



## ***Interactive comment on “Manganese redox cycling in Lake Imandra: impact on nitrogen and the trace metal sediment record” by J. Ingri et al.***

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This is very important and timing work aimed at addressing the fundamental mechanisms of element biogeochemistry in boreal subarctic lake. It is probably the first paper on trace element (TE) in sediments and water column of a high-latitude lake. Although this lake was thoroughly studied by Russian researchers in the past (including one co-author of the present manuscript), this manuscript clearly adds to our knowledge of subarctic lake geochemistry and as such deserves a publication in the special issue of the journal.

In view of novelty of the present work, especially concerning the sediments geochemistry, a short review on lake, not marine sediments, is necessary. It would be important to explain, what is actually known on sediments in arctic and subarctic lakes. In par-

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ticularly, what is known on polluted lakes in Canada, or in the Norilsk region? The work of Couture et al. (2010) may be also useful. (Couture, RM; Gobeil, C; Tessier, A. (2010). Arsenic, iron and sulfur co-diagenesis in lake sediments. *Geochimica et Cosmochimica Acta* 74, 1238-1255).

In the Introduction, the reader learns that there are 2 books (in Russian) by T. Moiseenko devoted to the geochemistry of this lake. A question arises, what is new in the present study. This should be briefly addressed.

The authors collected pore water samples from three different depths. Unless the sediment samples are extremely wet and contain high water amount, the extraction of the pore waters is not a simple task and should be explained in details. Was centrifugation used? How the anoxic conditions were maintained?

Long description of chemical composition of the water column may be shortening as chemical composition of the lake water should be available from numerous previous studies, including books of Moisseenko. In this regard, what is the difference of water column chemical composition parameters measured in 1995 in this study and during other periods, reported by earlier authors? Is there any temporal trend in major hydrochemical parameters?

#### Major recommendations.

-Discuss the possibility of release of the metals stored in contaminated sediments to the Arctic ocean

-The last sentence of the Abstract, that tracing direct influence of particles from different pollution sources, may be a general phenomenon applied to many other high latitude lakes.

A very important conclusion achieved in this work is that none of the analyzed TE shows a pattern that looks like the Fe/Ti ratio; as such, Mn-rich particles act as a scavenger for all these elements. An interesting question is how far this conclusion can

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be extended to other boreal lakes, notably those having high DOC (and, thus, Fe(III)) concentration?

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The authors discuss a lot the data in the temporal context (various periods, affected the sediment chemical composition). Is there any dating of collected sediments? Or probably similar sediments of adjacent lakes N Karelia and Kola Peninsula? What are the paleogeographic reconstructions? Some works of D.A. Subetto, on boreal lake sediments, may be helpful here.

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It appears only at the end of the paper that Mn oxide is the main carrier of the trace metals. However, the possible role of other TE carriers, Fe oxyhydroxides, organic detritus and aluminosilicate matrices is not at all discussed and not quantified – even if their role is minor compared to Mn oxydies.

The coupling between Mn and NH<sub>4</sub> cycle is very interesting. The authors present very complete and thorough analysis of these processes. However, most discussion is based on observations performed in marine environments. Is something known on the freshwater settings?

How reliable is ex-situ filtration of low-oxygen (anoxic) bottom waters? Filtration artifacts during separation dissolved vs. particulate phase may become important here.

A negligible role of particulate Fe in scavenging and remobilization of TE in the bottoms layers is, as the first glance, unexpected result given well known importance of Fe colloids and particles in TE transport in boreal waters. However, this result can be understood from the view point of very low concentration of DOC (and thus, Fe) in Imandra lake waters. Low concentration of dissolved and colloidal Fe, non-stabilized (in the case of Imandra) by DOM is therefore responsible for low concentrations of this metal in the water column. How general is this conclusion, can it be extended to other lakes of the northern regions?

Despite unequivocal dominating role of Mn oxides on TE behavior in bottom layers,

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no attempt is made to calculate the surface area of Mn oxy(hydr)oxides to evaluate the mass balance and surface capacity to accommodate all TE. What would be the proportion of metals incorporated inside the particles compared to that of adsorbed metals? For example, Ba and Mo are incorporated in the Mn phase (p.300, line 20) while Ni, Cu and Zn are more surface-related (section 5.2.2). The reasoning for this solely from the authors' data remains unclear. Overall, adsorption versus coprecipitation of trace metals with Fe and Mn oxides is not sufficiently discussed. It is possible that during massive precipitation of Mn oxide at the redox boundary, TE will be rather incorporated than simply adsorbed at the particle surfaces given i) higher efficiency of coprecipitation phenomena and ii) sufficient number of bulk sites available to accommodate all TE.

Figure 10: No data on pore water sediments at depth 8-10 cm are shown as stated in the end of section 3.1. Presented data on porewaters end up at 5 cm depth.

The authors have probably tested this, but it might be useful for the reader to address the issue of element pair correlations. Such correlations can be presented for the i) water column, ii) pore waters, and iii) sediments. Surprisingly there is no analysis and discussion of REE behavior.

Technical details: Last § of the Introduction; the authors state that there are five periods of Lake pollution. These periods should be briefly discussed. Analytical part: While the analysis performed in Lulea cast no doubt on their accuracy, analysis in laboratory of Kola Peninsula require at least the indication of uncertainties and detection limits. Which reference material was used to verify the correctness of the analysis? LKSD? SLRS-4? Phosphorus is potentially important carrier of trace metals in the sediments. Do the authors have any identification of P-phase in sediments? What are the results of organic versus mineral phosphorus analysis? P. 287, section 4.2.5: Is dissolved Fe and Mn concentration distribution independent on the redox status of the water column? First sentence of section 4.2.6: There is no data on porewater concentration in Fig. 12 – unlike what is stated in the manuscript. P. 290, lines 13-15: Please reference

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a figure illustrating this sentence The dissolve Mn peak 2 m above the sediments is, indeed, intriguing. Note that it is based on one single sampling, not the average. How significant is this double peak? The last sentence of section 5.2.1 is unclear. Section 5.2.3, Cobalt, not cobolt. The last sentence of Summary is unclear or unsupported by the data.

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