ND
14	28.3	15.0	10.5	25.6	20.0	0.6	28.3	2.44	0.59	ND
15	14.2	10.0	17.2	34.0	22.9	1.8	14.2	2.42	11.04	ND

ND: not determined

For the elutriate toxicity tests, responses of test organisms were compared to those of the control: deionized water with salt medium for algae test [27] and sterile standard water (hardness of about 100 mg/L) for paramecium test. For the whole sediment tests, responses of test organisms were compared to responses in the control sediment. The control sediment was obtained from the upper part of the Ushut River with a low level of anthropogenic activity in the water basin. Characteristics of the control sediment are presented in Table 2.

Statistical analysis. Statistical analysis was performed using Statistica 8.0® (StatSoft, Tulsa, OK, USA) and the data were expressed as mean \pm standard error for each toxicity endpoint for each treatment, for granulometric and chemical data – mean \pm standard deviation. Because distribution of the data was not normal (based on Shapiro–Wilk test), differences among samples were evaluated using the nonparametric Mann–Whitney U-test and Kruskal–Wallis analysis of variance (nonparametric ANOVA). Correlations between the parameters were evaluated using Spearman's rank order correlation coefficient. Differences were considered statistically significant at $p \leq 0.05$. Toxicity criterion was survival if less than 80% deviation of control was observed for all tests (Figs. 2–4).

The concentrations of metals and ammonia in the elutriate samples were compared to the USEPA water quality criteria [31]. The concentrations of metals and organic contaminants in the whole sediment were evaluated relative to the sediment quality guidelines (SQGs) described by MacDonald et al. [32] and de Deckere et al. [3]. MacDonald et al. [32] reported threshold effect concentrations (TECs), below which harmful effects are unlikely to be observed, and probable effect concentration (PECs), above which harmful effects are likely to be observed. De Deckere et al. [3] described SQGs in Flanders based on ecological and ecotoxicological data derived from a TRIAD monitoring network. Total petroleum hydrocarbons (TPHs) were compared with SQGs developed as the threshold effect concentration for freshwater sediments of the Middle Volga Region [33].

Results

Physical and Chemical Characteristics of Sediments. The analysis of grain size and TOC revealed that the proportion of sand ranged from 11% to 100%, clay ranged from < 0.001 to 4.2% and TOC ranged from < 0.001 to 7% (Table 2). In the forest area, the sediments were characterized as sandy (99.6%) with TOC = 0.4% on average. Sediments from the agricultural area mainly consisted of silt (45.9%), with clay and TOC 1.3% and 1.4%, respectively. Sediments from the oil production site were characterized as silty (76.6%) with TOC = 2.8%.

The results of the chemical analysis showed that the concentrations of metals were below those in the published sediment quality guidelines [3, 32] summarized in Table 2. With exception, Ni and Cd exceeded threshold effect concentrations (TECs) and Flemish SQGs by 69–77% (for Ni) and 34% (for Cd; Table 2). The concentrations of Cr were above TECs and Flemish SQGs in 43% samples (all samples from the oil production area).

