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Assessment of Present-Day Heavy Metals Pollution and Factors Controlling Surface Water Chemistry of Three Western Siberian Sphagnum-Dominated Raised Bogs

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Abstract: This study investigated the heavy metal concentrations in bog and stream water compared to present-day atmospheric deposition, and concentrations in peat and vegetation within three typical raised bogs in Western Siberia located in urban area, close to oil and gas facilities and in the natural background area. Our data showed that elevated heavy metals deposition occurs not only near industrial centres but also in remote areas, which is a sign of regional atmospheric deposition of heavy metals associated with long-range transport and wildfires. Present-day atmospheric depositions of heavy metals are not always consistent with their contents in waters, and the content of Zn, Pb, Cu and Cd in waters is more correlated with their concentrations in vegetation and in the upper peat layer; this indicates a significant role of biological processes in heavy metal cycling. Temperature plays an important role in increasing the mobility and vegetation uptake of heavy metals. Heavy metals removal is largely determined by the size of the bog and its stage of development, which determines bog–river interaction. The seasonal catchment-scale budget indicated that 80–97% of Zn and Pb and 47–74% of Cu and Cd from atmospheric inputs remained within the catchments.

Keywords: raised bogs; heavy metal cycling; sources of pollution; long-range transport; retention; temporal dynamics

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1. Introduction

The development of industry over the past 100–150 years has led to the active migration of a number of trace elements, extreme concentrations of which can have toxic or harmful effects on human health [1]. Mires are characterised by a high sorption capacity with respect to heavy metals; they are able to accumulate many pollutants in peat deposits [2,3]. It should be noted that most research has been devoted to the deposition of pollutants near emission sources, although it has been shown that heavy metal pollution may be associated with long-range transport [4–8]. Most studies are based on the assumption that the content of heavy metals in a peat deposit is stable over time and reflects only atmospheric deposition. However, [9] noted that the content of heavy metals can change during peat accumulation and is controlled by meteorological and hydrological conditions, as well as the biological activity of plants, which in turn is determined by the size of the bog [10,11]. Hansson et al. [12] showed that there is also a downwash of atmospherically deposited trace metals in peat during storm events.

According to some authors, climate change means there will be an increase in carbon release and export of stored contaminants to headwaters [13–17]. As pointed out in [18], leaching elements from peat depend on precipitation chemistry and water table level dynamics. Metal content in water within mires characterises different seasonal dynamics and also depends on acidity and redox potential [19]. Trace element release from solid peat within disturbed areas depends on the concentration of atmospherically derived sulphur [20]. Mechanisms to immobilise heavy metals in peat deposits have also been revealed, as a result of microbial sulphate reduction [21].

The excessive atmospheric deposition of Zn, Pb, Cu and Cd leads to a transformation of biogeochemical cycles of elements in ecosystems [18,20]. An intensive deposition of heavy metals also leads to their accumulation in vegetation and even to changes in plant communities [22], and plant litter decomposition is an important pathway of heavy metal cycling in ecosystems [23]. Cycling of heavy metals within mires is complex because many factors can influence metal behavior, including biotic and abiotic chemical processes, hydrology, climate, and the properties of metals themselves [23]. In this way, a question arises of whether mires will be a source of heavy metals, and under what conditions. Understanding this issue is especially important when restoring mires. Studies [24] have shown that restoration of a small part of forestry-drained peatland catchments for use as wetland buffer areas induced considerable increases in nutrient, carbon, and heavy metal exports.

The aim of this study was to investigate heavy metal concentrations in mire pore-water and streams in relation to present-day atmospheric deposition and concentrations in peat and vegetation in background areas and close to urban sites and oil and gas facilities. With these objectives in mind, we set out to answer the following questions. (1) What are the levels of present-day atmospheric depositions of heavy metals in the south-east of Western Siberia near and far from the main sources of pollution? (2) Are the concentrations of heavy metals in bog and stream waters the result of present-day atmospheric deposition of heavy metals, or are they related to heavy metals removal due to peat and litter decomposition? (3) What are the main factors controlling the pathway of heavy metal cycling in peat–vegetation–water systems and their retention within bogs?

2. Materials and Methods

2.1. Study Area

The study area is located within the southeast West Siberian Plain—an alluvial plain formed as a result of extensive meandering of large rivers (Figure 1). The territory is located in the southeast of the West Siberian Epipalaeozoic plate, which is part of the European plate [25,26]. The climate is continental with long, cold winters and short, hot summers; the average temperature ranges from −0.91 °C to +1.22 °C. The annual precipitation varies from south to north, from 416 to 719 mm. Average annual evapotranspiration reaches 332 mm [26]. Ombrotrophic and transitional mires dominate in the southeast of Western Siberia [27]. The study sites are located in a zone with no deep-lying relic permafrost rocks, where cryogenic processes are only seasonal and where the depth of seasonal soil freezing varies from 0.3 to 1.2 m. Atmospheric circulation is characterized by the predominance of the western transport of air masses, intense air-mass transformation, and interlatitudinal air transport due to the flat relief and openness of the territory from north and south.

In 2016–2020, the study was conducted within three typical Western Siberian pine–dwarf shrub–sphagnum raised bogs in the pristine north-eastern part of the Great Vasyugan Mire (GVM; 56°58′24.3″ N, 82°36′41.2″ E), within the Samus bog (SB, 56°45′49.4″ N, 84°46′17.3″ E) and the Bolshoe bog (BB, 58°47′51.7″ N, 81°11′50.8″ E). The largest area is dominated by *Pinus silvestris*, *Ledum palustre*, *Chamaedaphne calyculata*, *Andromeda polifolia* and *Sphagnum fuscum*. The depth of peat deposits varied from 2.5 to 3 m.

Three monitoring sites were organised to study the atmospheric deposition of heavy metals and to sample water, peat and vegetation, taking into account the prevailing wind directions (Figure 1) within the zones with the greatest industrial and infrastructure development in the south, near the Tomsk-Seversk urban agglomeration (Samus Bog); in the north, in the zone of the greatest accumulation of oil and gas facilities (Bolshoe Bog); and in the background area (Great Vasyugan Mire), at a distance of about 200 km from the main stationary sources of heavy metals.

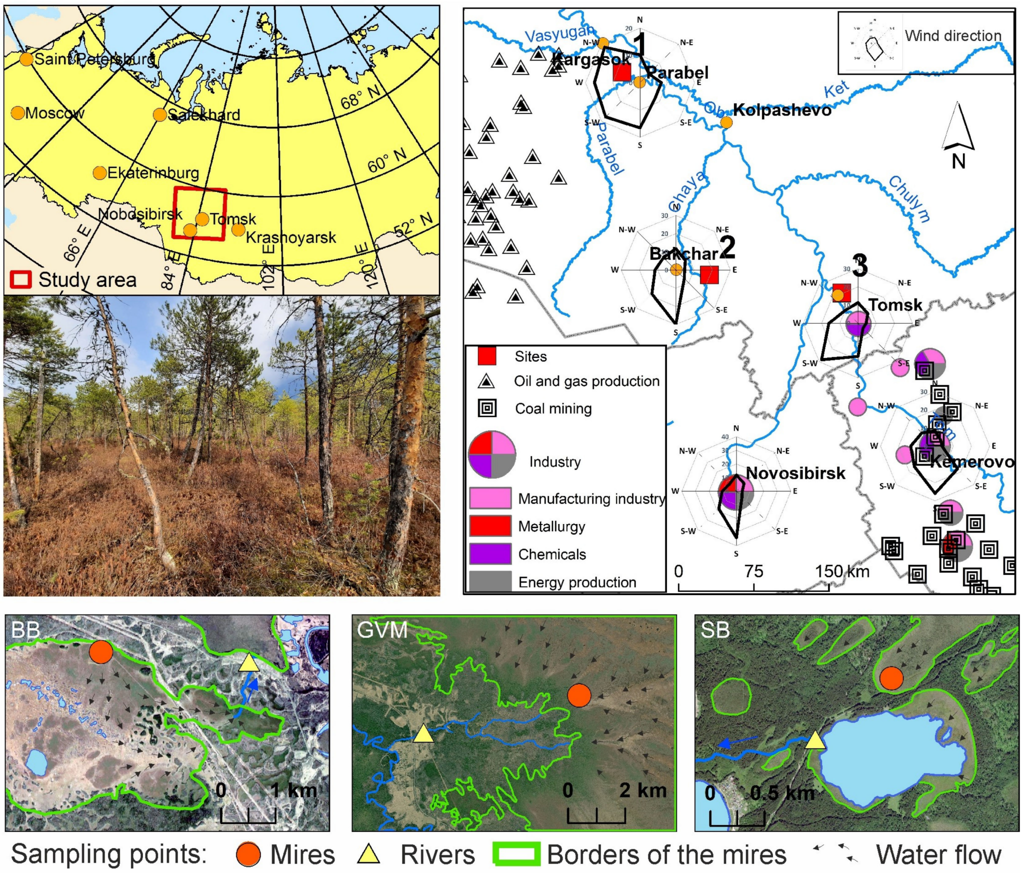

Figure 1. Location of the studied raised bogs in the south-eastern part of Western Siberia (1–BB, 2–GVM, 3–SB).

