Trace elements in lake sediment as signs of environmental impact from the electronic society: reference lakes

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Abstract

All compounds and elements that are presently tied up in the technosphere will sooner or later be a part of the natural element cycles in the biogeosphere. This project investigates traces of the electronic society in the environment by chemical and paleoecological methods. Here, we report some preliminary results regarding the background levels of selected elements typically found in electronic waste, in limnic water systems.

Four reference lakes located in boreal forest areas in Sweden were sampled for water and sediment. The sediment samples were kept in an anaerobic environment (N_2-gas) until and during processing, including sectioning. Lake water and pore water was acidified with HNO_3 and analysed for metals and metalloids with ICP-MS. Lake water was also analysed for basic chemical parameters (pH, alkalinity, electrical conductivity, O_2, TOC).

Some elements, which are common in electronic and electric equipment (EEE), were detected (i.e. Ag, As, Cd, Tl). However, the elements which can be expected to be most typical for EEE (Ga, Ge, In, Pd, Sb, Sn, Ta) could, with few exceptions, not be detected.

So far, the results show that it is possible to analyse some EEE-elements even in reference lakes.

Background

The modern society in the industrialised world is in some respects an e-society, i.e. a society dependent on electric and electronic equipment (EEE). The consumption of EEE has increased tremendously during the last decades and the growth will continue according to available forecasts (Taberman et al., 1995). Increased production and accompanied use of EEE are of course generating an increasing amount of waste with elements and compounds at concentrations and combinations not naturally occurring. This will most likely have environmental consequences since EEE hold a huge variety of chemical constituents, both elemental (metals/metalloids) and organic compounds (PCB, brominated flame retardants etc.) (Hedemalm et al., 1995). The potential environmental problems came to public awareness and motivated a change in the Swedish legislation in July 2001 when producer responsibility was introduced. However, although the legislation requires recycling of the majority of products it does not solve all environmental problems related to EEE. Far from all elements or organic compounds can be recycled due to technical or economical reasons (Sternbeck and Östlund, 1999). In addition, some components like flame-retardants, will also dissipate from the EEE during normal use (Lassen et al., 1999).

Project outline

The aim of this project is to study the environmental impact from the e-society as it is reflected by the quality of water and sediment in limnic environments. As for other sources of pollution, the composition of sediment profiles also serves as a historical record of the development of the e-society. In a first step, elements and organic compounds that can be used as chemical identifiers of the e-society have been determined simply by product information on the composition of typical EEE. The expected amount of waste, and its weathering rate, as well as trade statistics are included. Thus, the chronological development of the e-society is determined by commercial information in combination with field studies.

Very few, if any, elements or organic compounds found in the environment emanate solely from EEE, why it is important to relate their abundance to production. The elements most indicative of EEE-pollution are Ga, Ge, In, Pd and Sb (Sternbeck & Östlund, 1999) i. e. EEE are one of the most

common sources of these substances to the environment. Other elements, which are frequently used in EEE but have other significant applications as well, are for example Ag, Cd, and Tl. In this paper, preliminary result from chemical analysis of a few reference lakes will be presented.

Field sites

Four reference lakes (table 1) situated in boreal forest regions in Sweden were sampled. All four lakes are included in the Swedish National Monitoring Programme performed by the Swedish Environmental Protection Agency (SEPA). No lake, besides Lake Östra Skärsjön, had any identifiable source of contaminants in the watershed.

Lake Övre Skärsjön is situated in a mining area and it is to some extent influenced by an old mine tailing deposits. A few cottages are situated around the lake. Lake Remmarsjön has a small village (50-100 residents) close to the lake. The area around Lake Tväringen is uninhabited, but a sparsely trafficked road and a railroad are found right beside the lake to the west. Lake Stensjön has only a small road used for forestry close by and it seems to be the lake which can be expected to be least affected by local anthropogenic emissions.

Material and Methods

Sampling was performed in July and August 2002 during an unusually warm and sunny summer for Swedish climate conditions. This might limit the representativity of the samples because of unusually high evapotranspiration, leading to elevated concentrations.

