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Lead content in plant materials in the buffer zones of surface water bodies of Northwestern and Central regions of Lithuania

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Abstract

The lead (Pb) is a heavy metal, which causes severe disorders in humans and other organisms. Recently, the item of wetland buffer zone has emerged as an integrated development approach to nature conservation including buffer zone pollution by Pb. The main sources of Pb pollution in Lithuania are Pb ammunition used by hunters and natural and anthropogenic activities. Considering plant capability to accumulate Pb, they are used for bioindication. The objective of the study was to determine Pb content in the aboveground biomass of vegetation collected from the reference sites in the buffer zones of wetlands. The research was conducted in three localities of the different wetland buffer zones – drying ditch, natural pond, and stream, in the three parts of Lithuania: in the Northwestern part of Lithuania in the territory of the Žemaitija National Park, in the northern part of the Žemaitija Upland at the border of Latvia, and in the Central Lithuania, in the vicinity of the largest artificial waterbody – Kauno Marios and the Nemunas River. The content of Pb in the working solutions was determined by the atomic absorption method on an atomic absorption spectrometer at a wavelength of 283.0 nm. Significant differences were calculated using the three-way ANOVA (Tukey's HSD test). The relationships were calculated using a regression analysis, the data were significant at $P \leq 0.01$ and $P \leq 0.001$. The data of the research show that the content of Pb corresponds to the background content of uncontaminated sites, the values of which are reported by other scientists and is equal to 0.95–6.84 mg kg^{-1}. The average content of Pb in the buffer zones of various surface water source types was 3.75–3.76 mg kg^{-1}. The content of Pb in the plants at 20–30 m from the surface water bodies increased by 1.3–1.5 times, and then at 40 m it decreased by the same indicator.

Keywords: lead, vegetation, plants, wetlands, buffer zone, atomic absorption spectrometry.

Introduction

Plant material is widely used to assess the condition of the environment, including the content of heavy metals (Самойленко и др., 2018) because of the ability of plants to accumulate them (Kowalenko, 2004; Khalid et al., 2018). The places of lead (Pb) accumulation in plants may differ (Collin et al., 2022). For example, *Stevia rebaudiana* flowers contain twice as much Pb as leaves and stems (Hung et al., 2017; Collin et al., 2022), and blackberry (*Rubus fruticosus* L.) fruits contain 4.5 times less Pb than leaves (Hajar et al., 2014; Collin et al., 2022). Therefore, it is advisable to take a mixture of plant biomass for bioindication of the terrain. When bioindicating soils, it should be considered that only 0.05% Pb is plant-available, of its total content in the soil (Vysloužilová et al., 2003). To evaluate the pollution degree in the certain areas, the content of Pb, cadmium (Cd), zinc (Zn), and copper (Cu) in plants is used (Nikolova, 2015), changes in their concentrations of a Zn and Pb post-flotation tailings dump (Pietrzykowski et al., 2018; Szwalec et al., 2018) reveal the factors affecting the accumulation of elements in plants of urban ecosystems (Nevedrov et al., 2019), and, also, determine their accumulation close to water bodies (Molnárová et al., 2018).

Wetlands cover about 9% of the earth's surface. They are important components of watersheds and are vital for environmental, economic, social, and cultural reasons. Wetlands perform many environmental functions including helping to stabilise climatic conditions and flooding, storing carbon, maintaining good water quality in rivers, recharging groundwater, and acting as important sites for biodiversity (EC, 2019; Siddi, 2020; Tanneberger et al., 2021). They are estimated to contain ca. 35% of global terrestrial carbon. Wetlands sequester carbon from the atmosphere through plant photosynthesis and by acting as sediment traps for runoff (Richardson, 1994). Wetlands play a crucial role in preserving biodiversity of natural habitats. Their protection and restoration are

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supported by the Ramsar Convention, EU directives, and national legislation for nature protection. Wetlands are important for primary products such as agriculture, fishery, and forestry, also for recreation (e.g., swimming, boating, fishing, camping, and wildlife watching).