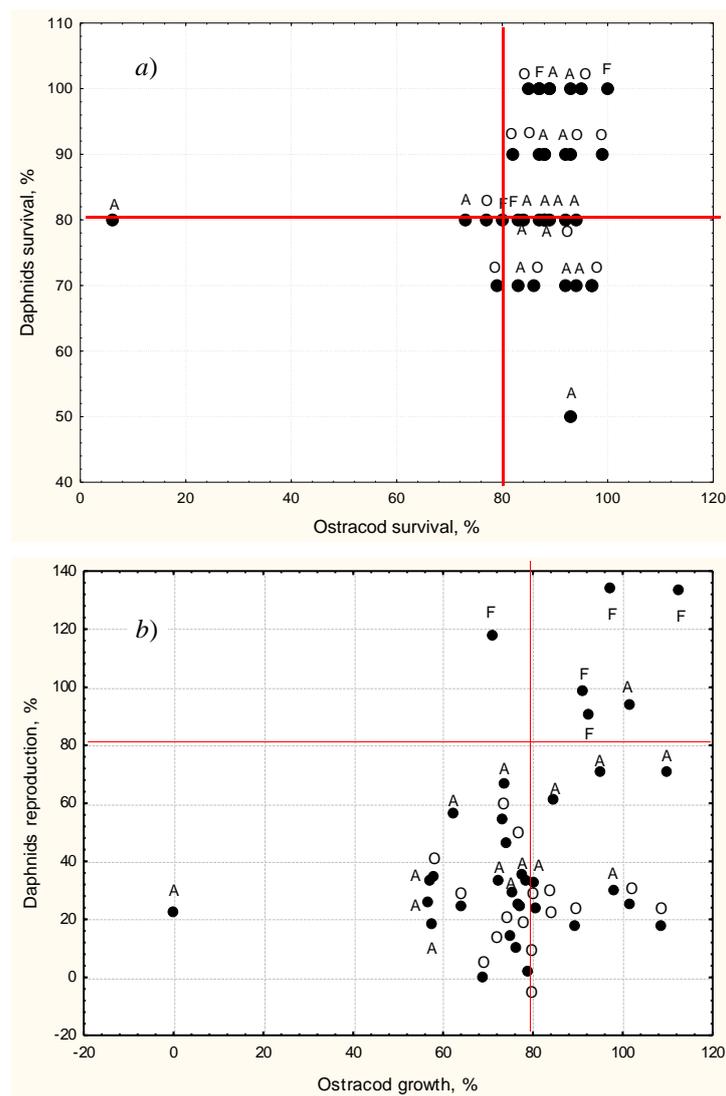


Fig. 2. Survival of ostracods compared to survival of daphnids (*a*) and ostracod growth compared to daphnid reproduction (*b*) (lines indicate criteria of toxicity; A – Agricultural area; F – Forest area; O – Oil production area)

Average metals and TPHs contents in the sediments increased from the forest area to the agricultural and oil production areas, but significant differences between the sampling stations (forest, agricultural, and oil production area) were noticed only in Fe, Zn, Ni, Cr, Pb, and TPHs.

The concentrations of PAHs were several orders of magnitude below TECs for most of the sediment samples, with only one sample containing fluorene in the content of 1.3 times above the TEC (Table 2). Concentrations of DDT were lower than the sensitivity of the detection method ($< 0.01 \mu\text{g}/\text{kg}$), in most cases. Only sediments from the Kazanka River (sites 7–9), had total DDTs concentrations in the range of 11–50 $\mu\text{g}/\text{kg}$, which is 2.2–9.6 times higher than TECs.

