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**ASSESSMENT OF GEOTHERMAL WASTEWATER
DISPOSAL EFFECTS
CASE STUDIES: NESJAVELLIR (ICELAND) AND
OLKARIA (KENYA) FIELDS**

MSc Thesis

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INTRODUCTION

The Geothermal Training Programme of the United Nations University (UNU) has operated in Iceland since 1979 with six months annual courses for professionals from developing countries. The aim is to assist developing countries with significant geothermal potential to build up groups of specialists that cover most aspects of geothermal exploration and development. During 1979-2004, 318 scientists and engineers from 39 countries have completed the six months courses. They have come from Asia (44%), Africa (26%), Central America (14%), and Central and Eastern Europe (16%). There is a steady flow of requests from all over the world for the six months training and we can only meet a portion of the requests. Most of the trainees are awarded UNU Fellowships financed by the UNU and the Government of Iceland.

Candidates for the six months specialized training must have at least a BSc degree and a minimum of one year practical experience in geothermal work in their home countries prior to the training. Many of our trainees have already completed their MSc or PhD degrees when they come to Iceland, but several excellent students who have only BSc degrees have made requests to come again to Iceland for a higher academic degree. In 1999, it was decided to start admitting one or two outstanding UNU Fellows per year to continue their studies and study for MSc degrees in geothermal science or engineering in co-operation with the University of Iceland. An agreement to this effect was signed with the University of Iceland. The six months studies at the UNU Geothermal Training Programme form a part of the graduate programme.

It is a pleasure to introduce the fifth UNU Fellow to complete the MSc studies at the University of Iceland under the co-operation agreement. Mr. Gabriel Wetang'ula, BSc in Natural Resources Management of the Kenya Electricity Generating Co. Ltd., completed the six months specialized training at the UNU Geothermal Training Programme in October 2001. His research report was entitled "Ecological risk assessment of Nesjavellir geothermal power plant wastewater disposal in Lake Thingvallavatn in SW-Iceland". After ten months of research work as environmental scientist in Olkaria, he came back to Iceland for MSc studies at the Faculty of Science of the University of Iceland in August 2002. He defended his MSc thesis presented here, entitled "Assessment of geothermal wastewater disposal effects case studies: Nesjavellir (Iceland) and Olkaria (Kenya) fields" in April 2004. His studies in Iceland were financed by a fellowship from the Government of Iceland through the UNU Geothermal Training Programme. We congratulate him on his achievements and wish him all the best for the future. We thank the Faculty of Science of the University of Iceland for the co-operation, and his supervisor for the dedication.

With warmest wishes from Iceland,

Ingvar B. Fridleifsson, director,
United Nations University
Geothermal Training

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ABSTRACT

Every geothermal installation produces a unique set of chemical effluents, which depend intricately upon the geochemistry and the exploitation history of the hydrothermal reservoir and on the individual plant design. Potentially adverse effects of geothermal energy utilization are chemical, - from gaseous components in steam that are discharged into the atmosphere and from aqueous components in spent water - and physical in the form of thermal stress, particularly in aquatic ecosystems. An environmental assessment of potential effects of current geothermal wastewater disposal options in the exploitation of the Nesjavellir geothermal field (Iceland) and the eastern sector of the Olkaria geothermal field (Kenya) is made. At Nesjavellir co-generation power plant hot wastewater 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, Vatnaskot, was done. Also an assessment of thermal stress at lake shoreline outflow sites was done. Recent increase in the volume of wastewater has caused a 15-17°C rise in water temperature at lake shoreline outflow sites. In calm periods during the ice free period and when the lake freezes over in the winter this causes temporal thermal stress near the outflow sites. 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. Olkaria East geothermal field is one of the sectors of the Greater Olkaria geothermal area in the central sector of the Kenya Rift Valley. The field supports the 45 MWe power station. Monitoring of trace elements in the wastewater has been an ongoing process as one of the pollution control measures since 1993. Results indicate that concentration level of most trace elements in wastewater from most wells is low in relation to plant and animal water quality criteria except for As, Mo and B. With the reinjection of the wastewater, which has also been an ongoing reservoir management strategy, any potential ecotoxicological effects that might emanate from elevated levels would be avoided.

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Part I: BACKGROUND

1.0 INTRODUCTION

1.1 Geothermal energy utilization overview

On a global scale geothermal resources constitute but a small, yet rapidly growing, energy resource. It is very important for some countries and an important renewable energy source. In the year 2000 geothermal energy constituted about 0.25% of the annual worldwide energy consumption (Fridleifsson, 2001). Geothermal energy, as natural steam and hot water, has been used for decades to generate electricity, and both in space heating and industrial processes. In 2000 a total of 21 countries were generating electric power from geothermal resources (Huttrer, 2001) and 58 countries were using geothermal energy directly (Lund and Freeston, 2001). The geothermal electrical installed capacity in the world is 7974 MW_e (year 2000), and the electrical energy generated is 49.3 billion kWh/year, representing 0.3 % of the world total electrical energy which was 15,342 billion kWh in 2000. In developing countries, where total installed electrical power is still small, geothermal energy still plays a significant role. Various countries have presented plans for increasing the use of geothermal resources for power generation. The total planned increase by 2005 is 3440 MW_e (Huttrer, 2001). The thermal capacity of non-electrical uses (greenhouses, aquaculture, district heating, industrial processes) is 15,14 MW_t (year 2000).

Geothermal systems consist of a body of hot aqueous fluid and hot rock (sometimes hot rock only) within the top few kilometres of the Earth's crust and are characterized by a particular rock-hydrological situation. Most often they develop by deep circulation of ground water, which usually consists of ancient to modern precipitation or seawater. So-called geopressurized systems host connate water¹ and hot-dry rock systems are essentially hot rock of low permeability. The ultimate source of heat to geothermal systems is the Earth's gravity field and decay of radioactive elements within the Earth. In individual convecting ground water systems the heat source may be hot rock towards the base of the water circulation or magma intrusions. The circulating ground water transports heat from the heat source to shallower depths forming a geothermal system in the process. During its circulation, the water composition is altered through interaction with the enclosing rock. The water may also receive chemical components from a degassing magma heat source. As a consequence of these processes, geothermal fluids may contain chemical constituents in such concentrations that they can have adverse effect on the environment, fauna and flora, the atmosphere and ground and surface waters if not properly disposed off. The environmental impact of geothermal power stations, which utilize high enthalpy reservoirs, is varied depending on the wastewater management option adopted.

1.2 Review of some trace element occurrences in the environment

Arsenic is a ubiquitous trace element found in the atmosphere, soils and rocks, natural waters and organisms. It is mobilized through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities. Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites. The most abundant arsenic ore mineral is arsenopyrite, FeAsS. Most environmental As problems are the result of mobilisation under natural conditions. However, man has had an important additional impact through mining activity, combustion of fossil fuels, the use of arsenical pesticides, herbicides and crop desiccants and the use of As as an additive to livestock feed, particularly for poultry. Arsenic is perhaps unique among the heavy metalloid and oxyanion-forming elements (As, Se, Cr, etc) in its sensitivity to mobilisation at

¹ Connate water is "fossil" water which has been out of contact with the atmosphere for a long period geologically. Water enclosed by deep rock formations. See Ellis and Mahon (1977) p. 28.

pH values typically found in groundwaters (pH 6.5–8.5) and under both oxidising and reducing conditions. Arsenic can occur in the environment in several oxidation states but in natural waters it is mostly found in inorganic form as oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. Organic As forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important (Smedley and Kinniburgh, 2002). Concentrations of As in fresh water vary by more than four orders of magnitude depending on the source of As, the amount available and the local geochemical environment. Under natural conditions, the greatest range and the highest concentrations of As are found in groundwaters as a result of the strong influence of water-rock interactions and the greater tendency in aquifers for the physical and geochemical conditions to be favourable for As mobilization and accumulation.

Concentrations of As 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 with river waters, increased concentrations are often 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 (Bright et al., 1996) and up to 1000 µg/L in geothermal areas (Robinson et al., 1995; Nimick et al., 1998). High As concentrations are also found in some alkaline closed-basin lakes as a result of extreme evaporation and/or geothermal inputs. Mono Lake in California, USA, for example, has concentrations of dissolved As 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).

Boron is a naturally occurring element found combined with other elements throughout the environment. Boron is neither transformed nor degraded in the environment, although changes in the specific form of boron and its transport may occur, depending on environmental conditions. Natural weathering of boron-containing rocks is a major source of boron compounds in water (Butterwick et al., 1989). Although few data are available quantifying boron releases from industrial sources, it is estimated that natural weathering releases more boron to the environment worldwide than anthropogenic sources. The quantity of boron released varies widely with the geographic variations in boron-rich deposits (Butterwick et al. 1989; ATSDR 1992).

Copper and its compounds are naturally present in the earth's crust but natural discharges to air and water, such as windblown dust, volcanic eruptions may be significant. It occurs naturally in many minerals, such as cuprite, malachite, azurite, chalcocite, and bornite. The copper content of ore deposits ranges from 0.5 to 5 % by weight, whereas igneous and crystalline rock contains 0.010% and 0.0055 % by weight respectively (Weant, 1985). Copper particulates released into the atmosphere by windblown dust, volcanic eruptions, and anthropogenic sources will settle out or be removed by precipitation. Copper is released into waterways by natural weathering of soil and rocks, disturbances in soil, or anthropogenic sources such as effluent from sewage treatment plants. Copper concentrations in drinking water vary widely as a result of variations in pH and hardness of the water supply; the levels range from a few ppb to 10 ppm. Therefore, it is important to consider the background levels that are commonly found in order to distinguish these from levels that can be attributed to anthropogenic activity (ATSDR, 2002).

Mercury is distributed throughout the environment by both natural and anthropogenic processes. The natural global bio-geochemical cycling of mercury is characterized by degassing of the element from soils and surface waters, followed by atmospheric transport, deposition of mercury back to land and surface water, and sorption of the compound to soil or sediment particulates. Mercury deposited on land and open water is in part revolatilized back into the atmosphere. This emission, deposition, and revolatilization create difficulties in tracing the movement of mercury to its sources. A degree of uncertainty exists with respect to estimates of the relative contributions of natural and anthropogenic sources of mercury emissions to the environment reported in the scientific literature (ATSDR, 1999). Anthropogenic emissions of mercury are estimated to be more than half of the total global emissions of 6,000 tons/year (Nriagu and Pacnya, 1988), with emissions from natural sources being 2,500 tons/year (Nriagu 1989). In contrast, WHO (1990, 1991) reported that the major source of atmospheric mercury is global degassing of mineral mercury from the lithosphere and hydrosphere at an estimated

rate of 2,700 - 6,000 metric tons/year, which is approximately 1.3 to 3 times the rate of release from anthropogenic sources. Most recently, Pirrone et al. (1996) estimated world emissions of mercury at 2,200 metric tons/year and concluded that natural sources, industrial sources, and the recycling of anthropogenic mercury each contribute about one-third of the current mercury burden in the global atmosphere. A major source of uncertainty in these estimates is that emissions from terrestrial and marine systems include a “recycled” anthropogenic source component (WHO, 1990). Natural weathering of mercury-bearing minerals in rocks is estimated to directly release about 800 metric tons of mercury per year to surface waters of the earth (Gavis and Ferguson, 1972). Atmospheric deposition of elemental mercury from both natural and anthropogenic sources has been identified as an indirect source of mercury to surface waters (WHO, 1991). Mercury associated with soils can be directly washed into surface waters during rain events. Surface runoff is an important mechanism for transporting mercury from soil into surface waters, particularly for soils with high humic content (Meili, 1991). Mercury may also be released to surface waters in effluents from a number of industrial processes.

Cadmium is a relatively rare element that is a minor nutrient for plants at low concentrations (Lane and Morel, 2000; Lee et al., 1995), but is toxic to aquatic life at only slightly higher concentrations. Volcanic activity is an important natural source of cadmium to the atmosphere. The annual global flux from this source has been estimated to be 820 tonnes (Nriagu, 1989). Levels of up to 4.5 mg/kg have been found in volcanic soils (Korte, 1983), but higher levels are present in sedimentary rocks. Cadmium present in various types of rocks and soils is widely distributed in the earth's crust in non-volcanic areas, at average concentrations ranging from 0.1 to 0.2 mg/kg in soils (GESAMP, 1984). In exceptional cases, values of 1 mg/kg in soil have also been found (OSPAR, 2002). In natural freshwaters, cadmium sometimes occurs at concentrations of less than 0.1 µg/L, but in environments impacted by man, concentrations can be several micrograms per litre or greater (Allen, 1994; Spry and Wiener, 1991).

Aluminium is released to the environment by both natural processes and anthropogenic sources. Because of its prominence as a major constituent of the earth's crust, natural processes far exceed the contribution of anthropogenic releases to the environmental distribution of aluminium (Lantzy and MacKenzie, 1979). Anthropogenic releases are primarily to the atmosphere. The largest source of airborne aluminium-containing particulates is the flux of dust from soil and the weathering of rocks (Sorenson et al., 1974). In addition, a significant amount of aluminium-containing dust is generated by volcanic activity. Aluminium is extremely immobile in many surface and near surface environments (Hem, 1978; Huang and Keller, 1972). It becomes mobile where conditions allow aluminous minerals to dissolve, as in acid sulfate soils, acid rain catchments (Driscoll and Schecher, 1990), acid mine waters (Stollenwerk, 1994) and acid areas in active geothermal fields (Martin et al., 2000). In geothermal systems the behaviour of Al is highly sensitive to fluid pH and Al is a major component of many of the principal minerals reacting and forming, both at the surface and in the subsurface in all stages of the alteration processes; in particular of minerals formed at the surface from the action of steam condensates (Martin et al., 1999). The mobility of Al is considerably enhanced in acid environments compared to those of near neutral alkali chloride fluids; as a consequence, prolonged exploitation of a geothermal field may greatly increase the ability of Al to move (Martin et al., 2000).

Lead is a major constituent of more than 200 identified minerals. Most of these are rare, and only three are found in sufficient abundance to form mineral deposits: galena (PbS) the simple sulfide, anglesite (PbSO₄) the sulfate, and cerussite (PbCO₃) the carbonate (US EPA, 1980c). Natural lead compounds are not usually mobile in normal ground or surface water because the lead leached from ores becomes adsorbed by ferric hydroxide or tends to combine with carbonate or sulfate ions to form insoluble compounds. The solubility of lead compounds in water depends heavily on pH and ranges from about 10,000,000 µg/L of lead at pH 5.5 to 1 µg/L at pH 9.0 (Hem, 1976). Lead does reach the aquatic environment through precipitation, fallout of lead dust, street runoff, and both industrial and municipal wastewater discharges (US EPA, 1980c).

The abundance of selenium in the earth's crust is 0.05-0.09 mg/kg, about 1/6000 of the total sulphur. However, the geographical distribution of Se is extremely variable. The total amount of Se in rocks comprises 40% of the total in the earth's crust, mainly in sandstone, quartzite and limestone. The worldwide Se content in eruptive rock is 0.01-7.0 mg/kg, 0.1-6.5 mg/kg in metamorphic rock, and 0.01-7.0 mg/kg in sedimentary rock. The average concentration of Se in freshwater around the world is 0.2 µg/L. The atmospheric Se in the polar regions and above the open sea, which could be regarded as an oceanic background value, is 0.04 ng/m³ (WHO, 1987). The major source of anthropogenic Se is probably the burning of fossil fuels. Selenium is released to water via sewage effluent, agricultural runoff, and industrial wastewater. Surface waters can receive selenium from the atmosphere by dry and wet deposition, from adjoining waters that may contain selenium, from surface runoff, and from subsurface drainage. Sewage treatment plants are another source of selenium releases to water. Selenium is released to soil primarily by leaching and weathering of the parent bedrock material, although dry and wet deposition also contribute to soil selenium levels. Natural atmospheric releases of selenium result from volatilization of selenium by plants and bacteria and from volcanic activity (ATSDR, 2001).

Zinc is commonly found in the earth's crust (most rocks, certain minerals, and some carbonate sediments), and natural releases to the environment can be significant. As a result of the weathering of these materials, soluble compounds of zinc are formed and may be released to water. The largest input of zinc to water results from erosion of soil particles containing natural traces of zinc (45,400 metric tons/year). Erosion resulting from human activities accounts for 70% of this soil loss; geologic or natural erosion constitutes the other 30%. However, this source of low levels of zinc is widely dispersed and is, therefore, unlikely to elevate aquatic concentrations significantly (US EPA, 1980a). In addition, zinc is one of the most widely used metals in the world. The environmental releases of zinc from anthropogenic sources far exceed releases from natural sources. On an annual worldwide basis, an estimated 77,000 - 375,000 metric tons of zinc are discharged into water from anthropogenic sources (Fishbein 1981; Mirenda 1986; Nriagu and Pacyna 1988).

1.3 Chemical constituents of geothermal fluids

Most geothermal energy developments involve bringing fluids to the surface in order to mine heat contained in the rock. In high-temperature liquid-dominated geothermal fields the volumes of resultant wastewater involved may be large: for example at Wairakei (New Zealand), a medium sized power station (156 MW_e) is about 5800 m³/hr. While for vapour-dominated and low temperature systems the wastewater is very much less: as is the case at Larderello in Tuscany, (Italy) which had no wastewater at all. For example in 2000 Larderello produced from 180 wells drilled in an area of 250 km² providing 830 kg/s of superheated steam at pressures 2-15 bar at temperatures 150-260°C, i.e. there is no wastewater at all. The installed capacity was 547 MWe in 27 units. Exploration showed that more superheated steam may be obtained at temperatures up to 350°C (Capetti et al., 2000).

The waste fluid is usually disposed off in waterways or evaporation ponds, or re-injected into the ground. Unless all waste borewater and cooling water blowdown is reinjected, geothermal fluid discharges may have an impact on the local and regional surface waters such as rivers, lakes and estuaries.

The chemical composition of geothermal fluids is extremely variable (Table 1). The chemistry of the fluid discharged is largely dependent on the geochemistry of the reservoir, and the operating conditions used for power generation and varies from one geothermal field to another (Webster, 1995). For example, fluids from the Salton Sea field (USA), which is hosted by evaporite deposits, are highly saline ([Cl] = 155 000 ppm) while those of the Krafla field (Iceland) are of low salinity ([Cl] = < 25 ppm). Chloride (Cl) is the major anion in most geothermal waters, at least if the salinity is relatively high. This element only forms soluble salts with cations that can be abundant in natural waters.

TABLE 1: Chemical constituents concentrations in world selected geothermal fluids

	SiO ₂ (mg/kg)	B (mg/kg)	Na (mg/kg)	K (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	F (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Fe (mg/kg)	Cl (mg/kg)	Al (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	As (mg/kg)	Hg (mg/kg)	Source
Nesjavellir NJ-11, Iceland	631		253	32.6	3.75	<0.09		0.0003	0.0017				0.00011	0.00072	0.134	0.00044	1
Nesjavellir NJ-13, Iceland	797	2.0	206.3	38.3	1.60	0.0049	1.58	0.0003	0.0017				0.00054	0.00023	0.160	0.000143	1
Krafla separator water								0.000197	0.0052	0.0075		1.46	0.0075	<0.000002	0.0595	0.0000039	2
Krafla, KJ-15, Iceland	738	9.89	8160	1720	1850	1.01		0.00184	0.0112	0.171	24.5		0.0868	0.000369	0.000171	0	3
Reykjanes, RN-09 Iceland	447	4.9	111.8	16.8	0.4	0.0024	0.47				41.5						4
Námafjall NJ-12, Iceland	480	0.6	212	27	1.5	0.0	1.9	0.007	0.017	0.05	197				-		5
Hveragerdi G-3, Iceland	773	12.9	805	144	2.46	0.05	76				1190	0.829	0.033	0.005	5.31	0.94	7
Olkaria OW-10, Kenya	502	4.9	503	67	0.35	0.03	64	0.007	0.015	0.01	586	0.491	0.037	0.008	4.19	0.52	6
Olkaria OW-16, Kenya	400	390	50400	17500	28000	54	15.0				155000				12	0.006	7
Salton Sea 1 California (US)																	
Cerro Prieto 5, (Mexico)	790	19	6950	1670	395	0.45	1.9				12900				2.3	0.00005	8
Wairakei 24 (New Zealand)	557	26.2	1256	200	26.7	0.02	6.9				2183				4.7	0.0002	7
Tongonan 202, Philippines	1034	235	6750	1710	211	0.08	-				12390						9
Zumil D-1, Guatemala	896	36.2	866	230	3.73	0.22	4.63				1506						10
1: Ólafsson (1992); 2: Árnannsson and Ólafsson, 2002; 3: Gudmundsson and Arnórsson (2002); 4: Orkustofnun data; 5: Bjarnson and Arnórsson (1986); 6: Simiyu and Tole (2000); 7: Ellis and Mahon (1977); Muffler and White (1968); Hunt (2001); 8: Truesdell et al. (1981); 9: Hedenquist (1990); 10: Arnórsson (1985)																	

Most high temperature geothermal water may contain high concentrations of at least one of the following toxic chemicals: aluminium (Al), boron (B), arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), and sometimes fluoride (F). The fluid concentrations of these components are largely controlled by their supply to the fluid. It is thus not surprising to have high concentrations of these components in geothermal fluids, which can extract the constituents from either the enclosing rock or degassing magma heat source. Waste geothermal fluids which often contain these constituents can have adverse impact on the environment if not disposed of properly.

High concentrations of trace metals are associated with high-temperature brines such as at Salton Sea in California and on the island of Nisyros, Greece. Arsenic associated with geothermal waters has been reported in several parts of the world, including hot springs from parts of the USA, Japan, New Zealand, Chile, Iceland, Kamchatka, France and Dominica (Criaud and Fouillac, 1989). Parts of Salta and Jujuy Provinces in NW Argentina also have thermal springs with high As concentrations. In the USA, occurrences of As linked to geothermal sources have been summarized by Welch et al. (2000). Reported occurrences include Honey Lake Basin, California (As up to 2600 µg/L), Coso Hot Springs, California (up to 7500 µg/L), Imperial Valley, California (up to 15,000 µg/L), Long Valley, California (up to 2500 µg/L) and Steamboat Springs, Nevada (up to 2700 µg/L).

