

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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Received and published: 20 January 2017

Response to anonymous Referee #1

The reviewer acknowledged “a very representative and complete dataset of chemical element concentrations on the snow of this region”. He/she also considers that our manuscript “. . . corresponds to the scope of the journal, especially in presenting such a novel dataset in a permafrost area where geochemical and hydrological processes are still poorly studied.”

However, the reviewer suggested to change the presentation of the data via i) distin-

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guishing the groups of chemical elements and ii) providing a better link between the different figures and between each figure and its relative text. We will greatly revise the presentation following this recommendation. Note however, that for the first time we present both dissolved ($< 0.45 \mu\text{m}$) and particulate composition of snow across a huge latitudinal gradient. Given the complexity of various simultaneously acting factors on snow chemical composition (marine aerosols, remote deserts and local industrial pollution), and the lack of distinct geochemical signature of each individual source measured in western Siberia, establishing the links between different factors and between different group of elements become a challenge and goes beyond the scope of this work. We did distinguish several groups of elements using additional sophisticated statistical tools, suggested by reviewer (see below). This helped to focus the presentation and facilitated the discussion.

The reviewer suggests that “The presentation of the data should be done in a more synthetic way and not as a list of chemical elements”. We agree and we will greatly revise the presentation focusing it on the groups of elements revealed by new statistics. For the dissolved part, these groups are 1) Pb, Al, Cr, REE; 2) Ti, Zr, V, As, Fe, Cu, Cd; 3) Na, Mg, Ca; 4) Cs, Mn, Rb, K, Co, Ba, and 5) Sr, Sb, Ni, Si, DOC, Mo which illustrate the combination of i) lithogenic silicate and refractory minerals subjected to leaching (1st and 2nd group), ii) soluble major ions (3rd group), and biogenic elements such as plant nutrients or highly labile components of the 4th group and 5th group. For the particulate fraction, new hierarchical cluster analysis revealed 5 groups of element depending on their leachability and the source (lithogenic silicates, local industry, marine aerosols).

The reviewer also suggested that “Proposing a working hypothesis could help to improve this presentation by given a clearer story-line to the manuscript.” The working hypothesis for this study was that the chemical composition of snow should reflect the contribution of three main sources of dissolved and particulate forms of chemical elements. From the one hand, these are marine aerosols and mineral dust from

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remote deserts provinces, provided via long-range atmospheric transport. From the other hand, these are local sources of pollution such as towns, gas and oil industry centers and roads. Formulating this hypothesis allowed to reduce the number of elements and discuss the group behavior.

The reviewer made a number of very constructive specific comments, among them: He/she stated that “The abstract should be revised in order to clearly state the objective in regard to the existing knowledge on snow chemical composition at these latitudes. You should clearly explain the added value of this work to the international community.” This study provides for the first time, elementary composition of both dissolved and particulate fraction of snow over significant (1700-km) gradient of very important sub-arctic zone. We demonstrate significant and previously underestimated atmospheric input of many major and trace elements to their riverine fluxes during spring flood. The fundamental meaning of this finding is that the impact of snow deposition strongly increased northward, in discontinuous and continuous permafrost zones of frozen peat bogs, which is 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. 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, which is largely ignored in most studies. Taking into account the snow deposition and its chemical composition, revealed for the first time for such a large arctic territory may change the dominant paradigm of increasing the nutrients and toxicants transport from the land to the ocean under climate warming in the Arctic.

The reviewer suggested improving the technical section by removing some redundancies and merging some parts. He/she also suggested that “Calculation of EF could be added and explained according to recent literature” and we carefully revised this part taking into consideration the recommended references of the group of Reimann and Probst. Here it is important to argue that, unlike the local pollution tracing in the Eu-

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ropean arctic within the Kola Ecogeochemistry project (Reimann, de Caritat) or small-scale stream bed sediments or soils (N'guessan et al., 2009; Moragues-Quiroga et al., 2017; Levitan et al., 2015) where the normalization to the local soil or bedrock was necessary, the present study deals with winter-period long-range atmospheric transport of soluble and mineral forms of elements. As such, following the common practice in this field, normalization to general shale or Earth crust, allows representing the true enrichment/depletion of the atmospheric aerosols. Note that the normalization of the snow particles elementary composition to that of local mineral soil, peat and moss is presented in Fig. 9 of the manuscript and discussed in L 356-382 of submitted version.