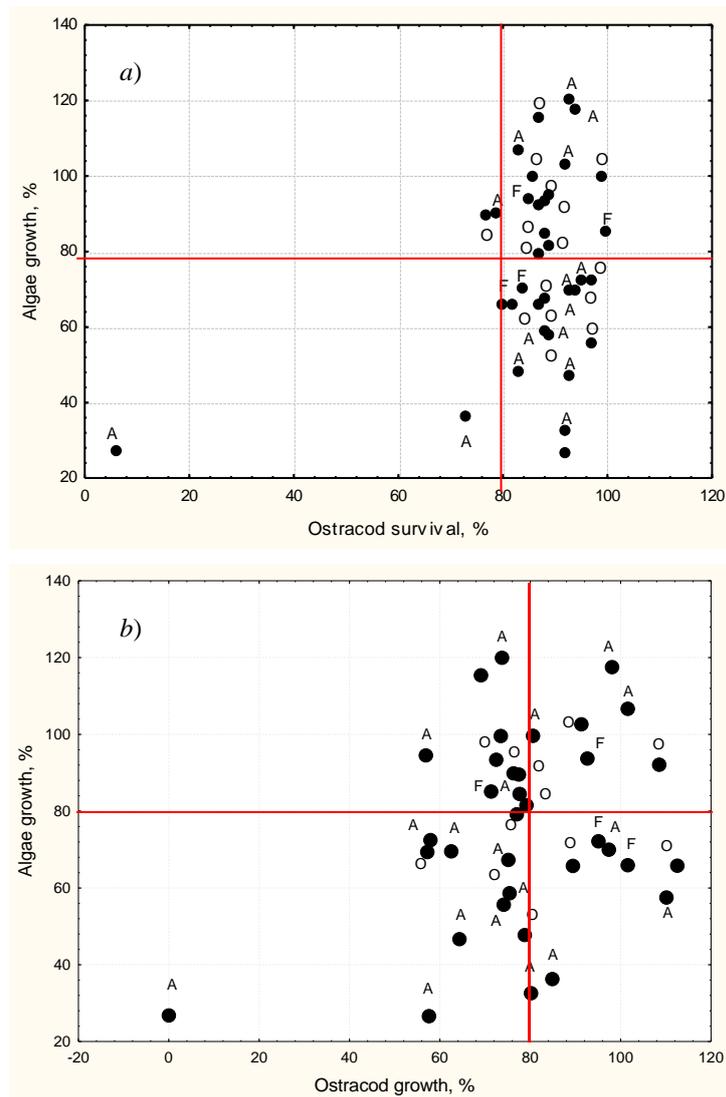


Fig. 3. Survival of ostracods compared to algae growth (a) and ostracod growth compared to algae growth (b) (lines indicate criteria of toxicity; A – Agricultural area; F – Forest area; O – Oil production area)

The concentrations of dissolved oxygen in the elutriate samples were > 5.5 mg/L, pH 6.8–7.6, conductivity 90–1309 $\mu\text{S}/\text{cm}$. About 80% of the elutriates were characterized as hard water, including 51% as very hard (Table 3).

The concentrations of ammonia and metals were typically below the USEPA chronic ambient water quality criteria (WQC). Exceptions were revealed for the following metals exceeding WQC: Fe (6%), Cd (6%), Cu (97%), and Al (82%).

Toxicity of elutriate and whole sediment samples. The number of batches tested was four for ostracods and ciliates and three for algae and daphnia tests. Test organisms, in an all tests met the acceptability criteria for controls indicated in Table 1.

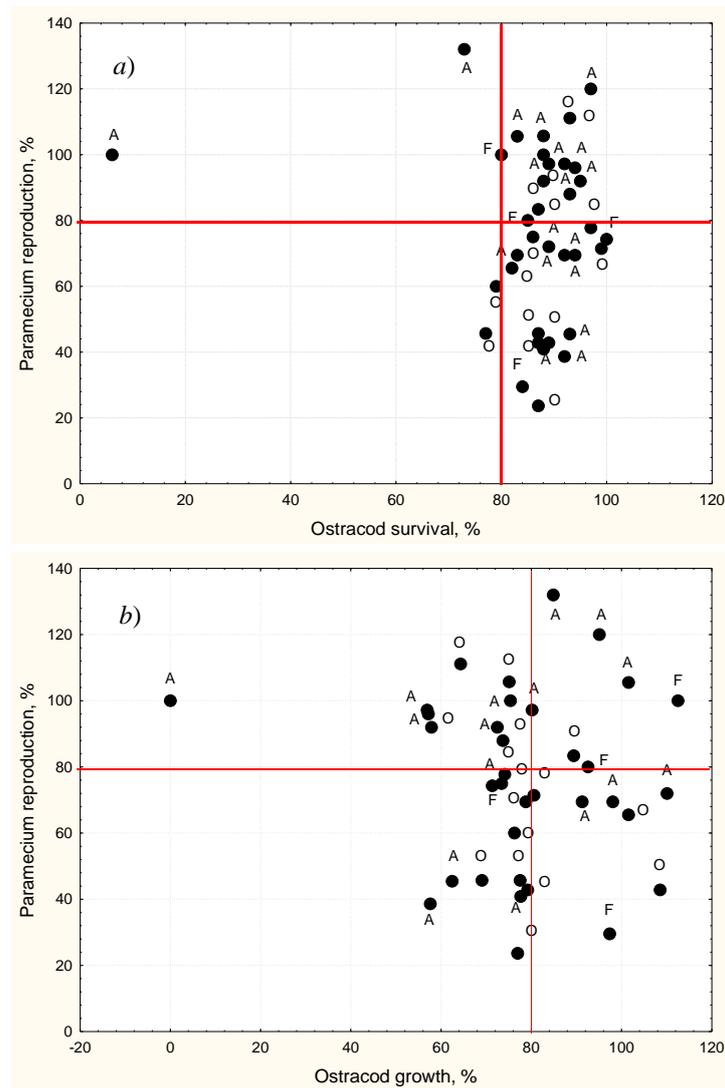


Fig. 4. Survival of ostracod compared to ciliate reproduction (a) and ostracod growth compared to ciliate reproduction (b) (lines indicate criteria of toxicity; A – Agricultural area; F – Forest area; O – Oil production area)

About 91% of the samples demonstrated toxicity at least for one species (based on a > 20% reduction relative to control). Toxicity was most frequently observed in daphnid reproduction (83% samples) and ostracod growth (60% of samples). The survival rate was a less sensitive endpoint for daphnids (23% toxic) and ostracods (9% toxic). A total of 51% of the samples were characterized by reduced reproduction of ciliates and 54% of the samples were marked by reduced algae growth.

