Accumulation of heavy metals and radionuclides in bottom sediments of monitoring streams in Lithuania

Guoda Mackevičienė

Institute of Ecology,
Akademijos 2,
LT-2600 Vilnius, Lithuania
E-mail: guoda@ekoi.lt

Nijolė Štriupkuvienė,
Gintaras Berlinskas

Ministry of Environment of Lithuania,
A. Juozapavičiaus 9,
LT-2600 Vilnius, Lithuania

To evaluate water quality changes in selected streams of Integrated Monitoring Sites (IMS) and an agrostation (AS), the level of heavy metals (Pb, Cd, Cu, Cr, Ni, Mn) and radionuclides (^{137}Cs, ^{134}Cs, ^{40}K, ^{90}Sr) was determined in bottom sediments. The heavy metal concentrations in surfice sediments of streams showed annual and seasonal changes and differences among the monitoring sites. The dynamics of accumulation level of heavy metals during 1996–1998 indicated that the concentration of cadmium gradually decreased in all localities. Accumulation of lead was observed at the Aukštaitija, Dzūkija and Žemaitija IMS. A downward trend was recorded in the contents of Pb, Cu, Cr and Ni and an upward trend in the Mn content at the Kėdainiai agrostation.

Activities of ^{137}Cs were relatively constant in sediments of the Aukštaitija and Dzūkija IMS, while three times higher concentration of radionuclides were determined in the Žemaitija IMS. The accumulation level of ^{137}Cs was significantly lower at the agrostation (LT06) than in the other monitoring sites. ^{90}Sr activity increased in the IMSs with the maximum being found at the Dzūkija station.

Key words: streams, bottom sediments, heavy metals, radionuclides, accumulation

INTRODUCTION

Contaminated sediments, in both freshwater and marine systems, are a significant issue worldwide. Contaminants can persist for many years in sediments, where they have the potential to adversely affect human health and the environment. Some chemicals continue to be released to surface waters from industrial and municipal sources, and polluted runoff streams from urban and agricultural areas continue to build up harmful levels of contamination in sediments.

In a comprehensive sediment assessment approach, five basic components should be considered: (1) benthic community structure, (2) laboratory bioassays for evaluating the toxicity of in-place pollutants, (3) bioaccumulation information, (4) knowledge of site stability, and (5) physico-chemical sediment properties [8].

Monitoring of the quality of stream water is part of a complex programme of biota monitoring in Lithuania [5]. The quality of surface water is under constant observation and evaluation by 70 indices and highest permissible concentrations in 47 streams [6].

Investigations of accumulation of heavy metals and radionuclides in bottom sediments as well as of the structure and abundance of benthofauna communities in the selected streams of stations of biota monitoring were carried out. The aim of the present work was to compile data on the ecological state of integrated monitoring and agrostationary streams and to evaluate the anthropogenic impact on the environment.

MATERIALS AND METHODS

Sediment samples were collected in spring and autumn in the surface layer (2–5 cm) of bottom sediments in the Versminis stream (Aukštaitija IMS, LT01) with a soft turfy bottom and in hard-bottomed (sand and gravel) Duburiai (Dzūkija IMS, LT02), Juodupis (Žemaitija IMS, LT03) and Greisupis (Kėdainiai AS, LT06) streams.

Heavy metal (Pb, Cd, Cu, Cr, Ni, Mn) concentrations in bottom sediments of the streams were determined by electrothermal atomic absorption spectrometry with AAS-30 (Carl Zeiss Jena) and AA-25 Plus (Varian) spectrophotometers with a graphite furnace in the trace level [1]. The sediment digest for metal analyses was prepared by heating samples with an Apion dry mode mineraliser. The mineralization takes place under atmospheric pressure. The principle of the mineralization is original, wholly universal and consists in heating a superoxidative gas mixture into the containers with samples heated to a chosen temperature in the range of 300–400 °C. The oxidative gas mixture consists of oxygen, nitrogen oxide and ozone and is prepared in the device by combustion of ammonia and by ozonation. As a by-product chemically pure nitric acid is formed, which can be used after distillation for dissolving the samples after mineralization. Concentrations of heavy metals in samples of bottom sediments were calculated in µg/g dry mass.

