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Hydrology and Earth System Sciences
Discussions
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Interactive comment on "Impact of snow deposition on major and trace element concentrations and fluxes in surface waters of Western Siberian Lowland" *by* Vladimir P. Shevchenko et al.

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The reviewer noted that "The topic and scope of this paper is a good fit for the journal." However, he/she suggested major revision of the manuscript via addressing the following issues. Specific suggestions of Reviewer No 2:

- Reviewer comment: Page 1, Line 15-31, The Abstract section needs a clear objective (at the beginning) as well as significance (at the end). Result descriptions should summarily focus on the objectives. - Author reply: We revised the Abstract as following: "Towards a better understanding of chemical composition of snow and its impact

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on surface water hydrochemistry in poorly studied Western Siberia Lowland (WSL), the surface layer of snow was sampled in February 2014 across a 1700-km latitudinal gradient (c.a. 56.5 to 68°N) in essentially pristine regions. We aimed at assessing the latitudinal effect on both dissolved and particulate forms of element in snow in order to quantify the possible source of atmospheric input to lake water solutes and elementary fluxes of rivers across the WSL. The concentration of dissolved+colloidal (< 0.45 μm) Fe, Co, Cu, As, La increased by a factor of 2 to 5 north of 63°N compared to southern regions. The pH and dissolved Ca, Mg, Sr, Mo and U in snow water increased with the increase in concentration of particulate fraction (PF). Principal Component Analyses of major and trace element concentration in both dissolved and particulate fractions revealed 2 factors not linked to the latitude. A hierarchical cluster analysis yielded several group of elements originated from alumino-silicate mineral matrix, carbonate minerals and marine aerosols or belonging to volatile atmospheric heavy metals, labile elements from weatherable minerals and nutrients. The main sources of mineral components in PF are desert and semi-desert regions of central Asia. Comparison of major and trace elements in dissolved fraction of snow with lakes and rivers of western Siberia across the latitudinal gradient revealed significant atmospheric input of a number of trace elements to the inland waters of the WSL. The snow water concentration of DIC, Cl, SO4, Mg, Ca, Cr, Co, Ni, Cu, Mo, Cd, Sb, Cs, W, Pb and U exceeded or were comparable with spring-time concentration in thermokarst lakes of the permafrost-affected WSL zone. The spring-time river fluxes of DIC, Cl, SO4, Na, Mg, Ca, Rb, Cs, metals (Cr, Co, Ni, Cu, Zn, Cd, Pb), metalloids (As, Sb), Mo and U in the discontinuous to continuous permafrost zone (64-68°N) can be explained solely by melting of accumulated snow. The impact of snow deposition on riverine fluxes of elements strongly increased northward, in discontinuous and continuous permafrost zones of frozen peat bogs. This was consistent with the decrease of the impact of rock lithology on river chemical composition in the permafrost zone of WSL, relative to the permafrost-free regions. Therefore, the present study demonstrates significant and previously underestimated atmospheric input of many major and trace elements to their riverine fluxes during spring flood. A broader impact of this result is that current estimations of river water fluxes response to the climate warming in high latitudes may be unwarranted without detailed analysis of winter precipitation."

- Reviewer comment: Significant editing is required to improve the grammar, syntax and English expression throughout the paper. - Author reply: The manuscript already received full English proofread via payed service at the Elsevier Webshop. We corrected a number of syntax and English expressions errors in the text following valuable recommendations of 1st reviewer, the Master Student review and Reviewer No 2. We performed all recommended corrections to L 39, 46, 48, 76, 105, 110, 134, 136, 171, 173, 178-180 etc. Note that in case of acceptance of our paper for HESS, it will received full English proofread as a part of payed Open access package.

- Reviewer comment: The second paragraph of the Introduction (Line 51-65) includes a lot of information and previous literature review. This could be improved by reorganizing or combining some of the previous reports in different regions. - Author reply: We greatly shortened and reorganized the Introduction (see revised ms as attachement)

- Reviewer comment: Line 51: "numerous studies ...western Siberia", probably in contradiction to the text on Line 61: "the trace ...Siberian snow remains at the beginning of exploration." - Author reply: We removed this line of text as unnecessary.

