

**Referee comment on BG discussion paper: Manganese redox cycling in Lake Imandra: impact on nitrogen and the trace metal sediment record by Ingri et al.**

General comments:

The study describes the geochemical cycling of major and trace elements in a boreal subarctic lake (L. Imandra) in the Kola peninsula. The manuscript therefore addresses important scientific questions relevant to the scope of BG. There are few previous published studies that have looked at the fate of major and trace elements in the region and lake Imandra in particular. The authors conclude from the study that the distribution and geochemical cycling of major and trace elements in L. Imandra is largely controlled by Mn redox cycling especially in the upper sediment layer and the overlying water. The observation is mainly based on previous published studies on similar systems and measurements of trace and major elements (including ancillary parameters) from a single sampling point during three seasons (April, August and October) in the lake nearly sixteen years ago (1995). I think the quality of the data set is good but no quality control measures (e.g. analysis of sediment or water certified reference materials) on the analytical measurements are reported.

Specific comments: Novelty

While this particular data set and its interpretation as it relates to the biogeochemistry of L. Imandra might be new (*vide infra*), the authors have not presented any novel ideas in the work. For example a study by Moiseenko 1999 (Moiseenko, 1999) on the fate of metals in the Arctic surface waters also points at the dominant role of Mn redox cycling in the fate of other trace metals (e.g. see figure 8 in that study).

Although the authors have extensively cited previous studies on redox cycling of trace metals in aquatic systems in general, I feel they have done a rather poor job of citing previous and especially recent work on the fate of major and trace elements in the region and specifically on L. Imandra by other workers (e.g. see (Malinovsky et al., 2002; Moiseenko, 1999; Moiseenko and Gashkina, 2007; Moiseenko et al., 2009a; Moiseenko et al., 2009b)). For example only three studies by Moiseenko et al. are cited in the study (two books in Russian and an unpublished report). I found more than four studies dealing with the fate of trace elements in the study region and specifically on L. Imandra, All published in peer-reviewed English language journals some as recently as 2009 (See reference list below)!

Presentation:

The presentation of the work is generally well structured but there are far too many figures in the manuscript (thirteen figures most of which have up to five subsets, i.e. a total of 79 figures in the manuscript!). The size of most of these figures (except figure 1 and figure 4) is too small to be clearly legible (e.g. I had difficult distinguishing between different curve labels in most of the graphs).

Other comments:

Dissolved organic matter (especially dissolved organic carbon) plays an important role in the cycling of trace metals in aquatic systems. I was therefore expecting the authors to report measurements of DOC and may be a discussion of its (DOC) role in the cycling of

trace metals (especially Cu which exists predominantly bound to organic ligands in most aquatic systems).

A discussion on how the difference in partition coefficients  $K_d$  of different trace metals studied affects their adsorption and hence transport would also have been helpful.

Finally I was expecting some budget calculations on the metal loads to the lake based on the data set and may be a comment on more recent trend since the study was done in 1995

More detailed comments:

*Abstract:*

The abstract is too vague and should be modified to better highlight more specifically the major findings and especially what is new in the study. Line 13 (*..Ba and Mo form a phase (or inner sphere complex) with Mn*). I think the statement about “inner sphere complex” is speculative as no study was done to confirm that and should be removed. Some budget calculations and numbers on metal loads to the lake would greatly improve the quality of the abstract.

*Introduction:*

The authors should a comment more on previous related work on L. Imandra and may be dwell less on more general studies on cycling of trace elements in aquatic waters. The aim of the study should also be more clearly stated. The *five periods* alluded to in line 17 in page 276 should be stated there after the end of that sentence.

The reference in line 27 (Moisenko et al., 2002) on page 276 (under study area) should probably be complimented with a more publicly accessible English language published study by the author e.g. (Moiseenko, 1999; Moiseenko et al., 2009a; Moiseenko et al., 2009b).

*Sampling and analytical Methods:*

This section seems to have been written in a hurry and aimed to a readership that is expected to be familiar with the abbreviations and places referred to rather than the BG readership in general. The authors should rewrite it with more care and pay more attention to detail.

The authors should state more clearly the polymer material the sampling containers were made of instead of *....25 l plastic cans!* ( line 22 and 23 page 278)

Page 280, line 3: what quality of acetic acid was used (trace metal grade?)

A number of abbreviations are not obvious and need to be clarified here e.g. Page 28 , line 19.

Page 280 line 24 and 25, GFAAS *Perkin Elmer 460 technique*.. this refers to an instrument not a technique.

Page 280: Does *Analytica* refer to a lab, where is the laboratory?

Page 280, line 1-6:

The methods used for nutrients analysis should be cited and the instrumentation used stated.

The authors should also detail the protocols they used to extract pore water and preserve its integrity.

Page 280, line 14. ICP-AES is an instrument not a technique.

Page 280, line 21: Is this sentence complete?

*Results:*

Page 282 section 4.1: are the five periods based on dated sediment records?

Page 282 line 24: I could not locate the reference (Moiseenko et al., 2000) in the reference list

*Discussion*

The discussion on page 290 section 5.1 and elsewhere on anaerobic ammonium oxidation is speculative. I also wonder whether the extensive speculative discussion on bacteria mediated redox process purported to occur in the lake is justified since there were no studies done on the bacteria community in the lake? I am of the opinion that the authors should limit their discussion to what the current data supports.

I am also not very comfortable with all the redox equations the authors claim explain the redox processes, as the data does not seem to support them.

### **References cited**

Malinovsky, D., Rodushkin, I., Moiseenko, T. and Ohlander, B., 2002. Aqueous transport and fate of pollutants in mining area: a case study of Khibiny apatite-nepheline mines, the Kola Peninsula, Russia. *Environmental Geology*, 43(1-2): 172-187.

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Moiseenko, T.I. and Gashkina, N.A., 2007. The distribution of trace elements in surface continental waters and the character of their migration in water. *Water Resources*, 34(4): 423-437.

Moiseenko, T.I., Gashkina, N.A., Sharov, A.N., Vandysh, O.I. and Kudryavtseva, L.P., 2009a. Anthropogenic transformations of the Arctic ecosystem of Lake Imandra: Tendencies for recovery after long period of pollution. *Water Resources*, 36(3): 296-309.

Moiseenko, T.I. et al., 2009b. Long-term modification of Arctic lake ecosystems: Reference condition, degradation under toxic impacts and recovery (case study Imandra Lakes, Russia). *Limnologica*, 39(1): 1-13.