

Geothermal Wastewater Disposal: Chemical Stress Assessment – Lake Thingvallavatn, Iceland

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ABSTRACT

Production of electricity and hot water for district heating by Nesjavellir geothermal co-generation power plant in SW-Iceland utilizes high temperature steam, which contains various trace elements. The effluent from the plant is either pumped into shallow drill holes or disposed off in the Nesjavellir stream, which disappears into the lava and finds its way into Lake Thingvallavatn, a rift lake of high conservational value. Measurement of quantities of chemical constituents in effluents and lakeshore outflow sites (springs), and in the biota at outflow sites, and at a control site, Vatnskot was done. Concentrations of SiO₂, As, Al and B are elevated in geothermal effluents but are diluted before the wastewater reaches the lake. There is no detectable rise or accumulation of trace elements in the biota at the geothermally influenced sites. However, taking into account the conservational value of Lake Thingvallavatn, sound wastewater management by deep re-injection and regular monitoring of thermal influence, chemical constituents in effluents and lake outflow sites water should be adopted.

1. INTRODUCTION

Nesjavellir geothermal co-generation power plant is located in the Nesjavellir geothermal field, a high enthalpy geothermal system within the Hengill Central Volcano in south-western Iceland, on the south of Lake Thingvallavatn (Figure 1). Thingvallavatn is a rift lake of high conservational value (Jónasson, 1992), fed 90% by underground springs with the main springs entering in the north at a temperature of 2.8-3.5°C. Warmer groundwater enters the lake in the southwest from the Hengill geothermal area (Ólafsson, 1992). Geothermal investigations at Nesjavellir commenced in 1946. However, it was not until 1986 that a decision was made to harness the geothermal heat for district heating in Reykjavík (Gunnarsson et al. 1992). By 1990, 14 production boreholes had been drilled, and all except one were successful. That year the Nesjavellir power plant was commissioned, generating about 100 MW_t, by producing about 560 l/s of 82°C hot water for district heating. Due to the chemical composition of the geothermal water it cannot be used directly. Cold groundwater is therefore heated in the power plant in heat exchangers, using both geothermal water and steam. Initially only four geothermal wells were connected to the plant, but gradually more wells have been connected as the capacity of the power plant has been increased. In 1995 the capacity was expanded to 150 MW_t and in 1998 to 200 MW_t and the production of 60 MW_e of electricity commenced (co-generation plant). The co-generation power plant has two functions. The first function is to heat cold

groundwater for space heating in Reykjavík and neighborhood while the second is to produce electricity with the geothermal steam. The electricity production phase is a steam cycle design currently generated by three steam turbines, each 30 MW. The steam is condensed in a tubular condenser and cooled to approximately 55°C with cold groundwater. The condensate is disposed of in shallow boreholes in the nearby lava field. The cooling water is pumped from a shallow fresh-water aquifer (Grámelur) in the lava field 6 km away from the power plant. The temperature of the cooling water is 5-7°C. The cooling water is heated to about 55°C in the condensers, and then piped through heat exchangers, for final heating to 87°C, using the 192°C hot geothermal water from the separators. In the heat exchangers the geothermal water is cooled to 55°C (Gislason, 2000). Used and unused brine at a flow rate of 115-143 kg/s at 46 - 100°C and 343-1776 l/s of cooling water at 49-69°C are discharged in the nearby Nesjavellir stream that disappears into Nesjahraun lava at Lækjarhvarf. About 126-140 kg/s of condensate at 48-68°C is also discharged into shallow drillholes that connect to surface groundwater (Wetang'ula and Snorrason, 2003). This mixes with groundwater, which flows some 3.8 km to Lake Thingvallavatn. Present installed capacity is 90 MW_e and 200 MW_t.

The study was done in the period July 2003-February 2004 with the following aims .

- To assess the levels of chemical constituents in Nesjavellir geothermal co-generation power plant wastewater, Lake Thingvallavatn outflow sites water, and in the biota (sediments, aquatic plants, gastropod snail and fish) and compare these concentrations with reference samples and previously published data.
- To evaluate the present concentrations of chemical constituents in geothermal wastewater and Lake Thingvallavatn outflow sites water relative to international drinking water standards and aquatic life water quality criteria.
- To evaluate the present concentration of trace elements in Lake Thingvallavatn outflow sites sediment relative to sediment quality guidelines for freshwater ecosystems and/or protection of aquatic organisms.

2. METHODOLOGY

2.1 Sampling and analysis of geothermal effluent and Lake Shoreline outflow sites water

At the start of June 2003 water sampling was initiated to describe spatial variability in the water quality at various study sites along the shore of Lake Thingvallavatn

influenced by geothermal wastewater disposal by Nesjavellir geothermal co-generation power plant. Approximately ten sites were verified as definite outflow points of warm wastewater into Lake Thingvallavatn with the main outflow being around Varmagjá. The sites represented a gradient of the influence of geothermal wastewater on Lake Thingvallavatn water quality.

Water samples for analysis of dissolved chemical constituents were collected from the geothermal wastewater at Nesjavellir geothermal co-generation power plant and at Lake Thingvallavatn shoreline outflow sites. At Nesjavellir power plant, wastewater samples were collected of separator water, cooling water (heated ground water from Grámelur), condensed steam (condensate) and a mixture of wastewater at Lækjarhvarf (a point where Nesjavellir effluent stream disappear into the lava and flow down the lake). On the southern shoreline of the lake, ten sites which had been identified as definite outflows were selected for trace elements sampling based on geothermal outflow sites identified during the temperature mapping survey (Figure 2). Water samples were collected from each site. The samples were passed through a $0.45\text{ }\mu\text{m}$ Nuclepore cellulose fibre filter to remove particulates, collected into pre-cleaned polyethylene sample bottles and preserved with concentrated suprapure Ultrex nitric acid. Based on analytical results of the past studies which did not take into account most of the trace elements, the concentrations of the following elements were determined in all samples using the by ICP-SMS (Fe, Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Ti and Zn), ICP-AES (Ca, K, Mg, Na, S, Si, B and Sr) and AFS (Hg). The analysis was carried out by Analytica Laboratory, Luleå, Sweden.

2.2 Sampling and analysis of Lake biota samples

Sediments were collected from two points at Varmagjá by use of a plastic sediment corer. No sediment was found at the Eldvik outflow. Samples of aquatic moss were collected from the Varmagjá and Eldvik outflow sites. The submerged aquatic plant *Myriophyllum alterniflorum* was collected from Varmagjá only. *Myriophyllum* was not found near the Eldvik outflow. The samples were freeze-dried and homogenized before digestion. The gastropod snail *Lymnaea peregra* samples were collected by picking them from stones in the water by use of plastic pincers. The snails were freeze-dried and homogenized before digestion.

Two fish species i.e. arctic charr *Salvelinus alpinus* and threespined stickleback *Gasterosteus aculeatus* were collected from Varmagjá and Eldvik. Fish sample preparation and processing was done at Natural History Museum Laboratory, Kopavogur, Iceland. When *Salvelinus alpinus* had been weighed and its length measured, its belly was opened and the liver extracted and weighed. Before analysis the livers were whipped to a homogenous mass. The fish was filleted after the removal of its skin. The sticklebacks were processed whole for analysis.

As, Cd, Co, Cr, Hg, Ni, Pb and Zn in gastropod snail, arctic charr liver, threespined sticklebacks, moss and *Myriophyllum alterniflora* were determined by inductively coupled plasma selective mass spectrometry (ICP-MS or ICP-SMS) while Cu and Mn were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Trace elements in arctic charr muscles were analysed by ICP-SMS. For elemental analysis of sediment, the following techniques were used: ICP-AES (Cr, Cu, Zn and Mo) and Inductively Coupled Plasma Quadropol Mass Spectrometry -ICP-QMS (As, Cd, Co, Hg, Ni and Pb).

3. RESULTS

3.1 Chemical constituents in wastewater and Lake outflow sites

The concentration of some trace elements in Nesjavellir geothermal co-generation power plant effluent and lake outflow sites are presented in Tables 1. The concentrations of aluminium, arsenic, boron and SiO_2 were high in separator water ($\text{Al} = 1880\text{ }\mu\text{g/L}$, $\text{As} = 50.3\text{ }\mu\text{g/L}$, $\text{B} = 2150\text{ }\mu\text{g/L}$, $\text{SiO}_2 = 483.4\text{ mg/L}$) and at Lækjarhvarf, where the effluent stream disappears into the lava ($\text{Al} = 922\text{ }\mu\text{g/L}$, $\text{As} = 52.4\text{ }\mu\text{g/L}$, $\text{B} = 974\text{ }\mu\text{g/L}$, $\text{SiO}_2 = 245.69\text{ mg/L}$); which was also reflected in the high pH of the effluent. As expected the concentration of these elements was much lower in the condensed steam ($\text{Al} = 19\text{ }\mu\text{g/L}$, $\text{As} = 0.148\text{ }\mu\text{g/L}$, $\text{B} = 72.2\text{ }\mu\text{g/L}$, $\text{SiO}_2 = 3.540\text{ mg/L}$) and in the cooling water (Figure 3).