The main criticism of this reviewer is on the results part. He/she suggested to “using the synthesis of such mathematical results to identify group of elements that behave in the same way and building the discussions on the elemental groups and not on the individual chemical element” using “a complementary hierarchical cluster analysis (Bini et al., 2011; Levitan et al., 2015; Schot and van der Wal, 1992; Gourdol et al., 2015; Moragues-Quiroga et al. 2017) to clearly state the significance of a given element to be part of a given group that is shown in the PCA analysis of Fig. 3 and S5. Following this important advice, we applied the methodology presented by Moragues-Quiroga (2017). Specifically, we conducted a hierarchical cluster analysis (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). We used the Ward's method (Ward, 1963) for the linkages rule, following previous studies (Gourdol et al., 2013; Lin et al., 2014). The Pearson correlation distance was used for the linkage distance, which is frequently used for clustering variables (Reimann et al., 2008). These choices are in agreement with the group search of the PCA loadings. However, the obtained results of the HCA (not shown here) did not confirm the PCA maps. The group presentation on the correlation circle F1 x F2 did not allow fractionating the PCA level because the first two PCA factors present only a part of the data structure when it looks for the relationships between the variables (element concentration) and the samples whereas the HCA takes into account the full

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set of data when it creates the groups as a function of the distances in the hyper-space without simplification of the structure by decomposition into the factors. Therefore, another analysis was conducted via constructing the data table on the basis of first two factors of the PCA. The HCA was applied on this new table which contained only the data structure described by two PCA factors. The results allowed partitioning of the variables. The criterion of non-intersection between the groups allowed to partition the chemical elements of the dissolved part into 6 groups presented in Figs 1 and 2 and the elements of the particulate fraction were distributed into 5 groups (Fig. 3 and 4). These groups characterize the elements according to their general chemical properties, their ability to mobilize in aqueous solution from the solid minerals, their affinity to the biota or their presence in the contaminated particles of industrial activity. Thus, the first two big groups of the dissolved fraction shown in Fig 1 and encircled in Fig. 2 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 mineral matrix (Cu, Cd, Pb). The 4th group includes major constituents of carbonate or marine aerosols matrix (elevated pH, Mg, Ca and Na). The 5th group includes 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) 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 (Fig. 1) For the particulate fraction, distinguishing the elements into 5 formal groups revealed by HCA shown in Fig. 3 and encircled in Fig. 4 is less certain and does not allow establishing clear link between the selected groups and physico-chemical properties of elements and their possible sources in the snow particles. Thus, in the 1st group, among three labile elements (Mg, Na and Ca) we identified V, which may exhibit elevated mobility in the form of anion in carbonate-bearing mineral particles. Divalent metals (Co, Ni, Mn) and Sr constitute the 2nd labile group of elements, yet this group also comprises Fe

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and Cr, which should be rather associated with the 3rd group of insoluble low mobile elements marking the presence of phosphates (REE and P), refractory Zr and volatile Pb. The 4th group of elements revealed by HCA of particles is composed of Sb, Cu and Zn. All these elements are strongly enriched in snow particles over the soil minerals (see 7 and Fig. 9a of submitted manuscript). The last group of elements in snow particles comprise both labile (Li) and biologically-important Mo, K, Rb, Ba, toxic volatile elements which could bear the signature of anthropogenic pollution (As, Cd) but also low mobile Ti and Ga. We could not identify the link of elements in this group to the degree of snow particles enrichment relative to main “local” substrates of the WSL (moss, peat and clays), see below.

The reviewer further proposed an interesting issue, “. . .to compare the distribution of the elements in both snow fractions with the distribution of the same elements in the lake and river waters to observe some similarity/dissimilarity that could be explained by contrasted behavior of elements after they are released from snow to river/lake water.” He/she argued that “Once the groups are significantly identified, we should replace the list of elements by the group number in order to clarify the results and discussion parts.” We thank the reviewer for suggesting this excellent strategy of interpretation. The comparison of dissolved element concentration in lakes and snow demonstrated that for lakes, the snow loading clearly exceeds the concentrations in lakes of Pb, Zn, Cu, Cd, Sb and Mo (Fig. 5 of submitted manuscript). However, these elements belong to 4(!) various group of elements in dissolved snow fraction, identified by THE HCA (Fig. 1 of this response). In rivers, the dissolved elements that can be dominated by snow input are SO₄, Cr, Co, Ni, Cu, Zn, Mo, Cd, Sb, Cs, W and Pb, which again, belong to 4 various group of elements identified by HCA.

