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Article

Dissolved Metal (Fe, Mn, Zn, Ni, Cu, Co, Cd, Pb) and Metalloid (As, Sb) in Snow Water across a 2800 km Latitudinal Profile of Western Siberia: Impact of Local Pollution and Global Transfer

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Abstract: Snow cover is known to be an efficient and unique natural archive of atmospheric input and an indicator of ecosystem status. In high latitude regions, thawing of snow provides a sizable contribution of dissolved trace metals to the hydrological network. Towards a better understanding of natural and anthropogenic control on heavy metals and metalloid input from the atmosphere to the inland waters of Siberian arctic and subarctic regions, we measured chemical composition of dissolved (<0.22 μm) fractions of snow across a 2800 km south–north gradient in Western Siberia. Iron, Mn, Co, Ni, and Cd demonstrated sizable (by a factor of 4–7) decrease in concentration northward, which can be explained by a decrease in overall population density and the influence of dry aerosol deposition. Many elements (Mn, Ni, Cu, Cd, Pb, As, and Sb) exhibited a prominent local maximum (a factor of 2–3) in the zone of intensive oil and gas extraction (61–62° N latitudinal belt), which can be linked to gas flaring and fly ash deposition. Overall, the snow water chemical composition reflected both local and global (long-range) atmospheric transfer processes. Based on mass balance calculation, we demonstrate that the winter time atmospheric input represents sizable contribution to the riverine export fluxes of dissolved (<0.45 μm) Mn, Co, Zn, Cd, Pb, and Sb during springtime and can appreciably shape the hydrochemical composition of the Ob River main stem and tributaries.

Keywords: snow; heavy metal; trace element; river flux; gas flaring; pollution; Western Siberia



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1. Introduction

Snow cover is known to be an efficient and unique natural archive and indicator of ecosystem status and atmospheric input [1–6]. Snow delivers from the atmosphere to the ground various soluble compounds, including metal pollutants [7,8]. Given its persistence over the frozen period of the year, snow records integral atmospheric input of solutes and delivers invaluable information on both short-range and long-range atmospheric transfer [9–17].

The importance of studying the chemical composition of dissolved (<0.22 μm or 0.45 μm) fraction of the snow water is that the snow input represents a non-negligible source of metal and metalloids in the river water and contributes to trace element delivery from the land to the ocean. Therefore, in order to evaluate the current status and possible future changes in dissolved metal export flux from the land to the ocean, high spatial resolution measurement of snow chemical composition are needed. This is especially true for arctic and subarctic regions, which are subjected to unprecedented changes due to

climate warming and susceptible to strong anthropogenic impact due to their vulnerability and low capacity to recover. According to the Arctic Monitoring and Assessment Programme [18], anthropogenic emissions are responsible for more than 50% of the total trace metal content in Arctic soils. For example, the Monchegorsk and Norilsk smelters affect the environment across several thousands of kilometers [19–22]. Among all Arctic regions, Western Siberia offers a unique possibility of performing large-scale spatial sampling due to its well-developed road infrastructure, linked to substantial oil and gas exploration activity. On the one hand, the Western Siberian Lowland (WSL), notably its northern part, is relatively weakly affected by human and heavy industrial activity (large towns, smelters, ore processing plants, forestry, and paper industry), compared with Northern Europe or NW European Russia. On the other hand, hydrocarbon extraction industry, notably accompanied by gas flaring, is capable of delivering various pollutants including metal and metalloids to adjacent territories [23]. These anthropogenic impacts on snow chemical composition can be further complemented by far-range atmospheric transfer of solid aerosols from southern desert and semi-desert regions of Central Asia [24].

In the present study, we used existing road infrastructure to sample a sizable (2800 km from the south to the north) transect of the WSL. We collected 36 integral (from the surface to the ground) snow cores and attempted to distinguish the effect of local (gas flaring, urban settlements) and global (long-range) atmospheric transfer. Via applying a mass balance approach for depth-averaged metal concentration, we estimated possible impact of winter time atmospheric input on metal (Fe, Mn, Ni, Co, Zn, Cd, and Pb) and metalloid (As and Sb) fluxes during the spring flood in the Ob River. We concluded that there is a sizable effect of atmospheric deposition on riverine export fluxes of some trace metals in Western Siberia.

Note that, compared with a previous study of snow chemical composition (upper 0–5 cm) in another part of Western Siberia [24], the originality of the present study consists in (i) sampling of much larger (~2800 km compared with 1700 km in previous work) latitudinal gradient in relatively pristine zones comprising forest, forest tundra, and tundra within the permafrost-free, discontinuous, and continuous permafrost regions; (ii) assessment of dissolved trace elements in integral (from the surface to the ground) snow samples.

2. Materials and Methods

The snow cores were collected along the latitudinal gradient south → north, from the vicinity of the Barnaul city (zone of forest steppe) to the Ob estuary (tundra zone) from 8 February 2020 to 19 February 2020. The integral 50–70 cm (from the surface to the ground, except the bottom 2–3 cm layer) snow core was collected at 36 locations, which were evenly distributed along the 2800 km transect (Figure 1). All sampled points were located more than 500 m from the road.