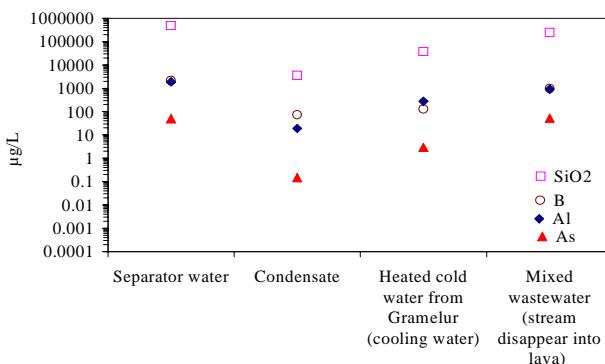


Figure 3 Concentration of "signal" chemical constituents SiO_2 , B , Al and As in Nesjavellir geothermal co-generation power plant wastewaters.

In separator water and stream effluent at Lækjarhvarf arsenic level were above the 0.025 mg/L (CCME, 1999) and 0.01 mg/L (US EPA, 2002; WHO, 1998) limits for drinking water quality guidelines, but in the lake shoreline outflow sites waters the As concentration was within the international drinking water quality guidelines. The arsenic concentration level in the effluent waters at Lækjarhvarf and water from lake outflow site 10 was above the $5.0\text{ }\mu\text{g/L}$ limit (CCME, 1999) water quality criteria for protection of aquatic life. The levels at sites 7, 8 & 9 (Figure 4a) were moderately high but within the aquatic life water quality criteria guidelines. The relatively high arsenic levels in these lake shoreline outflow site waters can be attributed to the geothermal wastewater input.

The aluminium concentration levels were low in the condensate and in waters from outflow sites 1-5 on the Lake Thingvallavatn shoreline. The Al level in separator water, heated ground water from Grámelur (cooling water), mixed effluents at Lækjarhvarf (where the stream disappears in the lava) and some lake shoreline outflow sites (7,8,9 & 10) was above the 0.1 mg/L (CCME, 1999) and $0.05-0.2\text{ mg/L}$ (US EPA, 2002) drinking water quality guidelines. These concentration levels and also Al concentration in water from site 6 were above the $5-100\text{ }\mu\text{g/L}$ limits for aquatic life water quality criteria for Al (CCME, 1999). Aluminium concentration in the water increased spatially from site 1 to site 10 (Figure 4b). High levels of Al in water from sites 6-10 may be due to high Al content in the separator water and the mixed effluent at Lækjarhvarf.

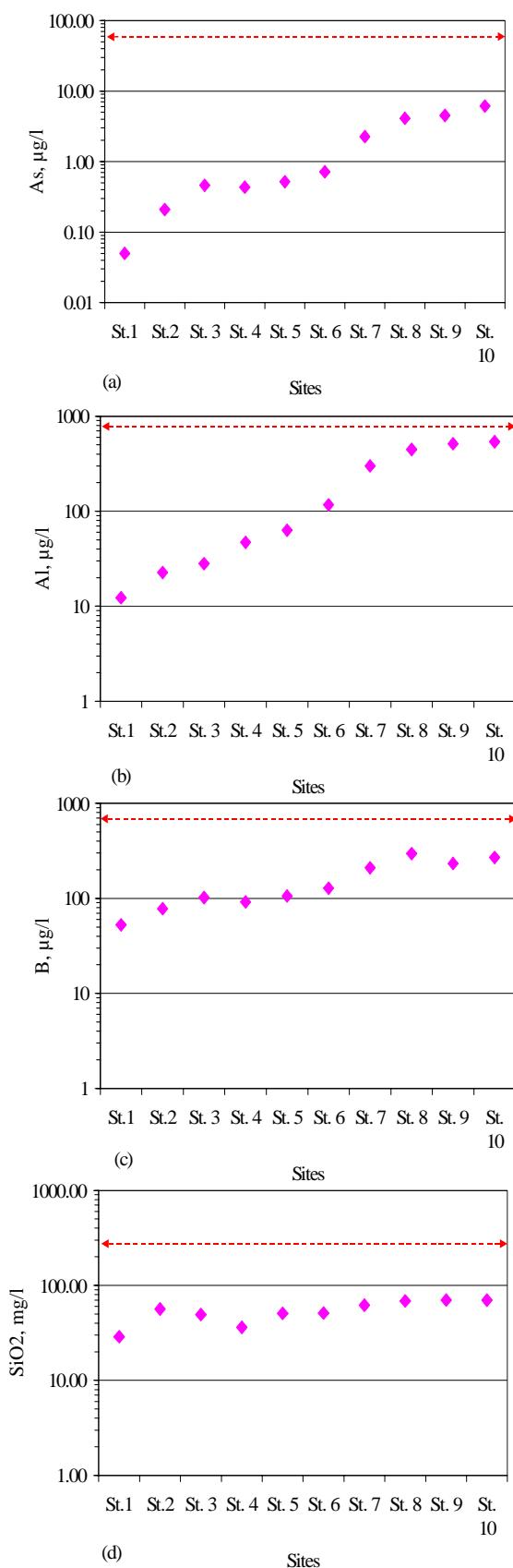


Figure 4 Spatial variation in the concentration of As, Al, B and SiO₂ at Lake Thingvallavatn outflow sites. Refer to Fig. 2 for location of sampling sites. Dotted line is the “derived” concentration assuming nothing occurs i.e. no dilution, no precipitation and dissolution as wastewater flows through Nesjahraun lava.

The highest boron concentration observed was 2150 µg/L and 974 µg/L in separator water and mixed effluent at Lækjarhvarf respectively.

Lowering of B concentration levels of mixed effluent to half that of separator water could be due to sorption of boron on the sediment and/ or dilution after mixing of separator and cooling water (heated groundwater from Gramelur). The B concentration of cooling water was around 128 µg/L, showing that it might be contaminated with geothermal effluent. Boron concentration levels were below the 5.0 mg/L (CCME, 1999) but above the 0.5 mg/L (WHO, 1998) drinking water quality guideline concentrations. At Lake Thingvallavatn shoreline outflow sites the boron concentration level was high at most sites. B concentration in water from sites 6-10 above 100 µg/L (Figure 4c). The highest concentration was observed in water from site 8 (Eldvik) although the concentrations there were still below those specified in drinking water quality criteria (CCME, 1999; WHO, 1998).

The cadmium concentration level in the geothermal effluent was <0.002 µg/L and thus below the 0.005 mg/L (CCME, 1999; US EPA, 2002) and 0.003 mg/L (WHO, 1998) drinking water quality criteria concentrations. At Lake Thingvallavatn shoreline outflow sites the concentration level was below the 0.017 µg/L (aquatic life) and 80 µg/L (livestock) water quality criteria concentration limits (CCME, 1999); and 0.005 mg/L (CCME, 1999; US EPA, 2002) and 0.003 mg/L (WHO, 1998) concentration specified in the drinking water quality criteria. Concentration level at the ten outflow sites can be categorized as “very low” (class 1 = <0.01 µg/L) except site 8 (Eldvik = 0.0158 µg/L) which was categorized as “low” (class 2 = 0.01-0.1 µg/L) with respect to Cd (SEPA, 1991).

The lead concentration level in the geothermal effluents was in the range 0.03 – 0.036 µg/L, thus below the 0.01 mg/L (CCME, 1999) and 0.001 mg/L (WHO, 1998) drinking water quality criteria concentration for lead. Lead concentration levels in lake shoreline outflow sites ranged from < 0.01 – 0.115 µg/L. This was thus below the 1-7 µg/L (aquatic life) and 100 µg/L (livestock) water quality criteria concentrations (CCME, 1999); drinking water quality criteria concentrations (CCME, 1999; WHO, 1998); and categorized as “very low” (class 1 = <0.2 µg/L) according to Swedish EPA guidelines for protection of lakes and watercourses for lead (SEPA, 1991).