Lake water

Water samples for determination of metals, pH, alkalinity, electrical conductivity, TOC etc were collected at three depths: 0.3 m below the surface, at the centre of the thermocline and close to the bottom (0.5-1.0 m above sediment surface) at the same site where sediment sampling was done. Samples for determination of the total concentrations of metals was sampled separately and were acidified with concentrated HNO_3 (final concentration 2 ml/l). Samples for measurements of pH and oxygen were sampled separately and measured at site with a portable probe. Glass bottles for determination of oxygen at laboratory were filled only at the surface and bottom depths.

At laboratory was oxygen determination performed by the Winkler method (using sodium azide). Alkalinity was determined by end-point titration to pH 5.4 with dilute HCl and bubbling with N_2-gas. Total organic carbon (TOC) and inorganic carbon (IC) were analysed with a Shimadzu TOC-5000. Total metal concentrations in lake water were analysed with ICP-MS (Agilent 4500) equipped with a Babington nebuliser (or, in some cases, an ultrasonic nebuliser). Rhodium was added to all solutions as internal standard and the data was evaluated quantitatively using external calibration.

Lake sediment

Two sediment cores from each lake were taken from the deepest part of each lake with a gravity corer (HTH-teknik, Vårvägen 37, SE-951 49 Luleå). In Lake Stensjön only one core could be collected due to technical problems. Each core was split in to two sub-cores and treated separately. In Lake Tväringen the samples were taken from the second deepest part, which was situated further away from the road and railroad. The sediment cores were kept in a nitrogen atmosphere until processed. The sediment sectioning was performed in a glove-bag with a continuous flow of N_2. Each core was sectioned into 1 cm thick slices (Lake Östra Skärsjön core A 0.5 cm) down to a depth of 10 cm. Each slice was then put into 100 ml polypropylene container. At least one sample was taken from the bottom of each core, usually at a depth of 25 to 30 cm. The samples were then quickly transferred to a clean, N_2-filled glove-bag, and put into acid-washed 40 ml centrifuge tubes (PPCO; Nalgene), flushed with N_2 and then centrifuged at 20,000 g for 30 mins. The pore water was collected and acidified with concentrated HNO_3 and then analysed for metals and metalloids. Trace metal analysis was conducted in the same way as for lake water besides that data were evaluated semi-quantitatively as well.

Results and discussion

Lake water

All lakes were stratified and had a well-developed thermocline. Lake Övre Skärsjön had the lowest pH and alkalinity. The very low values might be an effect of leaching from mine deposits. Among the four lakes, Lake

Tväringen seems to be the most well buffered lake. The general trend in lake water is decreasing pH and alkalinity from water surface to lake bottom. The lakes have TOC concentrations in low to medium high levels for Swedish conditions (table 2).
The surface waters contained the lowest metal concentrations compared to the thermocline and hypolimnion, as expected. Increased concentrations of ^{27}Al and ^{51}V close
to the bottom in all of the sampled lakes indicate that settling of allochtonous material from the watershed is the primary source. Figure 1 illustrates concentration profiles for ^{107}Ag, ^{111}Cd and ^{205}Tl in Lake Remmarsjön and Lake Tväringen. Data in table 3 can be compared with reference data from the literature presented in table 4. The higher concentrations of ^{75}As in Lake Remmaren are most likely due to bedrock geochemistry.

Pore water

The pore water contained some of the elements (Ag, As, Cd, Tl,) which are common in electronic and electric equipment (EEE) (table 5). However, the elements, which are expected to be most indicative for the e-society (Ga, Ge, In, Pd, Sb, Sn, Ta), could not be found at quantifiable levels (Sternbeck & Östlund, 1999).