It thus can be concluded that there is no direct link between the group of elements identified by cluster dendrogram in the snow water and the elements those concentration in rivers or lakes are significantly affected by snow deposition. We believe that a natural cause of this apparent inconsistency is different mechanisms controlling the

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element distribution in the aerosols such as local sources of pollution, remote desert provinces, leaching of soluble elements from particulate fraction and in surface waters (interaction of melted snow with upper peat and moss/lichen horizons; underground feeding, leaching of elements from silicate river suspended matter due to abrasion in spring flood).

The reviewer pointed out that “some literature should be added to strengthen the similar behavior of elements that are present in a given group and then should behave in the same manner in the environmental fractions that are analyzed (snow, lake and river water, particles)”. We thank the reviewer for pointing this out and we greatly extended the reference list (see References of this reply). There are a few elements that behave similarly in lakes, rivers and snow water (see our response to the previous comment). We would like to underline that the geochemical behavior (migration, correlation, degree of enrichment) of elements is fundamentally different in rivers, lakes and winter atmospheric aerosols. Comparative analysis of these processes is already considered in our previous publications on geochemistry of surface waters in western Siberia (Audry et al., 2011; Pokrovsky et al., 2011, 2013, 2014, 2015, 2016a,b; Shirokova et al., 2013) goes beyond the scope of the present manuscript.

The reviewer stated that “using EF is always a debate, especially regarding the choice of the reference that has to be used for the normalization. How representative of the area geological characteristics is the chosen reference? How could this impact the results? Some publication should be considered to explain your choice like Reimann and de Caritat (2005 – Environ Sci Technol) and N’guessan et al. (2009 – Sci Tot Environ). This could be added to the methods by describing the EF calculation”. We agree and will do so in the revised version. See our response to general comment above. We actually use 4 references for the area geological characteristics – average Earth crust, “local” moss, peat and underlying mineral horizon. The use of average crust 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

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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 (> 50) number of samples collected in previous studies across the 1700-km latitudinal gradient.

He/she further inquired “As you used in the discussion soil/peat profiles collected in the WSL should you not relate EF to a more local geological/pedological information rather than an average Earth Crust? This is thoroughly discussed in L 356-382 and illustrated in Fig. 9 of submitted manuscript. It is hard to provide more “local” geological and pedological reference than the moss, peat and underlying mineral deposits sampled along a similar transect. To our knowledge, such a thorough comparison of snow to the dominant local geogenic background has never been attempted in the arctic region over a large latitudinal profile.

Comments of reviewer on Discussion: “By filtering the snow and the lake/river water to $0.45 \mu\text{m}$, the dissolved fraction includes a colloidal load, which can play a crucial role in the concentration of trace elements. Then, the $<0.45 \mu\text{m}$ dissolved fraction of the snow water (which may not include colloids, see lines 364-370) is compared to the $<0.45 \mu\text{m}$ dissolved fraction of river water (in which the trace element concentrations can be heavily controlled by colloids). If the colloids are not present in the dissolved fraction of snow, it is known that their contribution can be important in river, especially during flooding periods. Then the environmental compartment, which releases the colloids

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[Discussion paper](#)



to the freshwater during the melting period is not considered in the fluxes calculation of the present study and could overestimate the contribution of the dissolved snow fraction to freshwater fluxes. This point needs to be clarified in the discussions.” We totally agree that the generation of colloids during springflood is mostly linked to DOC mobilization from organic topsoil and plant litter. We would like to point out that the $< 0.45 \mu\text{m}$ fraction of snow includes the colloids (1 kDa – $0.45 \mu\text{m}$) by definition. However, with typical concentration of DOC in snow water around 1-2 mg/L, the share of colloidal forms of metals will be an order of magnitude lower than that in river and lakes, having 10 to 30 mg/L of DOC. A thorough discussion of colloids in surface waters of western Siberia is presented in our recent work (Pokrovsky et al., 2016, *Geochim. Cosmochim. Acta*) and thus we avoided too extensive discussion in the present manuscript.