The site within the Great Vasyugan Mire was located at a distance of about 6 km from Polynyanka, a small village (population ~30 people) in the Tomsk region of Russia. The GVM study site was located within the basin of the small Klyuch River (F = 76 km^2) [28] and is part of a huge mire system with a total area of about 55,051 km^2 [29]. It was formed 10 thousand years ago, when a few small mires merged. In 2016, there was a wildfire approximately 8 km south from the sampling point within the drained section of the GVM and the adjacent forest. The most intense burning of the site occurred from August to October 2016, when 80% of the area was exposed to fire. The extent of the fire was 5.54 km^2 [30]. In addition, a fire also occurred in the eastern part of the GVM and the adjacent forest in October 2019, 20–27 km from the monitoring sites [31].

The Bolshoe bog (BB) is located 350 km north-west of Tomsk, 60 km east of the Ust-Silginsky gas condensate field in the village of Bolshaya Griva and 36 km south of Bondarka, where a refinery (an atmospheric distillation unit) owned by Vostokgazprom has been operating since 2003. The Bolshoe Bog is a 61 km^2 raised bog on the terrace of the Ob River [32]. The Samus bog (SB) is located 20 km northeast of Tomsk. The Samus bog (SB) is part of a lacustrine-bog system, 100 km from the Tomsk and 2 km from Samus village, which uses boiler and stove heating. The raised bog area is 0.58 km^2.

2.2. Methods

2.2.1. Atmospheric Deposition and Catchment-Scale Budget

The analysis of Cu, Pb, Zn, and Cd content in atmospheric deposition was carried out through passive sampling of dust sedimentation according to the content of particles per 1 m^2 [33]. The sampling was carried out during a time interval of 6–12 months using a 5 litre plastic dust trap installed at a 2 m height (Figure 2). The sampling was carried out at the same time interval for GVM, BB, SB (Table A1), with the exception of the BB in 2017–2018 and 2020, due to its long distance (400 km from Tomsk) and inaccessibility. The dust collectors were modelled on a design used by the United States Geological Survey for long-term monitoring of dust (suspended particulate matter) deposition in the southwestern United States [34]. Glass beads were placed in the dust trap on a grid fixed at 3–4 cm below the edge. Before installation, the dust collectors were thoroughly rinsed with distilled water. The marbles simulated the effect of a gravelly surface and prevented the dust that had filtered or washed into the bottom of the sampler from being blown away. The deposited particles were removed by rinsing the dust trap and the marbles in distilled water in a plastic bottle. In the laboratory, large organic particles (branches, leaves, needles) were removed, and the sample was filtered through pre-weighed filters, after which the filters were kept in an SH-FU-11MGE muffle furnace (South Korea) at 800 °C for 4 h. The mineral matter was then weighed and analysed for the Zn, Pb, Cu, and Cd content.

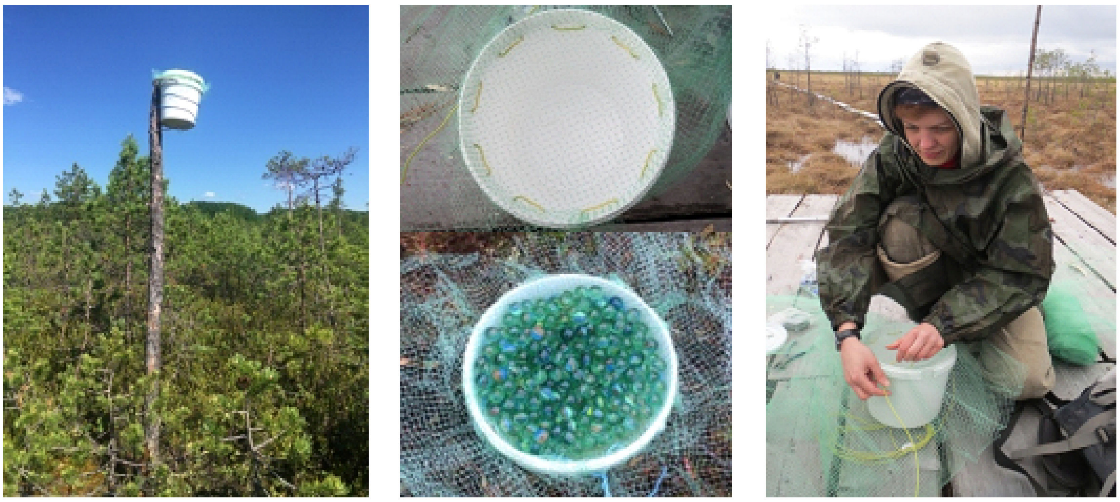

Figure 2. Monitoring of atmospheric dust deposition using the methodology of the US Geological Survey.

The total atmospheric deposition (dry + wet) of Cu, Pb, Zn, and Cd was estimated according to [33]:

$$A = \frac{(K_1\ V + K_2 m)}{tS} \tag{1}$$

where K_1 is the element concentration in the liquid part of the sample (µg/L); K_2 is the element concentration in the solid part of the sample (µg/kg); V is the volume of the liquid part of the sample (L); m is the mass of the solid part of the sample (g); t is the sampler installation period (months); and S is the surface area of the sampler (m^2). To assess the fate and behavior of heavy metals in the sites under study (GVM and SB), the catchment-scale atmospheric input–output budget for April–September 2020 was estimated. Catchment output values (stream discharge values) were calculated from river water concentrations of Cu, Pb, Zn, and Cd, catchment runoff (L/s km^2), the catchment area of the Klyuch River (GVM) and a small stream (SB). River discharge measurements in the closing sections of the catchments were carried out with OTT Hydromet (Germany) (Figure 1).

2.2.2. Water, Peat and Vegetation Sampling

Precipitation sampling was carried out within an area of long-term monitoring sites in the Great Vasyugan Mire (sedge–sphagnum bog 56°58′17.3″ N 82°37′04.5″ E), in the Samus bog (56°45′49.4″ N, 84°46′17.3″ E) and in the Bolshoe bog (58°47′51.7″ N, 81°11′50.8″ E). To take samples of atmospheric precipitation within the bogs, plastic 5 L samplers previously washed with distilled water were installed at a height of 2 m. The samples were taken at intervals of 2–5 days from April to October 2016–2020 during precipitation periods. During long dry periods, the samplers were periodically washed with distilled water. Precipitation samples were also taken in Polynanka village at a distance of 6 km from the bog monitoring point within the GVM. In total, 24 dust deposition and 79 liquid atmospheric precipitation samples were taken. A snow core was also selected for the entire depth in order to analyse the accumulation of Cu, Pb, Zn and Cd.

Water samples were taken from the peat deposits within the GVM, BB, and SB; and from the Klyuch River (56°57′49.1″ N, 82°31′15.4″ E) and headwater streams within BB (58°47′46.6″ N, 81°14′43.6″ E) and SB (56°45′31.8″ N, 84°45′33.4″ E). In dry periods, we took samples from Yakovo Lake, close to the outflow of the river.

Water samples were taken from depths of 30–50 cm in the peat deposits and the river/lake and transferred into glass and plastic bottles. One meter deep wells were drilled in the peat deposits. Before sampling, water was pumped from the water wells to avoid dilution due to atmospheric precipitation. Redox potential (Eh), pH (ORP200, PH200 HM Digital, South Korea) and water temperature (WTW, Oxi 3205, Germany) were measured immediately after sampling. The samples were preserved by adding HNO_3. Before analysis, the samples were stored at a temperature of 4–6 °C and filtered through a filter with pore diameter of 1–2.5 μm. A total of 104 water samples were taken from the bogs. Water level observations were carried out using an autonomous differential pressure sensor [35] in the GVM and in manual mode in the BB and SB areas. The temperature of the peat deposits was measured using DS18B20 sensors [35] installed within the GVM. The measurements were carried out at 4 h intervals in the year-round mode. Air temperature data were obtained from weather stations according to RIHMI-WDC (URL: http://meteo.ru/waisori/select.xhtml (accessed on 19 January 2023)).

Vegetation samples were selected by creating an average sample of 10 or more individuals from the shoots of the current year of each plant species in an area of least 10 m^2. The timing of sampling was determined by taking into account the fact that the maximum accumulation of elements by vegetation takes place in the first half of summer, with a further slight change in their concentrations by autumn [36]. An average peat sample was created from the 0–25 cm upper layer at each site in the bogs, consisting of 10 samples taken from the same location as the vegetation samples [37]. The sampling of vegetation and peat in the root layer was carried out with the aim of registering the influx of heavy metals into water during seasonal peat and litter decomposition. Peat cores were collected manually using a Russian peat borer with a 50 cm sample chamber.