The mercury concentrations ranged from <0.002 µg/L in heated ground water from Gramelur (cooling water) to 0.0056 µg/L in separator water. This is below the 0.001 mg/L (CCME, 1999; WHO, 1998) and 0.002 mg/L (US EPA, 2002) concentrations of drinking water quality standards. The maximum concentration levels in lake shoreline outflow sites waters was 0.0277 µg/L and thus below the 0.1 µg/L (aquatic life) and 3.0 µg/L (livestock) water quality criteria concentrations (CCME, 1999); and also below the drinking water quality criteria concentrations (WHO, 1998; US EPA, 2002).

The concentration levels of other trace constituents such as copper, chromium, molybdenum, nickel, manganese, and zinc were low in all geothermal effluents and Lake Thingvallavatn shoreline outflow site waters were below the international drinking water quality criteria concentrations (CCME, 1999; US EPA 2002; WHO, 1998). All these concentrations were below the 2-4 µg/L, 1.0 µg/L, 8.9 µg/L, 73 µg/L, 25-150 µg/L and 30 µg/L limits for Cu, Cr(VI), Cr(III), Mo, Ni, and Zn respectively according to

water quality criteria for aquatic life protection (CCME, 1999). The concentrations of Co, Mn, Ni and Zn in condensed steam were higher than in separator water which could be due to steel contamination. Elevated levels of Mn and Mo in the effluent at Lækjarhvarf could possibly be explained by the leaching of these elements from the rock in the streambed.

According to SEPA (1991) water quality criteria for metals in lakes and watercourse, the trace elements levels observed can be categorized as “moderately high” for arsenic at site 10 (class 3 = 5-15 µg/L), “low” for chromium (class 2 = 0.3-5 µg/L), “low” for copper (class 2 = 0.5-3 µg/L), “very low” for nickel (class 1 = < 0.7 µg/L) and “very low” for zinc (class 1 = <5.0 µg/L). Class 1 refers to metal concentrations in water which is intended to correspond to conditions in areas that have not been affected by human activities. Class 2 refers in most cases to increased concentrations of metals due to releases from local sources, or long distance transport via the atmosphere. But the levels that occur naturally in certain geologically unusual areas may fall into this class. In most cases, Class 2 levels are not high enough to cause measurable biological effects. Higher levels increase the risk of biological effects. Biological investigation is thus recommended in all areas with metal concentrations of Class 3 or higher (SEPA, 1991).

According to Icelandic government critical limits of trace metals for surface water for the protection of biota (Government News, 1999; B. No. 796/1999), the trace elements at lake outflow sites could be categorized as:- Cu and Cr (Level II- low probability of effects); Cd, Ni, Pb and Zn (Level I- Very low probability of effects); and As at site 1-2 (Level I), site 3-9 (Level II - Low probability of effects) and site 10 (Level III - Some effects expected in case of sensitive ecosystems) (see Table 2).

Concentration of SiO₂ in separator water, effluent at Lækjarhvarf and cooling water was 483.4 mg/L, 245.69 mg/L and 37.35 mg/L respectively. The SiO₂ concentration in the cooling water is two times higher than that of cold groundwater in inflow springs (Vatnsvík, Vellankatla, Flosagjá) on the northeastern and the northwestern sides of the lake reported in Ólafsson's (1992) study. This could be an indication that cold groundwater at Gramelur is being contaminated by geothermal water during flow. At Lake Thingvallavatn outflow sites, SiO₂ increased spatially from site 2 through site 10, with a maximum SiO₂ concentration of 70.11 mg/L at site 9 (Figure 4d). The SiO₂ concentration at Varmagjá was 56.33 mg/L, more than two twice the 24.6 mg/L reported in Ólafsson (1992) study.

SiO₂, Al, As, B concentration in effluent at Lækjarhvarf and lake outflow sites from wastewater mass balance

At Nesjavellir geothermal co-generation power plant separator and cooling water is disposed off into the Nesjavellir stream whose flows and disappears into Nesjahraun lava at Lækjarhvarf, while condensate is disposed off into shallow boreholes in the nearby lava field around the power plant. The stream carries surface drainage at 90 L/sec but effluent dilution will vary with runoff which may lead to flows of 1000 L/sec (Kjaran and Egilson, 1986). In order to derive some expected baseline concentrations of undesirable constituent and trace element at Lækjarhvarf and Thingvallavatn outflow sites upon disposal, the quantities of the constituents released from the power plant, their concentrations, initial dilution from their mixing, and their fate during surface and underground flow has been evaluated. From the results of measured

concentration levels of chemical constituents (Table 1), the “derived” concentration levels of SiO₂, Al, As and B at Lækjarhvarf from initial mixing was calculated based on effluent disposal flow rate data during sampling (183.8 kg/s and 1147.7 kg/s for separator water (used and unused) and cooling water, respectively); and the observed concentrations of the chemical constituents in separator and cooling wastewater. The underlying assumptions for computing the “calculated” concentration levels of the chemical constituents at Lækjarhvarf from wastewater disposal mass balance are that: (a) the stream is only receiving separator and cooling wastewater; (b) the stream channel is an isolated system where only mixing of the two wastewater types occurs with no other physical or chemical processes taking place during flow; and (c) flow is constant from the point of discharge up to Lækjarhvarf.

If the above assumptions hold, the “derived” SiO₂, Al, As and B concentration from the mix should have been 98.92 mg/L, 499.14 µg/L, 6.29 µg/L, 407.12 µg/L respectively (Table 3). The observed concentrations of SiO₂, Al, As and B at Lækjarhvarf (see Table 1, sample 4) was 2-7 times higher than the “derived” values. Partly this could be accounted for by external input of thermal waters high in these constituents from hot springs (Koldulaugagill and Nesjalaugagil) located above the point of wastewater discharge from the power plant into the stream. Trace elements concentration, thermal output, and flow rate of these two springs have not been determined but a SiO₂ concentration ranges from 41.1-636.7 mg/L and 18.6-139.5 mg/L in Koldulaugagill and Nesjalaugagil hot springs, respectively (Source: Reykjavík Energy).

The concentrations of aluminium, arsenic, boron and silica in water from ten geothermal outflow sites on the Lake Thingvallavatn shoreline show that levels of As, Al, B, and SiO₂ in the water increase from site 1 towards sites 10 (Figure 4). Assuming that: (a) the only wastewater that is mixing and flowing to the lake through the lava is the wastewater at Lækjarhvarf and the condensate disposed off into shallow boreholes in the nearby lava field close to the power plant; (b) no other physical or chemical processes take place in the lava during flow; (c) and no other groundwater is added to the system; and (d) all the wastewater reaches the lake; then “derived” chemical constituent concentration at all outflow sites assuming uniform water dispersion during outflow will be 46.7 µg/L, 823.73 µg/L, 875.86 µg/L and 219.34 mg/L for As, Al, B and SiO₂ respectively (see figure 4 – dotted line). The actual chemical constituent concentration levels at the outflow sites was much lower than the “derived” concentration (see Figure 4). The “derived” concentration levels were calculated from the wastewater disposal mass balances (measured concentrations; flow rates of condensate = 162.6 L/s and wastewater at Lækjarhvarf = 1331.5 L/sec with a combined flow of 1494.1 L/sec) during sampling. The groundwater flow towards Thingvallavatn has been estimated to be around 1600 L/sec (Kjaran and Egilson, 1986) thus considerable dilution takes place when the stream disappears and mixes with groundwater. Other chemical processes accounting for the difference in observed and “derived” constituent concentrations are discussed in the subsequent sections.

3.2 Concentrations of trace elements in the biota

3.2.1 Sediment

Trace elements concentrations in sediments (Table 4) were only determined at site 2 (Varmagjá) as no sediment was found at the Eldvik (sites 7 & 8). The concentration in the 3

sediment samples at Varmagja (site 2) was in the range 0.754-1.59 mg/kg, 0.136-0.277 mg/kg, 6.17-7.57 mg/kg, 64.9-73.2 mg/kg, 43.0-68.1 mg/kg, <0.4-0.0517 mg/kg, 9.9-13.2 mg/kg, 2.21-56 mg/kg, 27.2-157 mg/kg for arsenic, cadmium, cobalt, chromium, copper, mercury, nickel, lead and zinc respectively.

The arsenic concentration in sediment samples at Varmagjá did not deviate from concentration levels as the control station, Vatnskot for the period 1994, 1995 and 2000 (see Snorrason and Jonsson, 2000; Wetang'ula 2004). The same is true of cadmium, copper, mercury, lead and chromium (Table 5). The zinc concentration levels in sediments at Varmagja were significantly lower than at Vatnskot ($t = 5.26$, $p < 0.001$) (Table 5). Variations among replicate samples can be considerable in the present study, sediment sample 2003b-V had exceptionally high zinc concentration level (157 mg/kg) compared to samples 2003a-V (37.7 mg/kg) and 2003c-V (27.2 mg/kg). Similarly, sediment sample 2003b-V, had high Pb (56 mg/kg) compared to other samples. The Pb spikes of 56 mg/kg in sample 2003b-V at Varmagjá and 42 mg/kg at Vatnskot in 2000 could be regarded as outliers. This isolated high lead concentration in sediments at both Vatnskot and Varmagja could be due to sediment contamination by lead shots or sinkers used on fishing gears.