Sampling was performed using a metal-free technique, in a protected environment, using only plastic equipment and vinyl single-use gloves. First, a pit in the snow was dug with a plastic shovel to ensure the representability of the studied location and the evenness of the ground. Then, a two-person team sampled the snow in such a way that no contamination from external surfaces (other than the plastic shovel) was possible. The plastic shovel was inserted 2 cm above the ground in order to avoid touching the ground during sampling. The snow was collected via a 10 cm diameter PVC tube which was inserted into the snow until it made contact with the shovel surface, which was a few cm above the litter, to avoid any contamination from plant debris. Prior to sampling, the tube and the shovel were “rinsed” several times with fresh snow via inserting them into the snow cover 1–2 m from the sampling site.

Approximately 5 L of snow was collected into single-use polyethylene bags, which were double closed with a PVC collar. The polyethylene bags were thoroughly washed with 1 M HCl and abundant MilliQ water in a clean room, class A 10,000. Collected snow samples were transported to the laboratory in the frozen state and processed within 2 weeks after sampling. In the laboratory, the snow was melted at 18–20 °C of ambient temperature,

and immediately processed for analyses and filtration. The pH and conductivity were measured on unfiltered samples using Hanna portable instruments. The snow water was filtered through acetate cellulose filters (Millipore, 47 mm diameter) of 0.22 μm pore size. Blanks of MilliQ water from the clean room were also placed in polyethylene bags for the same amount of time as the melted snow (<3 h) and processed via filtration similar to the snow samples. The filtrates were acidified with double distilled HNO_3 acid and stored in pre-cleaned HDPE tubes for ICP MS analysis.

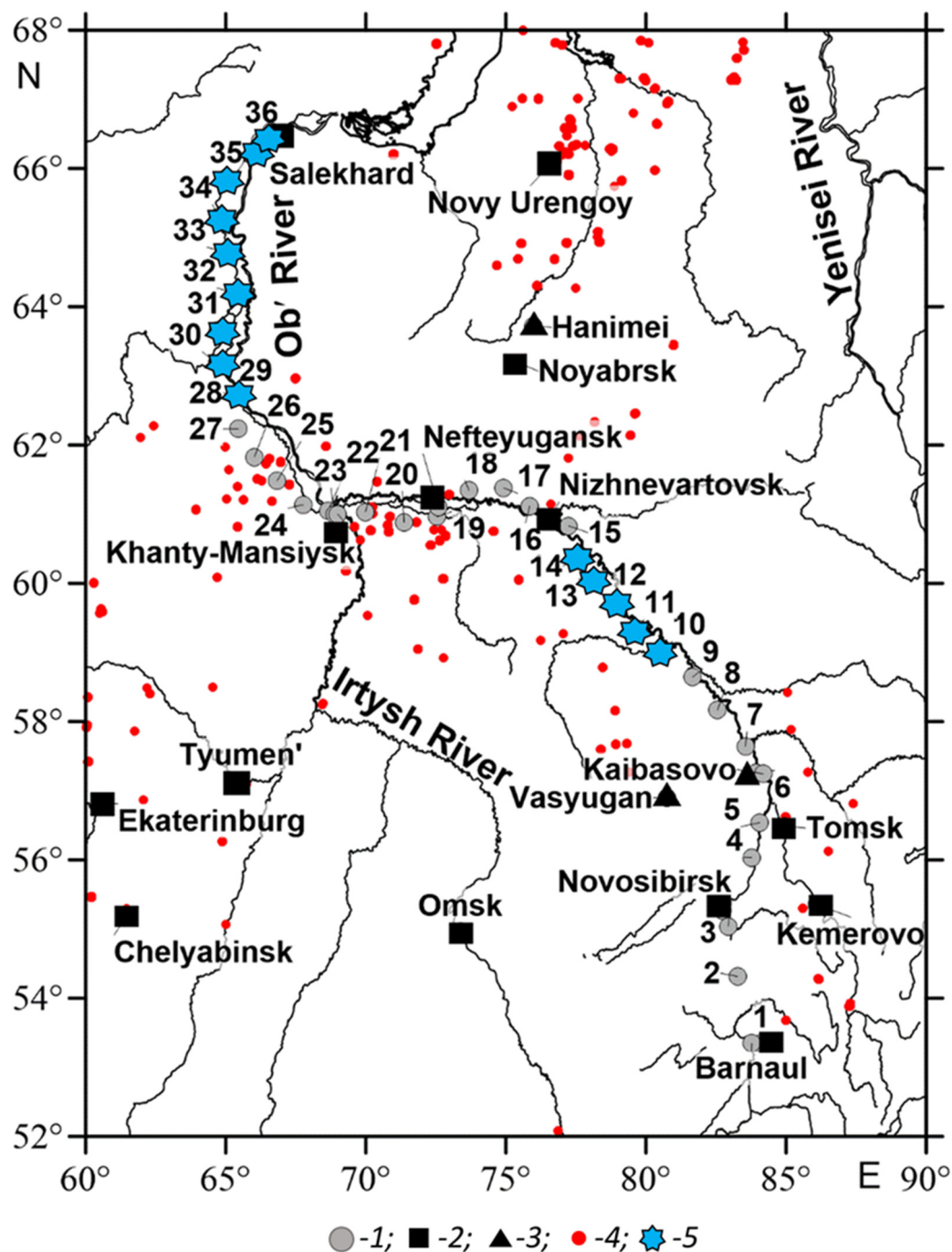


Figure 1. Studied area of the Western Siberian Lowland (WSL): 1—position of the sampling sites; 2—large cities; 3—scientific stations of Tomsk State University; 4—the position of gas flaring from site (<https://firms.modaps.eosdis.nasa.gov/download/accessed> on 25 July 2020); 5—sampling points taken from the so-called ‘zimnik’ which has no solid cover and is used only several months per year, with rather low traffic density.