The part that discussed the anthropogenic impact is like a list of potential industrial and urban sources but no real proof regarding the exact origin of the analyzed snow particles is given. The use of elemental ratios could be interesting to use especially with such a dataset to relate with known and existing anthropogenic/natural sources in the investigated region. This point is well taken. In agreement with the bulk of available information on metal pollutants in atmospheric precipitates (works of Reimann and de Caritat in the Kola Peninsula), we do agree that the anthropogenic pollution cannot be evidenced by mere enrichment factors. Moreover, we do not interpret the elevated concentrations of divalent metals, As and Sb as necessarily pollution from the industrial centers. Rather, volatile Pb, Cd, As may originate from long-range transport of desert material. We do discuss the fly ash (burning spheres) distribution in the context of gas flaring and road pollution (Section 4.2). Following recommendation of reviewer, 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 new 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

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snow sampled in this work.

The reviewer also provided a list of very useful detailed comments, most important of them are addressed below:

Line 286: what about Ga, Co and Cl, which present similar values in Fig. S4 than the element cited in the text? The riverine spring-time fluxes of Ga, Co and Cl in the southern, permafrost –free zone of the WSL can be provided by melted snow.

Line 298: Mg and Ca are not plotted in Fig. 6. Fig. 6 presents only the elements those fluxes in rivers are affected by snow deposition. See Fig. S4 of Supplement for Mg and Ca fluxes.

L365: I agree regarding the marine aerosols but what about the atmospheric deposition that come from anthropogenic or lithogenic origins? Could they be enriched in Fe- or organic-colloids? There is no known anthropogenic source of Fe north of 63°N. The lithogenic Fe from underlying clays is also unlikely since the mineral (clay, silt) horizons is permanently frozen in the continuous permafrost zone of the WSL.

Lines 398-399: Is this not an important conclusion of this study? This should appears in the abstract and the conclusions. We totally agree. The supply of mineral particles from the snow may also significantly enrich the rivers and lakes in dissolved alkaline earths, metal micronutrients, phosphorus and other elements given high reactivity of incoming silicate and carbonate grains in acidic (pH < 3-4), organic-rich (10 < DOC < 50 mg/L) surface waters of Western Siberia. Note that we currently collecting the dust from the Kazakhstan steppe for laboratory leaching by western Siberian surface waters.

Check the correspondence between the figures and the text: Ca and Mg do not appear in Figure 6. This is true. Shown in this figure are only the elements that are sizably affected by atmospheric deposition, averaged across full WSL territory. Ca and Mg appear only in Fig S4 C, for the continuous permafrost zone which shows indeed, the

similarity of snow deposition of Ca and Mg and the flux of these elements in rivers. In the revised version, we would like to place the Figure S4 in the main text.

References Bini, C., Sartori, G., Wahsha, M., Fontana, S., 2011. Background levels of trace elements and soil geochemistry at regional level in NE Italy. *J. Geochemical Explor.* 109, 125–133. <http://dx.doi.org/10.1016/j.gexplo.2010.07.008>. de Caritat, P., Reimann, C., Chekushin, C., Bogatyrev, I., Niskavaara, H., Braun, J., 1997. Mass balance between emission and deposition of airborne contaminants. *Environ. Sci. Technol.* 31, 2966–2972. Gourdol, L., Hissler, C., Hoffmann, L., Pfister, L., 2013. On the potential for the Partial Triadic Analysis to grasp the spatio-temporal variability of groundwater hydrochemistry. *Appl. Geochem.* 39, 93–107. <http://dx.doi.org/10.1016/j.apgeochem.2013.10.002>. Hartigan, J., 1975. *Clustering Algorithms*. John Wiley and Sons, NY. Kaufman, L., Rousseeuw, P.J., 2005. *Finding Groups in Data*. John Wiley and Sons Inc., NY (368pp). Levitan, D.M., Zipper, C.E., Donovan, P., Schreiber, M.E., Seal, R.R., Engle, M.a., Chermak, J.a., Bodnar, R.J., Johnson, D.K., Aylor, J.G., 2015. Statistical analysis of soil geochemical data to identify pathfinders associated with mineral deposits: an example from the Coles Hill uranium deposit, Virginia. USA. *J. Geochemical Explor.* 154, 238–251. <http://dx.doi.org/10.1016/j.gexplo.2014.12.012>. Lin, X., Wang, X., Zhang, B., Yao, W., 2014. Multivariate analysis of regolith sediment geochemical data from the Jinwozi gold field, north-western China. *J. Geochemical Explor.* 137, 48–54. <http://dx.doi.org/10.1016/j.gexplo.2013.11.006>. Moragues-Quiroga C., Juilleret J., Gourdol L., Pelt E., Perrone T., Aubert A., Morvan G., Chabaux F., Legout A., Stille P., Hissler C. 2017. Genesis and evolution of regoliths: Evidence from trace and major elements and Sr-Nd-Pb-U isotopes. *Catena* 149 (2017) 185–198 Pokrovsky O.S., Manasypov R.M., Loiko S.V., Shirokova L.S., 2016b. Organic and organo-mineral colloids of discontinuous permafrost zone. *Geochimica Cosmochimica Acta*, 188, 1–20. Reimann, C., Filzmoser, P., Garrett, R.G., Dutter, R., 2008. *Statistical Data Analysis Explained: Applied Environmental Statistics with R*. John Wiley and Sons Ltd., NY (343pp). Reimann, C., de Caritat, P., 2000. Intrinsic flaws of element enrichment fac-