The activities of ^{134}**Cs,** ^{137}**Cs** and ^{40}**K** were measured applying standard methods for radioecological analyses. Bottom sediments were dried at 90 °C, homogenised, weighed and placed into 100 ml polyethylene beakers. Radionuclide activity was determined using a gamma spectrometer with a HPGe or Ge+Li detector calibrated by mixed radionuclide standards. Gamma spectrum analysis, identification of nuclides and calculation of activities were performed using *Gamma Trac* or BS software. After gamma spectroscopy the activity of ^{90}**Sr** was determined. The samples were ashed at 610 °C for 15 h and dissolved in HCl. Yttrium-90 was extracted from the solution with 10% HDEHP. The activity of ^{90}Sr was counted in a low level anti-coincidence beta counter. The chemical yield of the Y carrier was determined by weighing [7].

RESULTS

Based on the evaluation of the data on annual changes of heavy metals, in 1998 we could state that the level of accumulation of xenobiotics at separate stations was different, though in most cases no significant changes were found (Table 1). The concentration of cadmium (Cd), one of the most toxic heavy metals, in stream sediments varied from 0.12 to 0.76 µg/g dry weight. As compared to spring, the concentration of Cd in autumn was 1.3–1.5 times higher (except for the Versminis stream at the Aukštaitija IMS). The Cd concentration in samples of soft turfy bottom was stable (0.18–0.19 µg/g). In 1998, the highest Cd concentration was found in Juodupis silt samples (Žemaitija IMS) where it was almost 3–4 times higher than at the other monitoring stations. The results obtained that year show that least polluted was the bottom of the Duburys stream (Dzūkija IMS).

A similar tendency is characteristic of the seasonal changes of the content of lead (Pb) in stream silt: the highest content of Pb was determined in spring (Table 1). The Pb concentration at the Aukštaitija IMS in the water sediments of the Versminis stream showed no seasonal changes. The highest amount of Pb was found at the Žemaitija IMS (11.4–19.3 µg/g), while it was lowest at the Kėdainiai AS (3.1 µg/g on average). Similar accumulation levels were found at the LT01 and LT02 monitoring stations with 6.3 and 5.6 µg/g of dry substance, respectively.

The levels of copper (Cu) at the LT02, LT03, and LT06 monitoring stations was almost stable and varied only from 2.4 to 9.4 µg/g. The highest levels of copper was accumulated by the Versminis stream silt (LT01), where the annual Cu concentration made up 7.1 µg/g. The lowest levels of the latter microelement were determined at the Kėdainiai AS and Žemaitija IMS. The concentration of chromium (Cr) at the Dzūkija and Žemaitija IMS and at the Kėdainiai AS was stable within a year. However, as compared to spring there was determined an increased level of this trace metal at the Aukštaitija IMS, and it was 1.4 times higher in autumn (Table 1). The highest level of Cr had been accumulated in the Versminis stream bottom sediments (LT01) (5.85 µg/g) and the lowest by

Table 1. **Concentrations of heavy metals (mg/g dry substances) in bottom sediments of monitoring streams in 1998**

Station	Date	Cr	Mn	Ni	Cu	Pb	Cd
Aukštaitija IMS	05.07	4.86	134	3.87	9.41	6.20	0.18
(LT01)	10.24	6.84	195	5.47	4.84	6.51	0.19
Dzūkija IMS	05.05	2.12	149	3.53	4.78	7.43	0.15
(LT02)	10.18	2.47	137	1.82	3.94	3.85	0.12
Žemaitija IMS	05.14	2.67	102	2.43	2.58	19.30	0.76
(LT03)	10.21	1.72	119	1.05	2.72	11.40	0.54
Kėdainiai AS	05.14	3.97	195	4.23	2.47	3.84	0.18
(LT06)	10.21	3.40	130	4.12	2.40	2.34	0.12

the Duburiai (LT02) and Juodupis (LT03) stream water sediments.