2.2.3. Laboratory and Statistical Analysis

The chemical analysis of the samples was carried out in the analytical laboratory of SibRIAP. Peat and plant samples were preliminarily oven-dried at 105–110 °C (ShSP-0.25-100, Russia) to constant mass and ground to a powdery state in a laboratory mill. To determine the concentrations of Zn, Pb, Cu, and Cd, peat and vegetation samples were digested with an acid mixture of HNO_3 and H_2O_2 and heated in a "Temos-Express" complex at 450 °C for about 1 h following complete mineralization of the residue. The water samples were evaporated to wet salts at 150–200 °C in the "Temos-Express" complex. The residues obtained as a result of the acid decomposition of peat, vegetation, and water samples were subsequently dissolved in HCl and tested using inversion voltammetry (STA, Russia) and inductively coupled plasma mass spectrometry (ICP-MC, ELAN DRC-e № W1520501, USA) at the Plasma Chemical Analytical Centre (Tomsk, Russia). The dissolved organic carbon (DOC) was determined using the H_2SO_4-K_2CrO_7 oxidation method with modification for determination by spectrophotometry (Specol-1300, Analytik Jena, Germany).

Quality assurance and control (QA/QC) procedures were carried out for estimation of Cu, Pb, Zn, and Cd content in water, vegetation, peat and dust samples. Sample analysis was carried out three times. The accuracy of the analysis depending on the concentration of trace elements was set in the range of 15–20%. The reproducibility of the results was assessed periodically by parallel comparative determination of Zn, Pb, Cu, and Cd concentrations in the same samples. The data were statistically analysed using the Pearson coefficient correlation, principal component analysis (PCA) and discriminant analysis.

3. Results

3.1. Atmospheric Deposition

The average atmospheric deposition of Zn was different across all monitoring sites and varied from 0.63 to 1.03 mg/(m^2*month) (Table A1). The highest average rate of Zn bulk deposition was found in the GVM (sedge–sphagnum bog) where it exceeded the values for areas affected by urban agglomeration (SB) and for oil–gas production areas (BB) by 1.6–2 times on average. Our data showed that Zn dust deposition usually decreases in winter. In 2017, bulk deposition of Zn halved in comparison with 2016. The bulk deposition of Zn generally remained constant in the following years, with the exception of 2019.

The average atmospheric deposition of Pb in 2016–2020 varied across all monitoring sites from 0.037 to 0.055 mg/(m^2*month)). The highest average rate of Pb bulk deposition was noted within the GVM and SB, decreasing by about 1.5 times within the BB. In winter, Pb deposition is generally reduced. There was a higher bulk deposition of Pb within the GVM in 2018, 2020 and for BB in 2019. Pb bulk deposition within the SB reached a maximum in 2020.

The average atmospheric deposition of Cu varied from 0.044 to 0.087 mg/(m^2*month). The highest average rate of Cu bulk deposition was found within the GVM and SB. Cu bulk deposition increased in 2017–2019 and decreased slightly in 2020. Studies have shown that Cu dust deposition, similar to Pb and Zn, usually decreases in winter.

Average atmospheric deposition of Cd varied from 0.00040 to 0.00087 mg/(m^2*month). The highest average rate of Cd bulk deposition was found within the GVM and SB, decreasing by 2 times within the BB. Bulk deposition of Cd increased within the GVM in the summer periods of 2019 and 2020, while the values were mostly stable within the SB and BB. As an exception, an increase in bulk deposition of Cd within the SB was observed in the cold winter period of 2018–2019.

3.2. Mire Water Chemistry

Waters of the bogs under study were characterised by low pH and EC values and an increase in pH in the GVM–SB–BB range. SB waters had a pH of 3.65 and the highest EC of 65 µS/cm. GVM waters had a pH of 3.77 and EC of 45 µS/cm (Table A2). Comparable DOC concentrations (55 mg/L) were found in the waters of BB and GVM, and the concentration was twice as high within SB. There were significant variations in Pb, Cu, Zn and Cd concentrations in the waters depending on the season (Figure A1). In general, the GVM was characterised by higher water table levels (WTL), and for the 2016–2020 sampling period, the WTL averaged 14 cm. In the SB, the WTL was 25 cm, and in the BB, it was 19 cm below ground level.

The average Zn content was 16.1 µg/L, increasing 1.5–1.6 times in the BB–GVM–SB series. There was a correlation between Zn and Cd, with the Pearson correlation coefficient of 0.93. Zn concentration in GVM and SB waters reached a maximum (56.6–95 µg/L) in 2017 (the year after the fire).

The average concentration of Pb in the waters of the studied bogs was 1.12 µg/L. The maximum Pb concentrations (4.16–6.95 µg/L) were in BB and GVM waters in 2016 due to a fire. There was a correlation between Pb and Cd, with the Pearson correlation coefficient of 0.77.

The average Cu content in the waters was 2.80 µg/L. Cu content increased 2.0 times in the GVM–BB–SB series. Despite the differences in mean concentrations, the variation within the studied bogs was similar, and Cu content in the waters of all of the studied bogs reached a maximum in the autumn of 2019.

The average Cd content in the waters was 0.064 µg/L. The average content of Cd increased by 1.4–3.6 times in the BB–GVM–SB series, which was consistent with the variation in Zn in the waters of the studied bogs. An increase in the concentration of Cd in the waters was observed in 2019 and 2020.

PCA showed that the Zn, Pb and Cd content in the porewater of the studied bogs in Western Siberia is affected by water temperature, peat deposit temperature, air temperature, and precipitation, and that pH and Eh determine Cu content in the waters (Figure 3).

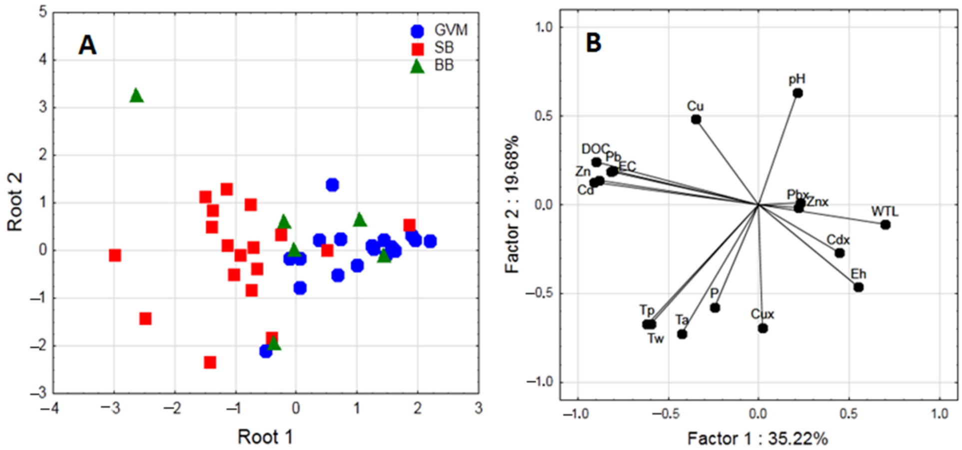

Figure 3. Discriminant analysis (**A**) and PCA (**B**) diagrams of water chemical composition of GVM, BB, SB (Zn, Cu, Pb, Cd content in water, µg/L; Zn_x, Cu_x, Pb_x, Cd_x content in precipitation, µg/L; Ta—air temperature, °C; Tp—peat temperature, mean at 1 m layer, °C; Tw—water temperature, °C; P—month sum of precipitation, mm; WTL—water table level, cm; EC—electrical conductivity, µS/cm; Eh—redox potential, mV; DOC—dissolved organic carbon in waters of bogs, mg/L).

3.3. Stream Water Chemistry

The pH value in the waters of the studied streams varied from 4.61 to 7.75. Stream waters were characterised by an increase in pH in the BB–SB–GVM range. SB stream waters were characterised by the lowest EC of 24 µS/cm, which was probably due to poor rock composition and the predominance of sandy deposits in the area. The Klyuch River and BB stream waters were characterised by a higher EC of 85–124 µS/cm, indicating input from deep mineral groundwater (Table A3). The waters of the studied streams within the GVM and BB had comparable DOC average values (56 mg/L), and there was a 2-fold decrease in DOC within the SB, which indicated a weak connection between the bog and the stream.

The average Zn content in stream waters was 18.8 µg/L, which exceeded the content in waters of bogs by 24%. There was an increase in Zn concentration in stream waters in the series from SB to BB and to the GVM. The highest Zn concentrations in the Klyuch River within the GVM were observed in May 2017 (254 µg/L). In general, 53% of the samples taken in the Klyuch River had higher Zn concentrations than in the GVM. In contrast to the GVM, within SB, higher Zn content in the stream waters compared to the bog was found only in 18% of the samples taken. The maximum concentration in stream waters within SB was also found in May 2017 (31.9 µg/L) (Figure A1). In the stream within the BB, the maximum Zn content was recorded in 2016 (43.1 µg/L). At the same time, the concentration in the river was higher than in the BB in 50% of the samples taken.