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

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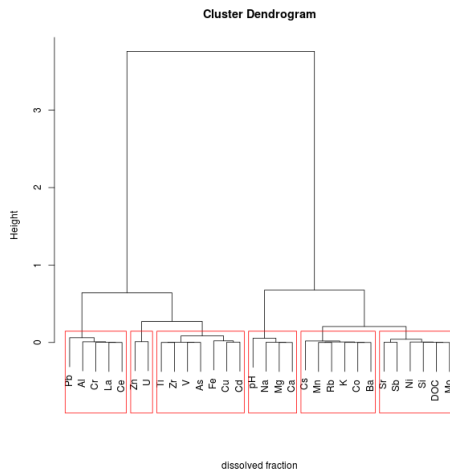


Figure 1. Dendrogram of a hierarchical cluster performed on variables of a reconstructed table for the dissolved fraction using Pearson correlation distance as distance measure and Ward's method for the linkage rule.

Fig. 1.

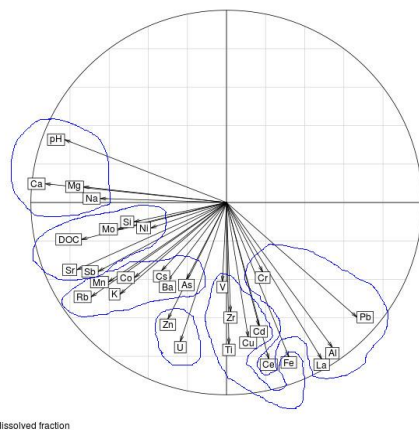


Figure 2. PCA Factorial map F1xF2 of elements of a reconstructed table for the dissolved fraction. Partition of elements into 6 groups revealed by a CAH is shown by a contour line.

Fig. 2.

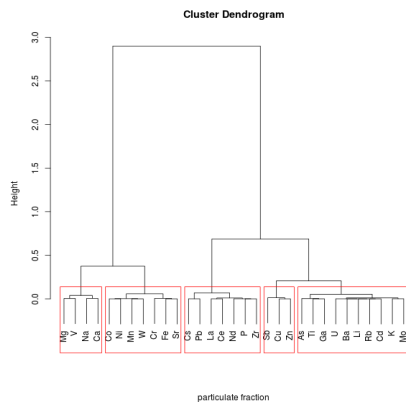
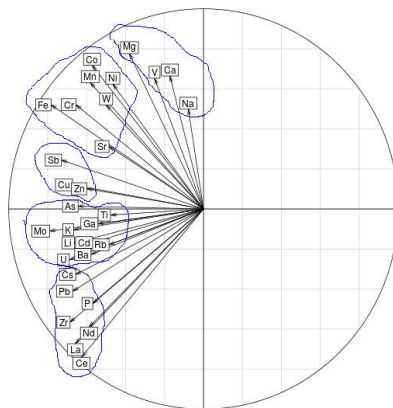


Figure 3. Dendrogram of a hierarchical cluster performed on variables of a reconstructed table for the particulate fraction using Pearson correlation distance as distance measure and Ward's method for the linkage rule.

Fig. 3.



particulate fraction

Figure 4. PCA Factorial map F1x2 of variables (elements) of a reconstructed table for the particulate fraction. Partition of elements into 5 groups revealed by a CAH is reported by a contour line.

Fig. 4.

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