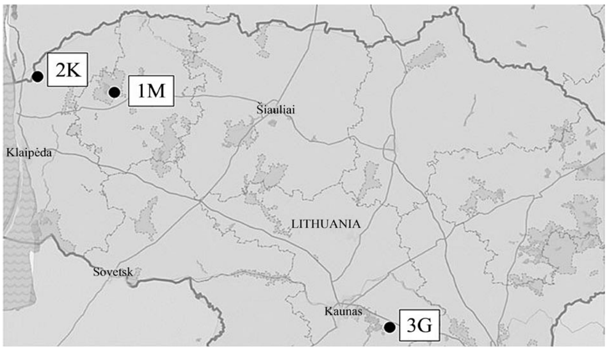
Wetlands support agricultural activities, because they are a source of water for irrigation and livestock and for domestic consumption. Wetlands improve water quality by trapping sediments filtering out pollutants and absorbing nutrients that would otherwise result in poor water quality for downstream users (Manzetti, 2020). They also provide a filter between surface water and shallow groundwater resources. In line with the EU commitments under the Air Convention – Convention on Long-range Transboundary Air Pollution (UNECE, 1979), the specific legislation led to reductions in emissions of heavy metals across Europe from 1990 levels. Between 2005 and 2019, emissions have continued to decline with Pb emissions decreasing by 44%, mercury (Hg) emissions by 45%, and Cd emissions by 33% across the EU-27 Member States. The 2030 Agenda for Sustainable Development (UNEP, 2016) is expected to strongly influence future policies and strategies and to ensure that the control of water pollution is elevated in international and national priorities. The wetlands filter nutrients from ground- and surface water that flows through them. Mineralisation of drained organic soils and excess use of fertilisers lead to pollution of adjacent surface waters like streams, rivers, lakes, groundwater, and sea with nutrients and pollutants. Wetland buffer zones are important for nutrients retention and cleaner waters. Buffer zones could be considered as effective barriers for diffuse nutrient pollution from agriculture and ought to be recognised for pollution management.

Recently, the item of wetland buffer zone has emerged as integrated development approach to nature conservation including water and buffer zone pollution by Pb. Lead is a toxic environmental contaminant, which enters water bodies from natural and anthropogenic activities. According to the European Chemicals Agency (ECHA, 2018), one of the main Pb sources among other potential sources of Pb exposure is Pb ammunition. ECHA concluded that expenditures related to limitation of the use of ammunitions over 20 years would reach 12 billion euros. Until today, it is unknown how many Pb is presented in wetland buffer zones excluding few small studies of the certain waterbodies.

The objective of the study was to determine Pb content in the aboveground biomass of vegetation collected from the reference sites in the buffer zones of wetlands in Lithuania.