- Reviewer comment: Results: the database was not clearly and continuously expressed. Too many small figures and supplement information. Readers have to obtain the data information here and there. Although it is difficult to think out a reasonable method to improve the description of big database, the authors still need to consider it. - Author reply: We strongly agree with this comment. We completely re-organized the results presentation, renumbered all figures and tables. The Results now follow the plan: 1) soluble fraction of element in snow water; 2) chemical composition of the particulate fraction and 3) assessing the impact of snow deposition on chemistry of lakes and rivers, see attached manuscript. We would like to point out that it is inevitable to have small figures for representing individual elements. It is not always possible to combine several elements on the same plots. However, following this recommendation, we removed significant number of figures from Supplement (altogether more than 12 plots) which allowed greatly simplifying the presentation of results.

- Reviewer comment: Page 6, Line 209-213: the PCA results seem inexplicable. Fe and Pb were attributed to lithogenic stable group; however, Ba and Si to highly mobile group. In the lithogenic group, Ti was not observed. - Author reply: The reviewer made a very good point. The PCA was not sufficiently powerful to explain the variability of major and trace elements in both dissolved and particulate phase of snow water. To address this issue, we used alternative technique to identify the group of elements that behaved in a similar way in snow water and snow particles. For this, we applied a complementary hierarchical cluster analysis (HCA) (e.g. Hartigan, 1975; Kaufman and Rousseeuw, 2005) which is widely adopted in geochemical interpretations of element concentration data (e.g. Bini et al., 2011; Levitan et al., 2015; Schot and van der Wal,1992; Moragues-Quiroga (2017). We used the Ward's method (Ward, 1963) for the linkages rule, following previous studies (Gourdol etal., 2013; Lin et al., 2014). The Pearson correlation distance was used for the linkage distance, which is frequently used for cluster variables (Reimann et al., 2008). These choices are in agreement with the group search of the PCA loadings. The HCA analysis was conducted on the basis of first two factors of the PCA. The criterion of non-intersection between the groups allowed partitioning the chemical elements of the dissolved part into 6 specific groups presented in Fig. 1 B. These groups characterize the elements according to their general chemical properties, ability to mobilize in aqueous solution from the solid minerals, affinity to the biota or their presence in the contaminated particles of industrial activity. Thus, the first two group of the dissolved fraction shown in Fig. 1 A and encircled in Fig. 1 B comprise low mobile elements likely originated from alumino-silicate mineral matrix (Al, Cr, REE, Ti, Zr, Fe, V) as well as some volatile heavy metals typically present in the solid aerosol particles (Cu, Cd, Pb). The 4th group includes

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major constituents of carbonate or marine aerosols matrix (elevated pH, Mg, Ca and Na). The 5th group is represented by typical macro- and micronutrients (K, Rb, Mn, Co, Ba). Finally, the last 6th group of elements comprises both labile elements linked to weatherable minerals (Sr, Sb, Si, Ni) and nutrients such as Sr, Ni, Si, DOC and Mo. Three of these elements are strongly enriched in snow particles relative to the Earth crust (Sr, Sb, Mo, see section 3.3 of revised manuscript), thus suggesting their possible leaching from atmospheric dust into the soluble fraction of snow. We could not find a straightforward explication of the common group of Zn and U in soluble snow fraction.

- Reviewer comment: If the mobile elements were used as indicator of marine aerosols, the element, Na should be also taken into account. - Author Reply: The PCA identified the second large group which was composed of DOC, K, Rb, Cs, Mn, Co, Ba, Sb, Co, Mo, Mg, Si, Sr, Na, Ca, pH. These highly mobile elements presumably reflect the marine aerosols and leaching from soluble soil minerals such as carbonates as well as plant biomass. In the HCA treatment, Na is located in the same group with Mg and Ca, the two major elements of marine aerosols (see Fig. 1 B).

- Reviewer comment: Page 8, Line 299-306: The introduction of EF calculation should be moved to the Method section. The authors should give some reasons to choose Al to be reference element, rather than Si or Ti in this study. Is there a good relation between Al and other trace elements? - Author Reply: Yes, there is a very good linear relation between Al and other immobile trace elements such as Ga, Zr, Th, Ti shown in Fig. 2 of Reply. The use of Al-normalized TE enrichment factor (EF) was for consistency with all previous results on snow particles composition in the Russian Arctic and subarctic: normalization to Al is the most common way of data presentation.