Selected trace elements (TE) in the dissolved fractions were measured without pre-concentration with an ICP-MS Triple Quad using both Ar and He modes to diminish the interference. Indium and rhenium were used as internal standards at concentrations of $\sim 3 \mu\text{g/L}$ and corrections for oxide and hydroxide ions were made for the REEs and the other trace elements [25]. The typical uncertainty for elemental concentration measurement ranged from 3–5% at 0.1–100 $\mu\text{g/L}$ to 5–10% at 0.001–0.01 $\mu\text{g/L}$. During the ICP-MS analyses, the international geostandards SLRS-6 (Riverine Water References Material for Trace Metals certified by the National Research Council of Canada) were measured after every 20 samples to assess the validity and reproducibility of the analyses. All certified trace element (Fe, Mn, Ni, Co, Cu, Zn, Cd, Pb, As, and Sb) concentrations of the SLRS-6 standard (e.g., [26]) and the measured concentrations agreed with an uncertainty of 10–20%. For all trace elements except Zn, the concentrations in the blanks were below or comparable with analytical detection limits ($\sim 0.1 \text{ ng L}^{-1}$). These values were at least 10 times lower than the average concentration of trace elements in snow samples. Zinc exhibited non-negligible concentrations in the blanks (0.03–1.3 $\mu\text{g L}^{-1}$); however, these concentrations were several times lower than those in snow water samples and as such Zn concentration corrections did not exceed 10% of the measured values.

Statistical analysis of the average values and the link between element concentration in the dissolved fraction and the latitude was carried out by comparison of different sampling locations using ANOVA and H-criterion of the Kruskal–Wallis and Mann–Whitney U tests, which allowed one to estimate the difference between two independent sets of data based on one given parameter following the approaches developed for lakes and rivers of Western Siberia [27–30]. The normality of data distribution was verified by a Shapiro–Wilk test; because the data were not distributed normally, we used nonparametric statistics. To identify potential drivers of snow water chemical composition, we performed a principal component analysis (PCA) in XLSTAT which is a statistical software that works as an add-on to Excel.

3. Results and Discussion

3.1. Spatial Variation and Possible Sources of Trace Element Concentration in the Snow

The latitude-averaged concentrations of dissolved and particulate fraction of snow samples are listed in Table 1. Concentrations of dissolved element in individual samples are listed in Table S1 of the Supplementary Materials.

Table 1. Physicochemical properties of dissolved ($<0.22 \mu\text{m}$) fraction of the snow water and mean (\pm SD) trace element concentrations ($n = 36$) in Western Siberia latitudinal transect.

pH	SC, $\mu\text{S cm}^{-1}$	Mn $\mu\text{g/L}$	Fe $\mu\text{g/L}$	Co $\mu\text{g/L}$	Ni $\mu\text{g/L}$	Cu $\mu\text{g/L}$	Zn $\mu\text{g/L}$	As $\mu\text{g/L}$	Cd $\mu\text{g/L}$	Sb $\mu\text{g/L}$	Pb $\mu\text{g/L}$
4.57 \pm 0.15	10.2 \pm 2.05	1.65 \pm 1.55	2.86 \pm 2.39	0.013 \pm 0.014	0.057 \pm 0.036	0.236 \pm 0.167	8.32 \pm 13.7	0.324 \pm 0.192	0.030 \pm 0.012	0.029 \pm 0.039	0.670 \pm 0.315

The specific conductivity (S.C.) ranged between 10–14 $\mu\text{S cm}^{-1}$ in the southern part of the profile (54–62° N) and decreased to 6–8 $\mu\text{S cm}^{-1}$ in the northern part of the profile. The concentration of solid particles [31] ranged from 1–4 mg/L in the southern part and remained relatively stable ($1.27 \pm 1.21 \text{ mg/L}$) in the northern part of the Ob River basin. The pH did not exhibit any systematic variation with latitude (4.53 ± 0.17 , median \pm IQR), Figure S1.

Iron, Mn, Co, Ni, and Cd demonstrated sizable (by a factor of 4–7) decrease in concentration northward (Figure 2a–e). This can be tentatively explained by a combination of both the decrease in overall population density and the degree of influence of dry aerosol deposition. Similar explanation has been put forward during our recent study of the uppermost (0–5 cm) snow cover in another latitudinal profile of Western Siberia [32]. Many elements (Ni, Mn, Cd, Cu, As, Sb, and Pb) exhibited a prominent local maximum (a factor of 2–3, see Figures 2b–d and 3a–d) in the zone of intensive oil and gas extraction (61–62° N latitudinal belt), which can be linked to gas flaring and fly ash deposition.