Geothermal waters in Yellowstone National Park have also been reported to contain high concentrations of arsenic. Arsenic concentrations of <1–7800 µg/L and 2830 µg/L in geysers and hot springs were reported (Smedley and Kinniburgh, 2002). These geothermal sources have given rise to high concentrations of As (up to 370 µg/L) in waters of the Madison River (Nimick et al., 1998). Geothermal waters at Lassen Volcanic National Park, California have As concentrations up to 27,000 µg/L (Thompson et al., 1985). Geothermal inputs from Long Valley, California are believed to be responsible for relatively high concentrations (20 µg/L) of As in the Los Angeles Aqueduct which provides the water supply for the city of Los Angeles (Wilkie and Hering, 1998). Geothermal inputs also contribute significantly to the high dissolved As concentrations (up to 20 mg/L) in Mono Lake, California (Maest et al., 1992).

Welch et al. (2000) noted a general relationship between As and salinity in geothermal waters from the USA. Despite a lack of good positive correlation between As and Cl, geothermal waters with As greater than 1000 µg/L mostly had Cl concentrations of 800 mg/L or more. Wilkie and Hering (1998) noted the high alkalinity and pH values (average pH 8.3) as well as high Cl and B concentrations of As-rich geothermal waters in Long Valley. Of 26 geothermal water samples analysed from 5 geothermal fields in Kyushu, Japan, As concentrations in the range 500 - 4600 µg/L have been reported. The waters are typically of NaCl type and the As is present in all but one sample overwhelmingly as As(III) (Yokoyama et al., 1993).

Robinson et al. (1995) found an As concentration of 3800 µg/L in waste geothermal brine from the main drain from the Wairakei geothermal field in New Zealand. River and lake waters receiving inputs of geothermal water from the Wairakei, Broadlands, Orakei Korako and Atiamuri geothermal fields had As concentrations up to 121 µg/L, although reported concentrations diminished significantly downstream away from the geothermal input areas.

High As concentrations have also been found in geothermal waters from the El Tatio system in the Antofagasta region of Chile. The geothermal area lies in a basin (altitude 4250 m) between the volcanoes of the Andes and the Serrania de Tucle. The geothermal waters are highly saline (NaCl solutions with Na concentrations in the range 2000 - 5000 µg/L). Arsenic concentrations of the waters are reported to be in the range 45,000 - 50,000 µg/L (Ellis and Mahon, 1977). As concentrations in the range 50 - 120 µg/L (in a 1963 study) for thermal waters from Iceland and in the range 100–5900 µg/L for thermal waters from Kamchatka have been reported (*see* Smedley and Kinniburgh, 2002).

High boron concentrations have also been found in many geothermal systems. For examples it was discovered that the high temperature reservoir in the Achuapan geothermal field in El Salvador contained highly saline water with potentially harmful minerals like B and As. The field produced wet

steam and the disposal of waste geothermal water represented a major problem. B and As concentration of 150 mg/L and 10.5 mg/L respectively were reported (Einarsson et al., 1975). The high concentration of boron in many geothermal systems is believed to derive from boron rich sediments or rocks that are metamorphosed (Smith, 2001). Boron rich waters occur in geothermal waters which have reacted with organic-rich sediments, such as at Ngwaha in New Zealand (Ellis and Mahon, 1977). Waters of geothermal systems hosted by basaltic rock are low in boron and arsenic and other trace elements but relatively high in both hydrogen sulphide and aluminium. This is exemplified by Krafla, Iceland (Gudmundsson and Arnórsson 2002; *see* Table 1). Arnórsson and Andrésdóttir (1995) reported the highest boron concentrations in well waters from high-temperature geothermal systems in the axial zones of the active volcanic belts, with B content of Icelandic basalts in the range 0.1-6.6 ppm. Most geothermal waters contain boron in the range 0.05-1 ppm, with the low values attributed to the low content of B in the basaltic rock.

On the other hand the thermal waters of Kizildere and environs in the Buyuk Menderes rift zone, Turkey have been reported to have high boron concentrations of up to 32 mg/L. Kizildere, which is the only commercial geothermal power plant in Turkey, discharges 6 million tons of geothermal wastewater from the steam separators annually into the nearby Buyuk Menderes River. Currently, the wastewater which has up to 24 mg/L boron is discharged into the river at a rate of 750-1,500 tons per hour with the temperature of the wastewater discharged approximately 140°C. The adverse effects of the high B content of the geothermal water has called for injection of the wastewater back into the geothermal reservoir (Demirel and Yildirim, 2002). Boron concentrations in the range 1-63 mg/L have been measured in Germencik geothermal field (Gemici and Tarcan, 2002; Filiz et al., 2000).

Aluminium is strongly immobile in many surface and near surface environments (Hem, 1978; Huang and Keller, 1972). It becomes mobile where conditions allow aluminous minerals to dissolve, as in acid sulfate soils, acid rain catchments (Driscoll and Schecher, 1990), acid mine waters (Stollenwerk, 1994) and acid areas in active geothermal fields (Ramahashay, 1968). In geothermal systems the behaviour of Al is highly sensitive to fluid pH and Al is a major component of many of the principal minerals reacting and forming, both at the surface and in the subsurface in all stages of the alteration processes; in particular of minerals formed at the surface from the action of steam condensates (Martin et al., 1999). The mobility of Al is considerably enhanced in the acid environment over that in the near neutral alkali chloride fluids as a consequence of prolonged exploitation of a geothermal field (Martin et al., 2000). In high-temperature geothermal waters Al concentrations decrease with increasing water salinity because such waters closely approach equilibrium with low-albite (Stefánsson and Arnórsson, 2000).

1.4 Aquatic ecosystems

Aquatic ecosystems are composed of the biological community (producers, consumers and decomposers), the physical and chemical (abiotic) components and their interactions. Within aquatic ecosystems, a complex interaction of physical and biochemical cycles exists, and changes do not occur in isolation. Aquatic ecosystems thus undergo constant change. However ecosystems have usually developed over a long period of time and organisms become adapted to their environment. In addition, ecosystems have an inherent capacity to withstand and assimilate stress based on their unique physical, chemical, and biological properties. Nonetheless, systems may become unbalanced by natural factors, which include drastic changes in climatic variations or by factors due to human activities. Any changes especially rapid ones, could have detrimental effects (CCME, 1999).

Adverse effects due to human activities, such as release of toxic chemicals in industrial effluents, may affect many components in aquatic ecosystems, the magnitude of which will depend on both biotic and abiotic site-specific characteristics. In evaluation aquatic ecosystems are always viewed as whole units, not in terms of isolated organisms affected by one or few pollutants. It's viewed as a complex system with aquatic and terrestrial components hence not studied in isolation (CCME, 1999).

As chemicals or substances are released into the environment through natural processes or human activities, they may enter aquatic ecosystems and partition into particulate phase. These particles may remain in the water or may be deposited into the bed sediments where the contaminants accumulate over time. Sediments may therefore act as long-term reservoirs for contaminants. Because sediments comprise an important component of aquatic ecosystems, providing habitat for a wide range of benthic and epibenthic organisms, exposure to certain substances in sediments represents a potentially significant hazard to the health of organisms. Effective assessment of this hazard requires understanding of the relationship between concentration of sediment-associated chemicals and the occurrence of adverse biological effects (CCME, 1999).

1.4.1 Potential effect of trace elements

Arsenic (As).

Epidemiological evidence has verified that arsenic is one of most carcinogenic and toxic substances in surface and ground waters. By European Union standards and USPHS Drinking Water Standards the maximum permissible As concentration in drinking water is 0.05 ppm and 0.01 ppm for aquaculture. However, from a toxicity assessment perspective, it is not sufficient to quantify total dissolved As, its chemical form must be determined (Arnórsson, 2003). Many studies of As speciation in natural waters have been carried out and most attempt to separate the inorganic species into arsenite (As^{III}) and arsenate (As^{V}). In lake and river waters, $\text{As}(\text{V})$ is generally a dominant species, though significant variations in speciation and concentration have been found. Concentrations and relative proportion of $\text{As}(\text{V})$ and $\text{As}(\text{III})$ vary according to changes in input sources, redox condition and biological activity (Smedley and Kinniburgh, 2002). In geothermal water, arsenic exists as arsenate, which is the thermodynamically stable form of arsenic and less toxic. This however could be reduced to $\text{As}(\text{III})$ by blue-green algae (cyano-bacteria) (Webster and Timperley, 1995).

In the aquatic environment, adverse effects of arsenic have been reported for a wide range of concentrations in water, sediments, and diets. Sandhu (1977) reported an intensive fish kill in a reservoir at Orangeburg, South Carolina (USA), after aerial spraying of arsenic defoliant in a nearby cotton field. The arsenic concentration in the water was elevated to 2500 $\mu\text{g/L}$, and catfish in the reservoir were reported to contain 5 and 12 mg/kg of As in skeletal muscle after 5 hour and 7 week exposure, respectively (wt basis not specified).

In Lake Rotorua, New Zealand, Tanner and Clayton (1990) reported elevated concentrations of arsenic in macrophytes (193-1200 mg/kg dw) and surface sediments (540-780 mg/kg dw) 24 years after an application of sodium arsenite herbicide. Arsenic levels in a nearby reference lake (Lake Rotokauri) were <20 mg/kg dw in macrophytes and 16.5-40 mg/kg dw in sediments.

Natural sources, such as hot springs and volcanic activity, can also contribute to elevated levels of arsenic in the environment. Lacayo et al. (1992) also determined arsenic levels in water, fish, and sediments from Xolotlan, Managua, Nicaragua, a lake which contained high levels of arsenic from such sources.

In Finfeather Lake, Texas which had been contaminated during 53 years of industrial production of arsenic-based cotton defoliant, fish population were affected by arsenic. Green sunfish *Lepomis cyanellus* in the system exhibited liver pathology related to arsenic. Large-mouth bass *Micropterus salmoides* from the lake had deformed fins, jaws, head, and eyes; waterborne arsenic concentrations at the time were 0.54 mg/L (Cantu et al., 1991). Low concentration of $\text{As}(\text{V})$ in water (1-15.2 $\mu\text{g/L}$) have been reported to inhibit certain aquatic plants, resulting in noticeable changes throughout the ecosystem. Sanders and Cibik (1985) have reported consequent changes in the composition and succession of species and in predator-prey relations in chronic studies.

U.S Department of the Interior (1998) reported the no-observed-adverse-effects levels (NOAEL)² for dietary concentrations of arsenic in several species of aquatic and terrestrial birds. The belted kingfisher *Ceryle alcyon* and great blue heron *Ardea herodias* are the most relevant species for aquatic habitats in the U.S. For those two species, the dietary NOAELs were 19 to 22 mg/kg ww when based on sodium arsenite in the diet and 3.4 to 3.9 mg/kg ww when based on copper acetoarsenite. Stanley et al. (1994) found that mallards fed arsenic as sodium arsenate showed reduced weight gain, reduced liver weight, delayed egg laying, reduced egg weight, and shell thinning. In adult mallards, toxicity from sodium arsenate in the diet was significant at 400 mg/kg dw.

Aluminium (Al)

Substantial knowledge exists that aluminium especially in inorganic form is detrimental to fish, invertebrates and plants. The inorganic soluble aluminium ions have been shown to be very toxic to many species of fish, amphibians, invertebrates and also affect algae. Aluminium doesn't biomagnify along the food chain but is shed when insects molt. Humic and organic substances have also been known to lower the effect of analyzed aluminium concentration. Numerous studies indicate that adverse effects of some kind occur in the interval 0.1- 0.3 mg/L of inorganic aluminium or even up to 5 mg/L and higher. Studies presenting total aluminium concentrations indicate in most cases effects at high nominal aluminium values. In some of these cases, the harmful aluminium is only a small part of the total aluminium. Several authors argue that it is hard to separate the aluminium effects from those of low pH, while others have concluded that low pH *per se* entails stronger stress than elevated aluminium concentrations. Aluminium sometimes counteracts the effects or ameliorates harmfully low pH levels (Hermann, 2001).

Fish are the only vertebrates to which, in their natural environment, aluminium is known to be acutely toxic. Aluminium is the principal antagonist in the death of fish in acid waters. The gill is the target organ and death is as a result of both extracellular (i.e. aluminium bound at the gill surface) and intracellular (i.e. aluminium instigates an accelerated death of gill epithelial cells) toxicity. Ionic binding is of major importance for the interaction between aluminium and the gill surface. Aluminium is also linked to a number of sublethal effects in fish including bone deformities, anaemia and neurodegeneration. The toxicity of aluminium is linked to its biological availability, which defines the reactions of aluminium in a biological system and the consequences of these reactions for a biological process and/or organism. The biological availability of aluminium in the natural environment is very much a product of its solution chemistry. Present understanding of the effect of aluminium in natural waters and its interactions with aquatic biota is based largely upon chemical equilibrium constants. The environment, however, and in particular the biological environment, is not in a steady state. Accordingly, true chemical equilibrium is seldom approached in natural systems like surface waters, and some ecotoxicological studies have indicated that a non-steady state aluminium chemistry may predominate in these systems. The same studies also indicate that a non-steady state transient aluminium chemistry may dictate the aluminium toxicity to fish in acidified freshwater systems (Lydersen et al., 2002).

Cadmium (Cd)

Fish represent the most sensitive aquatic organism to cadmium. In particular, Salmonids (*Salmo trutta*, *Salvelinus confluentus*, *Salvelinus fontinalis*) are more acutely sensitive to cadmium than any other freshwater animal species (Davies et al., 1993). The cladoceran, *Daphnia magna* is also very sensitive to cadmium, and thus the most acutely sensitive invertebrate species. A 21-day *Daphnia magna* test in which the test concentrations were not measured showed a 16 percent reduction in reproduction at 0.17 µg/L (Biesinger and Christensen, 1972). Siekierska and Urbanska-Jasik's (2002) study on cadmium effects on the ovarian structure of earthworms also revealed that Cd caused damage to the ovarian structure and affected oogenesis. Cadmium effects on the structure of ovaries were mostly dose-dependent and less clearly related to the exposure time. Effects on salmonids and many

² NOAEL: No-observed-adverse-effect level —the highest tested concentration at which no adverse effect was observed.

invertebrates have been observed at 5 µg/L (adjusted for hardness when available) or more (US EPA, 2001).

Hansen et al.'s (2002) study of effects of cadmium exposure on growth and survival of bull trout *Salvelinus confluentus* found that 0.786 µg/L caused increased mortality (37%) and reduced growth (28% reduction in weight change) in fish exposed for 55 days. Acute mortality due to Cd typically occurs as a result of ion regulatory dysfunction. Reductions in growth could be caused by physiological or behavioural stress during exposure to toxicants. Physiological or behavioural stress can result from a reduction in food consumption or food assimilation, or from increased metabolic costs associated with detoxification and homeostasis during chronic sublethal exposures. Therefore, a reduction in growth is a sensitive indicator of a reduction in an organism's fitness. This reduction in fitness may result in reduced survivability of an individual or population through a reduced ability to compete with other species or to avoid predators. All cadmium exposure concentrations caused significant whole body accumulation. For example, mean whole body Cd concentrations (µg/g tissue dry weight) from fish collected after 20, 40, 55 days Cd exposure was 0.456, 0.766 and 0.913 respectively (Hansen et al., 2002).

Growth reduction has been the major toxic effect of cadmium exposure to freshwater aquatic plants in the range of concentrations causing chronic effects on animals. Freshwater aquatic plants are affected by cadmium at concentrations ranging from 2 to 20,000 µg/L. Studies with macroalgae and microalgae revealed effects at 22.8 to 22,390 µg/L, respectively (US EPA, 2001).

Chromium (Cr)

Acute toxicity³ values of trivalent chromium range from 2,000 µg/L for *Daphnia magna* and the mayfly *Ephemerella subvaria* to 64,000 µg/L for the caddisfly *Hydropsyche betteni*, all three of which were determined in soft water. Studies on the effects of three levels of water hardness on the toxicity of trivalent chromium to *Daphnia magna* reported 48-hour acute values that ranged from 16,800 µg/L in soft water to 58,700 µg/L in hard water. The acute toxicity of trivalent chromium has been reported for several freshwater fish species. These values ranged from 3,330 µg/L for the guppy *Poecilia reticulata* in soft water to 71,900 µg/L for the bluegill *Lepomis macrochirus* in hard water. In hard water the chronic value of 1,020 µg/L for the fathead minnow *Plmephales promelas* is higher than the chronic value of 66 µg/L for *Daphnia magna*. The chronic toxicity⁴ value in soft water was 66 µg/L, but in hard water the lowest tested concentration (44 µg/L) inhibited reproduction (US EPA, 1980b). Toxicity studies of chromium to species of freshwater algae and eurasian watermilfoil indicate that algae are sensitive to hexavalent chromium. The concentrations of chromium that elucidate effects range from 10 µg/L for reduction in growth of a green alga *Chlamydomonas reinhardi* to 1,900 µg/L for root weight inhibition of eurasian watermilfoil *Myriophyllum spicatum*. Growth of the green alga, was reduced at a concentration of 10 µg/L. Inhibition of photosynthesis of a natural population of river algae exposed to 20 µg/L has also been reported (US EPA, 1980b).

Boron (B)

High boron concentrations of thermal waters cause environmental problems both in ground waters and surface waters. High concentrations in soil water boron may be deleterious for certain crops. Boron is necessary in small quantities for growth of plants, but in large concentrations it becomes toxic. Plants in general are far more sensitive than animals to boron toxicity. Plant boron resistance is divided into three groups according to plant species. Relative tolerances of boron are classified as sensitive, semi-tolerant and tolerant. As a general classification, boron concentrations of groundwater exceeding 1 mg/L are harmful to plants. The most sensitive crops can tolerate no more than 0.5-1.0 ppm B (Todd, 1980).

³ Acute toxicity - Adverse effects resulting from a single exposure to a toxic substance which results in severe biological harm.

⁴ Chronic toxicity- The capacity of a substance to cause long-term or delayed adverse health effects.

The waterweed *Elodea canadensis* is sensitive to even very low ambient concentrations of boron and was reported to show a reduced rate of photosynthesis in water containing 1 mg/L for a 28-day exposure (Perry et al., 1994). In addition, marsh pennywort *Hydrocotyle umbellata* exhibited reduced growth and yellowing of the leaves when exposed to <1 mg/L. Another ecological risk assessment for a natural community of aquatic plants showed that, at median spring and fall concentrations of 5.9 and 3.6 mg/L, the pattern of leaf tissue discoloration (yellowing) may indicate adverse ecological impacts on the vegetation (Powell et al., 1997).

The exact mechanism of boron toxicity in animals is not however fully understood. It is not known whether boric acid, the borate ions, or some other boron complex is the toxic boron compound (Maier and Knight, 1991). Available aquatic toxicity data for boron are limited and mostly confined to freshwater laboratory studies.

Little information is available on the toxicity of boron to aquatic invertebrates. In tests with *Daphnia magna*, the NOAEL and LOAEL⁵ were found to be about 6 and 13 mg/L respectively. A significant decrease in growth rate of midge *Chironomus decorus* larvae was found at boron concentrations of 20 mg/L and greater (Maier and Knight, 1991). Boron toxicity database for fish is extensive though it's mostly limited to evaluation of waterborne exposure to boron (without dietary exposure) and also does not include any definitive data relating boron levels in fish tissues to toxic effects. The available literature indicates that boron levels of 0.001-0.1 mg/L could reduce the reproductive potential of sensitive fish species, and concentrations exceeding 0.2 mg/L could impair the survival of developmental stages for other species (Channel catfish and Goldfish), under conditions providing continuous exposure from fertilization through 4 days, post hatching. Boron compounds are also more toxic to developmental and early post-hatched stages than adult fish (Birge and Black, 1977). However, Hamilton and Buhl (1990a) found no difference in the sensitivity of various life stages of fish (Coho salmon) exposed to boron for 96 hours.

In waterbirds such as mallards, adverse reproductive effects have been reported at dietary concentrations of 1000 mg/kg of boron. Hatching success of fertile eggs, body weights of ducklings at hatch, and survival of ducklings from hatching to day 7 were substantially reduced when breeding adults were maintained on a diet supplemented with 1000 mg/kg B. Mallard embryo mortality was greatest during the second half of incubation, when energy demands for embryonic growth were great. No adults died as a result of dietary boron treatment, showing that embryos and hatchlings were the most sensitive mallard life stages to boron toxicosis (Smith and Anders, 1989).

Lead (Pb)

The acute and chronic adverse effects of lead have been studied in a variety of freshwater organisms. Representative test animals include fish and various invertebrate species; rotifers, annelids, snails, cladocerans, copepods, isopods, mayflies, stoneflies, and caddisflies. Toxicity tests have also been conducted with freshwater plants from the algal, desmid and diatom groups. Acute tests were conducted at three different levels of water hardness with *Daphnia magna* demonstrating that daphnids were three times more sensitive to lead in soft water than in hard water. Rotifers tested for 96 hours in soft water were very resistant to lead; however, scuds *Gammarus pseudolimnaeus* are more sensitive to lead than any other invertebrate. Delayed larval development in the mud crab, *Rhithropanopeus harrisi*, has been observed after treatment with lead concentrations of 50 µg/L. In another study 1,000 µg/L of lead suppressed reproduction of two polychaete species, *Ctenodrilus serratus* and *Ophryotrocha disdema*, in a 21 day test. Acute toxicity tests have been conducted with different fish species and indicate a relationship between water hardness and the acute toxicity of lead to rainbow trout, fathead minnows and bluegills, with lead generally being much more toxic in soft water. However, 7 to 28-day soft water exposures of mayflies, stoneflies, and caddisflies to lead indicate that benthic insects are rather insensitive to lead (US EPA, 1980c).

⁵ LOAEL – Lowest-observed-adverse-effect level; the lowest dose in an experiment which produced an observable adverse effect.