The Pb content in stream waters averaged 0.82 µg/L, which was 1.4 times lower than the average concentration in the bogs. An increase in Pb concentrations in the streams was noted in the SB–BB–GVM series. The fluctuation in Pb concentrations in bogs and streams synchronises through the season.

The Pb concentration in the waters of the Klyuch River was on average 1.4 times less than that in the GVM waters, and only in 27% of cases was the concentration in the Klyuch River higher than that in the GVM. The maximum Pb concentration in the waters of the Klyuch River was recorded in August 2019, consistent with an increase in the Pb concentration in GVM waters and atmospheric precipitation. Within the SB, the Pb concentration in stream waters was two times lower than in the waters of the bogs. An increase in the Pb concentration in the stream relative to SB was observed in 18% of the samples taken. The maximum concentration of Pb in the stream waters within SB, similarly to the GVM, was observed in August 2019. High Pb concentrations in the stream were noticed in the BB in 2016 and 2019. On average, the concentration in stream waters was five times higher than that in the BB, and vice versa: there was a higher concentration of Pb in waters of bogs only in 25% of cases (Figure A1).

The average Cu content in stream water was 2.35 μg/L, which was, on average, 17% lower than in the bog area. The Cu concentration in rivers increased in the series from SB to GVM and to BB. In September 2016, an extreme increase in the Cu concentration in the river, of up to 17.5 μg/L, was noticed within the GVM; however, this was not consistent with an increase in Cu concentrations in waters of bogs and atmospheric precipitation, and was probably due to local pollution in dry conditions and low pH. In 57% of cases, the Klyuch River had higher Cu content than the GVM. Within the SB, the Cu content in the stream increased in comparison with the bog in 29% of the samples. The maximum concentration of Cu in the stream (7.57 μg/L) was recorded within the SB in May 2018, which was consistent with the Cu content in atmospheric precipitation. There was higher Cu content in the stream water within the BB than in the bog in 50% of samples. There was synchronicity in the seasonal dynamics of Cu content in bogs and rivers with a slight shift in time, but the correlation coefficient was very low.

The average Cd content in river waters was 0.046 μg/L. An increase in Cd concentration in river waters occurred in the series from SB to GVM and to BB. The Cd content in river waters was below the detection limit in 2016–2017. The maximum Cd content in streams was recorded in 2020, which was consistent with the content in precipitation. The Klyuch River had higher Cd content than the GVM waters in 53% of samples. The Cd content in stream waters was generally lower than that in waters within the SB. The samples collected in May 2018 and April and August 2019 were exceptions because of an increased input with precipitation. There was an increase in Cd concentration in water samples taken in the river within the BB during this period. The analysis showed higher Cd content in the river (1.4–9 times) than in the BB.

PCA analysis showed that water temperature, air temperature, pH and DOC affected Zn, Cu and Cd content in the streams studied in Western Siberia. The content of Zn and Cd in streams correlated well with DOC concentrations, the content of Cd and Zn in precipitation, and Zn in bog water (Figure 4).

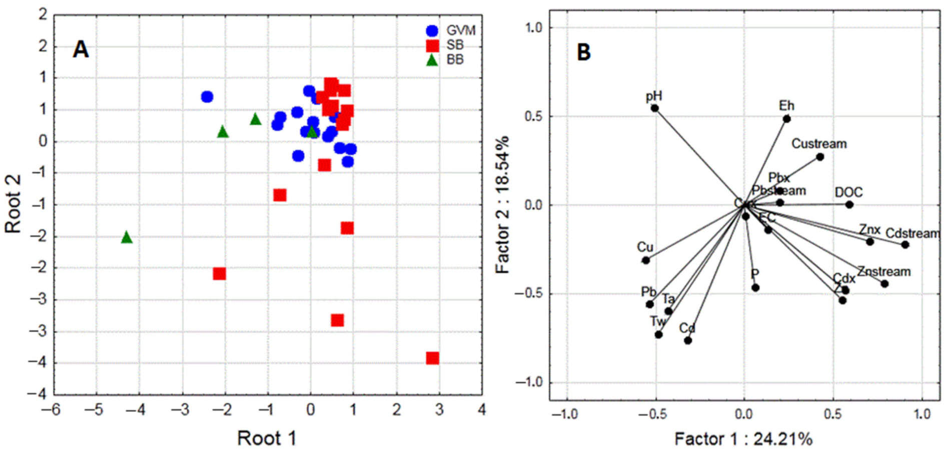

Figure 4. Discriminant analysis (**A**) and PCA (**B**) diagrams of the stream water chemical composition in GVM, BB and SB (Zn_{stream}, Cu_{stream}, Pb_{stream}, Cd_{stream} content in waters of streams, μg/L; Zn, Cu, Pb, Cd content in waters of bogs, μg/L; Zn_x, Cu_x, Pb_x, Cd_x content in precipitation, μg/L; T_a—air temperature, °C; T_p—peat temperature, mean at 1 m layer, °C; T_w—water temperature, °C; P—monthly sum of precipitation, mm; WTL—water table level, cm; EC—electrical conductivity, μS/cm; Eh—redox potential, mV; DOC—dissolved organic carbon in stream water, mg/L).

3.4. Peat and Vegetation Uptake

The content of heavy metals was examined in three plant species—*Pinus sylvestris*, *Chamaedaphne calyculata* and *Sphagnum fuscum*. Zn content in vegetation varied from 9.26 to 135 mg/kg. *Chamaedaphne calyculata* had minimal content. Higher Zn concentrations were characteristic of *Pinus sylvestris* and *Sphagnum fuscum*. The Pb content was 0.51–3.80 mg/kg, rising in the *Chamaedaphne calyculata*–*Pinus sylvestris*–*Sphagnum fuscum* series (Figure A2).

The Cu content in vegetation was 0.04–4.39 mg/kg, with minimum content in *Pinus sylvestris* and increases in *Chamaedaphne calyculata* and *Sphagnum fuscum*. The analysis showed ambiguous trends in the distribution of heavy metals in vegetation and peat in the studied bogs.

The maximum Zn content and increased Pb concentration were noted in the vegetation of the Samus bog near the urban area. The zone affected by oil and gas facilities had maximum concentrations of Pb and Cu in vegetation, with the exception of *Pinus sylvestris*. Surprisingly, the maximum Cd was observed in vegetation samples taken within the GVM. In the other bogs, the Cd content in all species was below the detection limit.

The upper peat layer had the highest Zn content within the SB, and Cu content in peat was minimal in this area. The Pb concentration in peat increased in the range from the GVM to BB and SB. The Cd concentration in peat was the highest in the GVM, and below the detection limit in the BB and SB. The content of heavy metals in vegetation is usually less than in the top layer of peat (0–25 cm); however, the GVM had a greater Zn content increase in *Pinus sylvestris* (1.77 times) than in the upper peat layer. The BB was characterised by increased Cd content in *Sphagnum fuscum* (1.21 times) and Cu in *Chamaedaphne calyculata* (by 1.22 times) and *Sphagnum fuscum* (by 1.80 times) in comparison with peat. An increase was observed within the SB relative to the peat Cd content in *Sphagnum fuscum* (1.22 times) and Cu in *Chamaedaphne calyculata* (2.21 times).

PCA showed that the content of Pb (0.76), Cd (0.69), Zn (0.74), Cu (0.48), DOC (0.89) and EC (0.71) in the waters of bogs directly correlated with concentrations of Pb (0.98) and Zn (0.95) in peat, the content of Pb (0.88) and Zn (0.93) in *Chamaedaphne calyculata*, Cu (0.73) and Zn (0.88) in *Pinus sylvestris*, and Pb (0.87) and Zn (0.95) in *Sphagnum fuscum* (Figure 5).

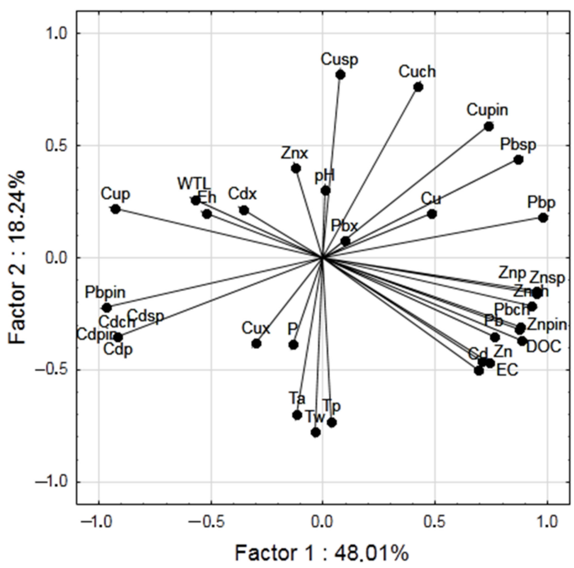

Figure 5. PCA diagram of Pb, Zn, Cu and Cd content in vegetation (Pb, Cu, Zn and Cd content in bog water; Pb_x, Cu_x, Zn_x, Cd_x—Pb, Cu, Zn, Cd content in precipitation; Pb_{ch}, Cu_{ch}, Zn_{ch}, Cd_{ch}—content in *Chamaedaphne calyculata*; Pb_{sp}, Cu_{sp}, Zn_{sp}, Cd_{sp}—content in *Sphagnum fuscum*, Pb_{pin}, Cu_{pin}, Zn_{pin}, Cd_{pin}—content in *Pinus sylvestris*; Pb_p, Cu_p, Zn_p, Cd_p—Pb, Cu, Zn, Cd content in the upper peat layer; WTL—water table level, cm; Ta—air temperature, °C; T_p—peat temperature, mean at 1 m layer, °C; Tw—water temperature of bogs, °C; P—monthly sum of precipitation, mm; EC—electrical conductivity in bog water, µS/cm; Eh—redox potential in bog water, mV).