The comparison of toxicity of samples from different types of areas indicated that 100% of samples from the oil production area, 94% of samples from the agricultural area, and 50% of samples from the forest area were toxic to at least one test organism. The percentage of toxic responses of species (high to low) for the forest area was as follows: ciliates = algae > ostracod (growth) > daphnids (reproduction). In the agricultural area: daphnids (reproduction) > algae > ciliates > ostracod (growth). In the oil production

Table 3. Chemical analysis and toxic unit of elutriate calculated based on USEPA ambient water quality criteria at a water hardness of 100 mg CaCO₃/L and pH of 7.8

Sample	Dissolved oxygen, mg/L	Conductivity, μ S/cm	pH	Hardness, mg CaCO ₃ /L	NH ₃ (TAN), mg/L	NH ₄ as unionized ammonia, mg/L	Metals toxic unit
Forest area							
1	7.5	513	7.2	94	0.56	0.005	7.1
2	7.3	490	7.1	100	1.50	0.011	10.1
3	6.8	568	7.4	92	< 0.05	ND	7.0
4	7.1	489	7.2	100	0.80	0.007	9.3
Agricultural area							
1	7.4	573	7.2	641	0.35	0.003	9.7
2	7.4	702	6.9	206	0.79	0.004	8.5
3	7.5	608	7.0	140	0.53	0.003	2.6
4	7.3	1144	7.0	321	0.44	0.003	5.9
5	6.4	530	7.6	140	3.60	0.080	7.1
6	6.8	760	7.7	140	0.24	0.007	4.3
7	7.3	1014	6.9	281	1.55	0.007	9.6
8	7.6	860	7.3	358	2.20	0.025	11.3
9	7.3	983	7.3	240	0.97	0.011	7.8
10	7.0	764	7.1	160	2.50	0.018	10.1
11	7.1	734	6.9	120	0.80	0.004	10.0
12	7.1	573	6.8	132	0.18	0.001	8.4
13	7.5	639	7.0	140	0.44	0.003	10.8
14	7.2	526	7.1	100	0.12	0.001	11.1
15	7.0	90	7.5	120	<0.05	ND	5.6
16	7.1	471	6.8	92	0.78	0.003	8.2
Oil production area							
1	6.3	591	7.5	194	1.82	0.032	5.4
2	7.3	704	7.0	168	1.03	0.006	8.2
3	6.5	659	7.3	220	1.98	0.022	75.6
4	5.6	569	7.5	163	0.74	0.013	3.3
5	7.7	853	7.3	188	4.3	0.049	2.3
6	5.8	896	7.2	188	0.07	0.001	6.5
7	5.8	642	7.3	218	0.39	0.004	6.6
8	7.8	236	7.6	200	0.54	0.012	10.2
9	7.3	430	6.8	213	0.94	0.003	7.9
10	6.2	551	7.3	167	3.00	0.034	6.0
11	6.1	908	7.3	420	0.72	0.008	7.7
12	6.0	1309	7.3	334	1.37	0.015	6.1
13	5.9	554	7.4	232	0.87	0.012	5.4
14	5.5	818	7.3	240	2.62	0.030	11.5
15	7.5	1070	7.3	461	3.37	0.038	14.8

area: daphnids (reproduction) > ostracod (growth) > ciliates > algae. Significant differences in terms of toxicity between all areas (forest, agricultural, and oil production) were noticed only for daphnid survival, reproduction, and ostracod growth.

The comparison of ostracod survival to daphnid survival, algae growth, and ciliate reproduction demonstrates the low level of toxicity for samples from all areas (Figs. 2–4). Only ostracod survival test demonstrated the absence of toxic effects in 89% of samples.

The sublethal endpoints for ostracod growth and daphnid reproduction indicated a higher frequency of toxicity in comparison with algae growth and ciliate reproduction.

The pairwise comparison of ostracod and daphnia toxicity tests based on survival (Fig. 2a) showed that the daphnia test was more sensitive than the ostracod test. The results presented in Figs. 2a, b indicate that 23% of the samples were toxic to daphnids and 11% of the samples to ostracods with survival endpoint, and in 83% of the samples to daphnids, and 56% of the samples to ostracods with reproduction or growth endpoints. A total of 40% of the elutriates were not toxic based on algae growth, ciliate reproduction and ostracod survival (Fig. 3a, 4a). In contrast, about 54–56% of the samples were toxic based on algal (Fig. 3b) and ostracod growth.