Chronic lead toxicity for freshwater fish has been reported with long-term effects on rainbow trout fry and fingerlings exposed to various concentrations of lead for 19 months in hard and soft water. During the 19-month exposures, most of the trout (60 to 100 %) developed spinal deformities in hard water at measured lead concentrations of 850 µg/L and above while in the soft water exposure of most trout (44 to 97 %) developed spinal deformities in water with measured lead concentrations as low as 31 µg/L. These results strongly demonstrate that lead is more chronically toxic in soft water than in hard water. Chronic tests have also been conducted with invertebrate species with the chronic values ranging from 12 to 174 µg/L. Both the acute and chronic toxicities of lead to freshwater animals decrease as water hardness increases. Delayed embryonic development, suppressed reproduction and inhibition of growth rate among fish, crab, polychaete worm, and plankton were also caused by lead. Lead has also been shown to be toxic to algae. Freshwater algae are affected by concentrations of lead above 500 µg/L. The adverse effect concentrations from these tests ranged from 500 to 28,000 µg/L. Cell division was delayed in the phytoplankton, *Platymonas subcordiformus*, after treatment with 2,500 µg/L for 72 hours. At 60,000 µg/L it caused both growth retardation and increased mortality (US EPA, 1980c). It would therefore appear that any adverse effects of lead on plants are very unlikely at concentrations lower than those that will induce chronic effects on freshwater animals.

Lead poisoning has been identified as the cause of death in hundreds of waterfowl. For example, mallards collected in the Coeur d'Alene River Wildlife Management Area, USA were found to contain lead shot with the vast majority of lead-poisoning deaths in the area being caused by ingestion of lead-contaminated sediments (Beyer et al., 2000). Lead in the form of lead shot was found to decrease immunocompetence in birds. A reduction in immunocompetence lowered fitness directly through increased mortality and indirectly through increased predation and parasitism. The activation of the immune system may thus be costly in itself and compete for energy for growth and development and therefore constitute additional stress during development (Fair and Myers, 2002).

Mercury (Hg)

Water concentrations are typically used to assess mercury hazards to fish and aquatic life. Gill and Bruland (1990) have shown that total dissolved mercury concentrations are not as useful in predicting concentrations in fish as are the dissolved concentrations of organic mercury compounds. The estimates of background total Hg concentrations in freshwater prior to 1980, were incorrectly measured in the range of 10 to 50 ng/L but now background concentrations are thought to be less than 10 ng/L. In some exceptionally pristine areas concentrations are less than 1 ng/L. An extraordinary range of estimated and measured effects of mercury in water exist. Differences in mercury toxicity between taxa are greater than differences between the organic and inorganic forms of mercury. Fish toxicity concentrations (96-h LC₅₀)⁶ vary by two orders of magnitude from 11 to 1800 µg/L. At 10° C, methylmercury is about seven times more toxic than Hg⁺² to fingerling rainbow trout. Eisler (1987) concluded that total mercury concentrations in water of 100 to 2000 µg/L were fatal to sensitive aquatic species, and the concentrations between 30 and 100 µg/L caused significant sublethal effects to fish. Mercury contamination in adult and juvenile fish has been shown to disrupt vital functions including reproduction, osmoregulation, orientation, searching for food, predator recognition and communication. Embryonic exposure to inorganic Hg or methylmercury caused a variety of teratogenic effects including cyclopia, tail flexures and cardiac malformations in medaka *Oryzias latipes* and mummichog *Fundulus heteroclitus* and jaw deformities, twinning and axial coiling in rainbow trout. Exposures of embryonic zebrafish *Danio rerio* to methylmercury produced finfold tissue abnormality and posterior tail flexures. Research on a variety of fish species reveal that embryonic exposures to sublethal concentrations of methylmercury produced significant effects on larval behaviour such as prey capture, predator avoidance and swimming activity (Samson et al., 2001).

⁶ LC₅₀ Median lethal concentration; estimated concentration at which 50 percent of exposed specimen would die. "LC" may be used with other percentages to indicate concentrations that produce mortality rates equal to those percentages.

Organomercury compounds, such as methyl or butyl mercury chloride are more toxic to aquatic plants than inorganic forms. In a study that exposed two-day-old sporelings of the red alga *Plumaria elegans* to mercuric chloride, 50% growth inhibition occurred after 6, 12 and 24 h at concentrations of 1.0, 0.5 and 0.25 mg/L respectively. Many wetlands accumulate mercury largely as a result of direct atmospheric deposition, or through transport from the watershed. Mosses typify much of the vegetation wetlands, and are key species because they tend to accumulate and retain more mercury than other plants. Plant uptake has a potential to contribute substantial mercury to food webs, and may also recycle considerable mercury through decomposition products. Determination of EC₅₀⁷ values in the presence of mercuric chloride, for various growth parameters of eurasian milfoil *Myriophyllum spicatum* grown in soil with overlying water revealed EC₅₀ values were 3.4 mg/L for root weight, 4.4 mg/L for shoot weight, 12.0 mg/L for root length, and 1.2 mg/L for shoot length. Exposure of the floating water cabbage *Pistia stratiotes* for two days to mercuric chloride at concentrations between 0.05 mg/L and 20.0 mg/L resulted in decreased chlorophyll content, protein, RNA, dry weight, catalase and protease activity, and increased production of free amino acids at the highest dose of mercury. In a study using the Canadian pond weed *Elodea canadensis* and the free floating duck weed *Lemna minor*, both plants were exposed for 14 and 28 days to varying concentrations of mercuric chloride. Water concentrations of 7.4 mg/L and 1.0 mg/L produced 50% damage to the two plants, respectively (Boening, 2000).

Copper (Cu)

Copper is an essential element for all living organisms but elevated levels in the environment may be harmful. Both deficient and excess amounts of copper cause adverse effects on all species. Copper is generally more toxic to aquatic organisms than birds and mammals. This is reflected by the relatively low ambient water quality criteria for copper and by the rarity of toxic effects through excess dietary exposure in birds and mammals under field conditions. Nevertheless, copper concentrations in bodies of aquatic birds and mammals are generally well regulated (Furness and Rainbow, 1990) and copper toxicity is likely to affect aquatic plants, invertebrates and fish. For example, Miller et al. (1992) reported reduced growth in females of white sucker *Catostomus commersoni* after sexual maturation, decreased egg size and fecundity, no significant increase in fecundity with age, and increased incidence of spawning failure at a waterborne copper concentration of 15 µg/L and sediment concentrations of 93 mg/kg. Nriagu (1979) also reported reduced egg production in fathead minnow *Pimephales promelas* at a relatively low copper concentration in water. Most aquatic organisms are relatively sensitive to copper even at low concentrations. Munkittrick et al. (1991) observed concentrations of 9.7 µg/L of copper and 232 µg/L of zinc in Manitouwadge Lake, Ontario, Canada which led to the complete absence of unionidae and several families of arthropods (Plecoptera, Ephemeroptera, Odonata, Trichoptera, Amphipoda).

Real et al (2003) studied the effect 44 mg/L of copper on a simple aquatic food chain using indoor experimental channels to identify the changes in periphyton community (metabolism, chlorophyll *a* content, abundance, composition and lipid and protein content) and in herbivore snail, *Stagnicola vulnerata* growth rate and reproduction. The results indicated algal community was sensitive to copper. Copper also affected growth rate, reproduction and embryo hatching on snails indicating that the effects on snails are more sensitive endpoints in assessing sublethal copper toxicity than effects on periphyton. Sherba et al. (2000) also observed food response in male and female crayfish *Cambarus bartonii* from an uncontaminated, freshwater lake preceding and following exposure to Cu concentrations of 0.02 mg/L and 0.2 mg/L. There was an increase in mortality in the higher concentration group and significant difference in mortality among the three copper concentrations. Females seemed to recover from Cu-induced impairment slightly faster than males, suggesting a more efficient mechanism for detoxifying copper. The toxic effects of copper persisted after removal of the toxicant and occurred at concentrations much lower than reported lethal levels.

⁷ EC₅₀: Median effective concentration; estimated concentration at which 50 percent of exposed specimens exhibit a particular effect. "EC" may be used with other percentages to indicate concentrations for which affected population is equal to those percentages.

Zinc (Zn)

Zinc is an essential element for all living organisms but elevated levels in the environment may be harmful. It is bioaccumulated by all organisms even in areas of low zinc concentrations. Both deficient and excessive amounts can cause adverse effects in all species. Zinc is most harmful to aquatic life during early life stages in soft water under conditions of low pH, low alkalinity, low dissolved oxygen, and elevated temperature. In contrast to its toxicity to sensitive aquatic organisms, zinc is relatively nontoxic to birds and mammals and tissue concentrations are homeostatically controlled (Eisler, 1993). Zinc poisoning occurs in birds when liver or kidney concentrations exceed 2,100 mg/kg (dw). Many studies have documented the toxicity of zinc and zinc-copper mixtures in effluents. Several studies have illustrated the potential impacts of zinc contaminated mine drainage on the aquatic environment. For example, acid mine drainage from the Iron Mountain Mine near Redding, California (USA) containing high concentration of zinc and copper caused numerous fish kills in the upper Sacramento River. Similarly toxic concentrations of zinc and copper from the Penn Mine area in Sierra Nevada of California caused sizable fish kills in the lower Mokelumne River Basin. During the fish kill zinc concentrations of 1.4 mg/L were measured 6.4 km down-stream from the mine (USDI, 1998). In fish significant adverse effects were observed in the most sensitive fish species at a waterborne zinc concentration of 10 mg/L. Larvae of rainbow trout *Oncorhynchus mykiss* exposed to 10 µg/L of zinc suffered 54 % mortality after a 28-day exposure (Spear, 1981), while acute 96-h LC₅₀ values for Chinook salmon *Oncorhynchus tshawytscha* were measured at > 1,270 µg/L (Hamilton and Buhl, 1990b).

Molybdenum (Mo)

Molybdenum is present in all plant and animal tissues and is considered an essential micronutrient for most life forms. Mounting evidence suggests that much of the primary production in the ocean and even some terrestrial environments is N-limited and thus the availability of dissolved Fe and/or Mo may govern primary production under N-limiting conditions (Gíslason and Eiríksdóttir, 2003). Aquatic organisms are relatively resistant to molybdenum and generally show no adverse effects on growth or survival at water concentrations lower than 50 mg/L. Molybdenum is considered essential for aquatic plant growth, but concentrations required are not known. Aquatic plants are relatively resistant to molybdenum toxicity. Concentrations observed to cause adverse effects in sensitive species were 50 mg/L for growth and 108 mg/L for development. In certain species of aquatic algae and invertebrates, a high bioconcentration of molybdenum has been recorded without apparent harm to the organism, however the hazard potential to organisms that feed on the bioconcentrators is not clear (Eisler, 1989).

Acute toxicity values for molybdenum indicate that it is relatively nontoxic to fish. The one exception was newly fertilized eggs of rainbow trout exposed for 28 days through 4 days posthatch; which had an LC₅₀ of 0.79 mg/L and an LC₁₀ of 0.12 mg/L. Molybdenum is more toxic to younger fish than older fish, although a study by Hamilton and Buhl (1990a) found that the 96-hr LC₅₀ values for all Chinook and coho salmon exceeded 1000 mg/L regardless of the quality of the dilution water (soft, fresh, brackish) or the life stage tested (eyed egg or fry). Addition of molybdenum to test mixtures of boron, selenite, and selenate seemed to increase the acute toxicity of these mixtures to Chinook and coho salmon.

Selenium (Se)

Based on the known margin of safety between normal and toxic dietary exposure selenium is more poisonous than both arsenic and mercury. Selenium is also an essential trace nutrient for animals, and it serves beneficial metabolic functions (Arthur and Beckett, 1994). Thus selenium deficiency as well as toxicity can cause adverse effects for fish and wildlife. Both toxicity and deficiency cause similar effects e.g. reproductive depression, anaemia, weight loss and immune dysfunction. Selenium is much less toxic to most plants and invertebrate animals than to vertebrates. The threshold of ecotoxicity of selenium is remarkably similar for fish and birds. Metabolic stress caused by winter weather can increase the susceptibility of birds and fish to selenium poisoning. Toxicity data collected under benign climatic conditions may thus underestimate sensitivity to selenium poisoning (Lemly, 1995).

Incidents of fish or wildlife poisoning studied in the field have been documented in the technical literature (see USDI, 1998 on Se review). In Belews Lake, North Carolina, USA a power plant cooling reservoir receiving return flow from a fly-ash settling basin and the ash-basin effluent contained about 150-200 µg/L selenium elevating the waterborne selenium in the main reservoir to about 10 µg/L. Of the twenty species of fish exposed to these contaminant conditions, 16 were extirpated, 2 had ceased reproducing, 1 was temporarily extirpated and one was unaffected. For most species, teratogenic⁸ effects and other abnormalities were observed in about 10-70 % of sample fish. The sublethal toxic effects such as generalized edema⁹ and abnormal ovarian tissue damage were also observed (Sorensen et al., 1984). In Hyco Reservoir, North Carolina, USA, another power plant cooling reservoir which received effluent from two fly-ash ponds that contained about 50-200 µg/L selenium in their water elevated the waterborne selenium in the Hyco reservoir to about 10 µg/L. As a consequence of this exposure, adult fish densities declined by 38-75 % and larval densities of fish declined by 98.6 % (Gillespie and Baumann, 1986). Waterborne selenium per se is not very toxic to fish and wildlife. When water is the only exposure route (e.g. standard aquatic toxicity test), toxicity threshold of selenium are generally > 1,000 µg/L (Maier et al., 1987). Much lower concentrations of selenium in water can be bioaccumulated to toxic levels in fish and wildlife via dietary exposure to the aquatic food chain. Field cases of selenium poisoning in fish and birds have been documented for waters averaging as little as 1-10 µg/L.

No study in the literature reports selenium toxicity thresholds for plants based on exposure in nature. In standard toxicity tests, sublethal effects of selenium exposure are initially observed for green algae at waterborne concentrations of 10 µg/L (selenate) and 75 µg/L (selenite). The growth of a green alga, *Selenastrum capricornutum*, was significantly reduced at tissue concentrations of 4 mg/kg (Williams et al., 1994). Toxicity profiles for aquatic macrophytes are not known, but sublethal toxic thresholds for aqua-cultured lettuce were 200 µg/L waterborne selenate and 3,000 µg/L waterborne selenite (Berry and Savage, 1986).

1.5 Heated water discharge effects on aquatic communities

Thermal pollution could be defined as any type of physical pollution associated with a change in the temperature of a medium, having in mind solely an increase in temperature resulting from the discharge of water warmed up by industrial works. Thermal pollution has been directly associated with the development of the heat and nuclear power engineering, whose operating objects discharge large volumes of warmed water into water reservoirs (Beznosov and Suzdaleva, 2001).

If hot wastewater from a standard steam cycle power plant is released directly into an existing natural waterway it inevitably leads to an increase in temperature. This changes various physical-chemical properties of water, such as density, viscosity, surface tension and solubility of gases. The influence of heating on aquatic ecosystems is ambiguous, and at different levels of heating it may be both positive and negative. The most important ecological factor is then to limit excessive heat dumping which will exceed the buffer capacity of the aquatic ecosystem. Of the many environmental factors influencing an ecosystem probably none exerts a more profound influence than temperature.

Due to its pivotal role in biological activity (development, growth and reproduction) temperature has long been recognized as an important environmental factor in both terrestrial and aquatic ecosystems. Seasonal temperature differences, characteristic of higher latitudes, strongly influence the biological activity of aquatic organisms and establish cyclical patterns that often mediate the scope of each activity. Over the long-term, changes to the thermal regime of the surrounding environment can effect the evolutionary, physiological and behavioural responses of individual organisms (Begon et al., 1990).

⁸ Interference with normal embryonic development.

⁹ Abnormal accumulation of fluid beneath the skin.

Temperature directly influences the metabolic rates, physiology, and life-history traits of aquatic species and helps to determine the rates of important community processes such as nutrient recycling and productivity (Allen, 1995). Thermal loads can cause negative processes in local areas of aquatic environment, such as over growth of blue-green algae deteriorating the water quality, change in the composition of plankton and dynamics of its numbers, disruption of fish and other aquatic communities. Fluctuation in water temperature induces behavioural and physiological responses in aquatic organisms. Permanent shifts in temperature regimes can render formerly suitable habitat unusable by native species.

Because of ecological importance of lake temperature, preventing or mitigating anthropogenic thermal degradation is a common concern for resource managers (Poole and Berman, 2001). In serious cases a permanent increase in water temperature levels can result in a complete change of the community whereby high temperature tolerant species take over. In milder cases water temperature variations between sites may create differences in the physiological and behavioural advantages among aquatic organisms hence influencing their competitive ability and distribution as indicated by the study of Taniguchi et al. (1998) showing that changes in competitive ability (measured as food consumption and aggression) could be temperature mediated.

Many studies have shown the effects of thermal discharges on aquatic communities. Squires et al's (1979) study of water temperature increases caused by thermal discharges in the Provo River in Utah, USA found a unique algal community which was attributed to this thermal discharge. The flora displayed an overall similarity in specific composition but with zonation related to local environmental conditions. Effects from elevated temperatures in river sections below the effluent area could not be distinctly isolated; however, the effluent area which extended 100-135 m downstream from the thermal discharge point exhibited a flora significantly different from that in other river areas. The effluent area was characterized by high diatom production. Esterly's (1975) study of thermal effluent effects on the benthos of Thomas Hill Reservoir, Missouri, USA found that the maximum surface water temperature was 37 °C while that of the bottom muds varied between 8-29 °C. Numerical abundance and biomass of benthos were greater in the control site than site affected by hot water but heated water had no apparent deleterious effects on the benthos.

Hickman and Klarer (1975) showed that thermal discharges caused an increase in the standing crop size of the epiphyton associated with sedges, *Scripus validus* and the mean primary productivity also increased. Thermal discharges were also found to cause changes in species composition and dominance in algal communities. The heated water approximately doubled the photosynthetic index of the non-heated site samples suggesting that the algal populations in the non-heated area were not photosynthesising at optimum temperatures. Continuous flow of heated water appeared to cause a decrease in photosynthetic efficiency in the heated area. Klarer and Hickman (1975) monitored water temperature, dissolved oxygen and water chemistry in a lake receiving heated water and found no large differences in these parameters except for water temperature and dissolved oxygen levels between the stations. However, there were increases in the dissolved silica, nitrate-nitrogen and phosphate-phosphorus levels at the heated stations while at a partially heated station only dissolved silica and nitrate-nitrogen increased. The epiphyton at all stations showed a spring maximum, a summer minimum, and a maximum in late summer. The heated water caused a decrease in the number of species and a corresponding increase in the importance of a few species at the heated stations. The major impact of the heated water, however, was an extension of the period of open water and the corresponding increase in mean yearly standing crop size in the heated areas.

Phytoplankton species also have an optimum temperature at which growth rate is maximal. The growth rate of phytoplankton generally increases with temperature only within a certain temperature range, and the temperature dependency of the growth rate differs between species. Species found growing at a higher temperature usually have a higher optimum temperature (Suzuki and Takahashi, 1995). Enzyme reaction rates generally increase with temperature, but metabolic costs such as respiration also increase. As a consequence of these responses to temperature, phytoplankton will exhibit an optimum temperature for growth. The different temperature ranges and temperature

dependencies of growth among species are thought to play an important role in algal competition. Several investigators have examined experimentally the influence of temperature on the growth rate of various species of marine diatoms. The effect of temperature on algal photosynthesis have also been reviewed by Davison (1991).

A study at Madras Atomic Power Station, India showed that thermal discharge affects benthic communities in three ways; reduction in composition of the assemblages; increased abundance of the so-called opportunistic or ephemeral species and alteration of population dynamics of the most abundant species. Death of almost all the macrofauna and flora species was observed during the hot season in an area impacted by the heated effluents. Much of the area that showed consistent thermal effects on benthic community structures, (Suresh et al., 1993) exhibited relatively high temperature values on the bottom due to the thermal discharges 7-10°C higher than in the ambient water. The different levels of heat dispersion in the sea water and the different thermal tolerance of the species in the study communities may have combined to produce no, little or great measurable responses to the thermal disturbances (Suresh et al., 1993).

On the other hand, studies performed at several Italian coastal sites with large power plants in general did not reveal any biologically important effects of the thermal discharges on different ecosystem components such as phytoplankton and zooplankton, benthos and fishes, although the proximity of the outfalls was not always considered (Cironi et al., 1995).

The responses of freshwater algae to temperature change have also been summarized by DeNicola (1996) and include a variety of effects that have been studied at the cellular, population and community level. Individual responses are highly dependent upon the variability in the physicochemical environment and spatio-temporal pattern in species distribution. Physiological responses to temperature include changes in concentrations of photosynthetic and respiratory enzymes, changes in cell quota and nutrient uptake, as well as alteration in fatty acids and proteins. Individual populations have been shown to exhibit minimum, maximum and optimum temperatures for growth that contribute to species composition and diversity and eventually lead to seasonal succession.

Several broad generalizations concerning periphyton responses to temperature have been summarized by DeNicola as follows: 1) as temperature increases, there is a shift in the dominance of algal classes from diatoms (<20°C) to green algae (15-30°C) to blue-green algae (>30°C); 2) species diversity increases from approximately 0 to 25° C and decreases at temperatures > 30°C; 3) the degree to which community composition changes with thermal input depends on the initial ambient temperature. Increases in temperature in environments near 25-30°C usually cause greater changes in community structure than in environments <25°C; 4) community structure usually recovers rapidly (< 1 yr) when temperature stress is discontinued; 5) biomass increases with temperature from approximately 0-30°C, and decreases at 30-40°C.

Temperature changes beyond threshold levels can also have variable effects on aquatic insect communities' diapause induction as a function of endocrine processes; hatching success which decreases at low or high extremes; larval growth, adult size and fecundity for which temperature influences the rate of feeding, assimilation and respiration, food conversion efficiencies and enzymatic kinetics; voltinism¹⁰ ; and timing of adult emergence which may be premature or delayed depending on temperature increase or decrease (Sweeney and Vannote, 1981).