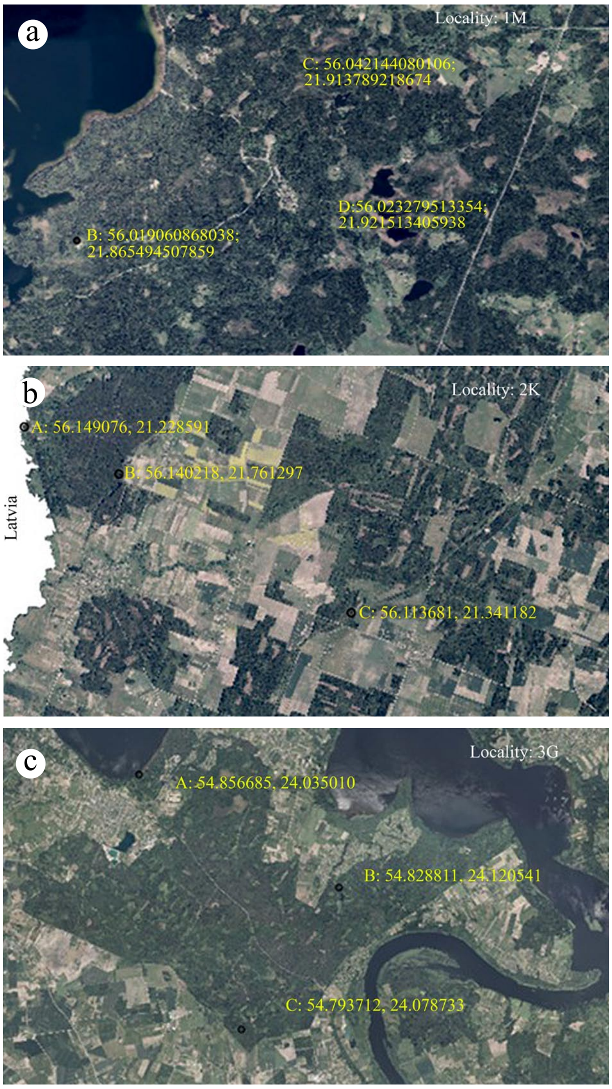
Material and methods

Study area. The experiment was conducted in three localities of the different wetland buffer zones: drying ditches, streams, lakes, fens, mires, bogs, wet forests, and peatlands, of Lithuania (Figure 1). Each experimental area was marked as 1M, 2K, and 3G (Figure 2). The sampling sites (n = 9) were established in each locality within transect of each buffer zone (i.e., an area of vegetation, which usually begins from the boundary of wetland dependent vegetation and extends outward, ending at the interface with another land use) with a width of 50 m.



1M – Northwestern part of Lithuania in the territory of the Žemaitija National Park; 2K – northern part of the Žemaitija Upland at the border of Latvia; 3G – Central Lithuania, the vicinity of the largest artificial waterbody – Kauno Marios and the Nemunas River

Figure 1. The experimental areas



1M: B – near the stream, D – drying ditch, C – natural pond surrounded by grasslands and forest stands (a); 2K: A – buffer zone of the drying ditch, B – stream, C – natural pond surrounded by arable land, meadows, and forest (b); 3G: A – stream flowing into the Kauno Marios, B – pond and stream intensively used for waterfowl hunting, C – drying ditch surrounded by grasslands and forests (c)

Figure 2. Localities of sampling points in the wetland buffer zones in Lithuania

The 1st experimental area (1M) is in the Northwestern part of Lithuania in the territory of the Žemaitija National Park. The total area of the model territory is 5,646 ha including 2,423.5 ha of forest, 717 ha of grassland, arable land, and shrubs, 120.4 ha of water bodies and 2,385.1 ha of protected area where human activities are limited or restricted. The mixed spruce-deciduous forests of the Žemaitija Upland prevail. The dominant forest species is Norway spruce (*Picea abies* (L.) H. Karst.). The mean annual temperature is +6.5°C, the long-term annual rate of precipitation 1.012 mm, and the growing season is 202 days. According to the Lithuanian classification (LRAM/VMT, 2009), the dominant forest soil site is sandy loam mesotrophic mineral soil of normal moisture (Ncl), and the forest type is *Oxalidosa*. The growing stock volume of 1st layer is 220 m^3, and the average stand stocking level is 0.7. Each buffer zone had 5 sampling points. The sample sites were established in the buffer zone of the drying ditch (D, 1–5 sample points), stream (B, 1–5 sample points), and the natural pond surrounded by grasslands and forest stands (C, 1–5 sample points).

The 2nd experimental area (2K) is in the northern part of the Žemaitija Upland at the border of Latvia. The local climate is affected by landscape and the nearness (18 km) of the Baltic Sea. The long-term annual precipitation is 897 mm, and during the growing season 642 mm; the mean annual temperature is +5.4°C, the mean temperature in the growing season +16.7°C, the mean temperature in January −3.5°C. The long-term period of stable snow cover is 90 days. The length of growing period is 202 days. The dominant soil group is *Arenosol* (Buivydaitė et al., 2001; WRB, 2014), the forest site is sandy loam mineral oligotrophic soils (Nbl) of normal moisture, and the dominant forest type is *Vaccinio-myrtillo Pinetum*. In the forest, the dominant tree species is Scots pine (*Pinus sylvestris* L.). The growing stock volume of 1st layer is 189 m^3 ha^{-1}, and the average stand stocking level is 0.7. The sample sites were established in the buffer zone of the drying ditch (A, 1–5 sample points), stream (B, 1–5 sample points), and the natural pond surrounded by arable land and meadows, and forest (C, 1–5 sample points).

