Reply to comments to Referee of "Trace metal distribution in pristine permafrostaffected soils of the Lena River Delta and its Hinterland, Northern Siberia, Russia"

by I. Antcibor et al.

C. Reimann (Referee)

clemens.reimann@ngu.no Received and published: 21 March 2013

General comments:

The paper describes soil properties (pH and texture) and trace element concentrations (12 elements: C, N, Cd, Pb, Ni, Cu, As, Fe, Mn, Zn, Co, Hg) from 7 soil profiles collected along a south-north transect in the Lena river delta and from 5 additional soil profiles collected on Samoylov Island. The authors try to establish background levels of the discussed trace elements for the Lena river delta based on their results and to unravel processes determining the trace element distribution within the profiles. Based on a comparison with values reported for the upper continental crust and "world soils" they come to the conclusion that they look at natural concentrations of trace elements in the Lena delta.

These are certainly interesting data from a little visited part of the world. Unfortunately, I have severe objections against the statistical treatment and presentation of the data.

We thank Prof. Clemens Reimann for providing helpful comments and suggestions to improve and clarify the manuscript. The suggestions were carefully considered and implemented in the text. Particularly, we used the exploratory data analysis which includes box plots and XY-plots to present our results.

Specific comments:

Introduction

Starts with "Heavy metals" – throughout the paper you use quite consistent the much better term "trace metals" – why here right at the start the ill-defined term "heavy metals" (see Duffus, 2002, Chapman, 2007)?

<u>Author's response</u>: The term "heavy metals" was replaced with the term "trace metals" as suggested.

Kola Peninsula: the classical reference to the distribution of trace metals in the environment surrounding the Nikel and Monchegorsk smelters is the Kola Atlas (Reimann et al., 1998).

<u>Author's response</u>: In the revised version of manuscript the references were used for the data comparison and discussion section, and included in the reference list as suggested.

Methods

The description is in parts a bit chaotic and needs some revision. You did certainly not first grind the samples to then determine the grain size composition.

<u>Author's response</u>: We considered this important comment in the section Methods in the part describing the sample preparation. The text was changed as suggested.

For the determination of the trace elements you used obviously an aqua regia extraction, this should be spelled out. DIN ISO 11466 is missing in the references.

<u>Author's response</u>: This change was performed as suggested. DIN ISO 11466 was added in the references.

(1) An aqua regia extraction does NOT result in "total metal concentrations". (2) I miss some words on quality control.

<u>Author's response</u>: (1) Objectively, an aqua regia extraction does not give results of "total metal concentration". Thus, according to Taraskevicius et al (2013), aqua regia method enables to extract nearly 90% of Cd, Cu and Zn, and from 79 to 89 % of Mn, Ni, Co, As and Pb. The term "total" was replaced with extraction of elements by aqua regia. (2) Quality control treatment included standards for each element, extended standard soil samples which are regularly analyzed and compared with other laboratories, laboratory sample replicates and reagent blanks. The detection limits for each element in mg kg⁻¹ were presented in the table of trace elements measurement. All information about quality control was included as suggested.

Statistical data analysis: the very first problem you meet here is that you are dealing with compositional data. Classical statistics are not suitable for the analysis of closed data. It is well established that PCA and correlation analysis are especially prone to fail (see, e.g., Aitchison, 1986, 1997).

<u>Author's response:</u> We considered carefully this important comment. In revised version of the manuscript we used exploratory data analysis techniques instead of ANOVA-test and principle component analysis as suggested in the next comment.

Trace elements in soils: *Table 5 shows mean values and standard deviations – these are not suitable measures of central tendency and variation for compositional data. You should use the median, and given that you have so relatively few results (between 2 and 8 samples for the calculations) provide minimum and maximum value so that the reader gets an unbiased impression of the variation. The statistical tests and p-values for results based on so few samples may look impressive but make little sense. I also react a bit to the fact that you first collect all the different horizons and then throw the trace element data together here. With the data at hand you should use simple EDA (exploratory data analysis) techniques to present and study your data graphically.*

<u>Author's response</u>: We thank referee for the valuable advice. The data was presented in a proper way as suggested.

It could for example be interesting to study a few transect (south-north) plots of your data – preferably top and bottom horizons plotted separately.

Author's response: This suggestion was adopted and implemented.

Looking at the sample names in the tables I get the impression that more than the reported locations have been sampled (TIK locations)? Are their additional data that are not presented here?

<u>Author's response</u>: It is true that there are more TIK locations (see: *Herzschuh et al., 2009*, Zubrzycki et al., 2012***) than were reported in this study. Unfortunately, there is no data available for other locations because of a limited amount of soil material. To avoid confusion, the station ID's of the present study were changed to a more appropriate form. The

correspondence table with ID names of the present study and the previous was added to the supplement of revised version of the manuscript.

* - Herzschuh, U., Bolshiyanov, D., Pestrjakova, L., Boersma, M., Abramova, K., Zubrzycki, S., Biskaborn, B., Klemm J., and Vakhrameeva, P. "Ecological state of permafrost lakes and their catchment along a North-South transect in north-central Yakutia: past and present", Polarforschung, 600, 22-24, 2009.

** - Zubrzycki, S., Kutzbach, L., Vakhrameeva, P., Pfeiffer, E.-M., 2012: Variability of Soil Organic Carbon Stocks of Different Permafrost Soils: Initial Results from a North-South Transect in Siberia. In: Hinkel, K.M. (Hrsg.) Proceedings of the 10th International Conference on Permafrost. Salekhard, 485-490

In Figure 2 the scales used for top and bottom soils are quite different – that makes comparison quite difficult for the reader.

Author's response: This change was performed as suggested.

Discussion

You compare here to rather outdated reference values, there exist much newer and better compilations, some even providing aqua regia data. When comparing to Taylor, Vinogradov or Bowen you compare to true total concentrations (as measured by XRF or INAA). Please use a recent compilation (e.g., Caritat et al., 2012), or the existing modern soil values from northwestern Russia as provided in the Kola atlas (Reimann et al., 1998) or the Barents atlas (Salminen et al., 2004).

<u>Author's response</u>: This important note was followed for comparison with our data and discussion section and as suggested. The new references were included at the reference list.

Note that you suddenly start to use the ill-defined term "heavy metals" quite a bit in the discussion.

Author's response: The comment was adopted and the term "heavy metals" was changed.

PCA: how was that carried out? Were the data opened prior to applying PCA? In addition you have very few samples and more variables than samples: this is a situation where PCA may not be an ideal multivariate technique. The PCA can also not be used to prove anything, it may suggest certain relations, but the proof would have to come from somewhere else.

<u>Author's response</u>: The OriginLab package version 8.6 was used to run the principle component analysis. The PCA was carried out using 13 observations (TIK01 – 1 station, TIK04 – 1 station, TIK21 – 1 station, TIK20 – 1 station, TIK05 – 2 stations, TIK14 – 1 station, TIK13 – 1 station, Samoylov – 5 stations) and 12 variables (trace metals, organic matter content and soil texture). We did not want to prove but to explore possible relationships among our variables and observations. Unfortunately, the data was not opened before to implement the PCA technique. We thank the referee for pellucid explanation of our mistake. The PCA analysis was not used anymore in revised version of the manuscript.

Conclusions

I do usually not expect to find references in the conclusion. Topics that still need references should be treated in the Discussion.

<u>Author's response:</u> The suggestion was adopted. The references were excluded in the section Conclusions.

REFERENCES quoted in the review

<u>Author's response</u>: We thank Prof. Reimann once more for providing references which helped to significantly improve the manuscript.