High but sub-lethal temperature can affect fish in a number of ways. The effects may reflect metabolic inefficiencies, susceptibility to disease and toxic effects of pollutants, changes in behavioural patterns, intra- and inter-specific competition, predator-prey relationships, community composition and parasite-host relationships (Dickerson and Vinyard, 1999). A study of ecological effects of hot water discharge of a steam electric generating plant in Crystal River, Florida on fishes found that species abundance was higher at non-affected sites than an affected station (Grimes and Mountain, 1971),

¹⁰ Number of generations per year based on larval growth rate.

while species diversity determination indicated higher diversity in winter at the affected station, but higher in summer at unaffected stations. Suppressed summer diversity was attributed to thermal stress on the community. Carr and Giesel (1975) found that both the numbers and biomass of juvenile fish in thermally affected creeks were 3-10 fold smaller than those obtained from the creek at ambient temperature.

A study of the thermal effluent effects on the community structure and nursery function of fish in an estuary showed decreasing numbers of species with decreasing distance from the thermal outfall (Jones et al., 1996). The thermal effluent only affected the species composition in the inner estuary, and estuary-opportunistic species. During winter/spring months, thermal effluent attracted some fish species to the warmer waters of the inner estuary. The extended growth season for such species and significantly higher growth rates promoted premature movement out of the inner estuary. The latter effects were postulated to lead to alteration of the population structures of the species by increasing their vulnerability to heavily localized fishing intensity, aggregation of natural predators and point-source pollution.

In a study of mosquitofish *Gambusia affinis* from thermally affected stations (28 to 40°C) and unaffected sites (12 to 29°C) for reproductive activity, sex ratios, size at sexual maturity, percentage of fat, and size structure, Bennett and Goodyear (1978) showed that mean brood size of populations from thermally affected areas generally varied inversely with water temperature. Size at sexual maturity and sex ratios were similar in all populations. Body fat content varied seasonally with each population with percentages of fat being higher in males and juveniles from thermally affected waters. Mean size of females from unaffected areas was found to be directly related to water temperature but the size structure of populations from unaffected waters varied inversely with temperature. Stauffer et al. (1974) studied the distribution of fish in two rivers in relation to thermal discharges from a fossil fuel power plant. They noted a slight decrease in diversity indices for stations located in the thermal discharge. The results showed that while a number of species were not affected; others avoided high temperatures but others were attracted to high temperatures.

Exposure of fish to thermal effluents can possibly compromise gametogenesis in fish (Luksiene et al., 2000). High temperature in Swedish and Lithuanian thermal effluent areas influenced gametogenesis of female perch *Perca fluviatilis*, roach *Rutilus rutilus* and pike *Esox lucius* negatively, indicating reduced reproductive capacity. Roach kept at high temperatures during the pre-spawning period in spring exhibited reduced gonadal size and atresia in the ovary. In the Lithuanian lake, at the Ignalina Nuclear Power Plant, gonads of female roach displayed highly arrhythmic development with stages of oogenesis. The sequence of seasonal development was disturbed, and high frequencies of atretic oocytes were observed already during early vitellogenesis. A similar pattern of damage was observed in roach sampled in a Swedish testing facility at a Baltic nuclear power plant where fish were exposed to cooling water in a large artificial enclosure (Luksiene and Sandstrom, 1994). Many females suffered from oocyte degeneration serious enough to inhibit complete spawning. Pathological changes in female roach gonads have been reported also from several Finnish coastal waters of the Baltic, including one area influenced by thermal effluent. The observed degenerations were associated with massive infections by a microsporidian parasite suggesting that microsporidian infections could be correlated positively with temperature (Wiklund et al., 1996). Most previous studies on cooling water effects on fish reproduction were made on populations living in reservoirs of a restricted volume, where the fish could not escape exposure. The reasons why fish gametogenesis can be damaged by exposure to higher than normal temperatures are not known. However, two alternative explanations deserve attention. Hormones control the reproductive processes, and endocrine homeostasis is known to be responsive to temperature changes. Gonadal steroid production measured *in vivo* is affected by temperature, and temperature modulates hormone action at all levels of the reproductive endocrine system (Van Der Kraak and Pankhurst, 1996).

In order to exploit a habitat efficiently, an animal needs to be active under the particular thermal conditions associated with it. Some species are capable of maintaining body temperature within a narrow range through behavioural or physiological adjustments, while others perform close to thermal

equilibrium with the environment (Huey and Kingsolver, 1989). Behavioural thermoregulation is not a widespread phenomenon in aquatic ectotherms (invertebrates and vertebrates except birds and mammals) since the required thermal heterogeneity is not always available (Hughes, 1998). Therefore, for most aquatic ectotherms, water temperature affects physiological rates and efficiencies and hence more complex organismal activities such as developmental rates (Blaxter, 1992), locomotor performance and growth almost directly (Ojanguren and Brana, 2000).

Temperature experienced during early life history phases also influences adult size and the balance of trade-offs such as egg size vs. fecundity, current vs. future reproduction and age at maturity (Van Winkle et al., 1997). Thus, a thermal regime acting on performance at various levels is likely to have strong ecological implications and thus evolutionary consequences for the populations (Gilchrist, 1995). Growth is an integrative process that results from digestion, absorption, assimilation, metabolic expenditure and excretion. All these functions are mediated by enzymatic activities that are strongly affected by temperature, and so thermal regime emerges as the main factor controlling the growth rate of fish (Elliott, 1994). In the mitigation of effects arising from heated water discharge on aquatic communities, the most important ecological factor will then be to limit excessive heat dumping that might exceed the buffer capacity of the aquatic ecosystem as a way of eliminating the profound influence of temperature on such communities.

Part II:
CHEMICAL AND THERMAL STRESS ASSESSMENT
– LAKE THINGVALLAVATN, ICELAND

2.0 PAST RESEARCH AT NESJAVELLIR AND THINGVALLAVATN

2.1 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, 2002), 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. Figure 2 shows the general design of the plant. 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 (Gíslason, 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.

2.2 Geothermally heated discharge and cold underground water

The underground flow of geothermal water through the Nesjahraun area has been subjected to a study model based on empirical data from tracer experiments and experimental drilling. Using a sodium fluorescein tracer the geothermal water has been traced from Lækjarhvarf down to some lakeshore springs (Kjara and Egilsson, 1986, 1987). According to these studies the flow was confined to a rather narrow area between Markagjá in the north and Stapavík in the south, the core of the flow being situated upwards of the Varmagjá area (Kjara and Egilsson, 1986, 1987; Ólafsson, 1992).

Temperature profiles from experimental drillholes in Nesjahraun show that the flow of the geothermal water is also confined vertically to a narrow zone a few metres above the cooler ground water table

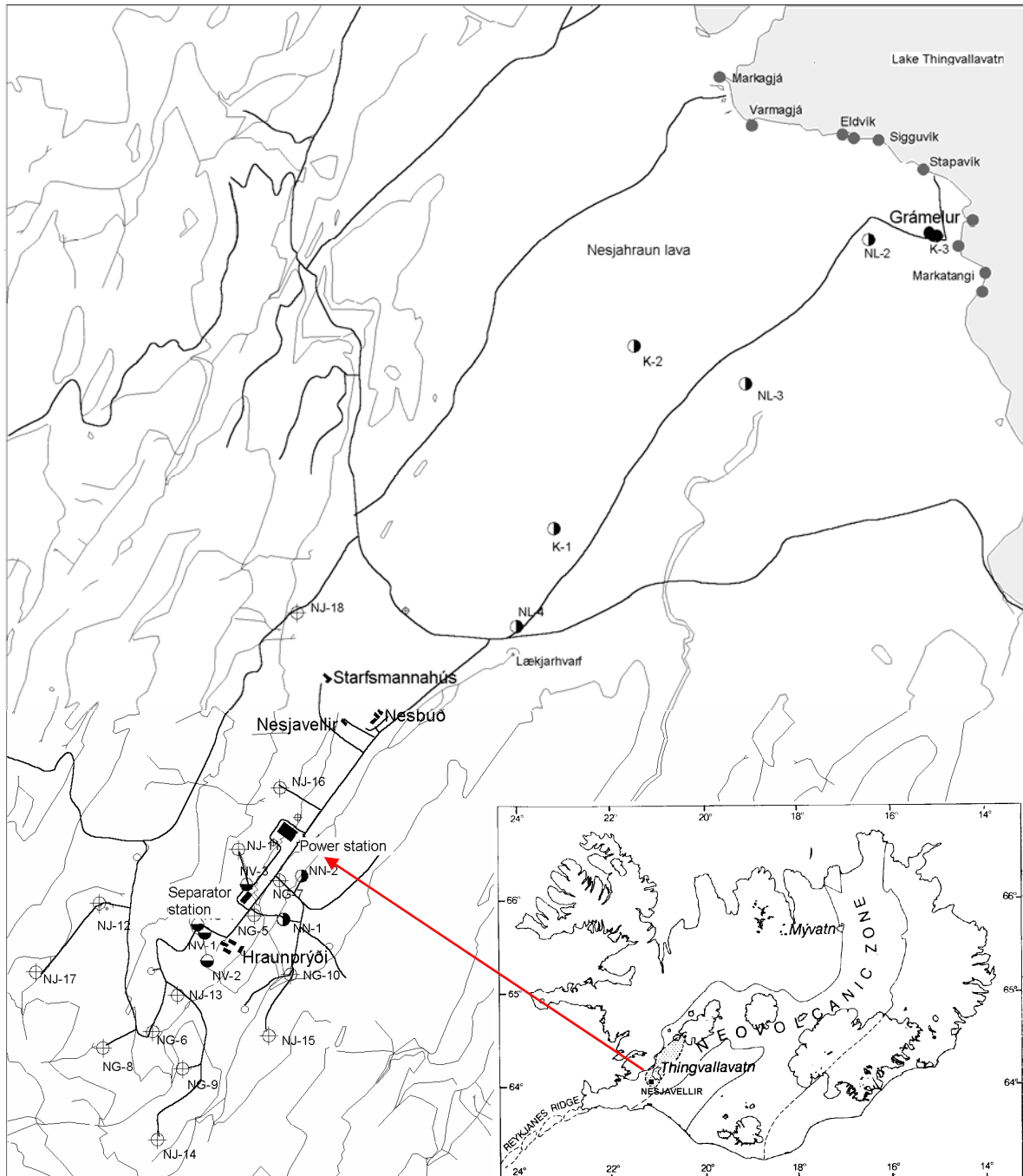


FIGURE 1: Location of Nesjavellir geothermal co-generation plant and Lake Thingvallavatn

(Hafstad, 2001). This means that the main, central stream of geothermal wastewater does not mix much with colder ground water. The most significant change in the system stems from the added disposal of “unusable” cooling water coming from the turbines generating electricity which were first deployed in October 1998. This addition now amounts to an average of 736.8-756.1 kg/s at 57.6-64.6°C but may be as high as 1447.6 kg/s of water (Wetang’ula and Snorrason, 2003). The effect of this is clearly seen in changes in temperature profiles of several monitoring drillholes in the Nesjavellir lava from spring 2000 to autumn 2001 (Hafstad, 2001), when the electricity generation facilities had been in full operation for less than a year. The data show a marked rise in the temperature of the central stream of geothermal water and an extension of the warm water tounge at the eastern and western edges (Wetang’ula and Snorrason, 2003).

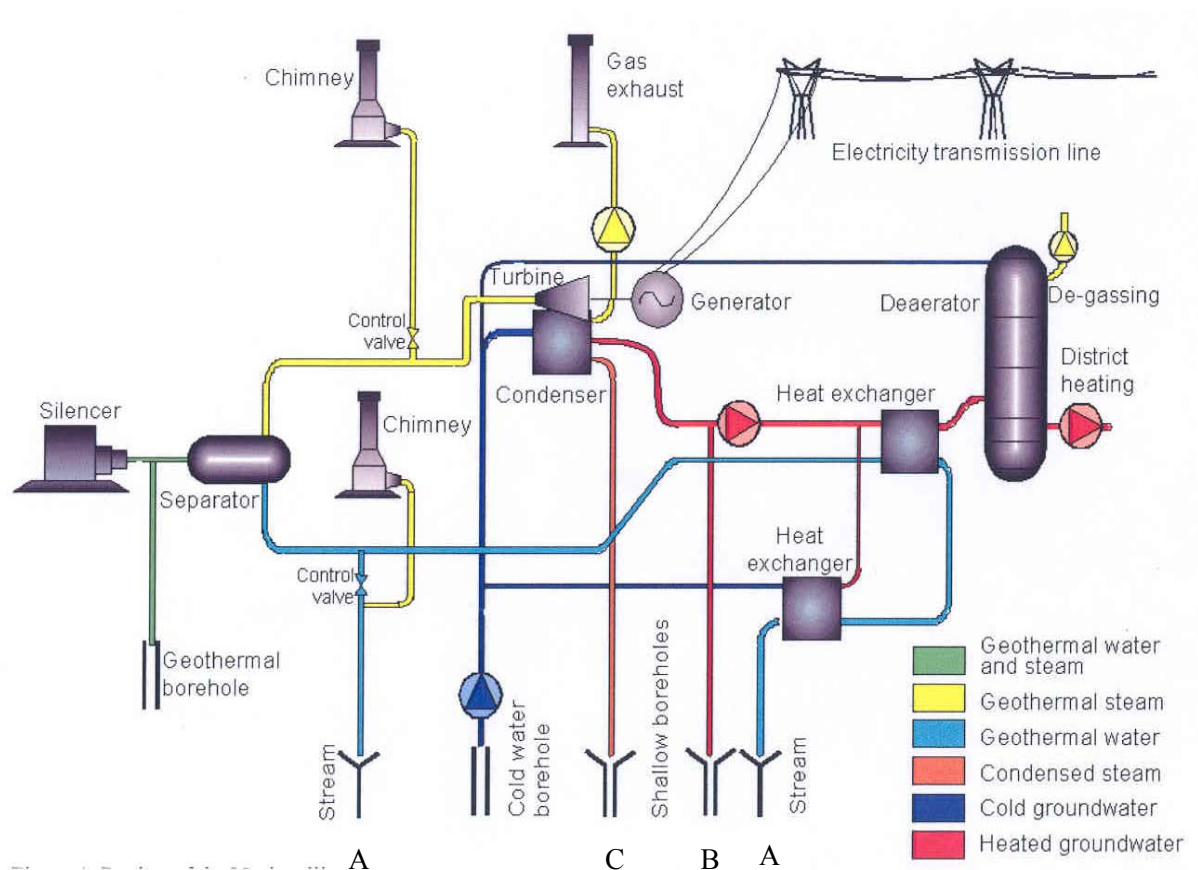


FIGURE 2: Nesjavellir geothermal co-generation power plant flow diagram;
A = separator water, B = Cooling water, C = condensate

2.3 Chemical constituents

Ólafsson (1992) determined some of the chemical constituents in Nesjavellir drillhole fluid, separator water and Lake Thingvallavatn shoreline springs water. A study of the chemical composition of effluents from 4 geothermal drillholes sampled in the Nesjavellir field in 1983-1984 showed concentrations of arsenic ranging from 5.6 to 310 µg/L. In the following years (1984-1991), during geothermal field development, arsenic concentrations rose slightly in two geothermally affected lakeshore springs, at Varmagjá (from 0.6 – 2.2 µg/L) and Eldvík (from 0.7 – 4.7 µg/L). The lead concentration in Varmagjá and Eldvík was between 0.03 and 0.1 µg/L. The reported cadmium concentration was 0.04 µg/L in Varmagjá in 1991. Ólafsson (1992) found a copper concentration of 1.2 µg/L in Varmagjá and 0.7-1.5 µg/L in Eldvík. Zinc in Varmagjá was 0.2 µg/L in 1984 and 1.1 µg/L in 1991.

From these results Ólafsson (1992) concluded that arsenic was the only constituent of the geothermal effluent likely to be of concern in Lake Thingvallavatn. Although the concentrations of chemical constituents in the affected springs were low and the arsenic concentration was within limits considered safe for the fresh water biota, precautionary monitoring measures were recommended (Snorrason and Jónsson, 1995).

During the summer of 1996 Björnsdóttir (1996) also determined concentrations of copper, zinc, lead and cadmium in separator water, condensate, effluent at Lækjarhvarf water and the water of Lake Thingvallavatn shoreline springs of Markagjá, Varmagjá and Eldvík (Table 2).

TABLE 2: Concentration of silica, aluminium and some trace constituents in Nesjavellir geothermal discharge and spring water by Nesjahraun

	SiO ₂ (mg/l)	Al (µg/l)	Ni (µg/l)	Mn (µg/l)	Cu (µg/l)	Zn (µg/l)	Pb (µg/l)	Cr (µg/l)	Cd (µg/l)	As (µg/l)	Hg (ng/l)	Source
Nesjavellir NJ-11			1.0	3.9	0.3	1.7	0.11		0.72	134	44	1
Nesjavellir NJ-13			0.2	1.7	0.3	1.7	0.54		0.23	160	143	1
Nesjavellir power station			1.3	1.2	1.2	1.2	0.09		0.05	120	261	1
Markagjá, 1984 & 1991	11.5/14.9		0.1/0.1	1.0/1.0	0.4/1.0	0.2/2.9	0.07/0.07		0.005/0.11	1.1/0.5	1.8/0.8	1
Varmagjá 1984 & 1991	32.3/37.9		0.2/0.1	0.1/0.2	1.2/1.2	0.2/1.1	0.06/0.03		0.006/0.04	0.6/2.2	0.9/8.0	1
Eldvík 1984/1991	33.6/47.7		0.1/0.1	0.1/1.2	0.7/1.5	0.3/0.3	0.05/0.1		0.004/0.06	0.7/4.7	0.9/2.5	1
Nesjavellir separator water					0.4	2.8	0.6		BDL			2
Cooled geothermal water					0.5	1.2	4.2		0.11			2
Lækjarhvarf					1.8	2.9	0.5		0.4			2
Markagjá 1996					1.0	4.2	0.4		0.2			2
Varmagjá 1996					0.6	3.0	1.0		0.04			2
Eldvík 1996					0.8	1.7	0.8		BDL			2
Separator water	807,000	1670	0.123	3.8	<0.1	1.94	<0.03	0.031	<0.005	20.9	<2.2	3
Markagjá	14,000	14.9	0.149	0.29	0.567	1.61	0.046	0.287	<0.005	0.035	<2.2	3
Varmagjá	49,000	1.54	0.138	0.08	0.56	<0.2	<0.03	0.479	<0.005	0.709	<2.2	3
Eldvík	64,000	349	0.166	0.49	1.02	0.636	0.146	0.46	<0.005	5.97	<2.2	3
Grámelur	40,000	291	0.561	0.33	1.6	28.4	0.054	0.31	<0.005	3.82	<2.2	3

1: Ólafsson (1992); 2: Björnsdóttir (1996); 3: VGK (2000); BDL: Below detection limit

During V GK's (2000) environmental impact assessment study for the expansion of the Nesjavellir power plant from 76 to 90 MWe the concentration of chemical constituents in separator water, lake shoreline spring water (Varmagjá and Eldvík), in the main fresh water source of the plant at Grámelur, and in water from Markagjá, which is not affected by geothermal activity (Table 2) were determined. The study revealed that chemicals, such as SiO₂, Al and As, were in high concentrations in the separator water from the plant; with Wetang'ula and Snorrason (2003) noting that such chemical constituents could be used potentially as markers for the level of influence of the geothermal wastewater on the ground water and natural springs in the Nesjavellir area. The concentration of aluminium in the separator water was rather high, 1670 µg/L, and in the Eldvík springs, the level was 349 µg/L much above the recommended 5-100 µg/L Canadian water quality guidelines for protection of aquatic life (CCME, 1999). The V GK study was the first where aluminium concentration in separator water from the power plant was measured.

2.4 Biological studies

The earlier conclusion of Ólafsson (1992) of potential ecotoxicological effects of Nesjavellir geothermal field developments on lake Thingvallavatn was followed by Snorrason and Jónsson's (1995, 1996, 2000) studies of trace metals in biological samples representative of the local biota (sediments; aquatic plant, *Myrophyllum alterniflorum*; a gastropod snail, *Lymnaea peregra*; and fish-small benthivorous arctic charr, *Salvelinus alpinus*) at Varmagjá (Thorsteinsvík) and at a control station, at Vatnskot, on the northern shore of the lake (Tables 3 and 4). In all the studies there were no significant differences in trace element concentrations at Thorsteinsvík and Vatnskot (control site) with the variations being attributed to background concentration. Gastropod snails are benthic dwellers feeding on sediments and form 80-90% of the diet of small benthivorous charr (Malmquist et al., 1992). Evidence of any bioaccumulation of metals from sediments and water should be detectable in either or both of the two organisms.

TABLE 3: Average concentrations of trace elements in sediment, an aquatic plant and a gastropod snail in Lake Thingvallavatn^a

	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	
Thorsteinsvík 1994	0.01	3.80	7.90	<0.01*	32.10	0.038	1.45	
Thorsteinsvík 1995	0.01	1.13	4.50	92.66	74.26	0.208	2.99	
Thorsteinsvík 2000	0.01	1.40	3.60	59.00	55.10	0.133	3.00	
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
Thorsteinsvík 1994	<0.14	2.20	2.00	56.20		0.49	1.60	
Thorsteinsvík 1995	0.0283	0.644	2.63	75.70	157.90	0.3785	0.38	14.20
Thorsteinsvík 2000	0.021	4.00	1.20	22.00	45.30	0.216	1.10	33.00
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
Thorsteinsvík 1994	<0.14	2.20	4.60	62.40		0.41	1.80	
Thorsteinsvík 1995	0.017	1.80	2.27	43.40	92.30	0.378	0.34	28.90
Thorsteinsvík 2000	0.191	5.40	2.10	70.00	68.00	0.468	<0.03	35.00
* Faulty measurement								

a) Snorrason and Jónsson (1995, 1996, 2000)

TABLE 4: Average concentrations of trace elements in liver of small benthivorous charr (wet weight samples) from Lake Thingvallavatn (see Snorrason and Jónsson (1995, 1996, 2000)

	Dry Wt. (%)	As (ng/g)	Se (µg/g)	Zn (µg/g)	Cu (µg/g)	Cd (ng/g)	Pb (ng/g)	Hg (ng/g)	Mn (µg/g)
<i>Vatnskot 1994</i>	22.21	153.00	4.96	37.30		76.80	<300	26.00	
<i>Vatnskot 1996</i>									
group 1 (3.7 yrs)		<750	2.71	31.60	32.20	<65	40.00	93.6*	1.82
group 2 (6.7 yrs)		<750	1.78	24.30	17.60	65.00	116.00	19.30	1.74
<i>Vatnskot 2000</i>									
group 1 (8.9 yrs)		200.00	3.90	35.40	84.00	108.00	<20	18.00	3.55
group 2 (3.8 yrs)		150.00	4.90	40.00	34.00	49.00	<20	13.00	0.15
<i>Thorsteinsvík 1994</i>	21.67	143.00	5.16	42.20		88.70	<300	18.10	
<i>Thorsteinsvík 1996</i>									
group 1 (5.6 yrs)		506.00	2.88	37.40	170.50	42.10	20.00	106.6*	1.88
group 2 (9.1 yrs)		926.00	2.48	33.90	364.90	61.40	44.00	12.00	1.63
<i>Thorsteinsvík 2000</i>									
group 1 (5.6 yrs)		360.00	5.00	39.00	296.00	91.00	<20	7.00	1.54
group 2 (4.0 yrs)		390.00	5.20	43.70	244.00	59.00	<20	6.00	2.35
group 3 (2.9 yrs)		370.00	5.40	40.80	200.00	74.00	60.00	7.00	1.71

* sample contamination or faulty measurement

3.0 STUDY OBJECTIVES

The present investigation of geothermal wastewater disposal at Nesjavellir, Thingvallavatn (Iceland) was stimulated by earlier findings. The aims of this present work were the following.