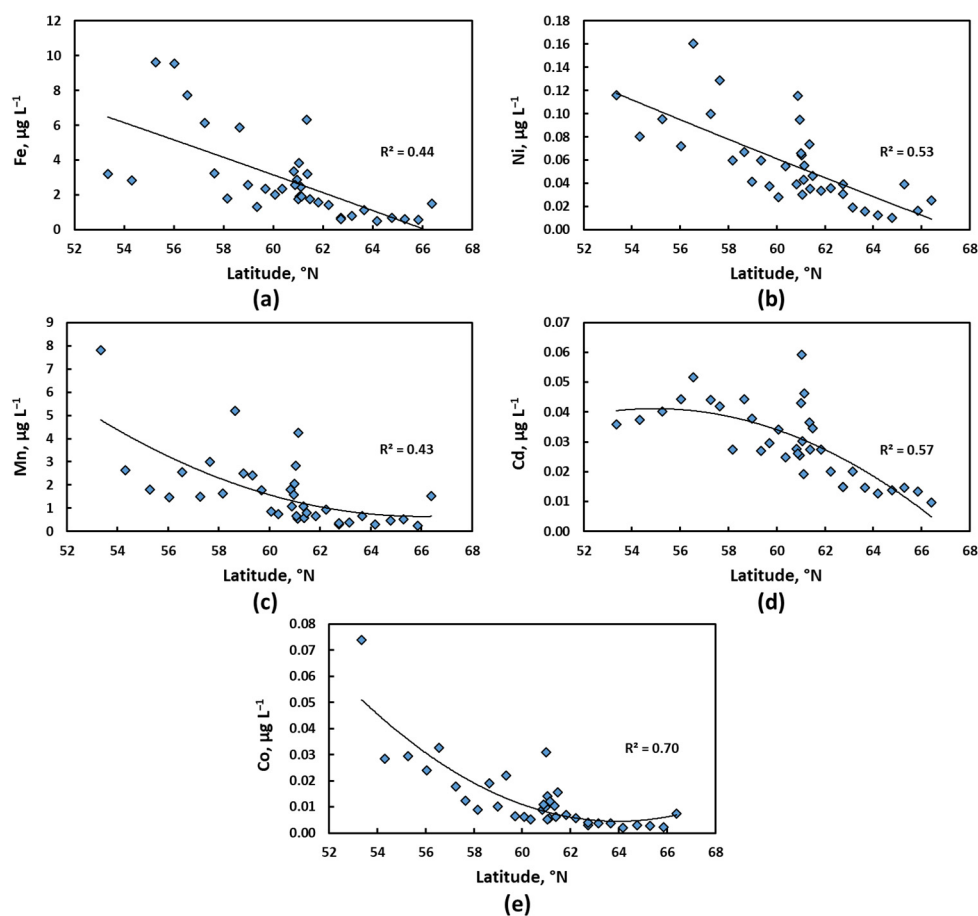


Figure 2. Examples of dissolved ($<0.22 \mu\text{m}$) metal concentrations in snow water as a function of latitude across the WSL. Fe (a); Ni (b); Mn (c); Cd (d); Co (e).

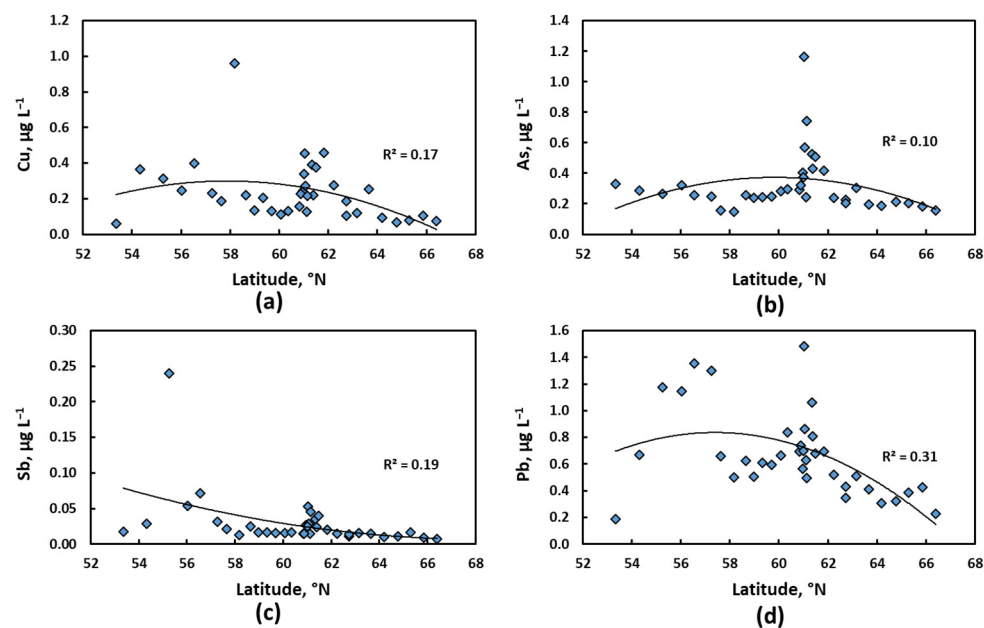


Figure 3. Examples of dissolved ($<0.22 \mu\text{m}$) metal concentrations in snow water as a function of latitude in the WSL. Cu (a); As (b); Sb (c); Pb (d).

