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# Sediment reference concentrations of seldom monitored trace elements (Ag, Be, In, Ga, Sb, Tl) in four Swedish boreal lakes — Comparison with commonly monitored elements

E. Grahn \*, S. Karlsson, A. Düker

Man-Technology-Environment Research Centre, Department of Natural Sciences, Örebro University, SE-701 82 Örebro, Sweden

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#### Abstract

This paper presents reference and recent acid-leachable concentrations of some seldom monitored trace elements (SMTE; Ag, Be, Ga, In, Sb and Tl) in sediments from four boreal oligotrophic lakes in a south to north transect in Sweden. For comparison commonly monitored trace elements (As, Cd, Co, Cr, Cu, Ni, Pb and Zn) are included as well as those of relevance for redistribution processes (Al, Ca, Fe, Mg and Mn).

Pore water pH and the corresponding solid/solution distribution coefficients ( $K_d$ ) indicated that redistribution of the elements due to acidification is minor. The depth of impact was defined as the level in the sediment where the mean values became constant on successive exclusion of metal concentrations in overlying strata. Reference concentrations were calculated below the depth of impact. The present concentration changes are estimated by the ratio between the average concentration above the depth of impact and the reference concentration.

Reference concentration ranges for the SMT-elements are (mg/kg, dry wt.): Ag 0.16-0.66; Be 1.6-3.7; Ga 2.0-5.1; In 0.05-0.22; Sb 0.05-0.11 and Tl 0.17-0.70. The concentration ratios for these elements ranged in the two most southern lakes from 1.5 to 4.5 and in the two northern ones from 0.6 to 1.6. A high correlation between  $K_{\rm d}$  for the SMT-elements, and iron, except for Sb and Tl, infer that the biogeochemistry of iron is quantitatively important for the accumulation of these elements.

The reference concentration ranges for the commonly monitored trace elements are (mg/kg, dry wt.): As 7.0–29.6; Cd 0.33–0.98; Co 5.7–23.8; Cr 15.2–26.1; Cu 27.6–58.4; Ni 5.4–20.8; Pb 44–96. The corresponding concentration ratios were 1.2–18 (second highest 3.9) in the two most southern lakes and 0.8–1.6 in the two northern ones. Declining ratios were found from south to north, most obvious for cobalt and zinc. The copper ratios did not show a regional pattern, partly because of the impact from old mine waste.

Increased concentrations of Ag, Be, Ga, In, Sb and Tl in recent sediments up to 4.5 times the reference levels in combination with the geographical pattern infer an elevated loading of these elements.

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Keywords: Seldom monitored trace elements; Lake sediment; Reference concentrations; Solid/solution distribution

#### 1. Introduction

Environmental pollution by commonly monitored trace elements (i.e. As, Cd, Co, Cr, Cu, Ni, Pb and Zn) has been in focus for decades. Increasing industrial use

<sup>\*</sup> Corresponding author. Tel.: +46 19 30 10 31; fax: +46 19 35 66. E-mail address: evastina.grahn@nat.oru.se (E. Grahn).

of seldom monitored trace elements (SMT-elements; Ag, Be, Ga, In, Sb and Tl) would in theory lead to increased environmental concentrations. A long-range atmospheric transport of them has been demonstrated since their levels have increased in the Arctic (Wolff et al., 1999; Planchon et al., 2002; Macdonald et al., 2005; Van de Velde et al., 2005) which indicates a global pollution. Combustion of fossil fuels and waste is a major source. An increasing fraction of the waste in industrialised countries consists of electric and electronic items (Ogilvie, 1997) where the SMT-elements are common. Since this sector is expected to maintain its rapid growth in the near future (Ogilvie, 1997) emissions are also expected to increase.

The pollution history of trace elements has been established in different environmental matrices such as ice cores from polar regions (Wolff et al., 1999; Planchon et al., 2002; Macdonald et al., 2005; Van de Velde et al., 2005), inland glaciers (Van de Velde et al., 1999; Rosman et al., 2000) and peat bogs (Shotyk et al., 1996; Shotyk and Krachler, 2004). The two latter matrices from central Europe have indicated increased deposition of some SMT-elements as a response to the growth of industry, but still at rather low amounts. Increased levels of, for example silver and antimony in peat cores from the last three thousand years emphasise the importance of accurate reference concentrations in environmental matrices that are used for quality assessment. Lacustrine sediments are frequently used for environmental quality monitoring but relatively little is known about the preindustrial and present concentrations of SMT-elements. In Sweden, Lithner and Holm (2003) reported lower concentrations of Ag, Be, In, Sb and Tl towards the north in a study of fresh lacustrine sediments, which would indicate atmospheric deposition. The concentrations of Ag, Au and Sb in fresh sediments from urbanised regions were higher than in samples from rural sites (Lithner et al., 2003) why also a local release of the SMT-elements could be important for their geographical abundance.

The magnitude of the concentration changes in sediments that are observed in a geographical context are not possible to determine without reference concentrations, although several approaches are feasible (cf. Roach, 2005). Due to the variability of natural trace metal concentrations in the Swedish bedrock, site-specific reference concentrations should be preferred instead of crustal averages. While the atmospheric deposition can be measured either in air samples or moss, the total loading to the sediment depends on both direct deposition on its surface and the mobility of trace metals in its catchment. This is in turn a function of biogeochemical processes, hydrological conditions and human impact

(e.g. acidification, and land use). The reference levels must, therefore, be determined most carefully.

In this study we present reference concentrations for the selected SMT-elements in lacustrine sediments in a south to north transect in a rural region in central Sweden were few recent chronological studies of trace metals in sediments exist. The impact of chemical redistribution by acidification is low why quantitative historical comparisons can be made within each lake as well as between them. Comparisons are made to Cd, Cu, Pb and Zn and the recent concentrations of the SMTelements are discussed.

#### 2. Material and methods

#### 2.1. Field sites

Four oligotrophic lakes (Fig. 1) in boreal forests in central Sweden (Tables 1 and 2) were sampled in July-August 2002. All of them serve as reference lakes in the Swedish National Environmental Monitoring Programme, why their properties are well documented. The need for lakes with sufficient background

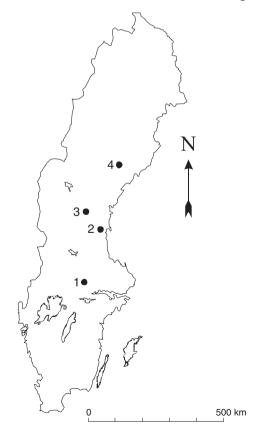


Fig. 1. Map of field sites in Sweden. 1 = Lake Övre Skärsjön, 2 = Lake Stensjön, 3 = Lake Tväringen, 4 = Lake Remmarsjön.

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