- 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;
- To evaluate whether trace element concentrations in fish tissue fish could be toxic if consumed;
- To evaluate the effects of geothermal wastewater disposal on lake water temperature at the outflow sites. Also discuss the potential effects of the trace constituents on organisms if the levels exceed the recommended water and sediment quality criteria.

4.0 METHODOLOGY

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. Temperature mapping was carried out on the southern shoreline of the lake from Markagjá to Grámelur (Figure 3) to determine geothermal water outflow sites by use of digital thermometer (Cole Parmer).

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. The sites were selected because in previous studies some of these sites had been mapped as geothermal outflow points. Varmagjá was selected because it has been considered the main site of geothermal influence because it is sheltered from the winds and thus warm water effects could easily be elucidated. Furthermore, previous studies of trace elements and ecology have carried out at this site (see Snorrason and Jónsson, 1995, 1996, 2000).

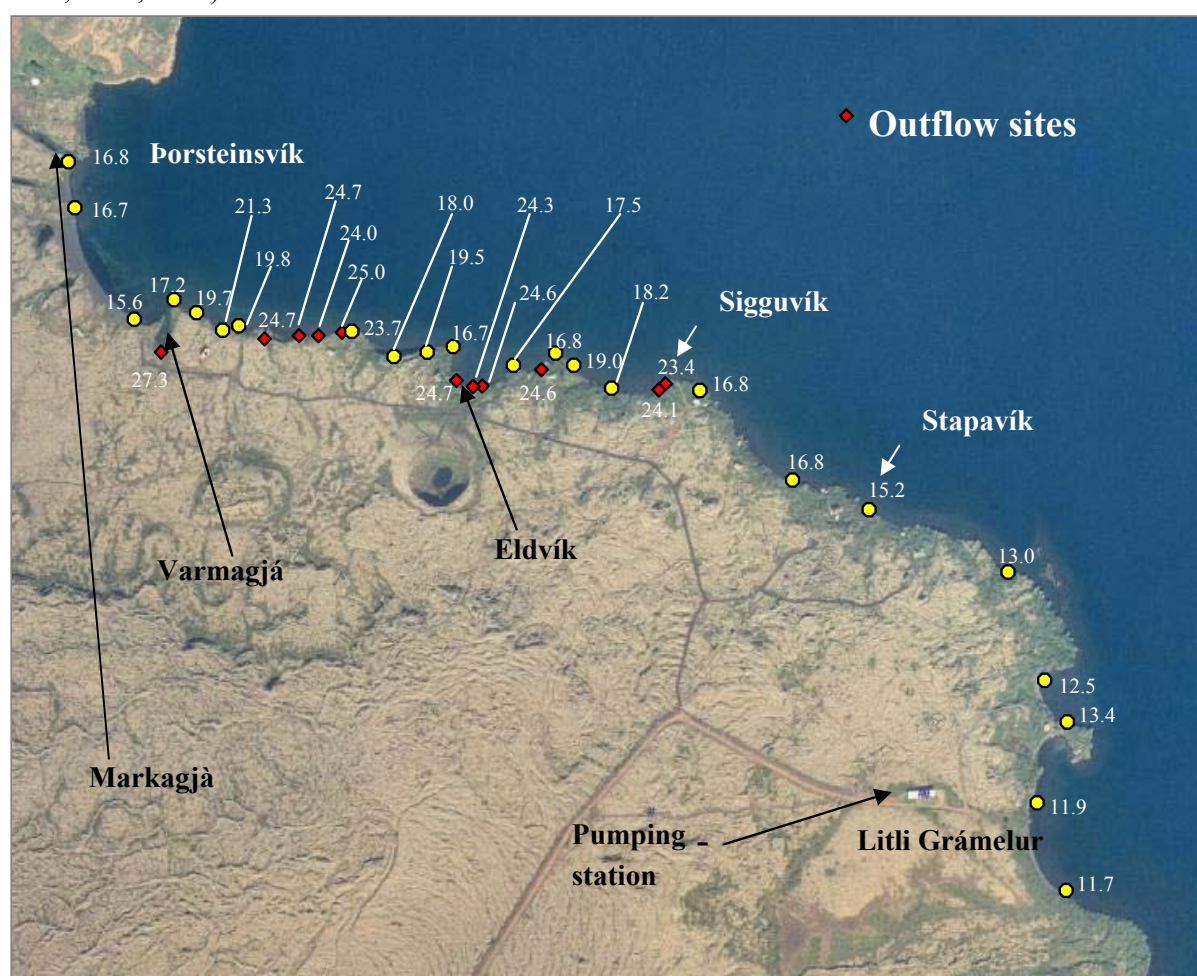


FIGURE 3: Spatial variations in water temperature along the southern shoreline of Lake Thingvallavatn. Red diamonds = Visible geothermal outflow sites, Yellow dots = Points with no visible outflow flows

4.1 Temperature and conductivity transect measurements

Water temperature profiles were measured along three different transects at 10, 25, 50 and 75 m distance from the mouth of Varmagjá and Eldvík outflow sites to determined the extent of geothermal

water influence into the lake. The logging was carried out with a YSI 650 Multiparameter Display System logger (YSI Environmental) was used to measure temperature (accuracy ± 0.15 , resolution 0.01°C), specific conductivity (accuracy $\pm 0.5\%$ of reading $+0.001\text{ mS/cm}$, resolution 0.001 or 0.1 mS/cm), dissolved oxygen – mg/L (accuracy 0 to 20 mg/L : $\pm 2\%$ of reading or 0.2 mg/L , whichever is greater, 20 to 50 mg/L : $\pm 6\%$ of reading, resolution 0.01 mg/L), pH (accuracy ± 0.2 unit, resolution 0.01 unit) and depth (accuracy $\pm 0.02\text{ m}$). In winter of 2004, surface water temperature mapping and temperature profiles were done at Markagjá and Varmagjá. Water temperature at Eldvík outflow site was also determined. pH was also measured with an Orion 290A pH meter (Orion Research Inc.). Alkalinity and dissolved oxygen were also determined in the laboratory using a 716 DMS Titrimetric (METROHM) titrator and the Winkler titration method respectively.

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

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 4). 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.

4.3 Biota samples

4.3.1 Sampling procedures

Sediment, aquatic plant and gastropod snail

Sediments were collected from two points at Varmagjá by use of a plastic sediment corer. No sediment was found at the Eldvík outflow. Samples of aquatic moss were collected from the Varmagjá and Eldvík outflow sites. The submerged aquatic plant *Myriophyllum alterniflorum* was collected from Varmagjá only. *Myriophyllum* was not found near the Eldvík 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.

Fish

Two fish species i.e. arctic charr *Salvelinus alpinus* and threespined stickleback *Gasterosteus aculeatus* were collected from Varmagjá and Eldvík. 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.



FIGURE 4: Sampling sites for trace elements and biological samples at lake outflow points. Biological samples (fish, aquatic plants, sediment and gastropod snail) were collected at Varmagjá and Eldvík sites

4.3.2 Sample digestion procedure

Sediments

The samples were dried at 105 °C according to the Swedish Standard SS 028113. For the following trace elements i.e. arsenic, cadmium, cobalt, copper, mercury, nickel, lead, zinc and sulphur; the samples were dried at 50 °C. Sample digestion was carried out in closed vessels using 1:1 nitric acid and water in a microwave digestion system based on the same procedure as described above. For the other elements (chromium and molybdenum) a 0.125 g sample was fused with 0.375 g LiBO₂ and dissolved in diluted HNO₃ according to ASTM D3682 Method (modified).

Aquatic plants, gastropod snail and fish

Biological samples of plants - *Myriophyllum alterniflorum* and moss, gastropod snail *Lymnaea peregra* and fish - threespined sticklebacks-*Gasterosteus aculeatus* and arctic charr- *Salvelinus alpinus* were digested before analysis. A microwave digestion procedure was applied to oven-dried samples (65°C, 24 hrs). A set of digestion blanks was prepared together with each batch of samples. Digestion of each sample (0.5 g of each biological sample, 5 ml nitric acid and 0.5 ml hydrogen peroxide weighed to PFA digestion vessel) was accomplished using a microwave oven (MDS-2000, CEM Corporation, Matthews, USA) for 1 h at 600 W power. The vessel was removed from the oven and cooled to room temperature. The digest was transferred to a plastic autosampler tube and diluted to 10 ml with high purity water Milli-Q water (Millipore Milli-Q, Bedford, USA). The sample was mixed, centrifuged at 4000 rpm for 5 min and further diluted five-fold for ICP-AES analysis and 10-fold for ICP-SMS (Rodushkin et al., 1999; Rodushkin, 1998).

4.3.3 Trace metal analysis of biological samples

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).

An ARL (Applied Research Laboratories SA, Ecublens, Switzerland) ICP-AES instrument was used with a Gilson 100 sampler changer. The device has 40 channels for simultaneous multielement detection. The ICP-SMS instrument used was the ELEMENT (Finnigan MAT, Bremen, Germany) equipped with an ASX 500 sample changer (CETAC Technologies, Omaha, USA). The device can be operated in low resolution mode (LRM, $m/\Delta m = 300$), medium (MRM, $m/\Delta m = 3000$) and high resolution mode (HRM, $m/\Delta m = 7500$). These resolution values are approximate (or “minimum” specification according to the manufacturer’s definition) and actual resolution depends on ion lens settings (Rodushkin et al., 1999; Rodushkin, 1998).

5.0 RESULTS

5.1 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 5 and 6. The concentrations of aluminium, arsenic, boron and SiO₂ were high in separator water (Al = 1880 µg/L, As = 50.3 µg/L, B = 2150 µg/L, SiO₂ = 483.4 mg/L) and at Lækjarhvarf, where the effluent stream disappears into the lava (Al = 922 µg/L, As = 52.4 µg/L, B = 974 µg/L, SiO₂ = 245.69 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 (Al = 19 µg/L, As = 0.148 µg/L, B = 72.2 µg/L, SiO₂ = 3.540 mg/L) and in the cooling water (Figure 5).

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 guide-lines. The arsenic concentration level in the effluent waters at Lækjarhvarf and water from lake outflow site 10 was above the 5.0 µg/L

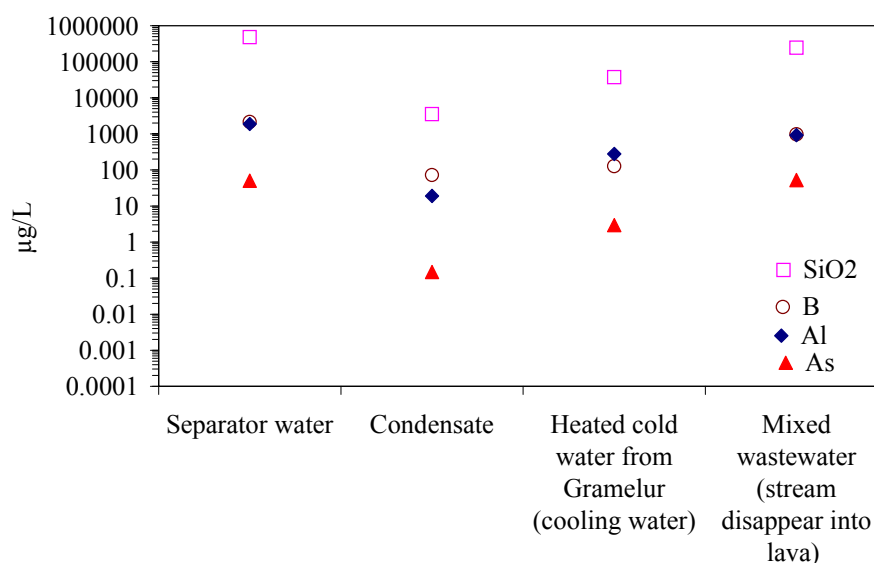


FIGURE 5: Concentration of “signal” chemical constituents SiO₂, B, Al and As in Nesjavellir geothermal co-generation power plant wastewaters

limit (CCME, 1999) water quality criteria for protection of aquatic life. The levels at sites 7, 8 & 9 (Figure 6a) 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.

TABLE 5: Trace elements concentration in Nesjavellir geothermal co-generation power plant wastewater (October 2003)

Sample	pH	Al (µg/l)	As (µg/l)	B (µg/l)	Ba (µg/l)	Cd (µg/l)	Co (µg/l)	Cr (µg/l)	Cu (µg/l)	Hg (µg/l)	Mn (µg/l)	Mo (µg/l)	Ni (µg/l)	Pb (µg/l)	Zn (µg/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	0.036	0.94
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	0.036	3.17
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	0.03	0.8
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	0.032	0.92

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

TABLE 6: Trace elements concentration in Lake Thingvallavatn shoreline outflow sites water (July 2003)

Sites ^a	pH	Al (µg/l)	As (µg/l)	B (µg/l)	Ba (µg/l)	Cd (µg/l)	Co (µg/l)	Cr (µg/l)	Cu (µg/l)	Hg (µg/l)	Mn (µg/l)	Mo (µg/l)	Ni (µg/l)	Pb (µg/l)	Zn (µg/l)
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	0.013	0.62
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	0.115	2.31
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	0.012	1.42
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	0.029	1.81
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	<0.01	0.86
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	0.012	1.06
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	0.027	5.01
8	8.08	447	4.11	296	0.96	0.0158	0.007	0.45	3	0.0055	0.703	1.03	0.401	0.045	2.54
9	8.11	513	4.51	233	1	<0.002	<0.005	0.457	1.8	0.0066	0.585	1.07	0.236	0.014	0.7
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	0.04	1.62

a) Information on sample locations are provided in Figure 4

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 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 µg/L limits for aquatic life water quality criteria for Al (CCME, 1999). Aluminium concentration in the water increased spatially from site 1 to site (Figure 6b). 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.

The highest boron concentrations observed were 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 Grámelur). 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 6c). The highest concentration was observed in water from site 8 (Eldvík) 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 $<0.002 \mu\text{g/L}$ 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 $0.017 \mu\text{g/L}$ (aquatic life) and $80 \mu\text{g/L}$ (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 = $<0.01 \mu\text{g/l}$) except site 8 (Eldvík = $0.0158 \mu\text{g/L}$) which was categorized as “low” (class 2 = $0.01\text{-}0.1 \mu\text{g/l}$) with respect to Cd (SEPA, 1991).

The lead concentration level in the geothermal effluents was in the range $0.03 - 0.036 \mu\text{g/L}$, 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 $< 0.01 - 0.115 \mu\text{g/L}$. This was thus below the $1\text{-}7 \mu\text{g/L}$ (aquatic life) and $100 \mu\text{g/L}$ (livestock) water quality criteria concentrations (CCME, 1999); drinking water quality criteria concentrations (CCME, 1999; WHO, 1998); and categorized as “very low” (class 1 = $<0.2 \mu\text{g/L}$) according to Swedish EPA guidelines for protection of lakes and watercourses for lead (SEPA, 1991).

The mercury concentrations ranged from $<0.002 \mu\text{g/L}$ in heated ground water from Grámelur (cooling water) to $0.0056 \mu\text{g/L}$ 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 $0.0277 \mu\text{g/L}$ and thus below the $0.1 \mu\text{g/L}$ (aquatic life) and $3.0 \mu\text{g/L}$ (livestock) water quality criteria concentrations (CCME, 1999); and also below the drinking water quality criteria concentrations (WHO, 1998; US EPA, 2002).

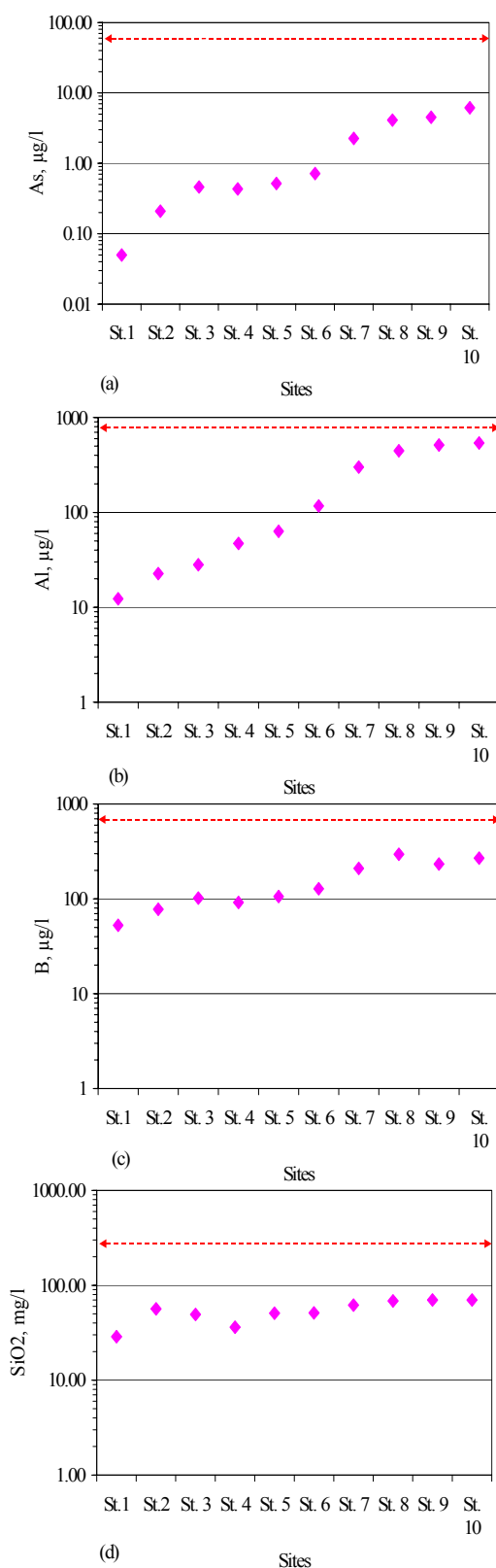


FIGURE 6: Spatial variation in the concentration of As, Al, B and SiO_2 at Lake Thingvallavatn outflow sites. Refer to Fig. 4 for location of sampling sites. Dotted line is the “derived” concentration assuming nothing occurs i.e. no delution, no precipitation and dissolution as wastewater flows through Nesjahraun lava

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, 1.0µg/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 7).

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 (Table 8). 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 Grámelur 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 6d). The SiO₂ concentration at Varmagjá was 56.33 mg/L, more than two times the 24.6 mg/L reported in Ólafsson (1992) study.

TABLE 7: Icelandic government critical limits for trace elements in surface water for the protection of biota (Government news B. No. 796/1999)

Element µg/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.

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

As shown in Figure 2, the 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 (Kjara and Egilsson, 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 5 and 8), 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 (Table 9). 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.

TABLE 8: Major chemical constituents in Nesjavellir geothermal co-generation power plant wastewater (October 2003) and Lake Thingvallavatn shoreline outflow sites water (July 2003)

	Ca (mg/l)	Fe (mg/l)	K (mg/l)	Mg (mg/l)	Na (mg/l)	S (mg/l)	SiO ₂ (mg/l)
<i>Nesjavellir power plant wastewater</i>							
Separator water	1.18	0.0121	26.8	0.509	131	777	483.4
Condensed steam	0.57	0.0332	<0.4	0.266	1.28	453	3.54
Heated groundwater from Grámelur	7.92	0.0228	2.29	4.26	16.7	40.6	37.35
Wastewater	7.07	0.0607	13.2	2.87	67.9	39.5	245.69
<i>Lake Thingvallavatn outflows</i>							
Site 1	8.38	0.0024	2.17	4.27	14	4.59	28.76
Site 2	11.9	0.0022	3.69	4.82	20	7.63	56.33
Site 3	11.8	0.002	3.58	5.06	19.5	6.96	49.34
Site 4	9.71	0.0022	2.63	4.09	16	4.9	36.15
Site 5	12.6	0.0024	3.67	5.45	20	7.2	50.74
Site 6	12.7	0.0031	3.64	5.66	20.8	7.13	51.14
Site 7	13.2	0.0077	4.04	5.96	24.1	7.55	61.92
Site 8	12.3	0.0119	4.35	5.54	26.6	7.75	68.51
Site 9	11.7	0.0118	4.25	5.26	25.8	7.63	70.11
Site 10	10.8	0.0135	4.55	4.94	27.3	7.74	69.91

If the above assumptions hold, the “derived” SiO₂, Al, As and B concentrations from the mix should have been 98.92 mg/L, 499.14 µg/L, 6.29 µg/L, 407.12 µg/L, respectively (Table 9). The observed concentrations of SiO₂, Al, As and B at Lækjarhvarf were 2-7 times higher than the “derived” values. This could partly be accounted for by external input of thermal waters high in these constituents from hot springs (Köldulaugagil and Nesjålaugagil) located above the point of wastewater discharge from the power plant into the stream. Trace element concentrations, thermal output, and flow rate of these two springs have not been determined but the SiO₂ concentration ranges from 41.1-636.7 mg/L and 18.6-139.5 mg/L in Köldulaugagil and Nesjålaugagil hot springs, respectively (Source: Reykjavik Energy).