3.2.2 Aquatic plants

Trace element concentrations in aquatic plants at Varmagja (site 2) and Eldvik (sites 7 and 8) are presented in Table 4. Two plant samples were an unidentified species of moss and *Myriophyllum alterniflorum*.

Moss

The concentration of all trace elements analysed in the moss at Varmagja (Table 4) can be categorized as "very low" (class 1) according to classification of metal concentrations in aquatic moss except for copper which is categorised as "high" (class 4 = 50-250 mg/kg). At Eldvik, trace elements concentration in moss are categorized as "very low" for Cd, Co, Ni, Pb and Zn; "moderately high" for As, Cr and Hg; and "high" for Cu (SEPA, 1991).

Myriophyllum alterniflorum

Myriophyllum alterniflorum was only available at Varmagja and the 2003 trace elements concentrations were 0.253 mg/kg, 0.191 mg/kg, 0.438 mg/kg, 1.13 mg/kg, 46.6 mg/kg, 0.021 mg/kg, 104 mg/kg, 1.0 mg/kg, 0.77 mg/kg, 24 mg/kg for As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn respectively. No significant difference was found in the concentration of trace elements arsenic, cadmium, copper, mercury, lead and zinc between Varmagja and the control station, Vatnskot (Table 5). In the present study the concentration levels of Cd, Cu and Ni were high in moss compared to *Myriophyllum alterniflorum*; while As, Co, Cr, Hg, Mn and Zn was high in *Myriophyllum alterniflorum* compared to moss. Difference between the two plant species in trace elements concentration could be due to trace elements preferential uptake by the respective plant species. The 1995 sample from Vatnskot had exceptionally high lead content (see Wetang'ula, 2004).

3.2.3 Gastropod snail

The concentration of trace elements in the gastropod snail, *Lymnaea peregra* at Varmagja and Eldvik are presented in table 4. Trace elements concentration level at Varmagjá and Eldvík was within the range of 2.83 mg/kg-4.24 mg/kg, 0.262 mg/kg -0.398 mg/kg, 48.1 mg/kg - 117 mg/kg, <0.01 mg/kg, 0.0679 mg/kg - 0.348 mg/kg, 23.7 mg/kg - 34.3 mg/kg for arsenic, cadmium, copper, mercury, lead and zinc respectively. There was no significant difference in trace elements concentration between Varmagjá and Eldvík and the control station, Vatnskot except in the case of cadmium (Table 5) which was higher at Varmagjá and Eldvík. Chromium concentration ranged from 0.953 mg/kg at Eldvik to 1.04 mg/kg at Varmagja. Manganese concentration at Varmagja and Eldvik were 32.7 and 87.2 mg/kg respectively. Nickel concentration levels at both sites were similar.

3.2.4 Fish tissues

Trace elements were analysed in two fish species in 2003; threespined sticklebacks *Gasterosteus aculeatus* and arctic charr *Salvelinus alpinus* (Table 4). Trace elements concentration in threespined sticklebacks (whole body samples) appear to be similar at Eldvík and Varmagjá. The trace elements concentrations in muscles and liver of arctic charr also appear quite similar at Varmagja and Eldvik. The results indicate that copper, manganese and zinc accumulate in fish liver compared to the muscles. There was no significant difference in trace element concentration in arctic charr liver between Varmagjá and Eldvík, and the control station, except for copper, which was higher at Varmagjá and Eldvík (Table 5).

4. DISCUSSION

4.1 Trace elements in geothermal effluent and lake outflow sites and processes controlling As, B, Al and SiO₂ concentration during flow

The most important processes affecting geothermal fluid composition include the overall irreversible dissolution of primary rock minerals and precipitation of secondary minerals. The dissolution process leads to increased concentration of aqueous components, including conservative species such as B. Other components brought into solution are again removed by precipitation (Arnórsson et al., 2000). It is important from an environmental perspective to understand the processes that control the aqueous concentrations of arsenic, boron, aluminium and silica in Nesjavellir geothermal co-generation power plant wastewater as it flows through the lava down Lake Thingvallavatn because results show that these constituents occur in elevated concentrations in the wastewater, a situation reflected to some extent in some of the lake outflow sites. The geographic concentration gradient seen in these constituents in outflow water gives an impression that the least diluted outflow is around sites 7-10. Compared to SiO₂, As, B and Al, B is considered to be a conservative component (Arnórsson 2000). Therefore it can be useful to view the reduction in SiO₂, As and Al with reference to the boron concentration (Figures 5-7).

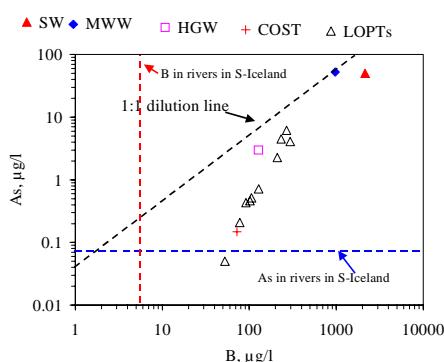


Figure 5 Relationship between As and B in Nesjavellir geothermal co-generation power plant wastewater and Lake Thingvallavatn outflow sites water. SW= Separator water, MWW= Mixed wastewater at Lækjarhvarf, HGW= Heated groundwater from Gramelur (cooling water), COST= Condensate, LOPTs= Lake outflow sites.

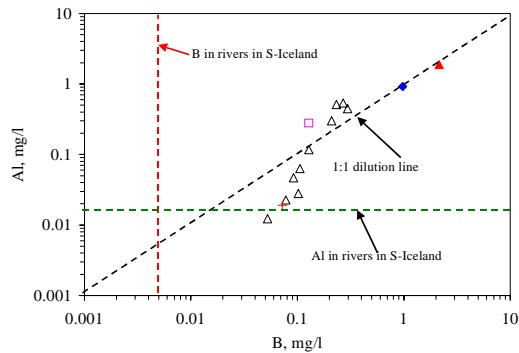


Figure 6 Relationship between Al and B in Lake Thingvallavatn outflow sites water and Nesjavellir geothermal co-generation power plant wastewater. The symbols refer to the legend on Fig. 5.

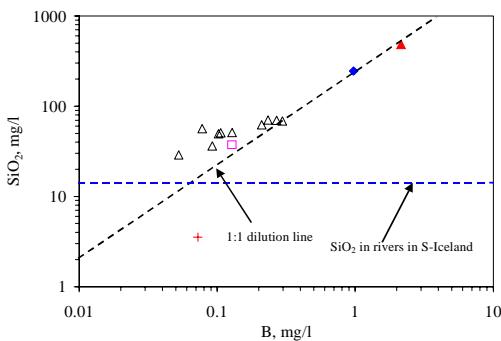


Figure 7 Relationship between SiO₂ and B in Nesjavellir geothermal co-generation power plant wastewater and Lake outflow sites water. The symbols refer to the legend on Fig. 5.

Judging by the concentrations of outflow sites 7-10 arsenic in the geothermal wastewater is reduced about 10 times as the wastewater flows towards the lake through the lava while the boron is only reduced around 4 times (Table 1, Figure 5). At sites 1-6 As concentration is much more reduced and at Markagjá the levels are down to what is

normally seen in rivers in the South of Iceland (Gislason et al., 2003). The reduction in arsenic concentration during flow could be accounted for by it being sorbed onto sediments in the lava (Nimick et al., 1998) and/or coprecipitated with (or adsorbed onto) Fe(III)-hydroxide. For example, the low As concentration of Amazon river water compared to that of other major rivers of the world, has been accounted for by its removal from solution by adsorption onto Fe(III)-hydroxide (Cutter et al., 2001). At the lake outflow sites arsenic concentrations in water do not show any relation to in situ pH (Table 1) nor with aqueous Fe concentrations. It is worthy noting that investigation in the vicinity of Lake Mývatn in north Iceland where effluent from two geothermal areas enter the nearby lava, showed that the As concentration diminishes rapidly after the mixing of geothermal effluent with the groundwater and the sole mechanism controlling the As concentration appeared to be dilution (see Ármannsson and Ólafsson, 2002)

Concentrations of arsenic in lake waters are typically close to or lower than those found in river water. Baseline concentrations have been found at <1 µg/L in Canada (Azcue et al., 1995). As concentration range of <0.03-0.28 µg/L have also been reported for three stations in Lake Mývatn in north Iceland (Ármannsson, 2003). Increased As concentrations have been found in lake waters affected by geothermal water and by mining activity. Ranges of typically 100 - 500 µg/L have been reported in some mining areas and up to 1000 µg/L in geothermal areas (Smedley and Kinniburgh, 2002). High arsenic concentrations are also found in some alkaline closed-basin lakes as a result of extreme evaporation and/or geothermal inputs. Mono Lake in the California, USA, for example, has concentrations of dissolved arsenic of 10,000 - 20,000 µg/L, with pH values in the range 9.5 - 10 as a result of inputs from geothermal springs and the weathering of volcanic rocks followed by evaporation (Maest et al., 1992). The As levels at site 7-10 around Eldvik were above the 1 µg/L which could be regarded as an As baseline in unpolluted lakes (Azcue et al., 1995) and above As concentration measured in Lake Myvatn (Ármannsson, 2003). The As concentration range 2.26-6.14 µg/L is in good agreement with the 4.7 µg/L As measured at Eldvík in 1991 (Ólafsson, 1992).