The 3rd experimental area (3G) is in the Central Lithuania, in the vicinity of the largest artificial waterbody – Kauno Marios and the Nemunas River. The agricultural area comprises cultivated fields, segetal and ruderal communities. The coldest month is January with an average maximum temperature of −1°C, and the average long-term precipitation is 721 mm. The highest relative humidity is in November (86.28%). The territory is dominated by broad-leaved and mixed pine-spruce forests (73.7%): *Picea abies*, *Pinus sylvestris*, and *Quercus robur*, and Norway spruce forests with a mixture of broad-leaved tree species. The dominant soil site is mineral oligotrophic soils (Nbl) of normal moisture and the dominant forest type is *Vaccinio-myrtillo Pinetum*. The average stand stocking level is 0.7. The sample sites were established in the buffer zone of the stream flowing into the Kauno Marios (A, 1–5 sample points), the pond and stream intensively used for waterfowl hunting (B, 1–5 sample points), and the drying ditch surrounded by grasslands and forests (C, 1–5 sample points).

Sampling procedure. In all three experimental areas, the vegetation samples were collected along a longitudinal grid developed along permanent plant sampling transects at 10 m interval (at 10, 20, 30, 40, and 50 m). Considering seasonal food preferences of beaver, edible vegetation parts as leaves, needles, shoots, and bark were collected. The collected vegetation species were willows (*Salix* spp.), aspen (*Populus tremula* L.), alder buckthorn (*Frangula alnus* Mill.), common oak (*Quercus robur* L.), small-leaved linden (*Tilia cordata* Mill.), Norway maple (*Acer platanoides* L.), European spruce (*Picea abies* (L. H. Karst.), alder (*Alnus* spp.), and grasses: bent grass (*Agrostis* spp.), common yarrow (*Achillea millefolium* L.), etc. About 200–300 g of vegetation biomass at the selected site was sampled and mixed by hand. The samples were stored in the marked bags and transported to the laboratory.

Sample preparation and analysis. All samples of plant biomass were dried at 65°C for 24 h to a constant weight. The dried mass was crushed in a Foss Tecator 1093 Cyclotec Sample Mill (Foss, Denmark). For the lead (Pb) content determination, samples were prepared as follows: wet mineralization with 50% nitric acid (HNO_3) with hydrogen peroxide (H_2O_2) and heating in a Foss KelROS Digestor (Foss) or OPSIS LiquidLINE (OPSIS AB, Sweden). The concentration of Pb in the working solutions was determined by the atomic absorption method on an Atomic Absorption Spectrometer AAnalyst 200 (PerkinElmer Inc., USA) at a wavelength of 283.0 nm.

Statistical analysis was conducted using packages from the software IBM SPSS Statistics, version 25 (IBM Corp., USA). Significant differences were calculated using the three-way analysis of variation (ANOVA) (Tukey's HSD test). The relationships were calculated using a regression analysis, the data were significant at $P \leq 0.01$ and $P \leq 0.001$.

Results and discussion

Contamination of soil and water by various heavy metals such as lead (Pb), silver (Ag), cadmium (Cd), and others is increasing day by day as a result of different human activities, like industrialisation and urbanisation. Lead is an example of potential heavy metal that is neither essential element nor has any role in the process of cell metabolism but is easily absorbed and accumulated in different parts of a plant (Nas, Ali, 2018). Figure 3 shows the distribution density of the values of all measurements of Pb for all three experimental areas. Thus, the largest part of Pb values falls within a range of 2.7–5.1 mg kg^{-1} and amounts to 2.4 mg kg^{-1}. However, the results of basic statistical calculations demonstrate that the interquartile range is only 1.79 mg kg^{-1} (Table 1).