The level of nickel (Ni) at the Kėdainiai AS showed no seasonal changes, whereas in autumn at the Dzūkija and Žemaitija IMS it was two times lower than in spring, while at the Aukštaitija IMS, on the contrary, it was 1.4 times higher than in spring. The highest content of Ni was found in the stream silt at the LT01 and LT02 monitoring sites.

The content of manganese (Mn) in stream bottom sediments in spring and in autumn changed. In autumn the Mn accumulation level at the LT01 and LT03 stations was 1.5 times higher than in spring, whereas it was 1.5 times lower in LT02 and LT06 streams. The highest level of Mn that year was registered at the Aukštaitija and Dzūkija IMS, while it was lowest at the Žemaitija IMS.

According to the general concentration, heavy metals can be arranged in the following decreasing order: Mn > Pb > Cu > Cr > Ni > Cd.

The activity of globally distributed artificial radionuclides ^{134}Cs, ^{137}Cs, ^{90}Sr as well as of radionuclide ^{40}K, a chemical analogue of ^{137}Cs, in the investigated bottom sediments is presented in Table 2. Seasonal activity changes of radionuclides in the permanent rivers are determined by isotope migration with sand and silt particles carried out by the stream. The analyses of the distribution of radionucles in hydroecosystems (water, hydrofits, bottom) showed that bottom sediments accumulate 88% of ^{137}Cs and 40% ^{90}Sr [10]. The activity of a globally distributed ^{137}Cs in the investigated monitoring sites fluctuated within a relatively wide interval (from 3.8 to 115 Bq/kg dry mass). By its geochemical characteristics, ^{137}Cs is rapidly dissolvable in water and easily makes ionic forms or colloids. Moreover, the suspended particles of detritus easily accumulate ^{137}Cs, which later settles down on the bottom [10]. Our data show that the activity of this metal was the least and relatively stable in the bottom of the Greisupis stream (3.8–3.9 Bq/kg). The maximal ^{137}Cs activity was determined in spring samples at the LT03 monitoring station (115 Bq/kg), which in autumn decreased by 29% (Table 2). The seasonal ^{137}Cs changes in bottom sediments at the LT01 and LT02 stations of the monitoring streams were insignificant.

A specific activity of the ^{134}Cs was found only in the autumn samples of silt in the Juodupis (Žemaitija IMS, 0.86 Bq/kg). This particular ^{134}Cs activity proved an influence of the Chernobyl Nuclear Power Plant accident on the radioecological pollution of the environment. This radionuclide belongs to a short-lived artificial group of radionuclides. The activity of ^{40}K (a chemical analogue of ^{137}Cs natural radionuclide) which is reflected in the investigated bottom sediments of streams shows natural fluctuations of radiation in the environment [4]. As compared to the end of the vegetation season, the activity of this radionuclid was higher at the beginning of the vegetation season in LT02, LT03 and LT06 bottom sediments of streams. However, at the Aukštaitija IMS, analogously to ^{137}Cs seasonal changes of accumulation, the activity of ^{40}K was lower in spring than in autumn.

The activity of the radioactive ^{90}Sr fluctuated in a relatively harrow interval in the investigated stream silt and reached 1.35–6.86 Bq/kg (Table 2). This radionuclide in all the investigated sites exhibited a 1.5–2.3 higher activity in spring than in autumn. The average annual ^{90}Sr concentrations at the integrated monitoring stations were similar (LT01, LT02, and LT03 – 3.46, 4.91 and 3.03 Bq/kg, respectively). The lowest ^{90}Sr activity was determined in the Kėdainiai AS Greisupis bottom sediments where the average annual activity made up 1.67 Bq/kg dry mass.