3.5. Catchment-Scale Budget

The budget indicates that many atmospheric inputs of the heavy metals were retained within the catchments. The relative amount of retention for Zn and Pb was 80–97%. For Cu and Cd, retention was lower: 47–74% (Table A4). Retention values and runoff water output for Zn and Pb were comparable in the studied watersheds, with the greatest differences for Cu and Cd. Runoff water output of Pb was 3–4%, and for Zn, it increased to 16–20% from TD. Runoff water output of Cd and Cu for the GVM was 38% and 26%, respectively, while within the SB, it increased to 48% and 53%. The amount of Zn exported from the bogs under study was the highest, varying from 0.41 to 0.46 mg/m^2. Seasonal stream water flux for Cu was found to be in the range of 0.12–0.21 mg/m^2. The range of seasonal Cd flux in streams at two sites was 0.0023–0.0032 mg/m^2. The runoff transport of Pb was very low: 0.02–0.04 mg/m^2.

4. Discussion

4.1. Regional Sources of Heavy Metals

Western Siberia, a region in the centre of Eurasia, is in the zone of influence of both local sources of heavy metals and long-range transport, which is determined by the peculiarities of atmospheric circulation and the amount of pollutants arriving with latitudinal and meridional transport of air masses. The monitoring of atmospheric deposition showed that there has mainly been a decrease in heavy metal emissions in Europe since the 1980s, due to tight controls and technological innovations [38–40]. Conversely, in Southeast Asia, there has been an increase in anthropogenic emissions and concentrations of heavy metals in the environment [41–43]. Over the past 30–40 years, China has seen active economic growth, and this is consistent with an increase in the concentrations of Pb in peat bog deposits in this country [42]. There are many studies on the accumulation of heavy metals in mires in Europe, Asia and North America, but only a few similar studies for Western Siberia [17,44–48]. The other studies mainly analysed dust deposition in snow and were carried out in the vicinity of industrial centres [49,50].

Analysis of the longitudinal distribution of heavy metals in the bogs of Western Siberia showed that the geochemical background within the study area was very uniform, and there was local industry pollution with heavy metals or long-range, anthropogenically induced transport [17]. In general, the overall flatness of the relief of Western Siberia contributes to a significant transfer of pollutants from north to south and from south to north, which means that the composition of atmospheric deposition varies significantly in time. There are sources of atmospheric deposition of particles in Mongolia and the steppes of Kazakhstan, but also in a number of industrial enterprises in the north and south of Western Siberia [17]. In general, research indicates an increase in the dust-aerosol mass in the air, the volume of which in the troposphere has almost doubled over the past hundred years [51]. Recently the most important sources of heavy metals in the atmosphere within the south-eastern part of Western Siberia have been fires, coal mining, oil and gas production, chemical and petrochemical industries, ferrous and non-ferrous metal smelting and refining, transport, and waste incineration [48,50,52–56]. The latest research suggests that ferrous and non-ferrous metallurgy is a source of Pb, Cu, Zn and Cd in atmospheric pollution [41,57,58]. According to [59,60], potentially toxic metals, notably Cu, Zn, Cd and Pb, have been mobilised in the environment by industrialisation, and especially through high-temperature processes, such as non-ferrous metal smelting and fossil fuel combustion. As noted in [61], the main sources of heavy metals in oil refineries are production processes that release solid particles, adsorbing heavy metals, into the environment. Solid particles are generated by primary oil recovery, fuel burning and oxidation, the elimination of gases by burning and the vacuum distillation of black oil and tar, as well as hydrocleaning, coke firing, fluid catalytic cracking, steam generation for thermoelectric power station generators and welding [61].

The prevailing wind direction in Western Siberia means that pollution from southern industrial centres (Novosibirsk, Kemerovo) is transported northward. The anthropogenic load is unevenly distributed in the Tomsk region. The largest volume of emissions originates from the oil and gas industry in the north and north-western part of Western Siberia (Tomsk region, Tumen region) [53,54], the petrochemical industry and the thermal power plants in the south (Tomsk and Seversk) [48,55]. The south-eastern part of Tomsk region is the most urbanised, because Tomsk city, with more than half of the region's population and large industrial enterprises, is located there [50]. Our data testify to an increase in atmospheric depositions of Pb, Cu, and Cd in the urban area. An increase in Zn in atmospheric depositions has been recorded due to the influence of oil and gas facilities. Surprisingly, higher atmospheric depositions of Zn and Cu, and levels of Pb and Cd depositions comparable to the amounts in the SB area near the Tomsk urban agglomeration, were noted within the Great Vasyugan Mire. As a rule, atmospheric deposition decreases in winter, although in some years there was an increase in atmospheric depositions of Zn and Cd in winter (mainly within SB), which may be associated with emissions from power plants and stove heating in winter. The high correlation (R = 0.7) between the bulk depositions of Pb and Cd within the GVM and the SB, however, indicates a common regional source of input. The atmospheric deposition data from our monitoring sites in Western Siberia were similar to the average values for Zn, Pb, and Cu observed in northern European countries with developed infrastructure and production [39,62,63]. Comparison with the data for Canada [64] demonstrated a lower atmospheric deposition of Cu and similar deposition of Zn in the bogs under study.

According to our data, the increased Zn, Pb and Cd in atmospheric depositions are also associated with their release into the atmosphere as a result of the 2016 and 2019 wildfires. In August–October 2016, there was a fire in the GVM, located 8–9 km south of the monitoring sites, and this caused increased Zn in dust deposits [30]. In 2017, bulk deposition of Zn halved in comparison with 2016. The bulk deposition of Zn remained generally constant in the following years, with the exception of 2019 due to the impact of wildfires in Eastern Siberia [31]. Cu bulk deposition increased in 2017–2019, decreasing slightly in 2020. The maximum bulk deposition of Pb was noted within the SB in 2020 and may have been related to increased emissions from vehicles as a result of increased recreational use of the territory due to the COVID-19 pandemic. There was an increase in the atmospheric deposition of Cd within the GVM in the summer periods of 2019 and 2020, while the values were mostly stable within the SB and BB. The increased Cd in atmospheric deposition was a result of 2019 wildfires, but also stove heating in nearby villages (SB) and the use of motor gasoline due to the location near roads (BB).

The effects of wildfires in Western Siberia on the increase in heavy metals in atmospheric fallout have been described in many papers. According to [65–67], the emission of heavy metals from wildfires can cause both local and regional air pollution. Pollutants migrate thousands of kilometres in the atmosphere due to the ability of some elements to be transported on submicron aerosols [68]. According to [69], the annual emission of heavy metals as a result of wildfires in Siberia ranges from 1–2 (Hg, Cd, As, Sb) to thousands of tons (Pb, Zn, Mn); Hg, Cd, As, Zn and Mg, and to a lesser extent, Cu and Pb, migrate actively during crown fires.

Our studies showed that the south-eastern part of Western Siberia has heavy metal precipitation not only near industrial centres, but also in remote areas, which is a sign of background heavy metal precipitation, as determined by the patterns of atmospheric circulation in the region.

4.2. Atmospheric Deposition vs. Water Chemistry

Our data showed that the values of present-day atmospheric depositions of heavy metals are not always consistent with their contents in the waters of bogs. The contents are more correlated with their concentrations in vegetation and in the upper layer of peat (0–25 cm); this proves a significant role of biological processes (peat and litter decomposition) in the migration of heavy metals in the peat–vegetation–water system. The maximum concentrations of Zn, Cu, Pb and Cd in water were registered within the Samus bog in the urban area, decreasing within the Great Vasyugan Mire and Bolshoe bog, whereas the GVM had higher atmospheric depositions of heavy metals. There was a closer correlation between the content of heavy metals in stream waters and atmospheric deposition of Zn and Pb in the GVM. The analysis showed higher Zn and Pb content in the waters of the Klyuch River within the background area of the GVM, an increase in Cu and Cd within the oil and gas facilities in the BB area. The concentration of heavy metals was minimal in the waters of the streams within the Samus bog close to Tomsk city. Periodically higher concentrations of Cu, Zn Pb, and Cd were registered in streams, compared to bogs (with the exception of SB). In general, the increase in the content of heavy metals near the urban area is consistent with the data obtained by [45], where the Tomsk urban agglomeration was found to have a significant effect on the accumulation of trace metals in the upper layers of peat, which can affect their content in water.