As shown in Table 1, the content of Pb in the plants in all experimental areas did not exceed 6.84 mg kg^{-1} DW (dry weight), and its minimum content was less than 1 mg kg^{-1} (0.95 mg kg^{-1}), while the range values were 5.89 mg kg^{-1}. This corresponds to the natural level of Pb content in the plants of uncontaminated areas of 0.1–10.0 mg kg^{-1} DW at an average concentration of 2 mg kg^{-1} (Кабата-Пендиас, Пендиас, 1989; Семёнова, 2020). Indeed, the content of Pb in the plants growing in the areas contaminated by industrial waste and transport exceeds the background value for uncontaminated areas by several times – 39.1 mg kg^{-1} (Nevedrov et al., 2019) and 39.2 mg kg^{-1} (Szwalec et al., 2018), and even

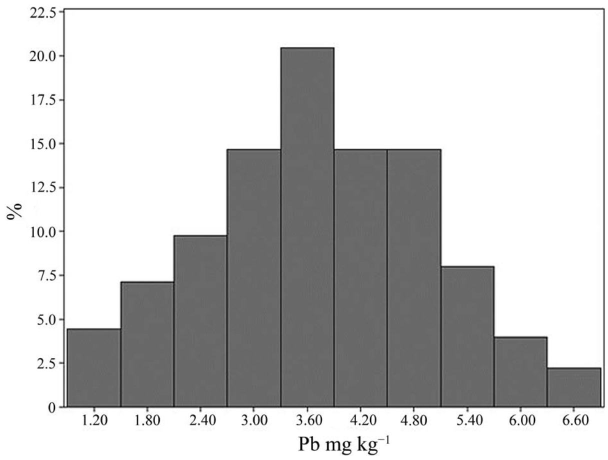


Figure 3. The distribution density of the content of lead (Pb) measurements in three experimental areas

ten times – 500 mg kg^{-1} (Pietrzykowski et al., 2018). Lithuanian researchers (Baltrėnaitė et al., 2010) have shown that the content of Pb in pine wood in the country does not exceed 0.05–2.80 mg kg^{-1}. The majority of Pb in tree wood comes from atmospheric pollution either directly through aerial interception or indirectly through the uptake of highly Pb-contaminated soil (Bindled et al., 2004; Baltrėnaitė et al., 2010). Soil scientists have been studying soil pollution with heavy metals from vehicle exhaust gases and found that such soils contain 504.40–819.60 mg kg^{-1} Pb (Motuzas et al., 2016).

The influence of three factors (locality, surface water source type near the buffer zone, and measurement interval) was studied using the three-way ANOVA (Table 2), which showed that significant results (P < 0.05 and P < 0.01) were available for the values of each individual factor and all their combinations.

Table 1. Minimum, maximum, and average lead (Pb) content in three experimental areas

Min	Max	Mean	Median	Mode	SD	Variance	Range	Interquartile range
					mg kg^{-1}			
0.95	6.84	3.73	3.75	1.64	1.26	1.58	5.89	1.79

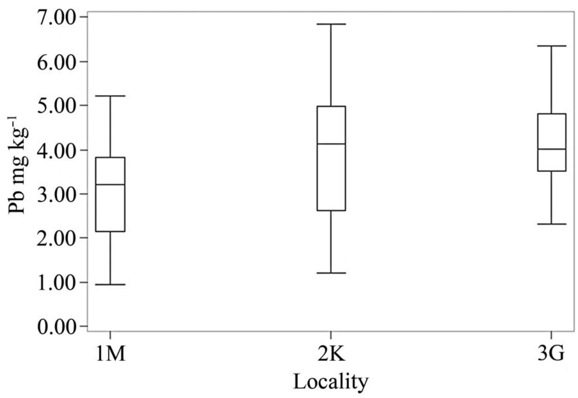
SD – standard deviation

Table 2. Statistical significance of three factors: locality (A), surface water source type near buffer zone (B), and measurement interval (C)

	DF	*F*-act.	*P*
Total	224		
Replication	4		
Treatments	44	39.41	**
Factor A (locality)	2	140.84	*
Factor B (surface water source type)	2	6.93	**
Factor C (measurement interval)	4	61.22	**
A × B	4	8.08	**
A × C	8	22.11	**
B × C	8	36.82	**
A × B × C	16	43.11	**
Error	176		

DF – degree of freedom; *, ** – significant at $P \leq 0.05$ and $P \leq 0.01$, respectively

The dependence of the Pb content in plant biomass on the geographic localities of buffer zones is shown in Figure 4.