Given that the soluble salt content (reflected by S.C.) exhibited much lower decrease northward compared with divalent metals (compare Figure S1e, Figures 2 and 3), the latter

are unlikely to originate from marine aerosols or soluble fraction of carbonate minerals. Such carbonate minerals (calcite and dolomite) are known to be present in Western Siberian solid aerosols and likely originate from far-range atmospheric transfer from the Kazakhstan and Mongolia desert regions [32]. Therefore, we hypothesize a local anthropogenic rather than global source of dissolved divalent metals (Mn, Co, Ni, Cd, and Pb). This source is most likely the products of flying ash dissolution or desorption from some solid particles. Note here that a northward decrease in concentration of solid particles was more pronounced than that of S.C. (a factor of 3.1 and 1.4, respectively).

In our previous study [31], we presented the variation of insoluble particles in the snowpack of the Ob River basin and showed that particulate matter consisted of biogenic debris and spores (evenly distributed over the transect) and lithogenic minerals (plagioclase and clay minerals) preferentially enriched in the southern part of the transect. The carbonate minerals (calcite and dolomite) were also reported in the upper layer of the snow pack from Western Siberia [32]. Note that in a previous study of the surface (0–5 cm) snow layer across another transect of the WSL, we found that Ca, Mg, Sr, Mn, and Co increase their concentration with an increase in particle concentration by a factor of maximum 10 [32]. A similar pronounced effect can be observed in the present Table S1, which encompasses the full depth of the snow core and thus represents more integral assessment of leaching potential of these elements from the mineral particles.

In the transect studied in this work, the proportion of anthropogenic particles (fly ash and black carbon) did not exhibit any systematic latitudinal pattern but was the highest near big towns and areas of hydrocarbon production [31]. In accord with these observations, here we hypothesize that a general northward decreasing trend in divalent metal (Mn, Co, Ni, and Cd) reflects possible leaching of these elements from aerosol minerals and desorption from anthropogenic particles linked to cities. In contrast, local maxima in concentration of elements not showing any systematic latitudinal trend (for As, Sb, Zn, Cu, and Pb) or elements exhibiting such a trend (Fe, Ni, and Cd) likely represent the point source of atmospheric pollution such as gas flaring. This is further confirmed by positive correlations ($p < 0.05$) between dissolved elements (Mn, Fe, Co, Ni, Zn, Cd, and Sb) and solid particle concentration in snow (Table S2, Figure S2).

Note that, in another part of Western Siberia, the surface (0–5 cm) layer of the snow pack sampled in 2014 demonstrated a single maximum of Sb, Cd, and Ni concentrations at c.a. 63–65° N, whereas As exhibited two maxima, at 63.5° N and 67.5° N [32]. Similar to the present study which demonstrated maxima of As, Ni, and Cd at 61° N, these patterns most likely reflect prominent ground source of local pollution such as gas flaring. To further examine these impacts, we tested a quantitative link between the distance to the gas flaring site and the element concentration in the snow water (Figure S3). None of the studied elements yielded significant ($p > 0.05$) correlation with the distance to the gas flare position. Note, however, that in this treatment we could not take into account the number of different gas flares around the sampling point and the dominant wind direction. Furthermore, one can expect a strong interference of gas flares' impact with that of large towns, especially in the southern part of Western Siberia.

Because of its exceptionally flat orographic context, extensive vegetation cover, and relative remoteness from the Arctic Coast, the atmospheric precipitates in winter are likely to bear a signature of remote desert and semi-desert regions of Central Asia (chiefly Kazakhstan and partially the Gobi desert). At the same time, the local centers of potential pollution include: (i) permanent (asphalt) roads (only in the southern part of studied transect, south of Khanty-Mansiisk); (ii) large towns with substantial heating centrals (operating on diesel and gas); and point gas flaring stations, especially abundant between Strezhevoy (station 14) and Priobie (station 28).

To better constrain possible local sources of pollution, we defined the distance to the nearest human-related object (gas flare, small settlement (within first 20 km from the sampling point), and large town) taking into account the dominant wind direction during winter (Table S3). In this case, a significant ($p < 0.05$; $R^2 > 0.3$) decrease in five element

(Fe, Co, Ni, Mn, and Cd) concentrations was observed as illustrated in Figure 4. The concentration of other trace metals (Cu, Zn, and Pb) and metalloids (As and Sb) did not show any link to the distance to local pollution. We thus suggest that these elements are essentially controlled by far-range atmospheric transfer and/or by multiple sources of local (<20 km) and near-local (20–100 km) pollution.