DISCUSSION

While investigating the dynamics of heavy metal accumulation in the monitoring stream bottom sedi-

Table 2. **Activities of radionuclides (A, Bq/kg dry substances) in bottom sediments of biota monitoring streams in 1998. P – error of estimation in %**

Station	Date	Cs-137		K-40		Sr-90	
		A	P	A	P	A	P
Aukštaitija IMS	05.07	12.2	11	142	10	2.10	12
(LT01)	10.24	15.3	3	324	4	4.81	15
Dzūkija IMS	05.05	40.3	5	602	5	2.95	12
(LT02)	10.18	36.2	8	338	10	6.86	15
Žemaitija IMS	05.14	115.0	9	501	9	2.08	12
(LT03)	10.21	82.1	7	487	9	3.98	15
Kėdainiai AS	05.14	3.9	18	649	5	1.35	12
(LT06)	10.21	3.8	15	567	5	1.99	15

ments (1996–1998), it was observed that their content in the surfice silt layer was different every year (Figs. 1 and 2). A gradual decrease of the accumulation level in all surfice layers of the investigated stream bottoms is characteristic of the inter-annual dynamics of cadmium, one of the most toxicant chemical stressors. At all the monitoring stations Cd content in the bottom sediments was lower than the maximum allowable concentration (MAC) [3]. The Cd concentration that was determined that year at the LT03 monitoring station (0.65 µg/g) was equivalent to the threshold concentration, which according to the literature sources has no negative effect on benthic community [3]. However, in the other monitoring stations the content of Cd during three years was 3–4 times lower than the transitional concentration (Fig. 1).

As compared to 1996, in 1998 at the monitoring stations the accumulation change of lead showed a significant increase. Though the area of the Kėdainiai AS is in a territory of economic activity, the content of Pb in the Greisupis silt was the lowest. Based on the three-year investigation data we can state that the accumulation level of copper in the bottom sediments was gradually decreasing, except for the station LT01, where the copper concentration that year increased by 37% as compared to 1997, and it was the highest (7.1 µg/g) among all the monitoring sites (Fig. 1).

In 1997–1998, the concentrations of chromium at the LT01, LT02, and LT06 stations were relatively stable. During three years, the highest Cr and Cu concentrations have been found in the LT01 monitoring stations, while they were lowest in the LT02 and LT03 monitoring stations. A significant decrease in the accumulation level of nickel was observed in 1996–1998 in the Žemaitija IMS, where the concentration of this metal that year was the lowest (1.74 µg/g). A slight increase in Ni content was observed in the stream silt at the LT01, LT02 and LT06 stations (Fig. 1). According to the published data [3], the background value of this heavy metal in the bottom surface of the water bodies makes up 31 µg/g, and the threshold concentration that has no negative effect on the bottom animals makes up 16 µg/g.

During the last three years, the accumulation level of manganese in the integrated monitoring stations significantly decreased (Fig. 2). The opposite tendency has been observed in the Kėdainiai AS, where the amount of Mn in the silt fraction that year increased up to 42% as compared to the previous year and to 78% against 1996. The threshold concentration of manganese made up 400 µg/g [3].

According to our investigations, the activity of ^{137}Cs in the Kėdainiai AS in 1996–1998 was decreasing. As compared to 1997, in 1998 a particular activity of this radionuclide in the Greisupis stream silt decreased by 63%. This might be related to a decrease of the pollution with radionuclides in this area. During the last three years, ^{137}Cs activity in the bottom sediments slightly decreased. However, an exception is the dynamics of this radionuclide in the Žemaitija IMS, where the average annual ^{137}Cs concentration that year was the highest and 1.5 times higher than the maximum allowable concentration for this station in 1996. The collected material