1M – Northwestern part of Lithuania in the territory of the Žemaitija National Park; 2K – northern part of the Žemaitija Upland at the border of Latvia; 3G – Central Lithuania, in the vicinity of the largest artificial waterbody Kauno Marios and the Nemunas River

Figure 4. Distribution of lead (Pb), limit values, and medians in three experimental areas

The largest range of values (1.20–6.84 mg kg^{-1}) falls on the buffer zone 2K – the northern part of the Žemaitija Upland; it was recorded that the highest Pb content of all measurements is 6.84 mg kg^{-1}.

Later, the influence of different surface water sources on the Pb content was analysed. It was found that the highest lead content (6.84 mg kg^{-1}) of all measurements was recorded near a natural pond – the Šventoji River (Figure 5).

The final analysis showed the Pb content in plants collected in different transections (Figure 6).

The minimum Pb value of 0.95 mg kg^{-1} was recorded in the northwest part of the Žemaitija National Park (1M) (Figure 4) – 40 m (Figure 6) from the stream (Figure 5). However, the minimum values up to 1.5 mg kg^{-1} are typical of all buffer zones (Figure 5) at 10 and 40–50 m from the surface water source (Figure 6) of the Northwestern region on the border with Latvia (1M) and the northern region of the Žemaitija Upland (2K) of Lithuania (Figure 4). In its central part near Kaunas (3D), most of the values were in a range of 3.5–4.8 mg kg^{-1}. Perhaps such values arose because of anthropogenic and technogenic pressure in this territory.

As shown in Figure 5, in the buffer zone of the dried ditch of all observation regions, the Pb content was

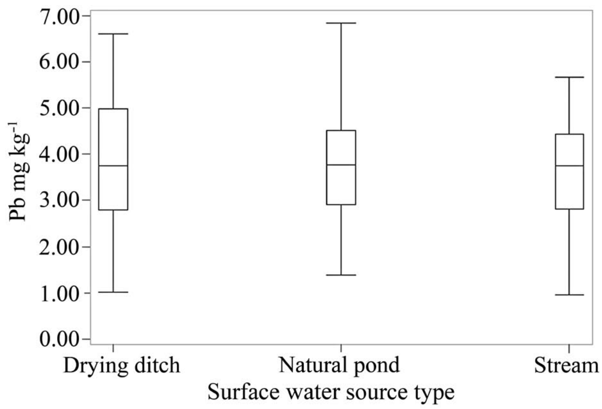


Figure 5. Distribution of lead (Pb), limit values, and medians of the surface water source type near the buffer zone

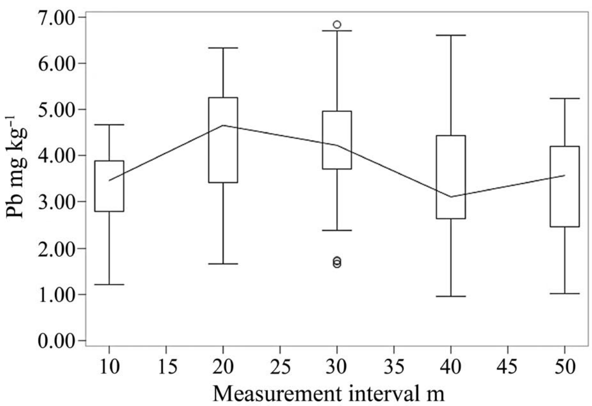


Figure 6. Distribution of lead (Pb), limit values, and the line between the medians points in the intervals of transect: 10, 20, 30, 40, and 50 m