Figures 4a and 4b reflect the same results of sample distribution based on toxic effects: the wide range of toxicity with ciliates (54% toxic samples) and ostracods (56% of toxic samples where growth inhibition was observed) and the absence of toxicity in most of samples based on ostracod survival.

Relationships between toxicity and chemistry. Correlation analysis between toxicity and contaminants in whole sediment (Spearman's criteria) did not show a significant relationship for survival of daphnids, ostracods or ciliates reproduction (Table 4). Negative correlations were found between daphnid reproduction and Cu, Ni, Cr, Pb, Co, As, TPHs, and TOC. Negative correlations were found between ostracod growth and Co and Pb. There was a positive correlation between algae growth and TPHs. Daphnid reproduction and ostracod growth were correlated with the small grain size of sediments: positive with sand and negative with silt and clay particles.

A significant negative correlation for daphnid reproduction was found between elutriate concentrations of unionized ammonia, hardness, conductivity and pH (Table 5), and between ammonia, Ni, and hardness for ostracod growth. A negative correlation for pH and a positive correlation to Fe were observed for algae growth.

Discussion

The low percentage of toxicity in the elutriate tests compared to the whole sediment tests using survival may be due to the relatively low concentrations of dissolved compounds (as indicated by the low concentrations of metals and ammonia in the elutriate samples (Table 2–3). In contrast, metals and hydrophobic compounds, such as petroleum hydrocarbons, may cause prolonged effects in the chronic whole sediment test demonstrated with inhibition of ostracod growth and inhibition of daphnid reproduction. The absence of correlation between metal, TPHs content in elutriate and toxicity for all species may be due to limited release of these materials from the sediment into water. The sediment structure (clay, fine particles) together with organic carbon, iron and manganese hydroxides are factors controlling bioavailability and can be responsible for the solid phase of metals [6]. In this study, the Ni correlation for elutriates and toxicity to daphnid reproduction and ostracod growth were observed. Ionized ammonia caused a toxic effect in the long-term tests with inhibiting daphnid reproduction and ostracod growth (Table 4–5).

Differences in the toxic responses at the same sites may be explained by the inter-species differences in tolerance to contaminants and mixtures present in the sediments, as well as conditions promoting their bioavailability, for example, dissolved oxygen,

Table 4. Correlations between toxicity and chemical content in whole sediment (significant differences in bold established at $p < 0.05$)

Whole sediment variables	Daphnid survival	Daphnid reproduction	Ostracod survival	Ostracod growth	Paramecium reproduction	Algae growth
Cu	< 0.01	-0.39	0.04	-0.01	-0.09	0.17
Zn	0.09	-0.32	0.01	-0.24	0.02	0.12
Ni	0.11	-0.61	-0.13	-0.15	-0.13	0.05
Cr	0.13	-0.64	-0.04	-0.23	-0.09	0.03
Cd	-0.27	0.07	-0.12	-0.21	0.21	-0.17
Al	0.14	-0.33	0.11	-0.10	-0.09	0.09
Li	0.16	-0.46	0.05	-0.20	0.15	0.03
Hg	0.21	-0.17	-0.16	-0.11	-0.31	0.28
Co	0.03	-0.64	0.01	-0.40	0.12	-0.23
As	-0.13	-0.34	-0.03	-0.22	-0.06	-0.24
Pb	-0.13	-0.48	-0.02	-0.39	-0.03	-0.07
Total petroleum hydrocarbons products	-0.03	-0.42	0.24	-0.14	0.06	0.34
Sum metal quotient	0.12	-0.63	-0.07	-0.2	-0.11	0.01
Total petroleum hydrocarbons quotient	-0.03	-0.42	0.24	-0.14	0.06	0.34
> 0.25 mm	0.09	0.45	-0.03	0.33	0.05	0.02
0.1–0.25 mm	-0.11	0.38	0.10	0.22	-0.09	0.18
0.05–0.1 mm	-0.11	-0.44	0.07	-0.39	-0.12	0.02
0.01–0.05 mm	-0.06	-0.53	-0.07	-0.34	-0.03	-0.06
0.001–0.01 mm	0.05	-0.59	-0.02	-0.38	0.09	-0.12
< 0.001 mm	0.18	-0.63	-0.11	-0.29	-0.01	-0.01
Total organic carbon	0.09	-0.45	-0.03	-0.24	-0.11	-0.19

pH, ionized ammonia and organic carbon [34, 35]. The pairwise correlation (Table 5) of toxicity and chemical content revealed that pH affected algae growth and daphnid reproduction. A shift in pH can lead to an increase in the bioavailability of some contaminants [35].