TABLE 9: Measured and derived concentration of SiO₂, 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 (µg/l)	As (µg/l)	B (µg/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.				

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 6). 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 6). The actual chemical constituent concentration levels at the outflow sites were much lower than the “derived” concentration (see Figure 6). 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 (Kjaraan 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.

5.3 Water temperature and conductivity

The summer water temperature along the shoreline from Markagjá to Grámelur ranged from 11.7°C around Grámelur to 27.2 at Varmagjá (Figure. 3). Water temperature at definite outflow sites ranged from 16.8°C at Markagjá (site 1) to 27.2°C at Varmagjá (site 2) (Figure 7). Conductivity of water at the outflow sites was lowest at site 1 (210µs) and highest at site 8 (322 µs) (Figure 7, Table 10). Conductivity at sites 7-10 was higher than at sites 1-6 (T-test, $p = 0.003$).

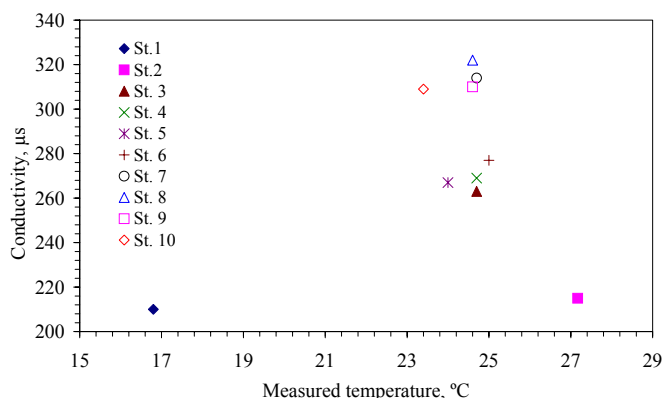


FIGURE 7: Relationship between conductivity and water temperature at major outflow sites. Measured temperature is the in situ temperature

Variation in conductivity and water temperature with depth at two sites; Varmagjá and Eldvík based on summer 2003 water temperature profiles (Figure 8)

show a general trend of conductivity and water temperature decrease with increasing depth and distance from the mouth of outflow sites. Water temperature profiles taken at the 10 m, 25 m, 50 m and 75 m marks along three different transects (Va T1, Va T2 and Va T3) from the mouth of Varmagjá (Figure 8) show a decrease in water temperature with increasing distance from the mouth.

At a distance of 10 m from the mouth, there is no stable pattern in water temperature with depth with the water temperature being in the range 14-25 °C (Figures 9a, 10a, 11a). Further away from the mouth of Varmagjá a pattern emerges where the warm water floats on top of the cooler, denser Lake water (Figures 9, 10 and 11). The same patterns are seen at Eldvík (Figure 12). Eldvík and Varmagjá, had similar temperature range at the respective points along the transects.

TABLE 10: Conductivity and water temperature at various major geothermal water outflow sites (July 2003)

Point	Conductivity (μ s)	Temperature (°C)
Site 1	210	16.8
Site 2	215	27.2
Site 3	263	24.7
Site 4	269	24.7
Site 5	267	24
Site 6	277	25
Site 7	314	24.7
Site 8	322	24.6
Site 9	310	24.6
Site 10	309	23.4

The winter 2004 water temperature profiles at Varmagjá also decrease with increasing depth and distance from the mouth. For example point V2, which is just close to the mouth, had a surface (30 cm depth) temperature in the range of 5-26°C. At profile points V4, V5 and V6 the pattern is regular with a layer of warm water floating on cold Lake water (Figure 13). Profile points V3 and V7, which were closer to the ice edge had an inverted gradient with temperatures < 1°C at depths down to 2 m which then increased to 3.5-4.0°C at the bottom (3.5 m depth). At Markagjá, the patterns were similar although the temperatures near the mouth are not as high as at Varmagjá (Figure 14).

Winter surface water temperatures around Varmagjá and Markagjá were high at the mouth but decreased with decreasing distance to the ice sheet (see Figure 8). The temperature range at Varmagjá was 0.6 °C near the ice edge to 26 °C at the mouth. At Markagjá, the surface water temperature range was 0.6°C and 16 °C at the ice edge and mouth respectively. Water temperature at Varmagjá and Eldvík outflow sites was 27.9 and 23.7°C, respectively, which is very similar to the summer temperatures. There were ice-free areas at all the definite outflow points.



FIGURE 8: Water temperature measurements at Varmagjá and Markagjá. Diamonds = surface temperature in winter 2004, stars = winter 2004 temperature profile points, Va T1 = temperature profile measurements along a transect in summer 2003

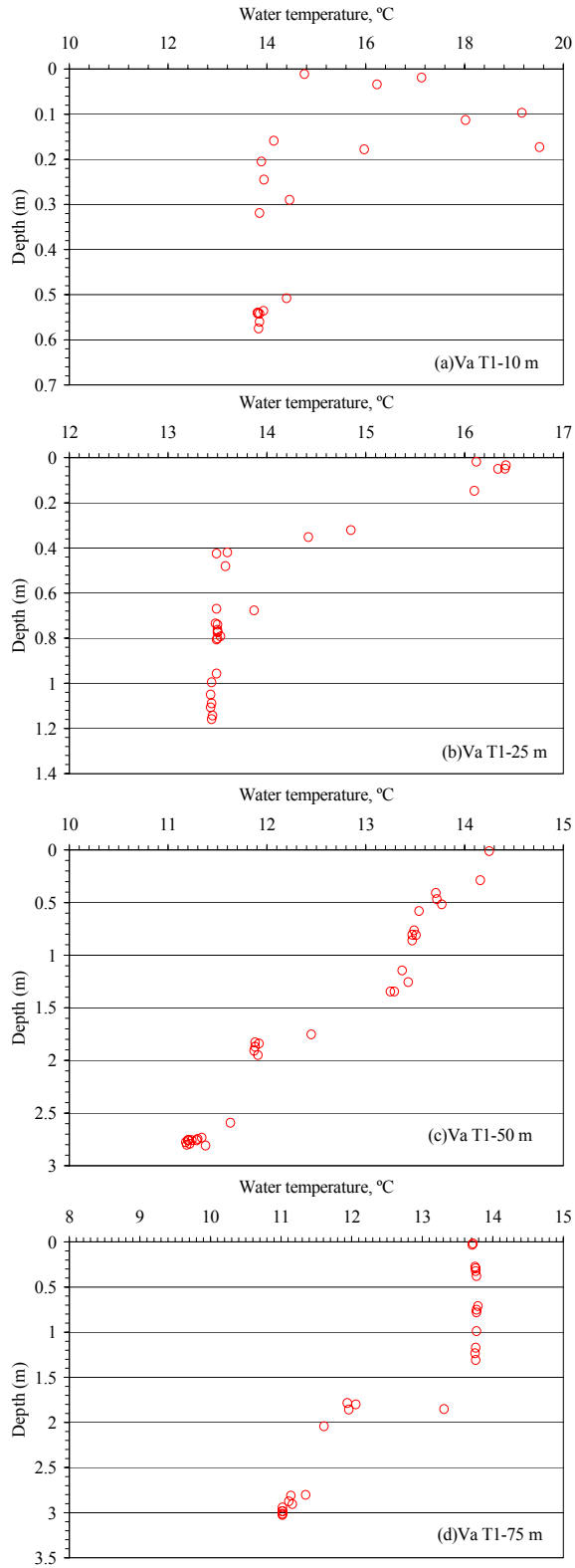


FIGURE 9: Summer (2003) temperature profiles on transect 1 at Varmagjá. Profiles were situated at 10, 25, 50 and 75 m distance from the outflow sites

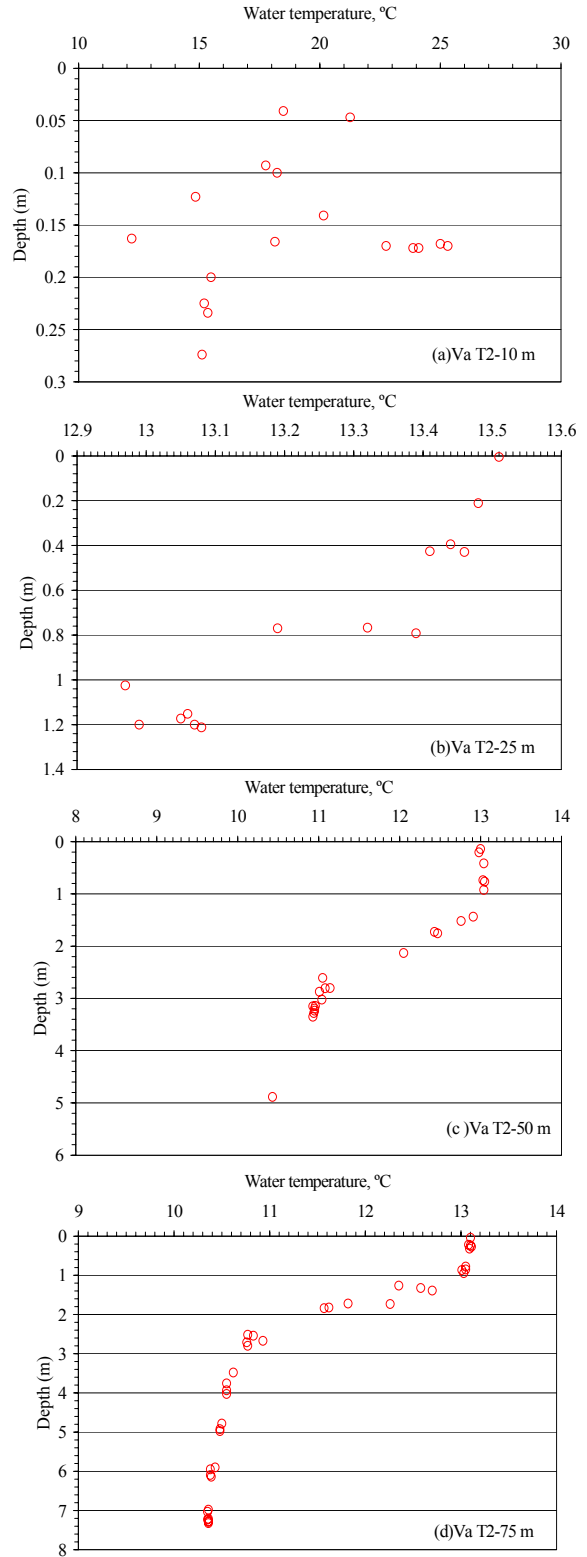


FIGURE 10: Summer (2003) temperature profiles on transect 2 at Varmagjá. Profiles were situated at 10, 25, 50 and 75 m distance from the outflow sites

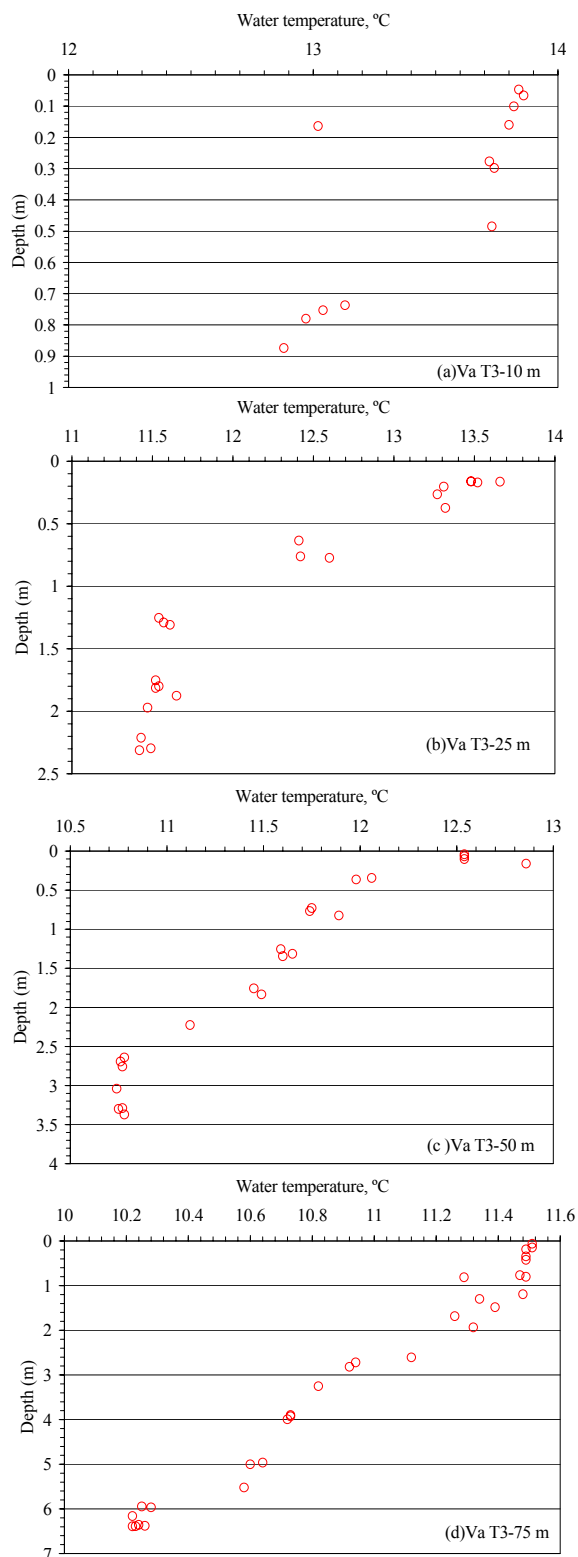


FIGURE 11: Summer (2003) temperature profiles on transect 3 at Varmagjá. Profiles were situated at 10, 25, 50 and 75 m distance from the outflow sites

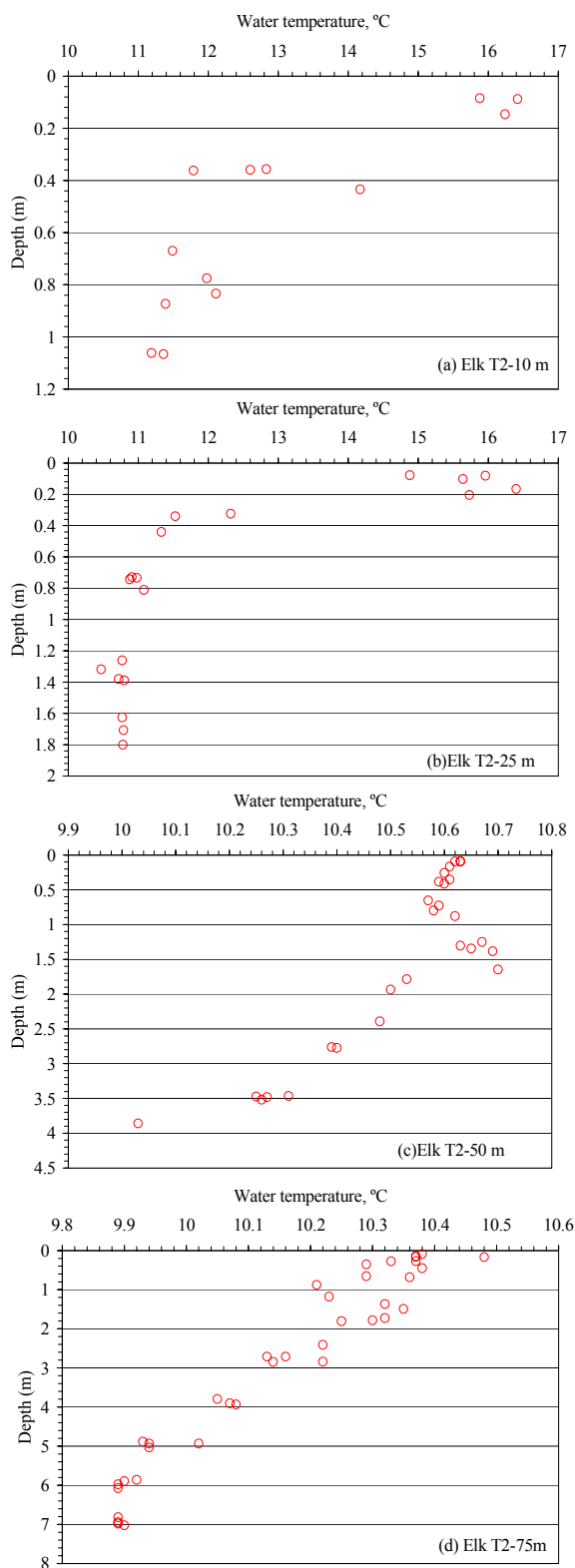


FIGURE 12: Summer (2003) temperature profiles on transect 2 at Eldvík. Profiles were situated at 10, 25, 50 and 75 m distance from the outflow sites

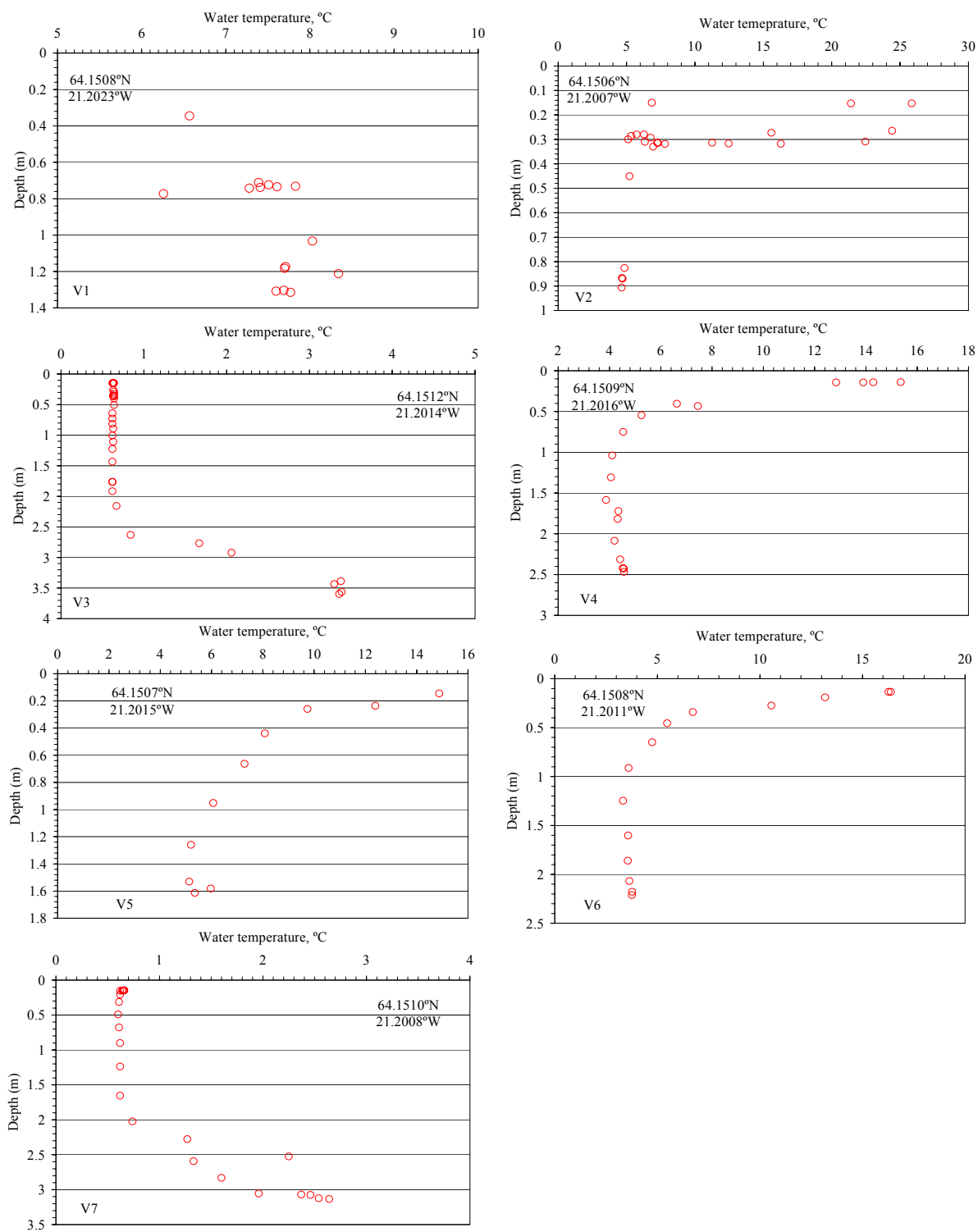


FIGURE 13: Winter (2004) temperature profiles at Varmagjá. Refer to Figure 8 for locations

5.4 Concentrations of trace elements in the biota

5.4.1 Sediments

Trace elements concentrations in sediments (Table 11) were only determined at site 2 (Varmagjá) as no sediment was found at the Eldvík sites 7 & 8. The concentration in the 3 sediment samples at Varmagjá (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 (Figures 15-20).

The arsenic concentration in sediment samples at Varmagjá did not deviate from concentration levels as the control station, Vatnaskot for the period 1994, 1995 and 2000. The same is true of cadmium, copper, mercury, lead and chromium (Table 15). The zinc concentration levels in sediments at Varmagjá were significantly lower than at Vatnaskot ($t = 5.26$, $p < 0.001$) (Figure 20, Table 15). 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 Vatnaskot in 2000 could be regarded as outliers. This isolated high lead concentration in sediments at both Vatnaskot and Varmagjá could be due to sediment contamination by lead shots or sinkers used on fishing gears.

5.4.2 Aquatic plants

Trace element concentrations in aquatic plants at Varmagjá (site 2) and Eldvík (sites 7 and 8) are presented in Table 12. Two plant samples were an unidentified species of moss and *Myriophyllum alterniflorum*.