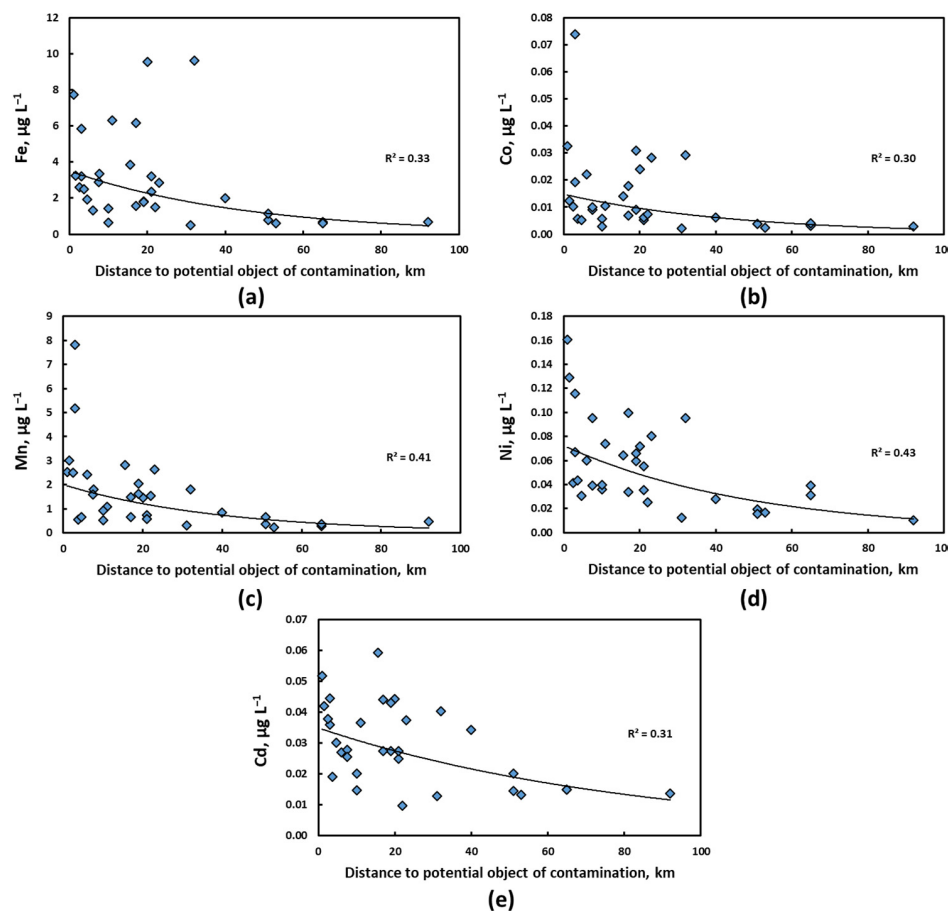


Figure 4. Examples of dissolved (<0.22 μm) metal concentrations in snow water as a function of distance to potential object of contamination in the WSL. Fe (a); Co (b); Mn (c); Ni (d); Cd (e).

A PCA treatment demonstrated two groups of parameters according to their spatial distribution in the snow water, although of low explicatory capacity (Figure S4, Table S4). The first group comprised Mn and Co solid particle concentration and latitude. The second factor acted on Fe, Cd, and Pb, and specific conductivity.

3.2. Assessment of Possible Snow Thaw Impact on Trace Element Concentration and Export by WSL Rivers

Obtained concentrations of dissolved fraction in the snow water can be compared with typical concentrations of trace elements in river water of the Ob River and tributaries, sampled during the end of the spring flood period [33]. This comparison (Figure 5, Table S5) revealed three groups of elements in the snow water depending on their potential to affect the riverine concentration. Iron, Co, and Ni in snow exhibited concentrations which were 10–15% lower than those in the Ob River water. Therefore, snowpack deposition of these metals could not appreciably affect their riverine export. In the northern sections of the transect, Mn, Co, Cu, As, and Sb from the snow could contribute between 10–30% to the river water concentrations. Finally, Zn, Cd, and Pb across the entire transect, as well as Mn and Co in the southern section of the transect, exhibited comparable or exceeded the concentration of these elements in the river water. This comparison illustrates the important possible contribution of snow water to the riverine transport of trace metals.