Al in the geothermal wastewater is only reduced by half when the wastewater reaches lake outflow sites 7-10 (Table 1, Figures 4 & 6). It appears, therefore, that in this part of the lava Al is being removed from the wastewater at a slower rate than boron. With regard to Al dissolution that might occur in groundwater system during flow, equilibrium with a solid phase has to be established that largely controls the extent to which Al dissolution can occur (Walker et al., 1988) and the equation below will be valid for alkaline conditions.



Brusewitz (1984) has also observed that transport and partitioning of Al in the environment is determined by the chemical properties of the element itself and the characteristics of the environmental matrix that affects solubility. At a pH >5.5, naturally occurring Al compounds exist predominantly in an undissolved form such as gibbsite, Al(OH)_3 , or as aluminosilicates. Aluminium is known to be only sparingly soluble in water between pH 6 and pH 8. Because the pH of about 95% of naturally-occurring water is between 6 and 9 and since high Al concentrations occur in surface water bodies only when the pH is < 5, the Al concentration in most natural waters is

extremely low (Filipek et al., 1987). In general, Al concentrations in surface waters at pH levels above 5.5 will be < 0.1 mg/L (Miller et al., 1984). This is not the case with Al concentrations at sites 7-10 which predominantly receive the geothermal input of Lækjarhvarf effluent water high Al concentration. At sites 1-6 the Al/B reduction ratio is reversed and at sites 1 and 2 the Al concentration has dropped to levels typical for rivers in S-Iceland (Gislason et al., 2003). In this part of the system Al is removed preferentially to B by Al(OH)_3 precipitation. The behaviour of Al could possibly be quantitatively interpreted by calculation of saturation for amorphous Al(OH)_3 . This was, however not determined in the present study, as the water samples were only analysed partially.

In natural freshwater ecosystems, surface water concentration of boron rarely exceeds 1 mg/L and is usually less than 0.1 mg/L; however in systems where boron has been mobilized by human activities, the concentrations may be much higher (Maier and Knight, 1991). In the present case, boron concentration at sites 7-10 was more than 0.2 mg/L which, as in the case of Al and As is due to high input from geothermal effluent. While the boron concentration at sites 1-6 are lower than at sites 7-10 (Table 1), it is still above levels in water from S-Iceland Rivers (Gislason et al., 2003). During flow sediments may adsorb the geothermal wastewater borne boron. Adsorption desorption reactions are the only significant mechanism that will influence the fate of boron in water. The extent of boron adsorption depends on the pH of the water and the chemical composition of the soil/sediment the water is flowing through. The greatest adsorption is generally observed at pH 7.5-9.0 (Keren and Mezuman, 1981). This could account for the low concentration level of boron at the lake outflow sites compared to its concentration level in geothermal effluents (Figure 5-7). Bingham et al. (1971) concluded that the single most important property of soil that will influence the mobility of boron is the abundance of amorphous aluminium oxide. The extent of boron adsorption has also been attributed to the levels of iron oxide (Sakata, 1987).

The SiO_2 -B relationship for outflow sites 7-10 (Figure 7) shows that the SiO_2 concentration in the power plant wastewater is reduced at a similar rate for boron. In the western part of the system (refer to Figure 2) the reduction of SiO_2 (Figure 4d) slows down compared to boron (Figure 4c) as the SiO_2 concentration approaches the levels for cold ground water in the area. Minerals of volcanic rocks, such as basalts are known to dissolve relatively rapidly, adding silica to solution. Silica solubility as a function of the temperature decreases drastically as the temperature decreases. The rates of dissolution and precipitation of amorphous silica changes as function of temperature, with considerable high rate at very high temperature and extremely slow rate at low temperatures (Arnórsson et al., 2000).

Mercury in geothermal fluids will exist in both water and steam/gas discharges due to its relatively high vapour pressure. Hg is also adsorbed readily onto hydrous oxides in sediment. This adsorption is considered to be the main control on Hg solubility under oxidizing conditions (Webster, 1995) which explains the Hg dilution effect as geothermal wastewater flows from the point of disposal, through the lava and down lake Thingvallavatn. Like As, dissolved Hg can bind to carbon forming strong complexes with organic ligands. In aquatic ecosystems, methyl mercury ions such as HgCH_3^+ and $\text{Hg}(\text{CH}_3)_2$ could form by progressive addition of the methyl (CH_3^+) groups to Hg by

bacteria and algae, leading to mercury accumulation through the food chain. It has also been observed that microbial reduction of adsorbed Hg can release Hg back into solution.

The regular east-west gradient (see Figure 2 for locations) in chemical constituent concentration levels at the outflow sites (Figure 4) may be due to differences in dilution effects of the geothermal wastewater during flow through the lava. It could also be true that the flow of condensate disposed of in the shallow drill holes and the effluents at Lækjarhvarf down the lake into the lava are quite distinct, with the latter, that was low in concentrations of the As, Al, B and SiO_2 , being confined around the Varmagjá/Markagjá area (sites 1-6) while the former, which had high concentration of these constituents is confined to the area around Eldvik (sites 7-10). What is evident then is that Eldvik is receiving waters high in chemical constituent concentration which could make one to hypothesize that the effluents at Lækjarhvarf and condensate disposed off in shallow drill holes to the west of Nesjavallalekur stream down the lake is controlled by defined faults in the Nesjahraun lava which hampers or prevents the mixing with other such streams. This hypothesis is further strengthened by the measured concentration of chemical constituents at Varmagjá and Eldvik for the period 1984 and 1991 when the original water heating plant was developed and built (Ólafsson, 1992). The data on spring water composition at Markagjá, Varmagjá and Eldvik (Ólafsson, 1992), show that the level of SiO_2 at Markagjá, Varmagjá and Eldvik in 1984 was 11.5 mg/L, 32.3 mg/L and 33.6 mg/L while in 1991 the SiO_2 levels had risen to 14.9 mg/L, 37.9 mg/L and 47.8 mg/L respectively. On the other hand, arsenic levels at Varmagjá and Eldvik in 1984 was 0.6 $\mu\text{g/L}$ and 0.7 $\mu\text{g/L}$ respectively while in 1991 As level had risen to 2.2 $\mu\text{g/L}$ and 4.7 $\mu\text{g/L}$ at Varmagjá and Eldvik respectively. It could be argued from these two studies that the core geothermal flow is around the Eldvik area not Varmagjá; dilution of geothermal water is less at Eldvik compared to Varmagjá; and /or the two sites receive geothermal water quite variable in the chemical constituent concentration which do not mix during flow from the point of discharge. Tracer tests with different tracer types are however needed to validate this hypothesis and at the same time qualify the Kjaran and Egilson (1986, 1987) groundwater flow model from Lækjarhvarf through Nesjahraun to the lakeshore outflow sites.

4.2 Concentration level of trace elements in the biota

4.2.1 Sediment

Making use of present and previous data one can now state that trace elements concentration levels in sediment at Varmagjá and the control station do not differ significantly except for zinc (Table 5), which was higher at control. Thus the variation observed is mostly attributed to natural variations in the background concentrations of the respective elements. The level of arsenic in sediment at Varmagjá was very low compared to the 540-780 mg/kg dw As in surface sediment of Lake Rotoroa, New Zealand, a lake that 24 years ago was affected by a sodium arsenite herbicide (Tanner and Clayton, 1990). A comprehensive evaluation of chemical concentrations in sediments that were associated with adverse biological effects (Long et al., 1995) have showed that arsenic concentrations of 8.2 mg/kg dw or less do not usually produce adverse effects, but concentrations of 70 mg/kg or higher usually do. In view of this effects of arsenic on the biota at Varmagjá are very unlikely.