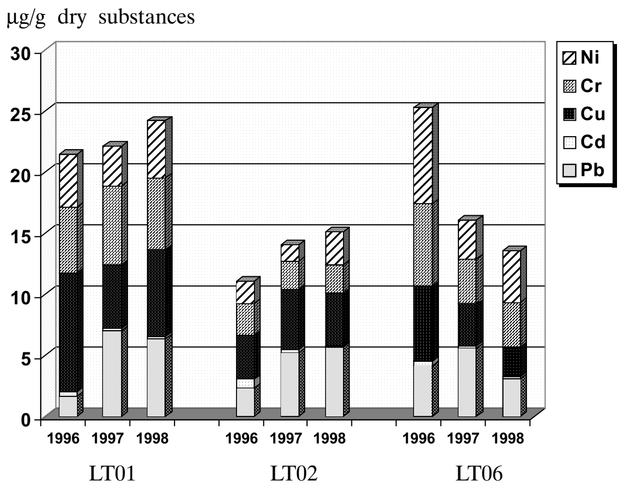

Fig. 1. Concentrations of heavy metals (Ni, Cr, Cu, Cd, Pb) in bottom sediments of monitoring streams at Aukštaitija IMS (LT01), Dzūkija IMS (LT02) and Kėdainiai (LT06) in 1996–1998

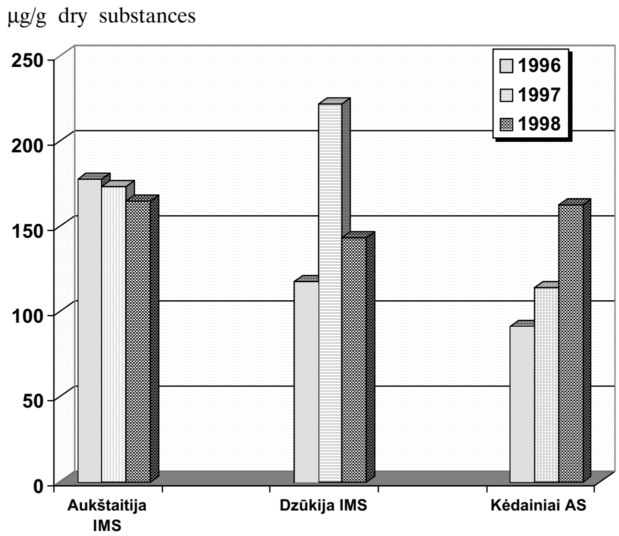

Fig. 2. Dynamics of Mn accumulation in bottom sediments of monitoring streams at Aukštaitija IMS, Dzūkija IMS and Kėdainiai AS in 1996–1998

allows us to maintain that the Plateliai National Park has formed as an accumulation zone of the artificial radionuclides emitted by the Chernobyl Nuclear Power Plant accident. This is proved only by the activity of ^{134}Cs which was found in this territory, and also by the zone of an increased radioactivity over the Žemaitija National Park, which was determined with the help of radioecological investigations of the air.

The level of ^{90}Sr accumulation in the stream silt fraction depends on the structure of the bottom of a waterbody and on the level of sediment mineralisation. In sandy-gravel bottoms, the accumulation of ^{90}Sr is lower than in silt [10]. While analysing the ^{90}Sr accumulation dynamics, we can see that during the last three years the particular activity of this radionuclide in the investigated streams was similar and ranged within a comparatively low interval (between 1.2 and 4.9 Bq/kg dry mass) (Fig. 3). The obtained results revealed a general tendency of accumulation level increase of this radionuclide at the integrated monitoring stations. As compared with the results of 1996, in 1998 the ^{90}Sr concentration in the stream silt fraction was 1.6–3.0 times higher. In the Kėdainiai AS during 1997–1998 the ^{90}Sr accumulation level was relatively stable (1.85–1.67 Bq/kg), but it was the lowest of all the monitoring stations.