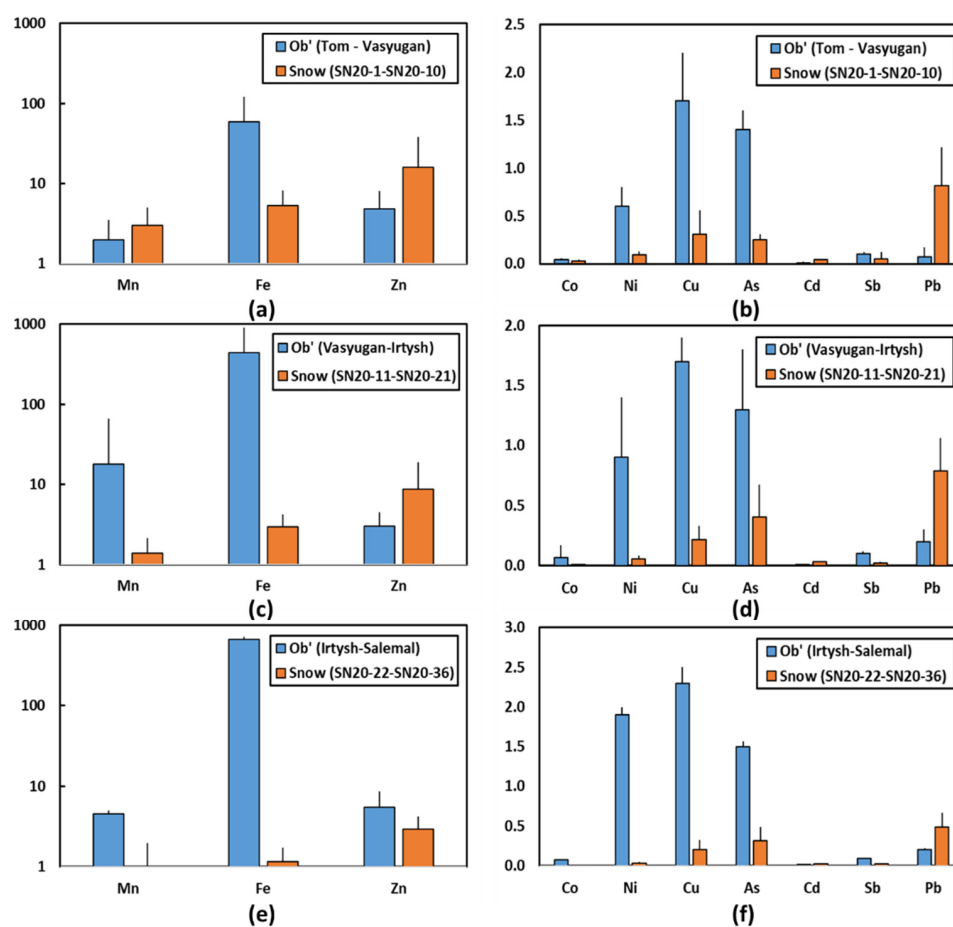


Figure 5. Histogram of metal concentrations in snow and river water (mean \pm sd) of Western Siberia: (a) concentration of Mn, Fe, and Zn (SN20-1–SN20-10); (b) concentration of Co, Ni, Cu, As, Cd, Sb, and Pb (SN20-1–SN20-10); (c) concentration of Mn, Fe, and Zn (SN20-11–SN20-21); (d) concentration of Co, Ni, Cu, As, Cd, Sb, and Pb (SN20-11–SN20-21); (e) concentration of Mn, Fe, and Zn (SN20-22–SN20-36); (f) concentration of Co, Ni, Cu, As, Cd, Sb, and Pb (SN20-22–SN20-36).

Overall, the snow water chemical composition reflects both local and global (long-range) atmospheric transfer processes. A northward decrease in Fe and divalent transition metals (Mn, Co, and Ni) and Cd in the snow water contrasts the latitudinal pattern of these elements in the Ob River and tributaries. The latter demonstrates a sizable increase in concentrations of Fe and divalent transition metals from the south to the north [33]. To quantify the snow water input to the springtime dissolved flux of the Ob River water, we accounted for the river runoff in spring and the snow pool of Western Siberia. The water stock in snow (in mm snow water accumulated during winter) is fairly well known for Western Siberia [32,34] and ranges from 110–120 mm in the zone 56–60° N to 140–150 mm in the northern part of the Ob River basin (60–68° N). The springtime river runoff (in mm during May and June) was approximated to be the same as for medium and small rivers of Western Siberia, as calculated in [35]. Here, we considered the average concentration of trace elements in the snow water in the southern (<60° N) and the northern (>60° N) parts of the Ob River basin.

The ratios of river fluxes in May–June to the amount of elements accumulated in the snow stock on the same territory are presented in the form of histograms (Figure 6). In the southern, permafrost-free zone, Mn, Co, Zn, Cd, Pb, and Sb fluxes in rivers can be provided essentially by snowmelt. The riverine flux of Zn, Cd, and Pb can be entirely controlled by snowmelt in the northern, discontinuous and continuous permafrost zones (north of 60–62° N). These comparisons demonstrate a paramount impact of wintertime atmospheric depositions on freshet riverine fluxes of dissolved metals in the WSL. Because the flood

period accounts for a sizable fraction of total annual lateral export of solutes in general and trace metals in particular [35], when foreseeing the consequences of climate change on river fluxes of metals, one has to account for collateral changes in snow quantity and chemical composition. This illustrates the intrinsic complexity of the response of elementary fluxes from the WSL to the Arctic Ocean due to ongoing environmental changes.