Moss

The concentration of all trace elements analysed in the moss at Varmagjá (Table 12) 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 Eldvík, trace elements concentration in moss are categorized as

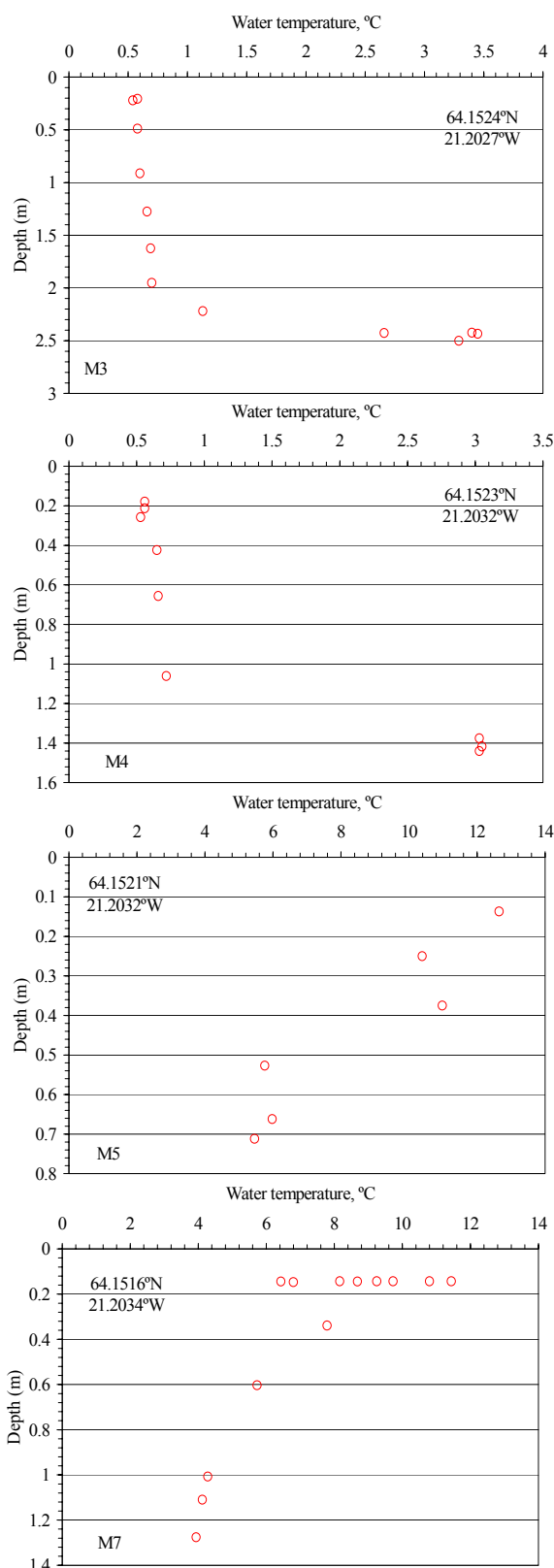


FIGURE 14: Winter (2004) temperature profiles at Markagjá. Refer to Figure 8 for locations

TABLE 11: Trace element concentrations in sediments at Varmagjá (site 2) in July 2003

Sample (no.)	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)
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

TABLE 12: Trace element concentrations in aquatic plants at Varmagjá (site 2) and Eldvík (site 7& 8) in July 2003

	TS (%)	As (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
<i>Moss</i>											
Varmagjá	7.7	0.241	0.852	0.101	1.05	115	0.0198	20	1.52	0.618	18.4
Eldvík	10.5	4.03	0.308	0.256	3.8	104	0.103	82.3	2.72	0.381	11.3
<i>Myriophyllum alterniflorum</i>											
Varmagjá	5.7	0.258	0.191	0.438	1.13	46.6	0.021	104	1	0.77	24

“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 Varmagjá 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 concentrations of trace elements arsenic, cadmium, copper, mercury, lead and zinc between Varmagjá and the control station, Vatnaskot (Table 15, Figures 15-20). 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 element concentrations could be due trace preferential uptake by the respective plant species. The 1995 sample from Vatnaskot had exceptionally high lead content (Figure 19).

5.4.3 Gastropod snail

The concentration of trace elements in the gastropod snail, *Lymnaea peregra* at Varmagjá and Eldvík are presented in Table 13. 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 (Figures 15-20).

There was no significant difference in trace elements concentration between Varmagjá and Eldvík and the control station, Vatnaskot except in the case of cadmium (Table 15) which was higher at Varmagjá and Eldvík. Chromium concentration ranged from 0.953 mg/kg at Eldvík to 1.04 mg/kg at Varmagjá. Manganese concentration at Varmagjá and Eldvík were 32.7 and 87.2 mg/kg respectively. Nickel concentration levels at both sites were similar.

TABLE 13: Trace element concentrations in gastropod snail, *Lymnaea peregra* at Varmagjá and Eldvík in July 2003

	TS (%)	As (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Varmagjá	18.3	2.83	0.398	0.935	1.04	117	<0.01	32.7	1.96	0.348	34.3
Eldvík	19.3	4.24	0.262	1.04	0.953	48.1	<0.01	87.2	1.97	0.0679	23.7

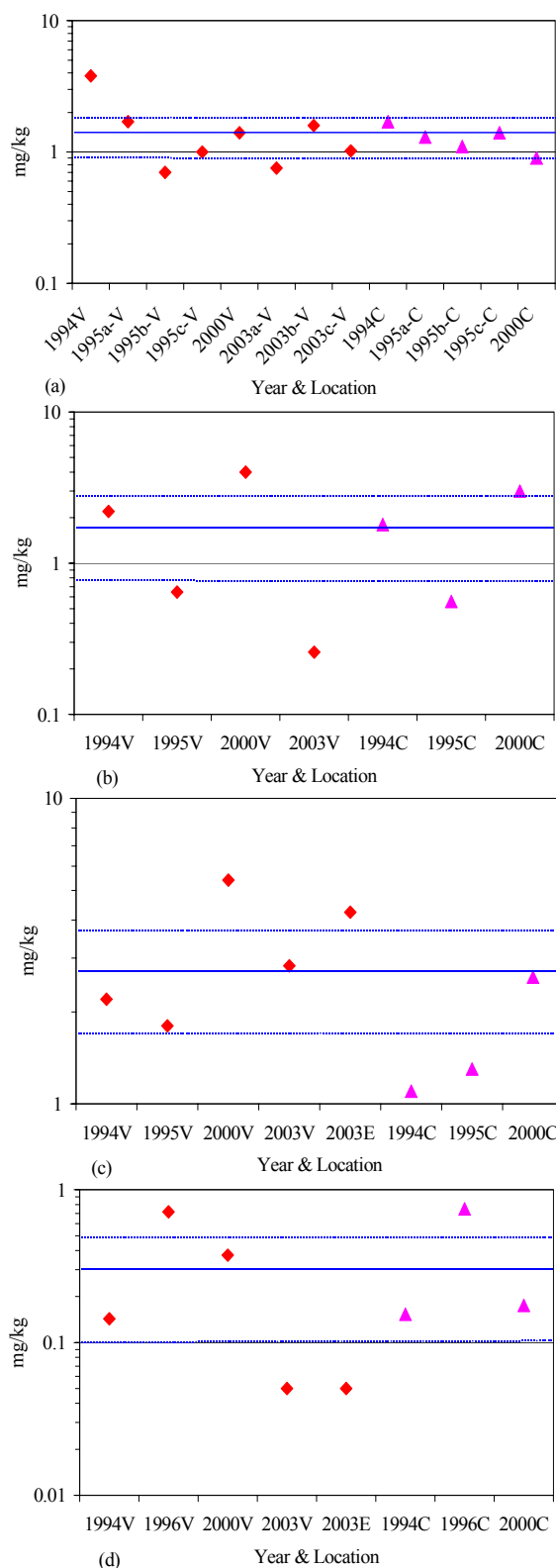


FIGURE 15: Concentration of arsenic in sediment (a), *Myriophyllum* (b), *Lymnaea* (c), and liver of arctic charr, *Salvelinus alpinus* (d), at Varmagjá (V), Eldvík (E), and a control station, Vatnskot (C), at the north shore of Lake Thingvallavatn. Thick line = Mean concentration, dotted lines = Concentration at 95% C.L. of sample mean

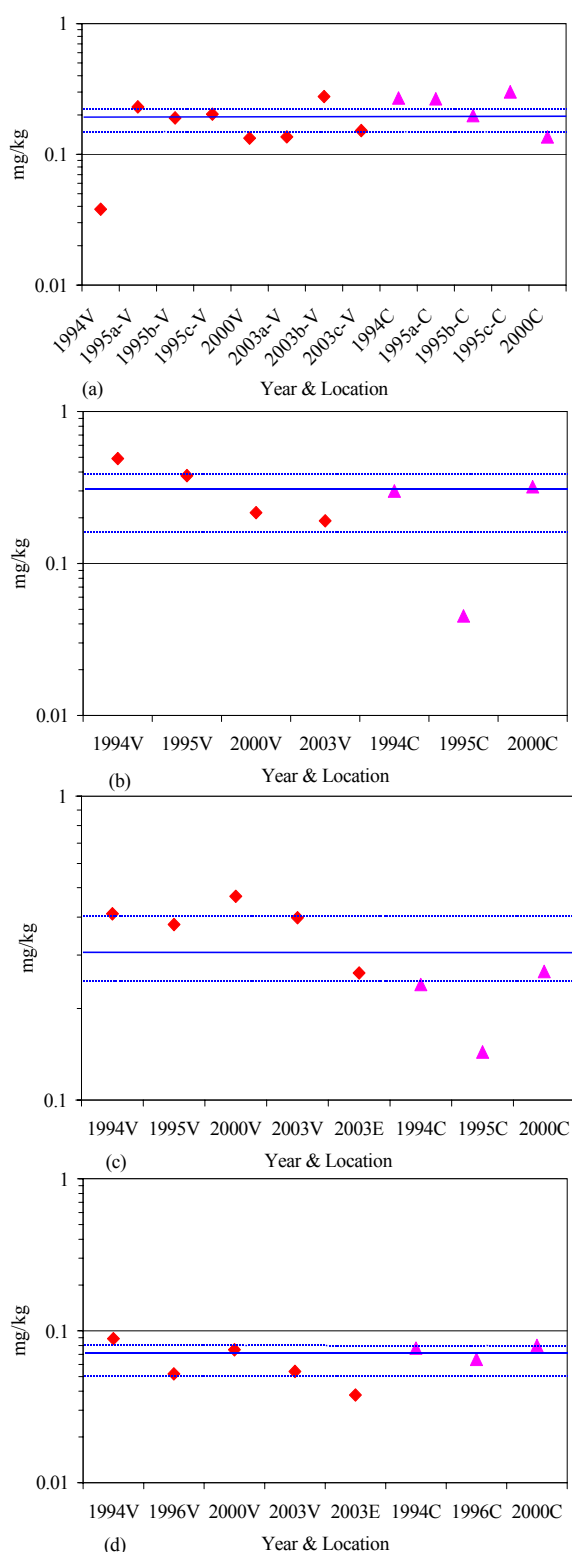


FIGURE 16: Concentration of cadmium in sediment (a), *Myriophyllum* (b), *Lymnaea* (c), and liver of arctic charr, *Salvelinus alpinus* (d), at Varmagjá (V), Eldvík (E), and a control station, Vatnskot (C), at the north shore of Lake Thingvallavatn. Thick line = Mean concentration, dotted lines = Concentration at 95% C.L. of sample mean

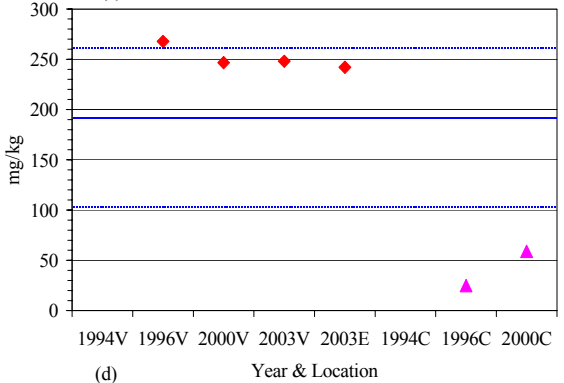
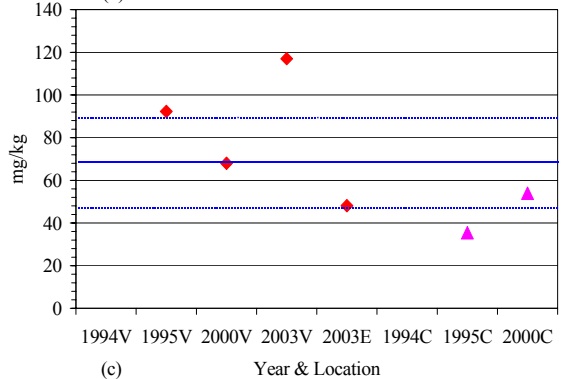
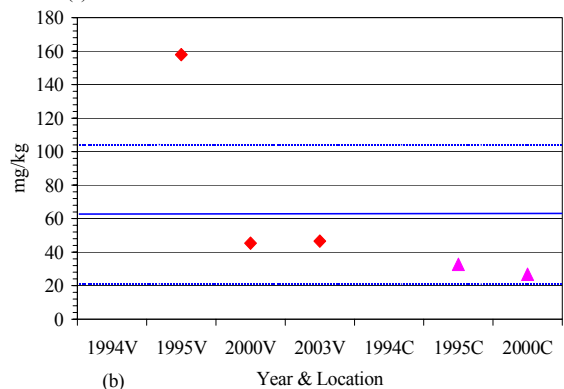
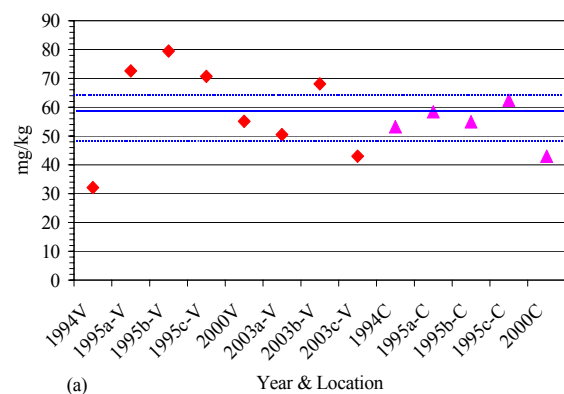


FIGURE 17: Concentration of copper in sediment (a), *Myriophyllum* (b), *Lymnaea* (c), and liver of arctic charr, *Salvelinus alpinus* (d); at Varmagjá (V), Eldvík (E), and a control station, Vatnskot (C), at the north shore of Lake Thingvallavatn; Thick line = Mean concentration, dotted lines = Concentration at 95% C.L of the sample mean

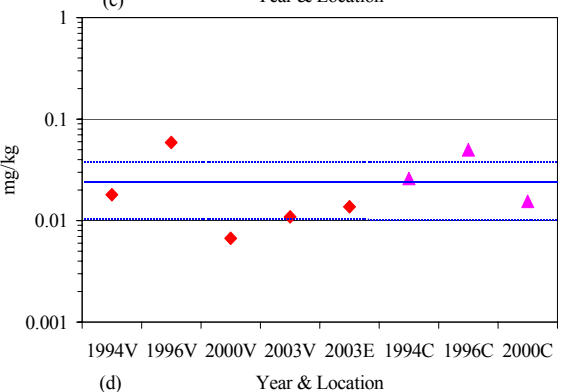
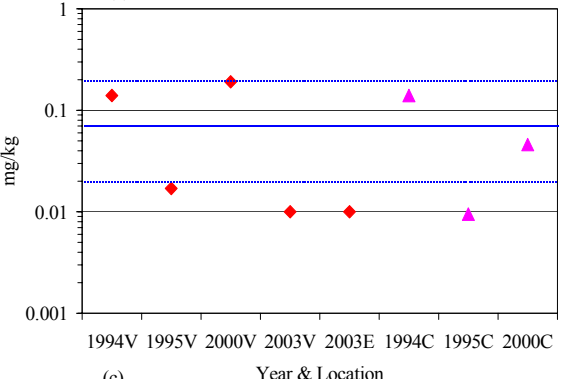
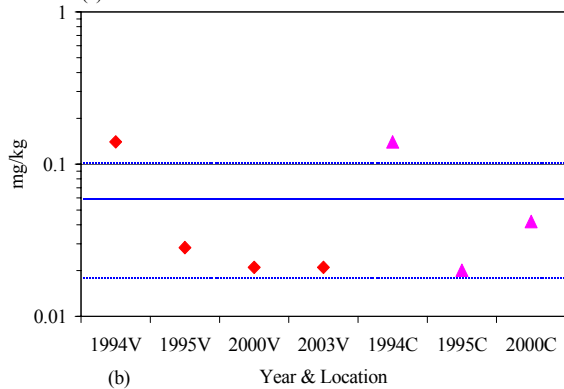
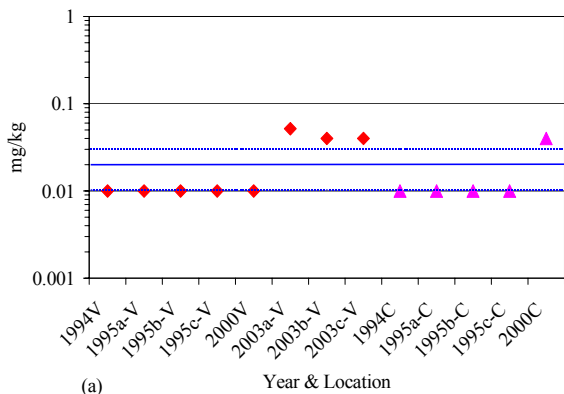


FIGURE 18: Concentration of mercury in sediment (a), *Myriophyllum* (b), *Lymnaea* (c), and liver of arctic charr, *Salvelinus alpinus* (d); at Varmagjá (V), Eldvík (E), and a control station, Vatnskot (C), at the north shore of Lake Thingvallavatn; Thick line = Mean concentration, dotted lines = Concentration at 95% C.L of the sample mean

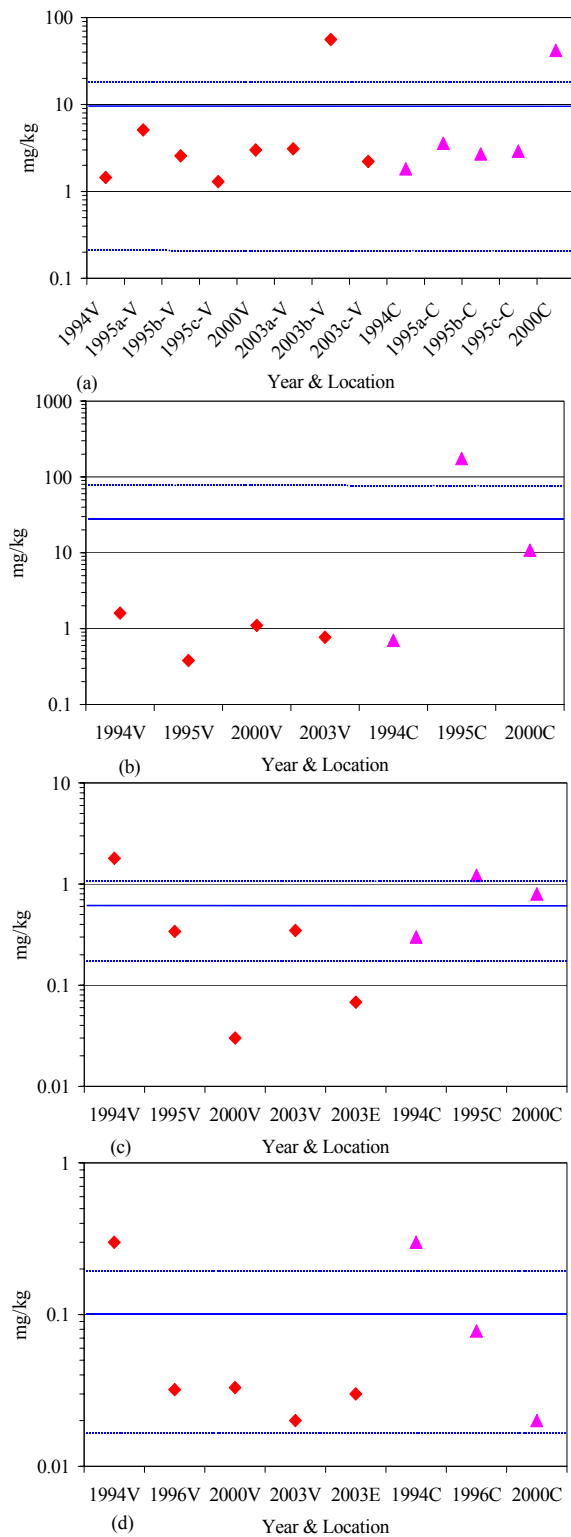


FIGURE 19: Concentration of lead in sediment (a), *Myriophyllum* (b), *Lymnaea* (c), and liver of arctic charr, *Salvelinus alpinus* (d); at Varmagjá (V), Eldvík (E), and a control station, Vatnskot (C), at the north shore of Lake Thingvallavatn; Thick line = Mean concentration, dotted lines = Concentration at 95% C.L. of the sample mean. The high Pb in (b) generated -21.16 as the lower C.L.