Sediments have been known to play an important role in arsenic cycling (Widerlund and Ingri, 1995). The fate of this element in sediments is related to the extent of biogeochemical transformations and its relative mobility under varying redox conditions. Upon its accumulation at the sediment-water interface, arsenic can be released to porewaters following the degradation of organic matter to which it may be associated. The sediment concentrations and fluxes of As to the overlying waters may, however, be buffered by its strong affinity for amorphous iron oxyhydroxides which accumulate in the oxic sediments (Sullivan and Aller, 1996) near the sediment-water interface.

Remobilization of arsenic in sediments following the reduction and dissolution of Fe(III) and/or Mn-oxides is well documented (Widerlund and Ingri, 1995) but, in general, the relative importance of these oxides as arsenic carriers remains unclear. Consequently, the redox conditions at or near the sediment-water interface will often determine whether the sediments serve as a sink or a source for arsenic.

Cadmium levels in the sediment samples 2003a-V, 2003b-V and 2003c-V (Table 4) were higher than the overlying water at Varmagjá and in geothermal effluent (Table 1). In surface and ground water, cadmium can exist as the hydrated ion, or as ionic complexes with other inorganic or organic substances. While soluble forms may migrate in water, cadmium is relatively non-mobile in insoluble complexes hence adsorbed to sediments (Elinder, 1985) accounting for difference in cadmium concentration in the water and the sediment.

The chromium concentration range in Varmagjá sediment samples (Table 4) have been below the 111 mg/kg Consensus based-probable effect concentrations (Ingersoll et al., 2000) and 110 mg/kg severe effects levels (Persaud et al., 1993) above which harmful effects are likely to be observed (see Table 7). Soluble chromium generally accounts for a very small percentage of the total chromium. Most of the soluble chromium is present as Cr(VI) and Cr(III) complexes. In the aquatic phase, Cr(III) occurs mostly as suspended solids adsorbed onto iron oxide (Fe_2O_3) (King, 1988). Chromium(VI) in water will eventually be reduced to Cr(III) by organic matter in the water if any leading to its elevated concentration in the sediment.

The Cu concentrations at both Varmagjá and Vatnaskot were above 34 mg/kg levels that on rare occasions have been found to impair the survival or reproduction of benthic invertebrates, but below the: - 270 mg/kg Cu concentrations or higher that usually do have negative effects (Long et al., 1995); the 197 mg/kg probable effect level (Smith et al., 1996; CCME, 1999); 149 mg/kg consensus based-probable effects concentration (Ingersoll et al., 2000); and 110 mg/kg severe effects levels (Persaud et al., 1993), concentrations above which are likely to be harmful. The Cu concentration levels at both Vatnaskot (Control) and Varmagjá could be due to the geochemical composition of parent material of the lakebed.

Much of the copper that enters environmental waters will be associated with particulate matter. The combined processes of complexation, adsorption, and precipitation control the level of free copper. The chemical conditions in most natural water are such that, even at relatively high copper concentrations, these processes will reduce the free copper concentration to extremely low values. Sediment is

thus an important sink and reservoir for copper. In relatively clean sediment, the copper concentration is <50 mg/kg; polluted sediment may contain several thousand ppm of copper. Iron oxides are the most important contributor to binding of copper by aerobic sediments (Perwak et al., 1980).

The concentration of mercury in sediments is low both at Varmagjá (Table 4) and Vatnaskot (Table 6). The measured Hg concentration was below the sediment quality guidelines for metals in freshwater ecosystems that reflect the probable effect concentrations (PECs) above which harmful effects are likely to be observed (Table 7). High natural concentrations are sometimes noted in geothermal areas. For example, the results of measurements at Yellowstone National Park showed contents as high as 500 mg/kg (dw) in sediments from springs and pools and 150 mg/kg in fine-grained muds from mudpots and mud volcanoes. Sediment is definitely a source of methylmercury to biota and the water column. Even low concentrations may result in bioaccumulation. Adsorption is considered to be the main process controlling mercury solubility under oxidizing conditions although complexes such as mercury chloride ($HgCl_2$) tend to be poorly adsorbed (Webster, 1995). Microbial reduction of adsorbed Hg in sediment can release it again in solution (Wang et al., 1991).

Lead concentration levels were generally low in sediment both at Varmagjá (Table 4) and Vatnaskot (Table 6). Sediment sample 2003b-V had high Pb (56 mg/kg) compared to other samples. The Pb spikes of 56 mg/kg in sample 2003b-V at Varmagjá and 42 mg/kg at Vatnaskot in 2000 are clear outliers and are most likely due to contamination in form of lead shots or sinkers used on fishing gear. These elevated concentrations are however still below the 91.3 mg/kg Pb probable effect level (Smith et al., 1996; CCME, 1999); 128 mg/kg consensus based-probable effects concentration (Ingersoll et al., 2000) and 250 mg/kg severe effect levels (Persaud et al., 1993) concentrations above which harmful effects will occur (Table 7).

Zinc concentration levels in sediments were significantly lower at Varmagjá (Table 4) than at the control station, Vatnaskot (Table 6). The reasons for this are unknown. The levels were however above the 150 mg/kg identified as a safe level for zinc in sediment but below the 410 mg/kg zinc concentration above which adverse effects are common (Long et al., 1995). The concentrations were also below the 315 mg/kg probable effect level concentration (Smith et al., 1996; CCME, 1999) and 459 mg/kg consensus based-probable effect concentration (Ingersoll et al., 2000) above which harmful effects are likely to be observed; and 820 mg/kg severe effects level (Persaud et al., 1993) (Table 7). Most of the zinc introduced into the aquatic environment is eventually deposited in sediments. Zinc partitions to sediments or suspended solids in surface waters through sorption onto hydrous iron and manganese oxides (Guy and Chakrabarti, 1976). Nickel concentration level in sediment was low in relation to sediment quality criteria for freshwater ecosystems (see Table 7).

The present evaluation of sediment trace elements concentration indicates that all elements levels are below the sediment quality guidelines (SQGs) limits for metals in freshwater ecosystems that reflect probable effect concentrations (Table 7). These are the concentrations above which harmful effects are likely to be observed. The effects are based on SQGs for the protection of sediment-

dwelling organisms in freshwater ecosystems and were previously grouped into two categories according to their original narrative intent, including threshold effect concentration (TEC) and probable effect concentration (PEC). The PECs guidelines were intended to identify contaminant concentration above which harmful effects on sediment-dwelling organisms were expected to occur frequently. They include probable effects levels (PELs; Smith et al., 1996), effect range low values (ERLs), effect range median values (ERM; Long et al., 1995), severe effect level (SEL; Persaud et al., 1993). Other SQGs derived have been consensus-based PECs (Ingersoll et al., 2000). The ERLs/ERMs and PELs relate the incidence of adverse biological effects to the sediment concentration of a specific chemical at a specific sampling site based on paired field and laboratory data. The developers of the ERLs/ERMs define sediment concentration below the ERL as being the "minimal-effects range," values between the ERL and ERM in the "possible-effects range," and values above the ERM in the "probable-effect range".

According to CCME (1995), sediments in which observed chemical concentrations are equal to or lower than the national sediment quality guideline are considered to be of acceptable quality and further investigation of these sediments would be of relatively low priority. Management options at these sites then should be to focus on the protection of the existing sediment quality conditions. However, in some cases, future biological testing may be required for validation of this conclusion, e.g. in sediments with low levels of TOC, when other factors are suspected to be increasing the bioavailability of sediment-associated chemicals, or when SQGs do not exist for particular chemicals that are observed in the sediment.

4.2.2 Aquatic plants

Two species of aquatic plants sampled for trace element analysis were moss and *Myriophyllum alterniflorum*. Moss was collected at both Varmagja and Eldvik while *Myriophyllum alterniflorum* which was not present at Eldvik, was collected from Varmagja only.

Moss

All trace metal concentrations levels in aquatic moss at Varmagja apart from Cu could be described as "very low" (class 1). The copper concentration level was categorised as "high" (class 4 = 50-250 mg/kg). At Eldvik, trace elements concentration level in moss can be classified as "very low" for Cd, Co, Ni, Pb and Zn; "moderately high" for As, Cr and Hg; and "high" for Cu (SEPA, 1991). The moderately high As and Hg at Eldvik could be due to the geothermal influence as the arsenic and mercury which are elevated in geothermal water also appeared to be higher at Eldvik.