Metal concentrations in Lake Östra Skärsjön, which had mine deposits in the catchment area, were difficult to interpret because of large concentration changes between each sample. However, concentrations of i.e. ^{208}Pb and ^{66}Zn, were higher than in the other three lakes, which is attributed to the mine waste. Higher levels of ^{75}As in Lake Remmarsjön were also reflected in the pore water. The EEE-elements in Lake Stensjön were often below the detection limit. In general, Lake Tväringen and Lake Stensjön seem to be the most pristine lakes. Figure 2 shows the concentration of ^{107}Ag, ^{111}Cd and ^{205}Tl in the pore water of Lake Remmarsjön and Lake Tväringen.

So far, only the pore water of the sediment samples has been analysed. Further interpretation of the results will be possible when metals/metalloids in the solid phase have been measured.

The data set with four lakes is still too small to give reliable results. The data set needs to be extended with more reference lakes and lakes impacted from diffuse urban pollution.

Conclusion

The results so far show that ICP-MS technique is likely to be sufficient to reach the goal of the project. Several metals which are typical representatives for metals in EEE (Ag, Cd, Tl) could be measured even in reference lakes. The most indicative of the e-society (Ga, Ge, In, Pd, Sb, Sn, Ta) have good opportunities to be found at detectable levels in lakes with more impact from diffuse pollution from populated areas.

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Tabel 1: Lake information (http://info1.ma.slu.se/db.html)

Lake name	Position	Area (km^2)	Maximum depth (m)	Average depth (m)
Lake Övre Skärsjön	15° 33' 12" E 59° 50' 15" N	1.7	32.7	5.7
Lake Remmarsjön	18° 16' 34" E 63° 51' 47" N	1.4	14.4	5.2
Lake Tväringen	15° 40' 35" E 62° 14' 39" N	1.7	19.0	4.5
Lake Stensjön	16° 34' 43" E 61° 38' 36" N	0.5	8.5	4.2

Tabel 2: Lake water chemistry

Lake	Level	pH[a.b)]	Electrical[b)] conductivity (µS/cm)	Alkalinity[c)] mmol/l	O_2[d)] (mg/l)	TOC (mg/l)
Övre Skärsjön	1 surface	5.57	21.92	0.01	8.3	7.5
	2 thermocline	5.24	23.34	0.01	-	7.7
	3 bottom	5.13	23.31	0.01	4.2	8.2
Remmarsjön	1 surface	6.00	18.33	0.09	7.8	8.3
	2 thermocline	5.73	17.86	0.08	3.8	7.7
	3 bottom	5.58	17.10	0.07	2.7	8.5
Tväringen	1 surface	6.76	19.34	0.12	9.8	6.4
	2 thermocline	6.16	24.99	0.17	2.4	6.8
	3 bottom	6.07	25.48	0.17	0.7	8.2
Stensjön	1 surface	6.34	19.34	0.04	7.7	6.9
	2 thermocline	5.71	15.85	0.05	3.5	6.1
	3 bottom	5.58	18.27	0.01	2.5	7.6

a) The data are from measurements in the laboratory
b) measurments was performed at room temperature
c) Average of two measurements from each sample except for a single measurement from Lake Stensjön 3.
d) Level 1 and 3 are average of two measurements from each sample except for a single measurement from Lake Övre Skärsjön level 3 which are based on one measurement. Level 2 are field measurments performed with a portable probe.

Table 3: Metal concentrations in lake water (µg/l).

Lake[a)]	^{75}As	SD	^{107}Ag	SD	^{111}Cd	SD	^{205}Tl	SD
Ö Skärsjön 1	0.35	0.01	0.01	5.49E-05	0.03	0.00	0.05	0.00
Ö Skärsjön 2	0.33	0.01	0.01	0.00	0.03	0.00	0.05	0.00
Ö Skärsjön 3	0,35	0.01	0.01	8.24E-05	0.03	3.95E-09	0.05	0.00
Remmarsjön 1	0.57	0.00	b.d	0.00	0.01	0.00	0.05	0.00
Remmarsjön 2	0.56	0.02	b.d	0.00	0.01	0.00	0.05	0.00
Remmarsjön 3	1.40	0.01	0.01	0.00	0.02	0.00	0.05	0.00
Tväringen 1	0.19	0.00	b.d	0.00	0.01	6.36E-09	0.05	0.00
Tväringen 2	0.22	0.01	b.d	0.00	0.01	0.00	0.05	0.00
Tväringen 3	0.27	0.01	b.d	0.00	0.02	0.00	0.05	0.00
Stensjön 1	0.15	1.80E-07	b.d	0.00	0.01	0.00	0.04	0.00
Stensjön 2	0.14	0.00	b.d	5.49E-05	0.01	0.00	0.04	0.00
Stensjön 3	0.24	0.01	0.01	0.00	0.01	0.00	0.05	1.29E-05