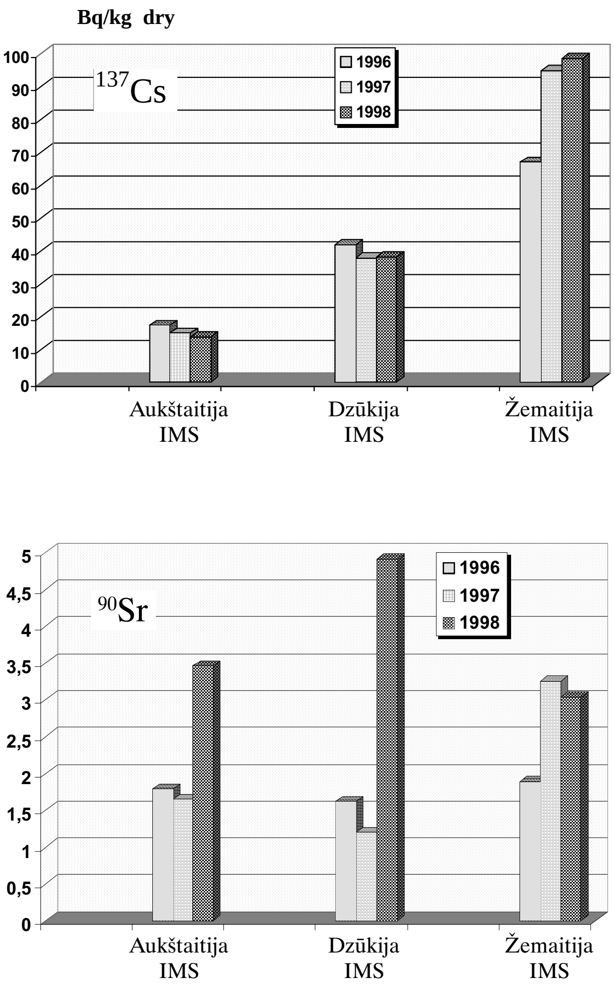

Fig. 3. Activities of radionuclides ^{137}Cs and ^{90}Sr in bottom sediments of monitoring streams at Aukštaitija IMS, Dzūkija IMS and Žemaitija IMS in 1996–1998

In 1994–1998, after assessing the biodiversity of macrozoobenthos according to the Shannon–Wiener (H, bits/ind.) and Simpson's indices (D) and water quality using the Trent and Mean Chandler biotic indices [9], it was established that the monitoring streams were clean waterbodies [2] (Arbačiauskas, unpublished report).

CONCLUSIONS

The heavy metal concentrations in surfice sediments of streams showed annual and seasonal changes and differences among the monitoring sites during 1996–1998:

• The concentration of cadmium gradually decreased at the stations of integrated monitoring (IMS) and at the agrostation (AS).

• A prominent accumulation of lead was observed in the Aukštaitija and Dzūkija IMS, the concentration of manganese increased at the Kėdainiai Agrostation. These changes may be caused by the anthropogenic impact, as well as by natural variations in the accumulation of Mn in the ecosystem.

• Activities of ^{137}Cs were relatively constant in bottom sediments of the Aukštaitija and Dzūkija IMS, while a three times higher ^{137}Cs concentration was determined at the Žemaitija IMS. The short-life artificial radionuclide activity ^{137}Cs (0.86 Bq/kg DW) was detectable only at the Žemaitija IMS, which may suggest radioactive contamination of the Plateliai National Park area by the Chernobyl Nuclear Power Plant.

• ^{90}Sr activity increased significantly in the IMS, the maximum being found at the Dzūkija station.

References

1. *Analytical Methods for Graphite Tube Atomizer* (ed. E. Rothery). Mulgrave, Victoria, Australija, 1988. 191 p.
2. Arbačiauskas K., Mackevičienė G., Štriupkuvienė N., Motiejūnas S., Kreslauskaitė R. Monitoring of streams: macrozoobenthos and accumulation of heavy metals and radionuclides in bottom sediments. *Proceedings of the Latvian Academy of sciences.* Section B. Supplement: Ecotoxicology Conference. 1998. Vol. 52. P. 109–112.