Myriophyllum alterniflorum

Judging from all available data there are no significant differences in the concentration of trace elements As, Hg, Cd, Pb, Cu and Zn in *Myriophyllum alterniflorum* at Varmagja and the control station, Vatnaskot (Tables 4-6). The variation observed can in most cases be classified as variation in natural background concentrations. The high lead values seen in two samples at Vatnaskot probably stem from point sources in the form of lead weights lost from fishing gears. The arsenic concentrations levels in both plant species at both Varmagja and Eldvik are very low compared to elevated concentrations of arsenic in macrophytes 193-1,200 mg/kg dw in lake Rotoroa, New Zealand, 24 years after an application of sodium arsenite herbicide (Tanner and Clayton, 1990).

4.2.3 Gastropod snail

There was no difference in concentration of As, Pb, Hg, Cu, Mn and Zn in the gastropod snail *Lymnaea peregra* at Varmagja and the control station, Vatnaskot (Table 5). Cadmium concentration levels were significantly higher at Varmagja. Chromium and nickel concentration level not previously determined was low and within similar concentration range at Varmagja and Eldvik (Table 4).

4.2.4 Fish tissues

Trace elements were analysed in two fish species; threespined sticklebacks *Gasterosteus aculeatus* and arctic charr *Salvelinus alpinus*. The results showed that concentration levels of trace elements As, Cd, Co, Cr, Hg, Mn, Ni, Pb, and Zn were low in fish tissues, muscles and liver at both Varmagja and Eldvik (Table 4). For example, arsenic in fish tissues, liver and muscle was less than the 0.27 mg/kg ww (1 mg/kg dw) that has been reported to be 85th percentile concentration of arsenic for freshwater fish (Schmitt and Brumbaugh, 1990) although the levels are known to be sometimes much higher in the biota collected near areas with high geothermal activity (Eisler, 1988). Judging from the combined data for the years 1994, 1996, 2000 (see Snorrason and Jonsson, 2000) and 2003, there was no significant difference in the arctic charr liver trace elements concentration for As, Cd, Hg, Pb, and Zn between Varmagja and the control station, Vatnaskot (Table 5) except for Cu which was considerably higher at Varmagja and Eldvik. The copper concentration levels in tissues of threespined sticklebacks and muscles of arctic charr were however below the average background copper concentration in freshwater fish i.e. 0.65 mg/kg ww or 2.6 mg/kg dw (Schmitt and Brumbaugh, 1990).

From Miller et al. (1992) study of the relationship between concentrations of copper and zinc in water, sediment, invertebrates, and fish; the water concentration was found to be a better indicator of metal concentration in fish tissue than sediment or invertebrate concentrations. In addition they found liver concentration to be a better indicator of chronic copper and zinc exposure than muscle. With regard to the present study, the Cu and Zn concentration was low in the sediment and gastropod snail. It can thus be hypothesized that arctic charr liver accumulates Cu and Zn preferentially to other trace elements during the detoxification process especially from gastropod snail, which is its major diet (Malmquist et al., 1992).

5. CONCLUSIONS

Concentration levels of chemical constituents measured in Nesjavellir geothermal co-generation power plant wastewater indicate that SiO₂, As, Al and B are elevated in geothermal effluents. From an ecotoxicological point of view, arsenic, aluminium and boron seem to be the only constituents of the geothermal effluents from the Nesjavellir geothermal co-generation power plant that could potentially affect the communities around the outflow sites. As the wastewater flows through Nesjahraun lava down to lake Thingvallavatn the concentration of these constituents are reduced through dilution with groundwater and through chemical reactions. In most cases the concentration levels of trace elements measured in Thingvallavatn shoreline outflow sites were within the acceptable international environmental quality guidelines for protection of aquatic life, watercourses and lakes. There was no statistically detectable rise or accumulation of trace elements in the biota at Varmagja and Eldvik, two of the geothermally influenced sites. In the year 2003 arsenic concentration in

one of the outflow site (site 10) water was slightly above the recommended 5.0 µg/L Canadian guideline limit for protection of aquatic life and within Level III of Icelandic government critical limits of trace elements in surface water for protection of biota. The level of aluminium was several times higher than the recommended 5-100 µg/L Canadian water quality guidelines for protection of aquatic life (CCME, 1999). The SiO₂, As, Al and B concentrations in outflow sites water increases spatially from Varmagja to Eldvik indicating that the area around Eldvík was the center of the chemical signals from the plant when the separator water is disposed off at Lækjarhvarf. However, taking into account the conservational value of Lake Thingvallavatn, sound wastewater management by deep re-injection and regular monitoring of chemical constituents in effluents and lake outflow sites water should be adopted.

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Table 1. Trace elements concentration in Nesjavellir geothermal co-generation power plant wastewater and Lake Thingvallavatn shoreline outflow sites water

	pH	Al	As	B	Ba	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb
Sample	Nesjavellir geothermal co-generation power plant wastewater (October 2003)													
	($\mu\text{g/l}$)	($\mu\text{g/l}$)	($\mu\text{g/l}$)	($\mu\text{g/l}$)	($\mu\text{g/l}$)	($\mu\text{g/l}$)	($\mu\text{g/l}$)	($\mu\text{g/l}$)	($\mu\text{g/l}$)	($\mu\text{g/l}$)	($\mu\text{g/l}$)	($\mu\text{g/l}$)	($\mu\text{g/l}$)	($\mu\text{g/l}$)
1*	9.39	1880	50.3	2150	0.21	<0.002	<0.005	0.065	1.27	0.0056	0.576	0.509	0.145	0.0
2	5.58	19	0.148	72.2	0.03	<0.002	0.044	0.048	0.29	0.0031	4.05	<0.05	0.771	0.0
3	7.58	278	2.96	128	0.38	<0.002	0.007	0.577	0.97	<0.002	0.85	0.85	0.384	0.0
4	9.12	922	52.4	974	0.68	<0.002	0.031	0.259	1.02	0.0052	7.99	2.19	0.292	0.0

*1: Separator water; 2: Condensed steam (condensate); 3: Cooling water; 4: Lækjarhvarf (Wastewater disappear in lava)

Sites ⁱ	Lake Thingvallavatn shoreline outflow sites water													
1	8.16	12.3	<0.05	52.6	0.46	0.0043	0.009	0.528	1.15	0.006	0.401	0.516	0.28	0.0
2	8.02	22.7	0.209	77.8	0.81	0.0023	0.004	0.568	0.27	<0.002	0.213	0.812	0.311	0.1
3	8.05	28.1	0.461	102	0.74	0.0042	<0.005	0.578	1.32	0.0063	0.295	0.767	0.453	0.0
4	8.02	47	0.433	91.8	0.5	<0.002	0.008	0.695	1.39	0.0027	0.355	0.687	0.413	0.0
5	8.10	63.1	0.518	106	0.75	<0.002	<0.005	0.58	0.92	0.0277	0.368	0.839	0.244	<0.
6	8.12	117	0.716	128	0.89	0.0021	<0.005	0.554	1.43	0.0077	0.377	0.915	0.367	0.0
7	8.10	300	2.26	210	1.18	0.0148	0.006	0.478	2.28	<0.002	0.504	0.995	0.406	0.0
8	8.08	447	4.11	296	0.96	0.0158	0.007	0.45	3	0.0055	0.703	1.03	0.401	0.0
9	8.11	513	4.51	233	1	<0.002	<0.005	0.457	1.8	0.0066	0.585	1.07	0.236	0.0
10	8.12	538	6.14	269	0.92	0.0114	0.006	0.434	2.51	0.0112	0.737	1.11	0.244	0.0

ⁱ Information on sample locations are provided in Fig. 2.

Table 2. Icelandic government critical limits for trace elements in surface water for the protection of biota (Government news B. No. 796/1999)

Element $\mu\text{g/l}$	Level I	Level II	Level III	Level IV	Level V
Cu	≤ 0.5	0.5-3.0	3-9	9-45	>45
Zn	≤ 5.0	5-20	20-60	60-300	>300
Cd	≤ 0.01	0.01-0.1	0.1-0.3	0.3-1.5	>1.5
Pb	≤ 0.2	0.2-1.0	1-0.3	3-15	>15
Cr	≤ 0.3	0.3-5.0	5-15	15-75	>75
Ni	≤ 0.7	0.7-1.5	1.5-4.5	4.5-22.5	>22.5
As	≤ 0.4	0.4-5.0	5-15	15-75	>75

Level I- Very low probability of effects

Level II- Low probability of effects

Level III- Some effects expected in case of sensitive ecosystems

Level IV- Effects expected

Level V- Permanently unacceptable levels for biota

Table 3. Measured and derived concentration of SiO_2 , Al, As and B in the Nesjavellir geothermal co-generation power plant at Lækjarhvarf where the stream disappears into the Nesjahraun lava.