Table 4: Reference data from unpolluted fresh water lakes.

As	Ag	Cd	Tl
≤ 0.4 µg/l[b)] (SEPA, 2000)	0.001-0.005 µg/l (Shafer et al, 1994)[a)] < 0.008 µg/l (Mukherjee & Lahermo, 1995)[a)]	≤ 0.01 µg/l[b)] (SEPA, 2000)	0.001-0.005 µg/l (Lin & Niragu, 1998) < 0.01 – 1 µg/l (WHO, 1996) 0.013 – 0.024 µg/l[c)] (Axner, 1993)

a) as in SEPA, 1996
b) representing class 1 (lowest impact level)
c) data from five lakes

Tabel 5: Metal concentration in pore water at 0-1 cm in four reference lakes (µg/l). A and B = core

Lake	^{75}As	SD	^{107}Ag	SD	^{111}Cd	SD	^{205}Tl	SD
Östra Skärsjön A[a)]	7.08	0.72	0.02	0.03	0.14	0.09	0.27	0.00
Östra Skärsjön B	2.02	0.59	0.13	0.00	0.19	0.01	0.21	0.02
Remmarsjön A	23.82	0.98	0.03	0.02	0.05	0.00	0.10	0.00
Remmarsjön B	22.60	0.09	b. d.	b. d.	0.18	0.00	0.08	0.00
Tväringen A	1.10	0.82	0.01	0.00	0.24	0.00	0.13	0.00
Tväringen B	0.78	1.08	b. d.	b. d.	0.00	0.00	0.10	0.00
Stensjön A	1.03	0.41	0.06	0.02	0.04	0.07	0.22	0.03
Stensjön B	0.36	0.05	b. d.	b. d.	0.16	0.03	0.18	0.02