The average Zn content in the waters of the studied bogs was 16.1 μg/L, which was significantly lower than the measurements obtained in the industrial region of Poland [18] and comparable with the data for Germany [14]. The studied bogs were characterised by an average 1.12 μg/L concentration of Pb in the waters, which was approximately 2–30 times lower than that of bogs in Poland and Germany [14,18]. The average Cu content in waters was 2.80 μg/L, about 10 times lower than the levels obtained in Poland and Germany [14,18]. The average Cd content in waters was 0.064 μg/L, which was 2–20 times less than the levels in Poland and Germany [18]. The Zn content in water in the studied bogs was comparable to measurements in Italy. However, the concentrations of Cu, Pb, and Cd were higher in the bogs of Italy [20].

The average content of Zn, Cu, Cd and Pb in the waters of the studied streams was generally comparable with the data published for Europe [14,16], and on average below the measured levels in Canada [70]. However, periodic extreme increases in Zn concentrations to 254 μg/L, which are a consequence of wildfires in the region, can be compared to the data obtained during a drought in the Copper Cliff Smelter zone [70]. Studies have shown a significant increase in Zn and Pb in GVM river waters in the year following a fire event that occurred 8 km south of the sampling point in 2016. This is because 2016 was characterized by dry conditions and low water levels, which contributed to the prolonged duration of the fire event from August to October 2016 [30]. A periodic increase in the Cu content of up to 17.5 μg/L in the studied streams was also noted in January of 2017, which was also due to the fire event in 2016 and the regional transfer of pollutants from industrial enterprises in the region. Our data showed that the export of heavy metals increases during high-discharge periods, especially after long dry and hot periods, which is consistent with the results obtained by [13]. This issue is especially relevant for the development of mire restoration projects; studies [24] have shown that mire restoration induced considerable increases in nutrient, carbon, and heavy metal exports. According to experimental data [12], there is a downwash of atmospherically deposited trace metals in peat under the influence of atmospheric precipitation. However, there was a difference in the retention of the added dissolved metals in the surface layer (0–2 cm): 21–85% for Pb, 18–63% for Cu, and 10–25% for Zn. In general, our studies have shown an active release of heavy metals from the bog area (GVM and partially BB) and the influx of heavy metals into headwater streams, which is due to a closer connection of the huge mire system (e.g., GVM and BB) with streams compared to small bogs [64,71]. It is necessary to conduct a detailed study of the concentrations of heavy metals and their seasonal dynamics in the waters of small bogs and in headwater streams.

4.3. Atmospheric Deposition vs. Peat and Vegetation Uptake

The content of Zn, Pb, Cu, and Cd in the vegetation of Western Siberian bogs is comparable with and lower than the published data. The content of Zn, Pb and Cu in sphagnum mosses is generally comparable with the data from Germany [72], but Cd had a lower concentration in the Western Siberian bogs under study. Our data showed an ambiguous trend in the distribution of heavy metals in vegetation and in peat. The content of heavy metals in vegetation and peat in the studied areas was not always consistent with the values of present-day atmospheric deposition, since their content in the upper layers of peat and vegetation, as a rule, results from the deposition of heavy metals in earlier periods.

The urban area had the maximum concentration of Zn and an increased concentration of Pb in vegetation, which is consistent with the data on the atmospheric deposition of Pb, but not of Zn. The maximum concentration of Cu in vegetation was noted in the zone of influence of oil and gas facilities. The atmospheric deposition of Cu, conversely, was higher in the GVM and SB areas, and was half as much within the BB. Surprisingly, the maximum Cd was registered in vegetation samples taken within the GVM, although this is consistent with the increased atmospheric deposition of Cd. The increase in heavy metals in bog vegetation in remote areas was associated with the long-range transport of pollution noted in [4,41], or in connection with low pH and, accordingly, with dissolution in water and the availability of heavy metals to vegetation [5,73]. A comparison with the data for *Sphagnum angustifolium* and *Sphagnum squarrosum* [55] showed lower heavy metal content in the bogs we studied, although the Zn content was very close. Similar Cu content in *Chamaedaphne calyculata* was found in [58].

Our research has shown that the content of heavy metals in vegetation is usually less than in the top layer of peat (0–25 cm); however, GVM demonstrated a greater Zn content increase in *Pinus sylvestris* (1.77 times) than in the upper peat layer. There were some differences in the content of heavy metals in peat compared with vegetation. A high Zn and Pb content was noted in the upper layer of peat in the Samus bog, which is located near the city of Tomsk. The maximum concentration of Cu in peat was observed for both the Bolshoe bog near oil and gas facilities and in remote areas at the GVM site, which is located some 200 km away from the main stationary sources of pollution. Cd was found in maximum concentrations in GVM peat. The content of heavy metals in the upper peat layer of the studied bogs was comparable to that in Western Siberia [53] and Estonia, except for Zn [3]. The content of Zn, Cu, Cd and Pb in the peat of the studied bogs was significantly lower than that in industrial regions in Poland [18], near a Cu-Ni smelter and at a background site in Finland [57], in rural and urban sites in Ireland [7], and near the Copper Cliff smelter in Canada [58]. There is comparable data on Zn content in peat within bogs in China [4] and Scotland [74], and the content of other metals is significantly higher.

4.4. Factors Controlling Heavy Metals Content and Release

Our studies have shown that in the south-eastern part of Western Siberia, higher heavy metal deposition is observed not only near industrial centres, but also in remote areas, which allows us to speak of background heavy metal deposition, which is determined by the patterns of atmospheric circulation in the region. Discriminant analysis showed that water chemical composition in bogs and streams is formed under the influence of periodic influx of heavy metals, and wildfires that happened in the region in 2016 and 2019 became important sources of heavy metals in waters. The mobility of heavy metals in the peat surface layer is linked to various factors, such as variation in pH [75], seasonal variations in redox conditions due to water table fluctuations [16,18], vegetation uptake [76], organic matter decay [9], litter decomposition [23] and changes in climate conditions.

Our data have shown significant variations in the levels of Pb, Cu, Zn observed in waters of the studied bogs in Western Siberia, depending on the season of the year, a pattern of concentration increase in the post-drought rewetting period, and are consistent with other findings [18,19,70]. The analysis of our data showed that WTL is in inverse correlation with the content of heavy metals in the waters of the studied bogs as a result of the dilution effect. Cu content in precipitation correlates with Cu concentration in the waters of the studied bogs. The data obtained are consistent with [75], which states that pH and mineralogy were found to affect Cu mobility in peat bogs. The mobility of heavy metals in peat deposits is also determined by a high affinity for binding with DOC [70,77].

Our data showed higher concentrations of Zn and Cd in streams (excluding SB) than in bogs, and elevated Cu and Pb content in the waters of the studied bogs due to their high affinity with DOC.

There is a synchronicity between the seasonal dynamics of Pb, Cu, Zn, and Cd concentrations in bogs and rivers, with a slight time shift. Similarly, there was an increase in Zn, Pb, and Cd content in the post-drought rewetting period [70]. An increase in Zn concentrations in Klyuch River waters was noted in May 2017 after the thawing of peat deposits, which was associated with the deposition of Zn as a result of a fire event in the autumn of 2016 [31].

According to our data, vegetation uptake of heavy metals in the studied bogs of Western Siberia depends on the water level and temperature. There is a direct correlation between Cd and WTL, and an inverse correlation for Zn, Pb and Cu, which characterises the bioaccumulation process while accelerating decomposition processes. Our studies showed a close relationship between Zn, Pb, Cu, and Cd in peat and vegetation, which is consistent with [58]. According to [58], elevated peat metal levels lead to increased metal uptake.

To sum up, our studies have shown that the temperature regime of bogs and the amount of precipitation, which determines the dynamics of WTL, play a leading role in increasing the mobility of heavy metals. The temperature regime changes dramatically with a decrease in WTL under drought conditions [70], and, as a rule, peat deposit temperature increases [78], which results in the acceleration of decomposition processes and an increase in heavy metals content in the waters. Element export patterns are mainly determined by seasonality and hydrologic preconditions, as microbial decomposition processes strongly depend on temperature [14].