- Reviewer comment: In addition, it is interesting to see that the EFs of Pb, Cu and Sb are larger than 100, and those of Sb, Zn and Cd larger than 1000, which clearly show serious anthropogenic pollution. However, in the introduction, the authors said that the region experiences lower anthropogenic disturbance, with fewer people and less industry. So, how to explain the high EFs? Probably it is a result of using average Earth

Crust as the background? - Author reply: Here, one has to distinguish the local pollution or anthropogenic disturbance that are known to produce the enrichment of atmospheric precipitates in toxic metals, for instance, in the vicinity (50-100 km) of Arctic smelters (works of de Caritatn, Reinmann), and long-range atmospheric pollution. We believe that the elevated concentrations of divalent metals, As and Sb should not be interpreted as necessarily pollution from the industrial centers. Rather, volatile Pb, Cd, As may originate from long-range transport of anthropogenic pollutants and the desert material. Therefore, we attempted to distinguish the well-known refractory, non-volatile heavy metals such as Cu, Ni and Co and more volatile elements such as Pb, Cd and As (i.e., Reimann et al., 2000) based on the HCA treatment. For both particulate and dissolved fraction, these elements are located in three or two different groups but never belong to one single group of inter-correlated elements. As such the available data do not evidence similar origin of Cu, Ni and Co, or Pb, Cd, and As in the snapshot of WSL snow sampled in this work. To further address this comment, we compared the element in snow samples to their concentration in local geological background rather than average earth crust (see Fig. 3 of Reply). Although the use of average crust for assessment of element enrichment in snow particles is justified by long-range transfer of snow components, it is known since the works of group of Reimann and de Caritat in NW Europe that the "average crust" is unlikely to represent the local background and the use of the "upper crust" average value can introduce a 2 to 3 order of magnitude uncertainty to any calculated EF (de Caritat et al., 1997; Reimann and de Caritat, 2000; Reimann et al., 2000). As such, western Siberia moss, peat and clay/loam horizons were used to assess relative enrichment of elements in snow particles. It can be assumed that the leaching of soluble forms of elements from these solid phases in winter is highly unlikely. The specificity of western Siberia is that the mineral ("geological") local substrate is completely frozen, even in summer, since the active (unfrozen) layer depth does not exceed the peat thickness, and in that case, the use of "organic" substrates is most relevant. All three WSL reference substances ("local" moss, peat and clays) represent latitudinal-averaged values based on large (>

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50) number of samples collected in previous studies across the 1700-km latitudinal gradient. The elementary ratios of snow particles to that in mineral soil, peat and moss of the WSL are illustrated in Fig. 3 A, B, and C, respectively.

- Reviewer comment: Discussion: The authors pointed out three objectives: latitudinal effect, mineralogical impact and different sources of metal input to lakes. So, the discussions should be related to these key issues. - Author reply: We totally agree with this remark. The revised discussion is constructed as following: 1) Dissolved fraction of snow, comparison with literature data and discussion of the origin of elements; 2) particulate transport of elements in snow, concentration of particulate fraction, its origin, and 3) Impact of snow deposition on river and lake chemistry and fluxes

- Reviewer comment: The current version of this section should be shorten, as some of text repeated the Results content. - Author reply: We agree and greatly revised this section via removing 20 lines of text, see the revised manuscript.

- Reviewer comment: Conclusions: This section should be compressed. It is not necessary to repeat too many details of data results. - Author reply: We agree and removed 13 lines of text from the Conclusions

- Reviewer comment: Quality/resolution could be improved for all figures. Figures 6, 7 and 8 could be merged together - Author reply: We strongly revised many figures and removed part of figures from the manuscript (see attachment)

The revised manuscript, which incorporates all the comments of MSc, Reviewer 1, and Reviewer 2, is attached as Supplement to this Reply.

Please also note the supplement to this comment:
http://www.hydrol-earth-syst-sci-discuss.net/hess-2016-578/hess-2016-578-AC4-supplement.pdf

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., doi:10.5194/hess-2016-578, 2016.