a) average between 0-0.5 cm and 0.5-1.0 cm

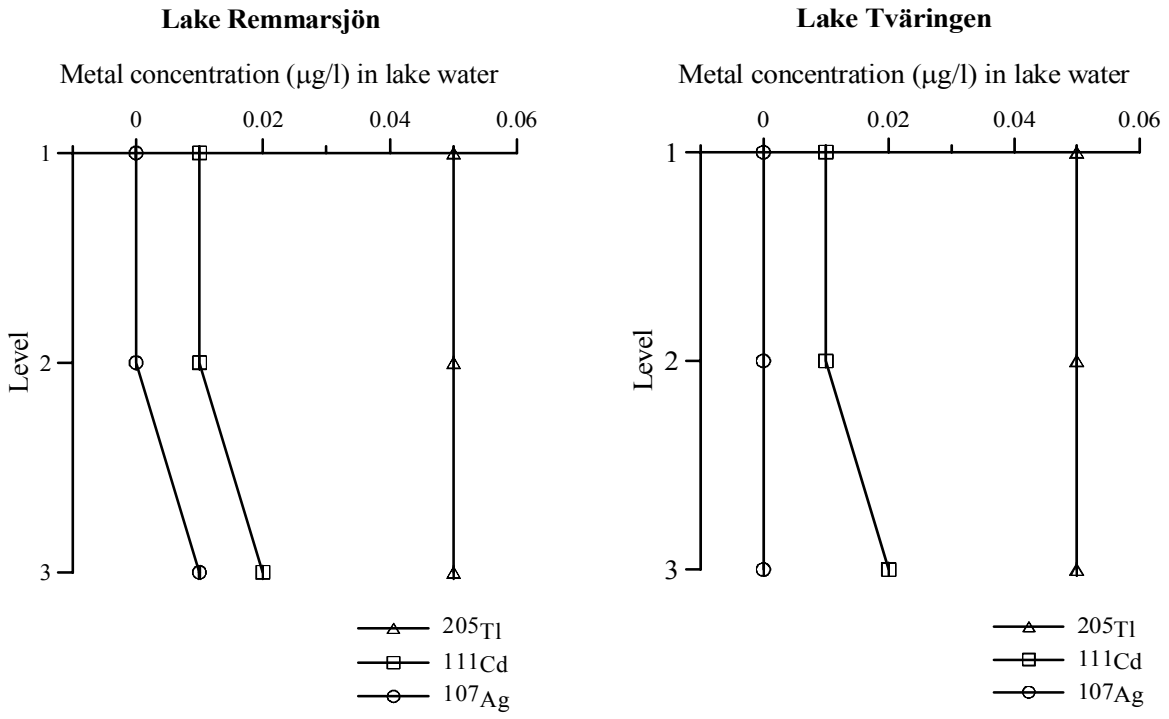

Figure 1: Concentrations profiles of Ag, Cd and Tl in lake water in Lake Remmarsjön and Lake Tväringen. The error bars represent the standard deviation.

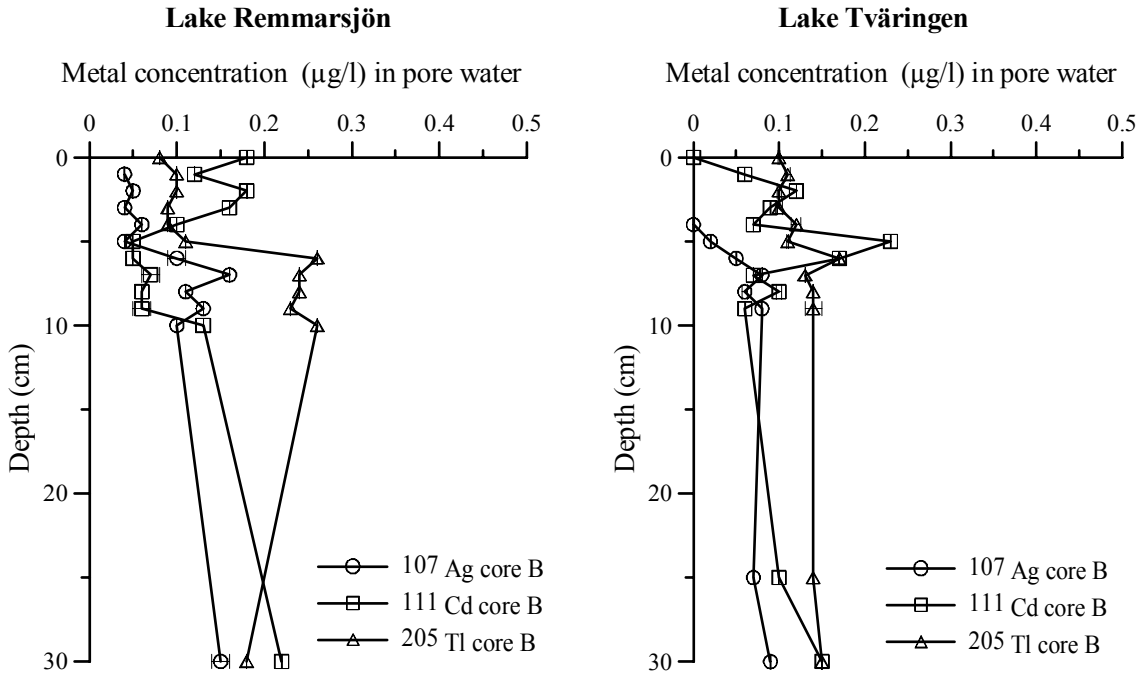

Figure 2: Concentrations profiles of Ag, Cd and Tl in the pore water of Lake Remmaren and Lake Tväringen. The error bars represent the standard deviation.