The seasonal catchment-scale budget for April–September 2020 within the GVM and SB showed that much of the atmospheric input of heavy metals was retained within the catchments. Relative retention for Zn and Pb was close to the published data [79,80], and lower values were noted for Cu and Cd within SB. Therefore, within the SB, a higher runoff output of Cu and Cd was noted, which is consistent with a decrease in retention. This suggests that the size of the bog and the pathway of heavy metal cycling in the peat–vegetation–water system within bogs is important for considering heavy metal retention. According to [11], a higher peat accumulation rate and dust deposition rates were observed in the more moderately sized Draftinge Mosse compared to the extensive Store Mosse, suggesting that the size of the bog is important in peat palaeodust studies. The paper [11] also noted that the smaller bog responded more rapidly to hydrological changes, indicating that the size of the bog affects the buffering capacity.

A detailed analysis of the data showed that the waters of the small Samus bog had 1.5–2.5 times higher content of heavy metals in comparison with other bogs; conversely, the concentrations in the stream waters were minimal. On the contrary, we found a lower concentration of heavy metals as a result of dilution in the waters of the medium-sized Bolshoe bog and the huge Great Vasyugan Mire, which is associated with a high WTL, whereas in the streams, the concentration of heavy metals was higher. This is because the WTL is lower within small bogs, and heavy metals are, therefore, mainly consumed by vegetation directly from peat, while in a large bog (such as the GVM and BB), the water table level is close to the surface, and the waters have low pH, so that heavy metals are dissolved in the waters and carried out into headwater streams. This suggests that the size of the bog and the pathway of heavy metal cycling in the peat—vegetation—water systems within bogs is important for considering heavy metal content in water.

5. Conclusions

Our studies have shown that in the south-eastern part of Western Siberia, heavy metals deposition is elevated not only near industrial centres but also in remote areas, which is an indication of regional atmospheric deposition of heavy metals associated with long-range transport and wildfires. Surprisingly, atmospheric depositions of Zn and Cu within the Great Vasyugan Mire were higher than in the urban and oil and gas facility areas, and the data on the amount of deposition of Pb and Cd were comparable to those for the urban area. The GVM waters had an average concentration of Zn and Cd comparable to that of the zone with oil and gas facilities, while stream waters had an elevated content of Zn and Pb. The maximum Cd content was noted in vegetation and the upper peat layer of the GVM, and the Cu content was deemed comparable to the data obtained within the oil and gas facilities.

The analysis showed that the values of present-day atmospheric depositions of heavy metals are not always consistent with their contents in waters, and the contents in waters of bogs are more correlated with their concentrations in vegetation and in the upper layer of peat (0–25 cm). This indicates a significant role of biological processes (peat and litter decomposition) in the migration of heavy metals in the peat–vegetation–water system. PCA showed that Zn, Pb and Cd content in the porewater of the studied bogs in Western Siberia is affected by water temperature, peat deposit temperature, air temperature, and precipitation, and that pH and Eh determine Cu content in the waters.

Higher concentrations of Zn were noted in streams (excluding SB) than in bogs; conversely, an increase in the content of Cd, Cu and Pb in waters of bogs was observed due to their high affinity with DOC. There is a direct correlation with the content of Zn in streams and bogs, and the content of Zn and Cd in streams correlates well with Zn and Cd in precipitation. There is a synchronicity between the seasonal dynamics of Zn, Pb, Cu, and Cd concentrations in bogs and streams, with a slight time shift. Similarly, there was an increase in Zn, Pb, and Cd in the post-drought rewetting period. The seasonal catchment-scale budget within the GVM and SB indicated that much of the atmospheric inputs of heavy metals were retained within the catchments. The relative amount of retention within the GVM and SB was 80–97% for Zn and Pb, and 47–74% for Cu and Cd. To sum up, the accumulation of heavy metals in bogs depends on the amount of atmospheric deposition, uptake by vegetation, hydrological conditions and the temperature regime of the peat deposits. Additionally, heavy metals removal is largely determined by the size of the bog and its stage of development, which determines bog–river interaction.

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Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Average monthly atmospheric deposition of Zn, Pb, Cu and Cd in 2016–2020.

<table>
<tr><th>Site</th><th>Type</th><th>Summer 16</th><th>Winter 16–17</th><th>Summer 17</th><th>Winter 17–18</th><th>Summer 18</th><th>Winter 18–19</th><th>Summer 19</th><th>Winter 19–20</th><th>Summer 20</th><th>Mean [2]</th></tr>
<tr><td colspan="12">Zn, mg/(m^{2}month)</td></tr>
<tr><td>GVM</td><td>Background</td><td>3.63</td><td>0.62</td><td>1.89</td><td>0.25</td><td>0.64</td><td>0.21</td><td>1.05</td><td>0.54</td><td>0.47</td><td>1.03</td></tr>
<tr><td>SB</td><td>Urban</td><td>0.20</td><td>0.32</td><td>0.61</td><td>0.26</td><td>0.46</td><td>0.44</td><td>1.16</td><td>0.29</td><td>0.34</td><td>0.45</td></tr>
<tr><td>BB</td><td>Oil-gas facilities</td><td>0.81</td><td>0.50</td><td colspan="2">0.35</td><td colspan="2">0.50</td><td>1.51</td><td>0.12</td><td>-</td><td>0.63</td></tr>
<tr><td colspan="12">Pb, mg/(m^{2}month)</td></tr>
<tr><td>GVM</td><td>Background</td><td>0.053</td><td>0.013</td><td>0.060</td><td>0.028</td><td>0.093</td><td>0.041</td><td>0.050</td><td>0.048</td><td>0.093</td><td>0.053</td></tr>
<tr><td>SB</td><td>Urban</td><td>0.024</td><td>0.006</td><td>0.016</td><td>0.025</td><td>0.071</td><td>0.069</td><td>0.083</td><td>0.045</td><td>0.16</td><td>0.055</td></tr>
<tr><td>BB</td><td>Oil-gas facilities</td><td>0.038</td><td>0.033</td><td colspan="2">0.035</td><td colspan="2">0.033</td><td>0.073</td><td>0.007</td><td>-</td><td>0.037</td></tr>
</table>

Table A1. *Cont.*

Site	Type	Summer 16	Winter 16–17	Summer 17	Winter 17–18	Summer 18	Winter 18–19	Summer 19	Winter 19–20	Summer 20	Mean [2]
					Cu, mg/(m^{2}month)						
GVM	Background	0.065	0.045	0.170	0.051	0.093	0.026	0.162	0.094	0.078	0.087
SB	Urban	0.050	0.019	0.150	0.055	0.068	0.036	0.095	0.058	0.067	0.066
BB	Oil-gas facilities	0.086	0.032	0.041		0.022		0.059	0.023	-	0.044
					Cd, mg/(m^{2}month)						
GVM	Background	0 [1]	0	0	0.0003	0.0008	0.0006	0.0016	0.0005	0.0014	0.00087
SB	Urban	0	0	0	0.0007	0.0009	0.0015	0.0003	0.0009	0.0008	0.00085
BB	Oil-gas facilities	0	0	0		0.0007		0.0004	0.0001	-	0.00040

Note: [1]–average bulk deposition of Cd was not determined due to the content below the instrument detection limit. [2]–determined for the period of data availability.

Table A2. Concentrations of Pb, Cu, Cd, Zn, pH, EC and DOC in the waters of bogs under study (north-eastern part of Great Vasyugan Mire, Samus bog and Bolshoe bog) in 2016–2020, N–number of water samples.

Study Sites	N		Pb	Cd	Cu	Zn	pH	EC, µS/cm	DOC, mg/L
			µg/L						
GVM	30	Mean	0.83	0.046	1.74	14.0	3.77	45	55.2
		Range	0.16–6.95	0.001–0.093	0.27–6.61	3.22–56.6	2.0–4.47	19–78	29.9–72.8
SB	17	Mean	1.34	0.114	3.53	21.0	3.65	65	100.5
		Range	0.39–2.38	0.001–0.22	0.22–6.90	2.69–95.1	2.20–4.37	40–87	58.8–126.9
BB	6	Mean	1.19	0.032	3.14	13.2	3.76	38	55.9
		Range	0.31–4.16	0.022–0.046	0.53–6.84	5.08–41.9	3.22–4.03	23–52	46.0–66.6

Table A3. Stream water concentrations of Pb, Cu, Cd, Zn, pH, EC and DOC (N–number of water samples).

Study Sites	N		Pb	Cd	Cu	Zn	pH	EC, µS/cm	DOC, mg/L
			µg/L						
GVM	30	Mean	0.92	0.043	2.10	27.2	6.64	124	56.0
		Range	0.108–10.5	0.013–0.073	0.029–17.5	2.42–253.7	5.79–7.75	51–423	27.3–85.6
SB	17	Mean	0.62	0.034	1.96	7.06	6.25	24	25.8
		Range	0.052–2.69	0.001–0.12	0.34–7.57	0.61–31.9	5.0–7.63	18–35	14.6–47.5
BB	4	Mean	0.89	0.060	2.98	22.2	5.14	85	56.2
		Range	0.65–1.05	0.047–0.077	1.02–4.24	8.17–43.1	4.61–6.30	33–223	36–80.6

Table A4. Total seasonal input–output budgets, retention of atmospheric inputs and transfer of heavy metals in river catchments within GVM and SB in April–September 2020.