2.78–4.98 mg kg^{-1}, and the median was 3.75 mg kg^{-1}. The same values of Pb were near the stream, but the range of values was already 2.82–4.43 mg kg^{-1}. The median is slightly higher in the buffer zone of natural pond – 3.76 mg kg^{-1}. This value of the median is more than 1.5 times higher than the previously indicated value of uncontaminated territories – 2 mg kg^{-1} (Семёнова, 2020). This may indicate a fluctuating exposure to a source of Pb pollution or its point locality. Registration buffer zone associations were significant ($P \leq 0.01$). Significance ($P < 0.001$) was also shown by the factor C – the interval of the sampling transects from the surface water source. Thus, Figure 6 shows that at 20–30 m from the surface water source the average content was higher (medians 4.66–4.22 mg kg^{-1}, respectively) than at points 10, 40, and 50 m (medians 3.46, 3.10, and 3.57 mg kg^{-1}, respectively). Thus, at a distance of 20–30 m from the source, the Pb content in plants increased by 1.5–1.3 times, respectively.

In the future, perhaps it might be worth to investigate the difference in the content of Pb in plants of buffer zone lands of other use.

Conclusions

1. The content of lead (Pb) in plant biomass in three regions of Lithuania: in the Northwestern part of Lithuania in the territory of the Žemaitija National Park, in the northern part of the Žemaitija Upland at the border of Latvia, and in the Central Lithuania, in the vicinity of the largest artificial waterbody – Kauno Marios and the Nemunas River, was equal to 0.95–6.84 mg kg^{-1} and corresponded to the background content of uncontaminated sites.

2. The average content of Pb in the plant biomass in buffer zones of various types (drying ditch, natural pond, and stream) was 3.75–3.76 mg kg^{-1}.

3. The content of Pb in plants at 20–30 m from the water source increased by 1.3–1.5 times, and then at 40 m it decreased by the same indicator.

Further studies should demonstrate the relationship between the Pb content in surface water bodies and buffer zones to determine their impact on agricultural land.

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Švino koncentracija Lietuvos Šiaurės Vakarų ir Vidurio regionų paviršinių vandens telkinių buferinėse zonose

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Santrauka

Švinas (Pb) yra sunkusis metalas, sukeliantis rimtus žmonių ir kitų organizmų sutrikimus. Pastaruoju metu įgyvendinant integruotas gamtos apsaugos plėtros priemones, iš jų vandens ir buferinės zonos taršą Pb, iškilo pelkių buferinės zonos aktualumas. Lietuvos šlapynėse pagrindinis Pb taršos šaltinis yra jo akumuliacija dėl medžioklėje naudojamų šaudmenų, antropogeninės veiklos ir natūralių procesų. Augalai geba kaupti Pb, todėl jie priskiriami vienoms geriausių bioindikacijos priemonių. Tyrimo tikslas – nustatyti Pb kiekį augmenijoje, surinktoje iš etaloninių vietų šlapynių buferinėse zonose. Tyrimas atliktas trijose skirtingų šlapynių buferinių zonų vietovėse Lietuvoje: Šiaurės Vakarų, Šiaurinės Žemaitijos aukštumos ir centrinės dalies. Tyrimo metu švino kiekis tirpaluose buvo nustatytas atominės absorbcijos metodu atominės absorbcijos spektrometru, bangos ilgis 283,0 nm. Reikšmingi skirtumai buvo nustatyti taikant trijų veiksnių ANOVA (*Tukey HSD* testą). Regresinės analizės metodu buvo nustatyta, kad duomenys reikšmingi, kai $P \leq 0{,}01$ ir $P \leq 0{,}001$. Tyrimo duomenimis, Pb kiekis atitinka foninį kiekį neužterštose vietose, kurių ribos nurodomos kitose šalyse, ir yra lygus 0,95–6,84 mg kg^{-1}. Vidutinis Pb kiekis įvairių tipų buferinėse zonose (nusausinimo grioviuose, šaltiniuose ir upeliuose) yra 3,75–3,76 mg kg^{-1}. Švino kiekis augaluose 20–30 m atstumu nuo šlapynės padidėja 1,3–1,5 karto, o už 40 m tiek pat sumažėja.

Reikšminiai žodžiai: švinas, augmenija, šlapynės, buferinė zona, atominės absorbcijos spektrometrija.