The increasing concentrations TOC were correlated with reduced daphnid reproduction. Organic carbon and fine clay particles can sorb metals, but the redox equilibrium and bioturbation activity of ostracods and daphnids may promote release of contaminants. All clay minerals, as well as TOC and fine fraction, and coating of iron and manganese hydroxides are the factors affecting metal and organic compound bioavailability [1]. Significant negative correlations between daphnid reproduction and some of the metals in sediments were observed; at the same time, there was no correlation between metals in elutriates and the toxic response for any species (Table 5).

Only Ni, Cr, and Cd exceeded SQGs, suggesting potential additive effects. Figure 5 illustrates the reduced daphnid reproduction with increased metal PEC quotients. A similar relationship was observed between metal PEC quotients and response of the amphipod *Hyalella azteca* survival or growth [36].

Table 5. Correlations between toxicity and elutriate chemical content (significant differences in bold established at $p < 0.05$)

Elutriate Variables	Daphnid survival	Daphnid reproduction	Ostracod survival	Ostracod growth	Paramecium reproduction	Algae growth
Dissolved oxygen	-0.09	0.46	0.27	-0.26	0.17	0.17
Conductivity	-0.19	-0.37	-0.11	-0.26	-0.11	-0.05
pH	0.11	-0.37	-0.16	-0.16	0.08	-0.40
Hardness	-0.13	-0.56	0.02	-0.51	-0.25	-0.10
NH ₃ as total ammonia nitrogen	-0.08	-0.40	0.03	-0.55	-0.07	-0.11
NH ₄ as unionized ammonia	< -0.01	-0.49	-0.03	-0.49	-0.05	-0.26
Fe	-0.15	0.62	-0.03	0.19	-0.15	0.37
Mn	-0.07	0.63	-0.04	0.14	-0.09	0.29
Al	-0.19	0.48	-0.09	0.05	0.11	-0.08
Cd	-0.06	0.03	0.29	-0.20	0.05	0.07
Cr	0.04	0.06	-0.17	<0.01	0.16	-0.10
Cu	-0.12	0.14	0.06	-0.30	-0.11	0.13
Ni	-0.18	-0.30	-0.17	-0.35	0.21	-0.07
Pb	0.43	-0.23	-0.09	0.20	-0.28	0.32
Zn	0.60	-0.15	-0.05	0.21	-0.22	0.11
Metal toxic units	0.12	0.24	0.03	-0.13	-0.15	0.24

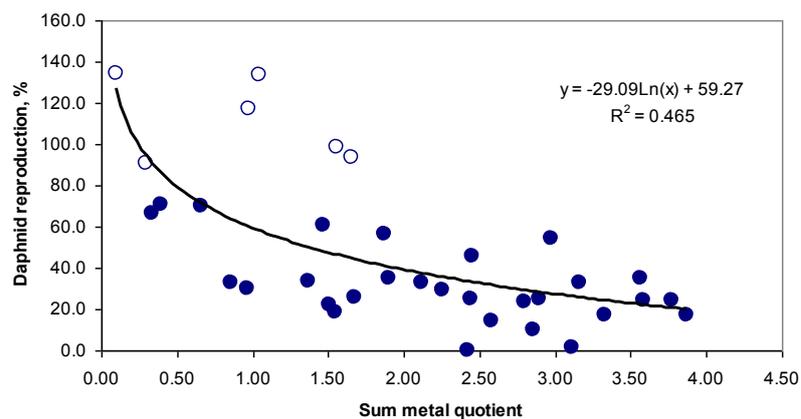


Fig. 5. The relation between the sum probable effect concentration quotient for metals and daphnids reproduction (closed symbols represent samples identified as toxic)

Ho and Burgess [5] in their summary of various sediment toxicity tests report that metals contributed to the toxicity in 16% to 35% of the samples and nonionic organic chemicals contributed to toxicity in 42% to 70% of the samples. Probably, sediment toxicity in the present study was caused by contaminants that were not evaluated, such as pyrethroid insecticides. This gap in sediment chemical monitoring will be evaluated in future investigations.