	Zn	Cd	Cu	Pb
Great Vasyugan Mire				
Total deposition (TD) input mg/m^2	2.82	0.0084	0.47	0.56
Runoff water output mg/m^2	0.46	0.0032	0.12	0.02
Output/input (%)	16	38	26	3
Retention (input–output), mg/m^2	2.36	0.0052	0.34	0.54
Retention/TD, %	84	62	74	97
Samus bog				
Total deposition (TD) input mg/m^2	2.04	0.0048	0.40	0.96
Runoff water output mg/m^2	0.41	0.0023	0.21	0.04
Output/input (%)	20	48	53	4
Retention (input–output), mg/m^2	1.63	0.0025	0.19	0.92
Retention/TD, %	80	52	47	96

Appendix B

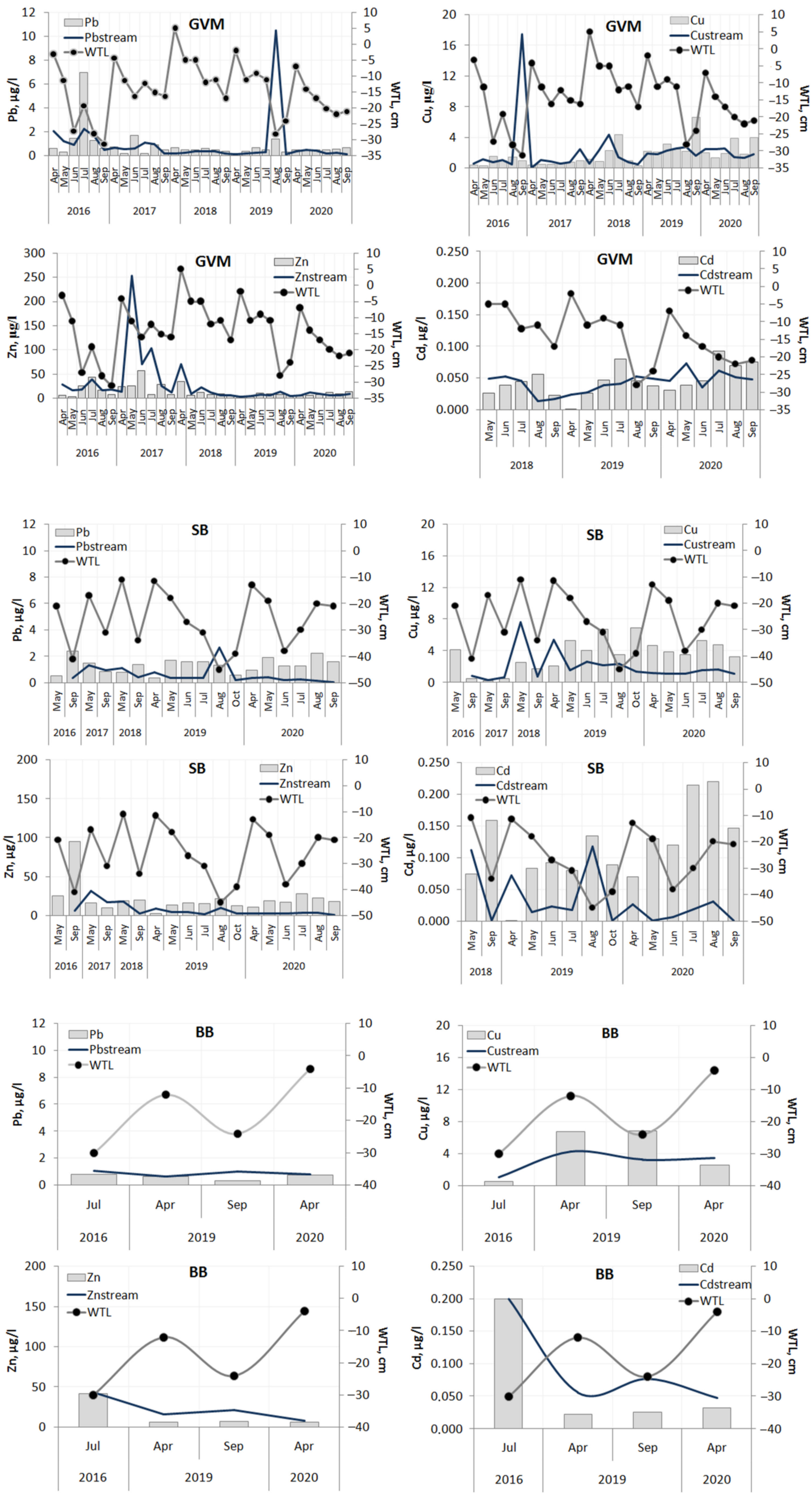

Figure A1. Seasonal variation in Zn, Cu and Pb content in waters and WTL of studied bogs in comparison with streams.

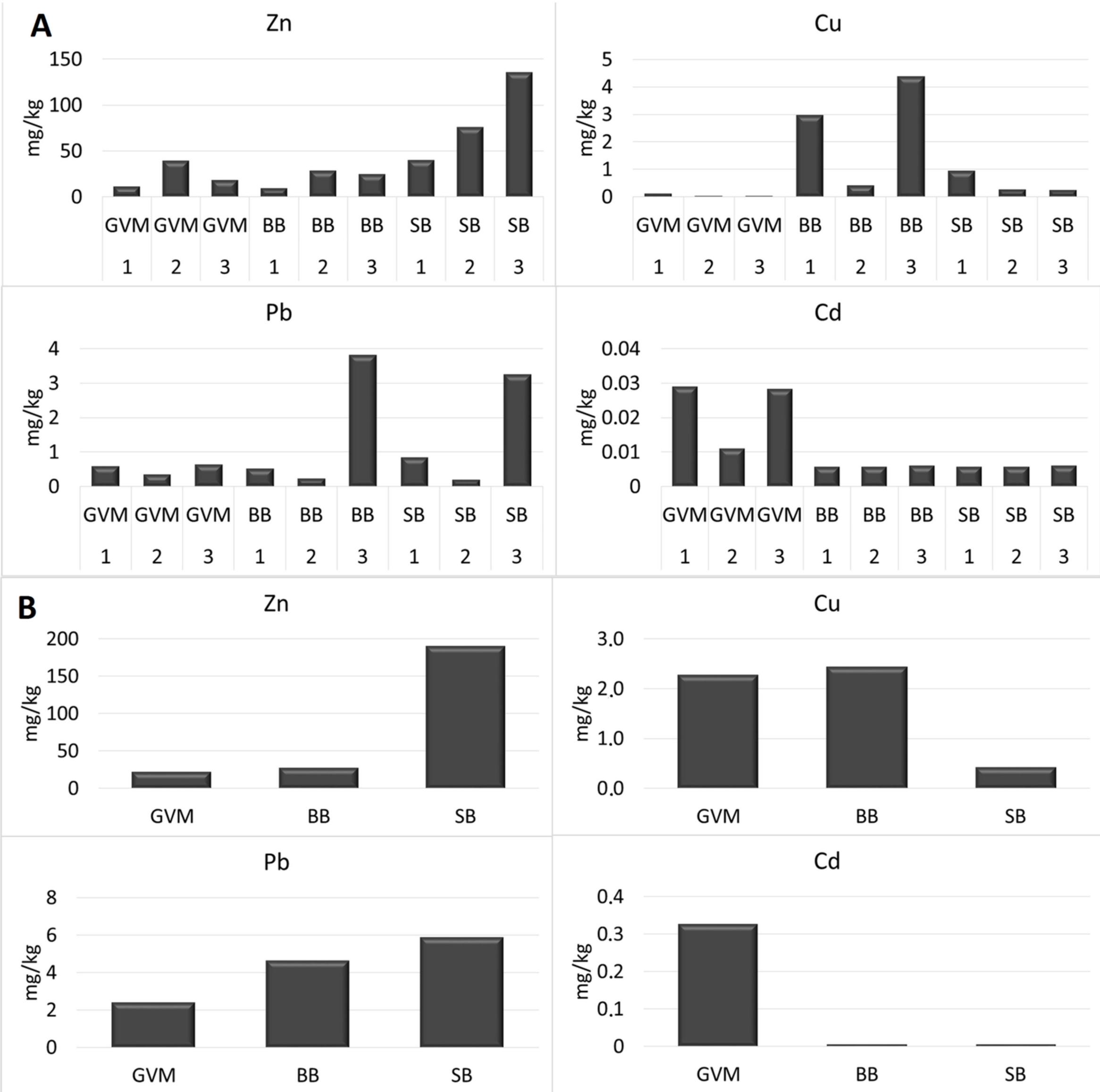

Figure A2. The concentration of Zn, Pb, Cu and Cd in vegetation (**A**) and upper peat layer (**B**). 1—*Chamaedaphne calyculata*, 2—*Pinus sylvestris*, 3—*Sphagnum fuscum*.

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