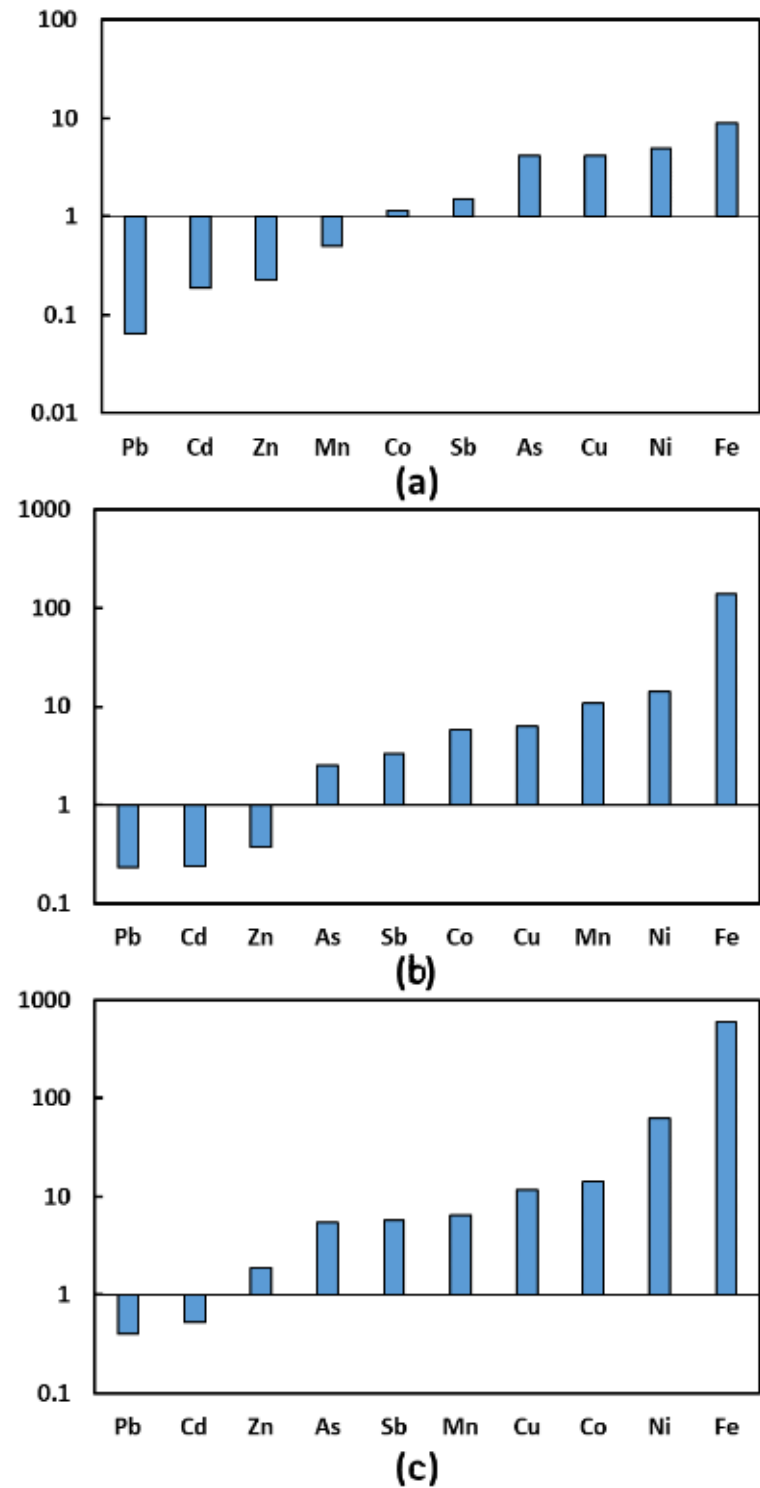


Figure 6. The ratio of mean dissolved flux of rivers in three latitudinal zones (53–60 (a), 60–62 (b), and 62–66° N (c)) of the WSL to the stock of dissolved fraction of snow. For this calculation, the snow volume (in millimeters of water) accumulated over full winter and mean river runoff during May and June were used.

4. Conclusions

The chemical composition of the full depth of the snow pack was studied across a 2800 km latitudinal gradient of the Ob River basin. There was a decreasing trend of Mn, Fe, Co, Ni, and Cd concentration in the snow water (<0.45 μm) northward. Some divalent metals (Cu, Ni, Pb, and Cd) and metalloids (As, Sb) demonstrated a local enrichment at 61–62° N, presumably originated from anthropogenic sources of pollution. However, we could not establish a quantitative link between the distance to gas flaring sites and the element concentration in the snow water. This may be explained by strong interferences with large towns, especially in the southern part of Western Siberia.

A northward decrease in Fe and divalent transition metals (Mn, Co, and Ni) and Cd in the snow water contrasted the latitudinal pattern of these elements in the Ob River and tributaries (according to available literature data). In the southern, permafrost-free zone, Mn, Co, Zn, Cd, Pb, and Sb fluxes in the Ob River during the May–June period can be supplied essentially by dissolved fraction of the snowmelt. The impact of snowmelt on river export fluxes in spring strongly increases northward for Zn, Cd, and Pb. In the permafrost zone, entire riverine fluxes of these elements during spring flood can be provided by the snowmelt.

Altogether, the obtained results suggest large complexity of the riverine export and atmospheric deposition of trace metals under climate warming scenario and require comprehensive analysis of dissolved metals in rain waters during different seasons across the region.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w14010094/s1>, Figure S1: Examples of the concentration of SC, pH in snow water as a function of latitude, Figure S2: Examples of Mn, Fe, Co, and Ni in snow water as a function of particulate fraction, Figure S3: Examples of the concentration of SC, Mn, Ni, Fe, Cu, Cd, Co, Zn, As, Pb, and Sb in snow water as a function of distance to gas flaring, Figure S4: PCA factorial map F1 \times F2 of elements of a reconstructed table for the dissolved fraction, Table S1: Physicochemical properties of dissolved (<0.22 μm) fraction of the snow water trace element concentrations ($\mu\text{g/L}$) in Western Siberia latitudinal transect, Table S2: Spearman correlations $p < 0.05$, Table S3: The distance between the sampling point and some nearest possible sources of pollution, Table S4: Results of PCA treatment of all data, Table S5: Mean ($\pm\text{SD}$) concentration ($\mu\text{g L}^{-1}$) of metals in river water and snow water in the three distinct parts of the Ob River main stem upstream and downstream of its confluence with Vasyugan and Irtysh.

Author Contributions: Conceptualization, V.P.S. and O.S.P.; field sampling, S.N.V., I.V.K., A.G.L. and O.S.P.; analysis of collected samples, I.V.K., A.G.L. and F.C.; visualization, I.V.K.; writing and editing O.S.P., I.V.K. and V.P.S. All authors have read and agreed to the published version of the manuscript.

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