	SiO ₂ (mg/l)	Al ($\mu\text{g/l}$)	As ($\mu\text{g/l}$)	B ($\mu\text{g/l}$)
Measured concentration at Lækjarhvarf	245.69	922	52.4	974
Derived concentration at Lækjarhvarf after mixing of separator and cooling water in the flow channel (Nesjavellir stream)	79.79	430.41	7.46	320.37

"Derived" concentration is calculated from the disposal flow rates of separator and cooling water in the stream and the respective concentration of each chemical constituent.

Table 4. Trace elements concentration in sediments, aquatic plants, gastropod snail and fish at Varmagja (site 2) and Eldvik (sites 7 & 8) in July 2003.

	TS (%)	As (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Mo (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Sample	Sediments at Varmagja (site 2)										
2003a-V	14.2	0.754	0.136	7.57	73.2	50.5	0.0517	<6.0	13.2	3.1	37.7
2003b-V	11.4	1.59	0.277	7.14	64.9	68.1	<0.04	<6.0	12.5	56	157
2003c-V	11.6	1.02	0.152	6.17	67.3	43.	<0.04	<6.0	9.9	2.21	27.2
	Aquatic plants										
	Moss										
Varmagja	7.7	0.241	0.852	0.101	1.05	115	0.0198		1.52	0.618	18.4
Eldvik	10.5	4.03	0.308	0.256	3.8	104	0.103		2.72	0.381	11.3
	<i>Myriophyllum alterniflorum</i>										
Varmagja	5.7	0.258	0.191	0.438	1.13	46.6	0.021		1	0.77	24
	Gastropod snail, <i>Lymnea peregra</i>										
Varmagja	18.3	2.83	0.398	0.935	1.04	117	<0.01		1.96	0.348	34.3
Eldvik	19.3	4.24	0.262	1.04	0.953	48.1	<0.01		1.97	0.0679	23.7
	Fish										
	Threespined sticklebacks, <i>Gasterosteus aculeatus</i>										
Varmagja	25	<0.2	<0.003	0.0084	<0.02	0.462	0.02		0.0327	0.187	32
Eldvik	22.5	<0.1	<0.003	0.0077	<0.02	0.409	0.0149		<0.02	0.0401	38.5
	Fish muscle (Artic charr, <i>Salvelinus alpinus</i>)										
Varmagja	21.4	<0.09	0.0044	0.0233	<0.02	0.346	0.025		<0.02	<0.02	5.67
Eldvik	17.1	<0.05	<0.003	0.0278	<0.02	0.245	0.0125		<0.02	<0.02	4.89
	Fish liver (Artic charr, <i>Salvelinus alpinus</i>)										
Varmagja		<0.05	0.054	0.161	0.03	248	0.0109		0.0311	<0.02	30.7
Eldvik		<0.05	0.0378	0.204	0.0265	242	0.0137		0.0453	<0.03	25.8

Table 5. Comparison of concentration levels of trace elements in biota at geothermally affected sites (Varmagjá, Eldvík) and a control site (Vatnaskot) based on samples from 1994-2003 (see Wetang'ula, 2004).

Elements	Sediment		<i>Myriophyllum</i>		<i>Lymnaea</i>		Arctic charr liver	
	t-value	p-value	t-value	p-value	t-value	p-value	t-value	p-value
As	0.56271	0.58399	0.00942	0.99279	1.93713	0.09393	0.38464	0.71192
Cd	1.59844	0.13593	0.83306	0.43671	2.97649	0.02062	1.20228	0.26834
Cu	0.68264	0.50780	1.22539	0.28765	1.97013	0.10591	2.92097	0.03298
Hg	0.76568	0.45866	0.30852	0.76812	0.15256	0.88305	0.62154	0.55394
Pb	0.12156	0.90526	0.92249	0.39186	0.60168	0.56636	0.47179	0.65143
Zn	5.25964	0.00020	2.24735	0.06568	1.21684	0.26310	0.17472	0.86624
Cr	1.17138	0.26418	-	-	-	-	-	-
Mn	-	-	0.91724	0.41092	0.90494	0.40699	1.49872	0.19422

Table 6. Average concentrations of trace elements in sediment, an aquatic plant and a gastropod snail at a control station Vatnskot in Lake Thingvallavatnⁱ

	Hg (µg/g)	As (µg/g)	Se (µg/g)	Zn (µg/g)	Cu (µg/g)	Cd (µg/g)	Pb (µg/g)	Mn (µg/g)
Lake sediments								
Vatnskot 1994	0.01	1.70	3.80	170.00	53.20	0.27	1.82	
Vatnskot 1995	0.01	1.30	3.90	190.66	56.56	0.255	3.07	
Vatnskot 2000	0.04	0.90	1.00	193.00	43.30	0.136	42.00	
Aquatic plant - <i>Myrophyllum alterniflora</i>								
Vatnskot 1994	<0.14	1.80	1.80	81.30		0.30	0.70	
Vatnskot 1995	0.0201	0.558	1.39	87.00	32.70	0.0452	175.00	190.80
Vatnskot 2000	0.042	3.00	1.61	140.00	26.80	0.32	10.80	*1055.00
Gastropod snail (<i>Lymnaea peregra</i>)								
Vatnskot 1994	<0.14	1.10	3.40	53.90		0.24	<0.3	
Vatnskot 1995	0.0095	1.30	1.58	60.50	35.40	0.144	1.22	85.30
Vatnskot 2000	0.046	2.60	3.13	116.00	54.00	0.265	0.80	118.00

* Faulty measurement

Table 7. Sediment quality guidelines for metals in freshwater ecosystems that reflect probable effect concentrations (PECs) above which harmful effects are likely to be observed.

	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Hg (mg/kg)	Ni (mg/kg)	Zn (mg/kg)
Probable effect level ⁱ	17	3.53	90	197	91.3	0.486	36	315
Severe effects level ⁱⁱ	33	10	110	110	250	2.0	75	820
Effects range median ⁱⁱⁱ	70	9.6	370	270	218	0.71	51.6	410
Consensus based-PEC ^{iv}	33.0*	4.98*	111*	149*	128*	1.06*	48.6*	459*
Interim sediment quality guideline ^v	5.9	0.6	37.3	35.7	35	0.17		123

* = >75% correct classification as toxic.

ⁱ Smith et al., 1996; CCME, 1999ⁱⁱ Persaud et al., 1993ⁱⁱⁱ Long et al., 1995^{iv} Ingersoll et al., 2000^v CCME, 1999

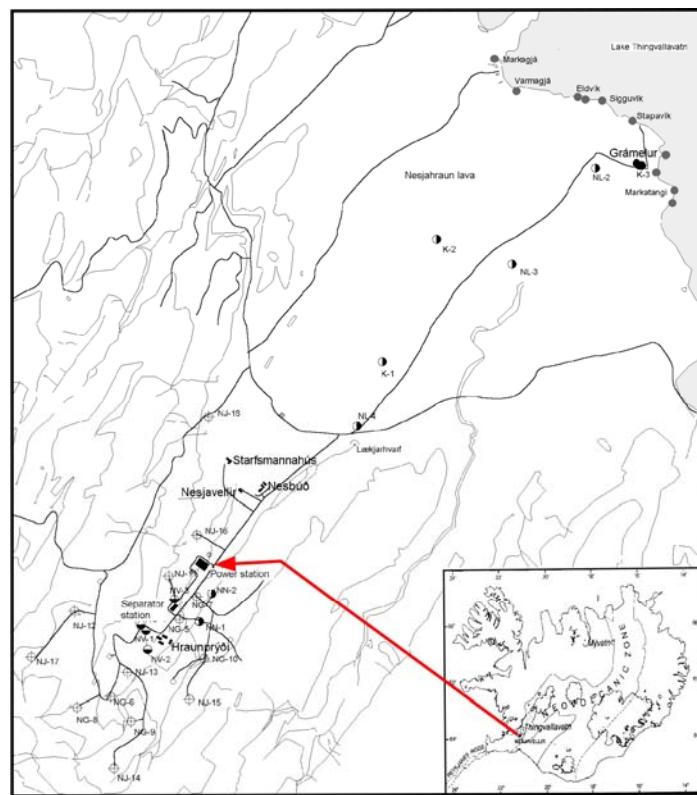


Figure 1. Location of Nesjavellir geothermal co-generation plant and Lake Thingvallavatn



Figure 2. Sampling sites for trace elements and biological samples at lake outflow points. Biological samples (fish, aquatic plants, sediment and gastropod snail) were collected at Varmagja and Eldvik Sites.