Algae tolerance to crude oil contamination may explain the positive correlation observed between algae growth and TPHs [37, 38] and their ability to take part in the process of bioremediation.

Samples from the rivers with oil production activity have higher petroleum hydrocarbons and the metals Ni and Cr. Total petroleum hydrocarbons affected toxicity in the chronic tests (daphnid reproduction and ostracod growth), and as well as in shorter tests (ciliate reproduction; Figs. 2, 4). Positive correlation between ostracod growth and *H. azteca* 14-d survival was demonstrated in the freshwater sediments from Peninsula Harbor [15]. The ostracod test detected toxicity better or at the same level as the conventional amphipod or midge tests [14, 17–19]. Chial et al [16] investigated oil-contaminated sediments with 14-d amphipod *H. azteca* and 6-day ostracod tests where ostracods seemed to be more sensitive, based on mortality, than amphipods to oil contaminated sediments. In the present study, daphnids showed much higher sensitivity in the long-term reproduction test than the ostracods in the growth inhibition test, especially in oil contaminated sediments. The reason may be a longer time that daphnids were in contact with sediments.

On the contrary, the algae test did not demonstrate selectivity to samples from the type of activity in the water basin (Fig. 3). Only 47% of samples from the oil production area were toxic instead of 63% of toxic samples from the agricultural area. The sum PEC metals quotient in the oil production and agricultural areas varied in the range of 2.4–3.8 and 0.3–2.3, respectively (Table 2). The increased toxicity in the agricultural area can be owing to the increased level of Cd in sediments (a significant difference between Cd in the agricultural area and the others). The sensitivity of algae (*Chlorella vulgaris*, *Chlorella pyrenoidosa*, and *Scenedesmus acutus*) to Cd is well known [39–41]. Kudlak et al. [42] reported high sensitivity of ostracods to Cd in comparison with other metals.

This study showed variations in the toxicity responses between species with different sensitivity to contaminants in sediments. Daphnid reproduction and ostracod growth are sensitive to metals, but algae and ciliates may have responded to other chemicals that were not determined in the study.

The toxicity test conducted with the whole sediment is more susceptible to contaminants sorbing to clay particles connected with sulfide or organic substances; however, elutriate tests provide an efficient, cost-effective alternative to whole sediment toxicity tests, being, therefore, easily used as a screening tool for monitoring sediment toxicity. A more intensive assessment of a site found to have consistently toxic sediment through elutriate testing may likely require the use of additional environmental measures, including whole sediment testing, to determine the level and extent of toxicity [34].

Nevertheless, the test battery used in this study with different types of exposures (elutriate, whole sediment), time of exposure (acute and chronic test), toxicity endpoints (survival, growth, and reproduction) proved to be more efficient in eliciting the toxicity of contaminated sediments than any of the tests alone. Other authors have made similar conclusions from their toxicity studies [19, 35, 43, 44].

Conclusions

The sediments from rivers in the Middle Volga Region contained Ni, Cr and Cd in a range that exceeds SQGs. The content of Fe, Zn, Ni, Cr, Pb, and TPHs was significantly increased in the sediments from the forest area, compared to the agricultural and to the oil production area. The concentrations of PAHs were typically three orders of

magnitude lower than SQGs. The concentrations of DDT were typically below detection in most of the sites.

The most polluted sediments were observed in the area of oil production. The comparison of toxicity of samples from different types of areas indicated that 100% of samples from the oil production area, 94% of samples from the agricultural area, and 50% of samples from the forest area were toxic to at least one test organism.

The possible reason of toxicity to daphnid reproduction may be Cu ($R^2 = 0.39$), Ni ($R^2 = 0.61$), Cr ($R^2 = 0.64$), Pb ($R^2 = 0.48$), Co ($R^2 = 0.64$), As ($R^2 = 0.34$), TPHs ($R^2 = 0.42$), and ammonia ($R^2 = -0.49$), hardness ($R^2 = 0.56$), pH ($R^2 = 0.37$) in elutriates. Inhibition of ostracod growth may be connected with the presence of Co ($R^2 = 0.40$) and Pb ($R^2 = 0.39$) in sediment and ammonia ($R^2 = 0.55$), Ni ($R^2 = 0.35$) and hardness ($R^2 = 0.51$) in elutriate. The reason for the observed toxicity to ciliate reproduction and algae growth was not revealed.