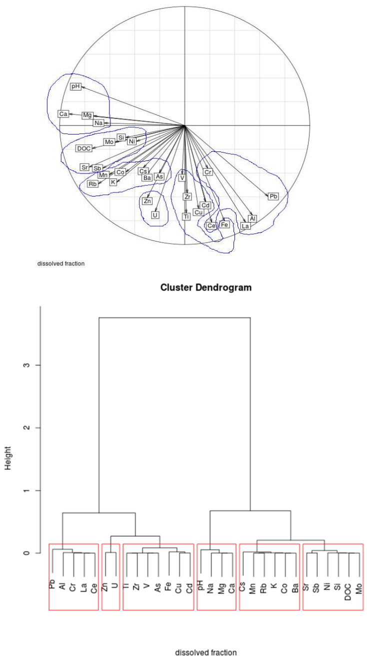

Figure 1 Reply: PCA Factorial map F1xF2 of elements of a reconstructed table for the dissolved fraction. Partition of elements into 6 groups revealed by a CAH is shown by a contour line. **B:** Dendrogram of a hierarchical cluster performed on variables of a reconstructed table for the dissolved fraction using the Pearson correlation as a distance measure and Ward's method for the linkage rule.

Fig. 1.

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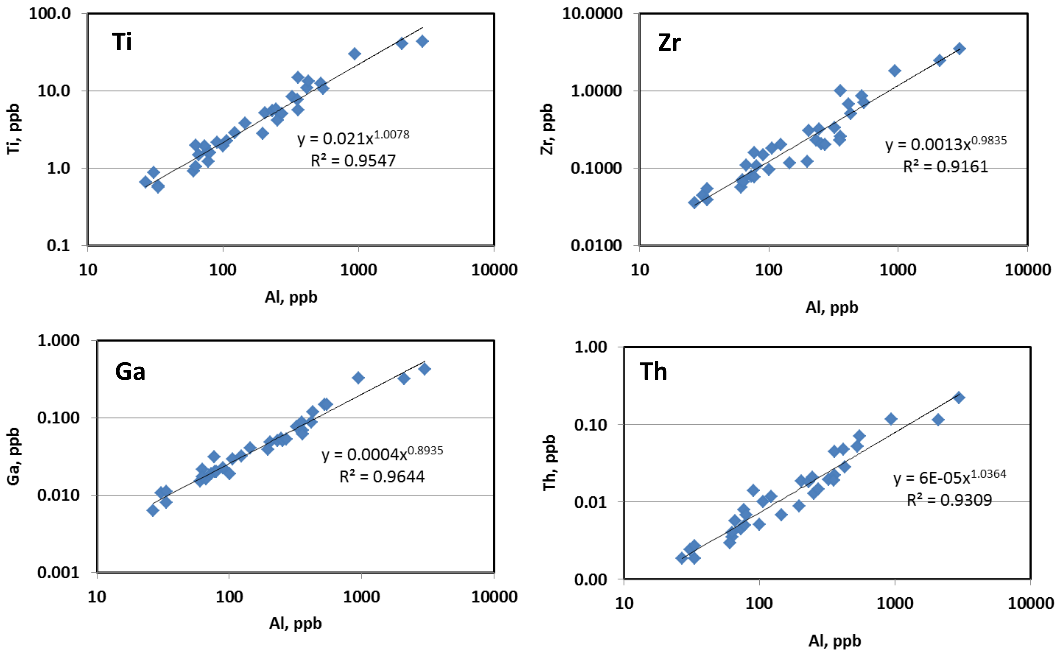

Figure 2. Relationship between Al concentration in the particulate fraction and that of Ti, Zr, Ga and Th

Fig. 2.

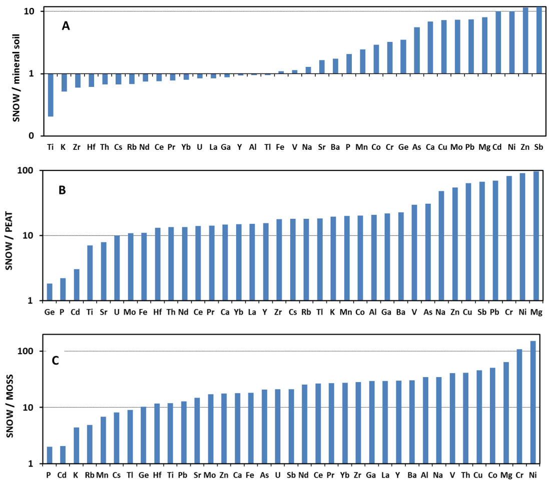

Figure 3. The ratios of the average concentrations of elements in snow particles (neglecting sample SF22) to those in mineral soil (A), peat (B) and mosses (C) of WSL. The peat, moss, and underlying mineral horizons data are averaged over the latitude of 55 to 68°N as described in Stepanova et al (2015). Note normal Y scale for mineral soil (A) and log Y scale for peat and moss (B, C).

Fig. 3.

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