3. *Guidelines for the protection and management of aquatic sediment quality in Ontario. Environment in Ontario.* 1993. P. 1–10.
4. Lukšienė B., Tarasiukas N., Šalavėjus S., Špirkauskaitė N., Lujanienė G., Lujanas V., Šukytė J. Radionuklidų migracijos ir kaupimosi Kuršių marių, Kauno marių ir Baltijos jūros rytinės dalies ekosistemose tyrimai. *Lietuvos užterštumas radionuklidais ir jo pasekmės*. Vilnius: Academia, 1992. P. 100–106.
5. *Manual for Integrated Monitoring. Programme Phase 1993–1996. Environmental Report 5.* Environmental Data Centre, National Board of Water and the Environment. Helsinki, 1993. 114 p.
6. Standard methods for the examination of water and wastewater. 1992.
7. Suomela J., Wallberg L. & Melin J. *Method for Determination of ^{90}Sr in Food and Environmental Samples by Cerenkov Counting.* SSI Report. 1993. P. 96–111.
8. Ulrich F. Managing Contaminated Sediments II. Integrated Process Studies. *Journal of Soils and Sediments*. 2001. Vol. 1, N 2. P. 111–115.
9. Water Quality Assessments: A Guide to the Use of Biota, Sediments and Water in Environmental Monitoring (ed. O. Chapman) UNESCO/WHO/UNEP. London, 1992. 585 p.
10. Марчюлёнене Д., Душаускене-Дуж Р., Мотеюнене Э., Швобене Р. Радиохемоэкологическая ситуация в оз. Друкшяй – водоеме-охладителе Игналинской АЭС. Вильнюс: Academia, 1992. 215 c.

Guoda Mackevičienė, Nijolė Štriupkuvienė, Gintaras Berlinskas

SUNKIŲJŲ METALŲ IR RADIONUKLIDŲ AKUMULIACIJA MONITORINGO UPELIŲ DUGNO NUOSĖDOSE

Santrauka

Ištirti sunkiųjų metalų (Cd, Pb, Cu, Cr, Ni ir Mn) bei radionuklidų (^{137}Cs, ^{134}Cs, ^{40}K, ^{90}Sr) akumuliacijos lygiai integruoto monitoringo teritorijų ir agrostacionarų upelių organinės kilmės dugno nuosėdose. Įvertinus 1998 m. pokyčius, išryškėjo bendra Cd, Cu, Cr ir Ni santykinai stabilios sezoninės kaitos tendencija, tuo tarpu Pb ir Mn kiekiai buvo didesni pavasarį, palyginti su rudeniu. Tarpmetinei 1996–1998 m. dinamikai būdingas palaipsnis kadmio koncentracijos mažėjimas ir švino akumuliacijos lygio didėjimas integruoto monitoringo teritorijų upeliuose. Pagal vidutinį akumuliacijos lygį tirti sunkieji metalai yra išsidėstę šia mažėjančia tvarka: Mn > Pb > Cu > Cr > > Ni > Cd.

Globaliai pasiskirsčiusio technogeninio radionuklido cezio (^{137}Cs) tarpmetinei dinamikai būdingas santykinis specifinio aktyvumo stabilumas ir gerokai didesnis akumuliacijos lygis Žemaitijos integruoto monitoringo teritorijoje, kurioje aptiktas ir ^{134}Cs aktyvumas. Stebima stroncio (^{90}Sr) koncentracijos tirtų upelių dugno nuosėdose didėjimo tendencija. Nustatytos metalų koncentracijos daugelyje tirtų atvejų yra mažesnės už slenkstines ir neturi poveikio upelių bentofaunai.