The samples were more frequently toxic in the whole sediment exposures compared to the elutriate exposures. The whole sediment induced a higher toxic response than the elutriates: 86% samples were toxic in whole sediment toxicity tests in comparison with 54% of the samples in elutriate tests. The highest sensitivity was observed for daphnid reproduction, mostly in the oil production areas. Significant differences in terms of toxicity between all areas were noticed only for daphnid survival, reproduction and ostracod growth.

The results of the present study highlight the importance of integrative evaluation of freshwater sediments, which allow a comprehensive evaluation of sediment quality.

The results of this study can be used for development of a sediment monitoring program in Russia (Republic of Tatarstan) and as information for the decision of sediment manipulation in contaminated areas.

The future sediment investigations will concern a more detailed assessment to identify sediment toxicity with application of the following methods: toxicity identification evaluations [47], measurements of acid volatile sulfide and simultaneously extracted metals [45] and spiked sediments [26].

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**Сравнение токсичности донных отложений рек
с различным уровнем антропогенной нагрузки в элюатном
и контактном тестах (Среднее Поволжье, Россия)**

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Аннотация

Проведена характеристика химического состава, токсичности в элюатных и контактных тестах 35 образцов донных отложений, отобранных по программе мониторинга рек Среднего Поволжья (Республика Татарстан, Россия). Область исследования включала лесной район с отсутствием значительной антропогенной нагрузки и районы с преобладанием определенного вида деятельности на водосборе (аграрная) и (нефтедобывающая). Токсичность исследуемых образцов определяли с помощью элюатных тестов на водорослях *Chlorella vulgaris* и инфузориях *Paramecium caudatum*, а также в ходе контактных тестов на рачках *Daphnia magna* и остракодах *Heterocypris incongruens*. Было показано, что содержание металлов в 43% проб донных отложений превышало нормативы качества, принятые в США (probable effect concentration (ПЕС)), в то время как содержание полициклических ароматических углеводородов (ПАУ) и хлорорганических пестицидов в большинстве проб было ниже соответствующих нормативов. Выявлена корреляционная зависимость между токсичностью у дафний (ингибирование репродукции), остракодов (ингибирование роста) и содержанием

металлов и аммония в донных отложениях и водных вытяжках. Токсичность продемонстрировали 86% проб в контактных тестах и 54% проб в элюатных тестах. Около 91% проб были токсичны по результатам, по крайней мере, одного теста; наиболее часто токсичность проявлялась в ингибировании размножения дафний (83% проб) и роста остракод (56% проб). Токсичность наблюдалась в 23% и 11% проб по критерию выживаемости дафний и остракод соответственно, а также в 54% проб по критерию размножения инфузорий и ингибированию роста водорослей. Наиболее загрязненными донные отложения были в районе нефтедобычи. Сравнение токсичности проб, отобранных в районах с разными типами антропогенной нагрузки на водосборе, показало, что 100% проб из района нефтедобычи, 94% проб из аграрных районов и 50% проб из лесного района были токсичными по результатам хотя бы одного теста.

Ключевые слова: донные отложения, оценка токсичности, *Chlorella vulgaris*, *Paramecium caudatum*, *Daphnia magna*, *Heterocypris incongruens*, тяжелые металлы, нефтепродукты, Среднее Поволжье

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Подписи к рисункам

Рис. 1. Участки, где были взяты пробы донных отложений: А – аграрный район; Л – лесной район; Н – район нефтедобычи.

Рис. 2. Выживаемость остракод по сравнению с дафниями (*a*) и рост остракод по отношению к размножению дафний (*b*) (критерии токсичности показаны линиями; А – аграрный район; Л – лесной район; Н – район нефтедобычи).

Рис. 3. Выживаемость остракод по сравнению с ростом водорослей (*a*) и рост остракод по отношению к росту водорослей (*b*) (критерии токсичности показаны линиями; А – аграрный район; Л – лесной район; Н – район нефтедобычи).

Рис. 4. Выживаемость остракод по сравнению с размножением инфузорий (*a*) и рост остракод по отношению к размножению инфузорий (*b*) (критерии токсичности показаны линиями; А – аграрный район; Л – лесной район; Н – район нефтедобычи).

Рис. 5. Отношение между коэффициентом воздействия суммарной возможной концентрации металлов и размножением дафний (токсические образцы показаны цветом).

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