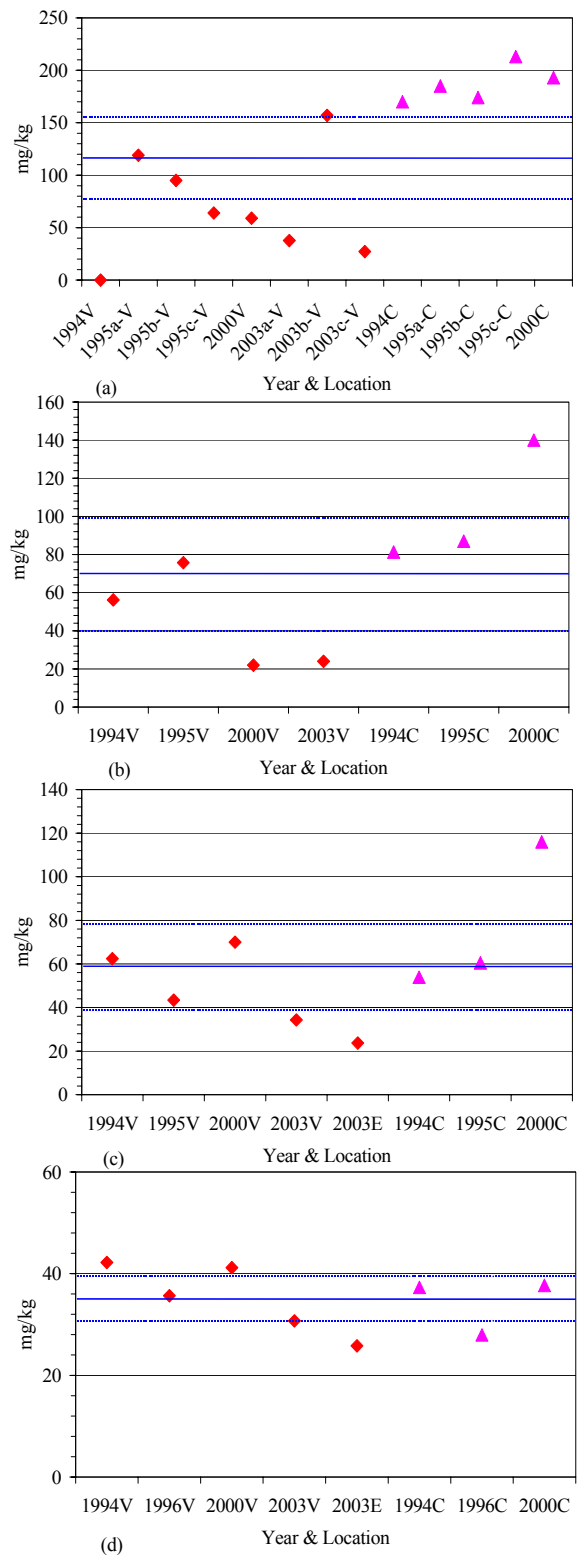


FIGURE 20: Concentration of zinc in sediment (a), *Myriophyllum* (b), *Lymnaea* (c), and liver of arctic charr, *Salvelinus alpinus* (d); at Varmagjá (V), Eldvík (E), and a control station, Vatnskot (C), at the north shore of Lake Thingvallavatn; Thick line = Mean concentration, dotted lines = Concentration at 95% C.L. of the sample mean

TABLE 14: Trace element concentrations in fish at Varmagjá and Eldvík in July 2003

	TS (%)	As (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
<i>Threespined sticklebacks, Gasterosteus aculeatus</i>											
Varmagjá	25	<0.2	<0.003	0.0084	<0.02	0.462	0.02	7.53	0.0327	0.187	32
Eldvík	22.5	<0.1	<0.003	0.0077	<0.02	0.409	0.0149	12.3	<0.02	0.0401	38.5
<i>Fish muscle (Arctic charr, Salvelinus alpinus)</i>											
Varmagjá	21.4	<0.09	0.0044	0.0233	<0.02	0.346	0.025	<0.02	<0.02	<0.02	5.67
Eldvík	17.1	<0.05	<0.003	0.0278	<0.02	0.245	0.0125	0.07	<0.02	<0.02	4.89
<i>Fish liver (Arctic charr, Salvelinus alpinus)</i>											
Varmagjá		<0.05	0.054	0.161	0.03	248	0.0109	1.47	0.0311	<0.02	30.7
Eldvík		<0.05	0.0378	0.204	0.0265	242	0.0137	1.3	0.0453	<0.03	25.8

TABLE 15: Comparison of concentration levels of trace elements in biota at geothermally affected sites (Varmagjá, Eldvík) and a control site (Vatnskot) based on samples from 1994-2003

Elements	Sediment		<i>Myriophyllum</i>		<i>Lymnaea</i>		Arctic charr liver	
	<i>t</i> -value	<i>p</i> -value	<i>t</i> -value	<i>p</i> -value	<i>t</i> -value	<i>p</i> -value	<i>t</i> -value	<i>p</i> -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

5.4.4 Fish tissues

Trace elements were analysed in two fish species in 2003; threespined sticklebacks *Gasterosteus aculeatus* and arctic charr *Salvelinus alpinus* (Table 14). 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 Varmagjá and Eldvík. 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, Vatnskot except for copper, which was higher at Varmagjá and Eldvík (Figures 15-20, Table 15).

6.0 DISCUSSION

6.1 Trace elements in geothermal effluent and at 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, 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 SiO_2 , As, B and Al, B is considered to be a conservative component (Arnórsson 2000). Therefore it can be useful to view the reduction in SiO_2 , As and Al with reference to the boron concentration (Figures 21-23).

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 (Figure 21). 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 (Gíslason 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 (Mamtaz and Bache, 2001; Decarlo and Thomas, 1985). 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 6) nor with aqueous Fe concentrations (Table 8). 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 $<1 \mu\text{g/L}$ in Canada (Azcue et al., 1995). As concentration range of <0.03 - $0.28 \mu\text{g/L}$ 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 - $500 \mu\text{g/L}$ have been reported in some mining areas and up to $1000 \mu\text{g/L}$ 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 $10,000$ - $20,000 \mu\text{g/L}$, 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 Eldvík were above the $1 \mu\text{g/L}$ which could be regarded as an As baseline in unpolluted lakes (Azcue et al., 1995) and above As concentration measured in Lake Mývatn (Ármannsson, 2003). The As concentration range 2.26 - $6.14 \mu\text{g/L}$ is in good agreement with the $4.7 \mu\text{g/L}$ 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 (Figures 6 and 22). It appears, therefore, that in this part of the lava Al is being removed

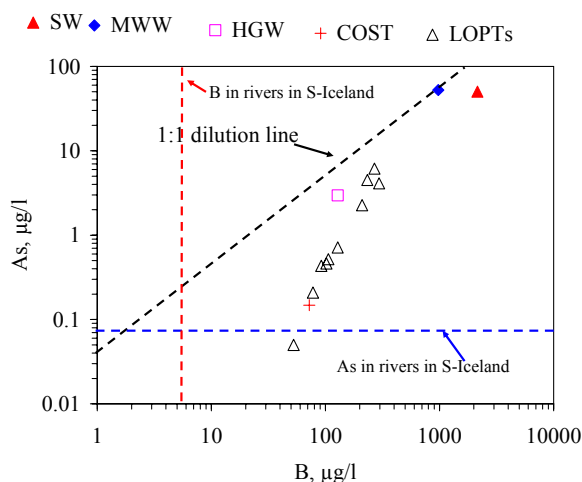


FIGURE 21: Relationship between As and B in Nesjavellir geothermal co-generation power plant wastewater and Lake Thingvallavatn outflow sites water. SW= Separator water, MWW= Mixed wastewater at Lækjarhvarf, HGW= Heated groundwater from Grámelur (cooling water), COST= Condensate. LOPTs= Lake outflow sites

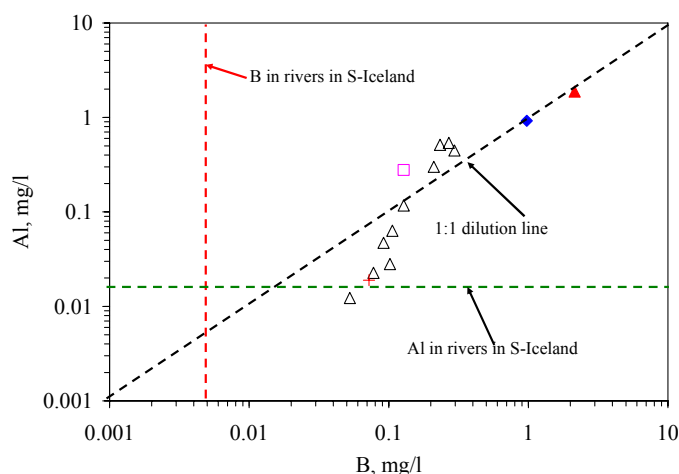


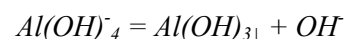
FIGURE 22: Relationship between Al and B in Lake Thingvallavatn outflow sites water and Nesjavellir geothermal co-generation power plant wastewater. The symbols refer to the legend on Figure 21

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, $\text{Al}(\text{OH})_3$, 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 (Gíslason et al., 2003). In this part of the system Al is removed preferentially to B by $\text{Al}(\text{OH})_3$ precipitation. The behaviour of Al could possibly be quantitatively interpreted by calculation of saturation for amorphous $\text{Al}(\text{OH})_3$. 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, it is still above levels in water from S-Iceland Rivers (Gíslason 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. 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 shows that the SiO_2 concentration in the power plant wastewater is reduced at a similar rate for boron (Figure 23). In the western part of the system the reduction of SiO_2 slows down compared to boron 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

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 of 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

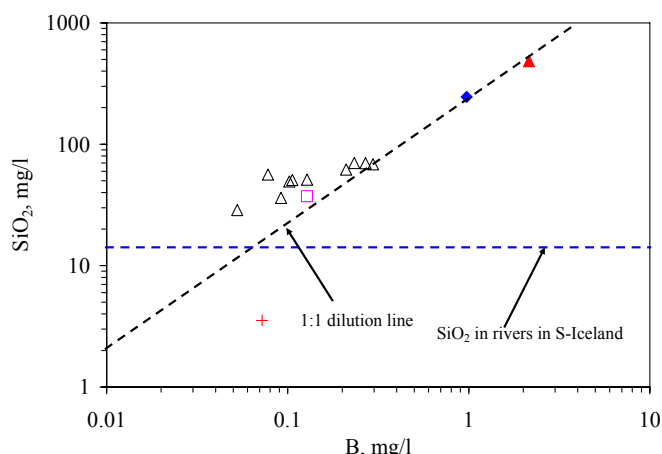


FIGURE 23: Relationship between SiO_2 and B in Nesjavellir geothermal co-generation power plant wastewater and Lake outflow sites water. The symbols refer to the legend on Figure 21

changes as function of temperature, with considerable high rate at very high temperature and extremely slow rate at low temperatures (Arnórsson, 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 in chemical constituent concentration levels at the outflow sites 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 Eldvík (sites 7-10). What is evident then is that Eldvík 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 Nesjavallalaekur 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 Eldvík 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 Eldvík (Ólafsson, 1992), show that the level of SiO_2 at Markagjá, Varmagjá and Eldvík 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 Eldvík 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 Eldvík respectively. It could be argued from these two studies that the core geothermal flow is around the Eldvík area not Varmagjá; dilution of geothermal water is less at Eldvík 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.

6.2 Variation in water temperature and conductivity at outflow sites

From the temperature measurements at the various sites along the southern shoreline of Lake Thingvallavatn, it is evident that the inflow of warm water has elevated the spring temperatures in

relation to the overall lake temperature which usually varies between 6 and 11°C in summer and autumn but cools to near 0°C in winter. From the start of electricity production the water temperature at major outflow sites has increased by 15-17°C and is now about 15-28°C above the ambient lake temperature. Results from the temperature profile transects taken at both Varmagjá and Eldvík show spatial pattern in water temperature increase during calm periods, i.e. the warm geothermal affected water is floating atop the cold, dense lake water. During winter when most parts of the lake freeze over, most of the areas around the outflow sites especially Markagjá, Varmagjá and Eldvík were ice-free. While the spatial distribution pattern of the warm water is similar as in the summer the situation near the ice-edge is in sharp contrast with the inverted temperature gradient. Judging by elevated temperatures in monitoring drill holes (Hafstad, 2001) at the edges of the warm water area, the horizontal extension of water temperatures at outflow sites to Markagjá in the west and Stappavík in the east could be expected. It is somewhat surprising to see a sharp increase in temperature but only a moderate increase in concentration of the geothermal signal elements at Varmagjá. These levels further support the suggestion that Varmagjá could be the main outflow for the condensed steam component of power plant effluents. This would need verification by a tracer study.

The effects of elevated outflow sites temperatures, - thermal stress-, on lake Thingvallavatn will only be on a local scale and somewhat temporal in nature (see Figure 8). In calm weather tongues of warm water floating on the surface form temporarily. Such layering is likely to break down quickly due to wave action when the wind picks up (Snorrason, 1982). The elevated temperatures have affected the winter ice sheet along the shore between Markagjá and Grámelur with more extensive, permanent openings. Any large scale effects of elevated outflow sites temperature on the Thingvallavatn ecosystem are not expected. Efficient water mixing causes temperature drop to the normal lake temperature short distance away from outflow sites. Hence, the normal cold water adapted benthic algal communities will not be affected on large scale (Jónsson, 1992). However, changes can be expected to the benthic communities of plants and animals in the nearest neighbourhood of the outflow sites particularly in Varmagjá, which, due to its isolation from the lake, is somewhat sheltered from wave action. Here the environment will favour species that tolerate a wider range of temperatures and large short term fluctuations in temperature.

Conductivity of both Varmagjá and Eldvík water also decreases with increased depth. Electrical conductivity of water being a measure of total dissolved solids (TDS) in water implies that the higher conductivity of the upper water layer is indicative of its TDS content. This high TDS content can be attributed to the geothermal outflow input.

6.3 Concentration level of trace elements in the biota

6.3.1 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 Vatnaskot do not differ significantly except for zinc, which was higher at Vatnaskot. 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 Rotorua, 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 and Morgan, 1991; 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 (Table 16). In view of this effects of arsenic on the biota at Varmagjá are very unlikely.

TABLE 16: 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)
PEL = Probable effect level (Smith et al., 1996; CCME, 1999)	17	3.53	90	197	91.3	0.486	36	315
SEL = Severe effects level (Persaud et al., 1993)	33	10	110	110	250	2.0	75	820
ERM = Effects range median (Long & Morgan, 1991)	85	9	145	390	110	1.3	50	270
ERM = Effects range median (Long et al., 1995)	70	9.6	370	270	218	0.71	51.6	410
CB-PEC = Consensus based-PEC (Ingersoll et al., 2000)	33.0*	4.98*	111*	149*	128*	1.06*	48.6*	459*
ER-L = Effect range low (Long et al., 1995)	8.2	1.2	81	34	46.7	0.15	20.9	150
ISQG = Interim sediment quality guideline (CCME, 1999)	5.9	0.6	37.3	35.7	35	0.17		123

* = >75% correct classification as toxic.

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; Sullivan and Aller, 1996) 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 were higher than the overlying water at Varmagjá and in geothermal effluent. 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 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 16). 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 (Fe₂O₃) (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 Vatnskot 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 severe effects levels (Persaud et al., 1993), concentrations above which are likely to be harmful. The Cu concentration levels at both Vatnskot (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 and Vatnskot. 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 16). 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 and Vatnskot. 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 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.

Zinc concentration levels in sediments were significantly lower at Varmagjá than at the control station, Vatnskot. 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). 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.

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 (see Table 16). 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; Long and Morgan, 1991), effect range median values (ERM; Long and Morgan, 1991; 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.

6.3.2 Aquatic plants

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

Moss

All trace metal concentrations levels in aquatic moss at Varmagjá 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 Eldvík, 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 Eldvík could be due to the geothermal influence as the arsenic and mercury which are elevated in geothermal water also appeared to be higher at Eldvík.

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 Varmagjá and the control station, Vatnskot. The variation observed can in most cases be classified as variation in natural background concentrations. The high lead values seen in two samples at Vatnskot probably stem from point sources in the form of lead weights lost from fishing gears. The arsenic concentrations levels in both plant species and both Varmagjá and Eldvík are very low compared to elevated concentrations of arsenic in macrophytes 193-1,200 mg/kg (dw) in lake Rotorua, New Zealand, 24 years after an application of sodium arsenite herbicide (Tanner and Clayton, 1990).

6.3.3 Gastropod snail

There was no difference in concentration of As, Pb, Hg, Cu, Mn and Zn in the gastropod snail *Lymnaea peregra* at Varmagjá and the control station, Vatnskot. Cadmium concentration levels were significantly higher at Varmagjá. Chromium and nickel concentration level not previously determined was low and within similar concentration range at Varmagjá and Eldvík.

6.3.4 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 Varmagjá and

Eldvík. 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 and 2003, there was no significant difference in the arctic charr liver trace elements concentration for As, Cd, Hg, Pb, and Zn between Varmagjá and the control station, Vatnskot except for Cu which was considerably higher at Varmagjá and Eldvík. 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).

Evaluation of trace element concentration levels in fish tissues at Varmagjá and Eldvík based on US EPA risk levels for noncancer hazard quotient of 1 and Food and Drug Administration (FDA) tolerance/action or guidance levels (US EPA, 1997), indicated that the trace element concentrations levels in fish tissues were below the levels assumed to cause potential adverse effects to humans from consumption of fish that become contaminated through exposure to contaminated sediments (Table 17).

TABLE 17: Guideline values for screening level hazard of chemicals amounts in fish tissues (US EPA, 1997)

	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Hg (mg/kg)	Ni (mg/kg)	Zn (mg/kg)
EPA Noncancer Hazard Quotient = 1	3.2	5.4	54	400		1.1	220	3200
FDA Guidance/ Action/Tolerance level	68	3.0	11		1.3	1.0	70	

7.0 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 Varmagjá and Eldvík, 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 Varmagjá to Eldvík

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.

Water temperature measurements show that the large volume of geothermal wastewater (40.9°C - 84.0°C) disposed off after the generation of electricity started has caused a rise in both summer and winter water temperature at lake shoreline outflow sites. At definite outflow sites temperature was in the range 23.4-27.3°C irrespective of season. The temperature at the outflow sites did not correlate well with the concentration of boron, the most conservative signal element. The highest temperature was found in Varmagjá. This discrepancy may stem from the fact that the condensed steam, which is low in concentration of these chemicals, is disposed off in shallow drillholes near the power plant and this may flow through the Nesjahraun lava somewhat west of the main flow from Lækjarhvarf. The results show that the spatial distribution of thermal stress in the Lake varies seasonally. In the summertime water temperature profiles showed a decrease in water temperature with increasing depth and distance from the shore. In calm weather warm water floats on top of the cool lake water and a warm water tongue can extend some distance (> 75m) from major outflow sites. During windy spells the warm water probably mixes quickly with the lake water thus lowering thermal stress effects. During winter, when ice covers most of the lake, small areas close to warm water outflow points remain ice-free. In these situations a wall of cold water forms at the ice edge, resisting the warm water outflow and causing a deepening of the thermal effect near outflow sites. In order to define the potential effects of the warm water on the local biota the short-term and seasonal dynamics of the thermal stress need to be charted in more detail. The thermal influence at the lake outflow sites will be averted once plans to re-inject all the geothermal wastewater and to further cool unusable cooling water are realised. 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.

Part III:
**EVALUATION OF TRACE ELEMENT LEVELS AND
THEIR ECOTOXICOLOGICAL RELEVANCE IN
GEOTHERMAL WASTEWATER OF OLKARIA EAST FIELD, KENYA**

8.0 INTRODUCTION

Olkaria East field is one of the seven sectors of the Greater Olkaria geothermal area located in the central part of the Kenya Rift Valley to the south of Lake Naivasha, 120 km northwest of Nairobi. Other sectors are Northeast, Northwest, Southwest, Southeast, Central and Olkaria Domes fields for management purposes. Exploration for geothermal work started in the early 1950s when two wells were drilled at Olkaria. Olkaria East field supports a 45 MWe Olkaria I geothermal power plant fully commissioned in 1985. Thirty-three wells have been drilled, seven of which are make-up wells. The large volume of waste geothermal fluids generated during electricity production has been a major environmental concern especially with regard to Hells Gate National Park gazetted in 1984. An important aspect of the environmental management of geothermal development in this area has been the existence of Hells Gate National Park which supports wildlife species such as Buffalo (*Syncerus cafer*), Zebra (*Equus burchellis*), Grant's gazelle (*Gazelle grantii*), Thomson's gazelle (*Gazelle thomsonii*), Coke's hartebeest (*Alcephalus buselaphus*), Maasai giraffe (*Giraffa reticulata*) among others. It has been estimated that geothermal fluid is discharged from the 45 MW power station at flow rate of about 120 m³/h (Merz and McLellan – Virkir, 1977). Each well under production is equipped with a wellhead separator and stabilizing pond systems for wastewater and solid residue settlement. Most of the separated water drains through open concrete channels into one main evaporation or infiltration lagoon for containment before reinjection. Such wastewater if not properly disposed off could be a potential ecotoxicological hazard to both fauna and flora due to the environmentally significant trace elements they may contain.

In mitigating environmental effects that might arise due to plant and animals exposure to such constituents in geothermal wastewater, Kenya Electricity Generating Company Ltd (KenGen) initiated a monitoring programme for the concentration levels of environmentally significant chemical elements in well discharge and separation plant discharge on a quarterly basis. This monitoring which has been in progress since 1993 was adopted as one of the pollution control measures (Were, 1998).

Prediction of potential environmental effects of geothermal wastewater with special emphasis on the Olkaria geothermal field have been made in various studies (Simiyu, 1995, 2000; Simiyu and Tole, 2000). For example Simiyu and Tole (2000) indicated that soils in contact with geothermal fluids concentrate elements by factors of between 13 and 6000 in comparison to metal concentrations in overlying water columns. The present study is an evaluation of trace element levels in wastewater from selected geothermal wells in the Olkaria East field and their ecotoxicological relevance. This is in relation to plant and animals water quality criteria (CCME, 1999) and other laboratory and/or field ecotoxicological studies. Trace element concentration data is from different sources: - the present study analysis from the 19/08/2002 and 21/08/2003 sampling; an ongoing KenGen environmental monitoring programme and; other published literature (e.g. Simiyu 1995, 2000; Simiyu and Tole, 2000).

9.0 METHODOLOGY

The sampling of wastewater for trace elements analysis in study was in two parts. First sampling took place on 19th August 2002 while the second one was on 21st August 2003. Geothermal wastewater from infiltration ponds of wells OW-2, OW-5, OW-7/8, OW-10, OW-16, OW-21, OW-22, OW-23, OW-24/28 and OW-32 in Olkaria East field were sampled (Figure 24). All sampling bottles and

equipment were thoroughly acid washed before sampling. Bottles were filled with 10% HNO₃, left to stand overnight and then rinsed carefully with distilled water. In the two separate sampling periods, the samples were shipped to Iceland and then to *Analytica* Laboratory in Sweden for trace elements analysis. The samples were passed through a 0.45 µm Nuclepore cellulose fibre filter to remove particulates and preserved with concentrated Ultrex Supra pure nitric acid. The determination of unstable parameters such as pH was carried out in the Olkaria Geochemistry Laboratory. Based on the results of the past studies which did not take into account most of the elements, the concentration of the following trace and major elements were determined 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).

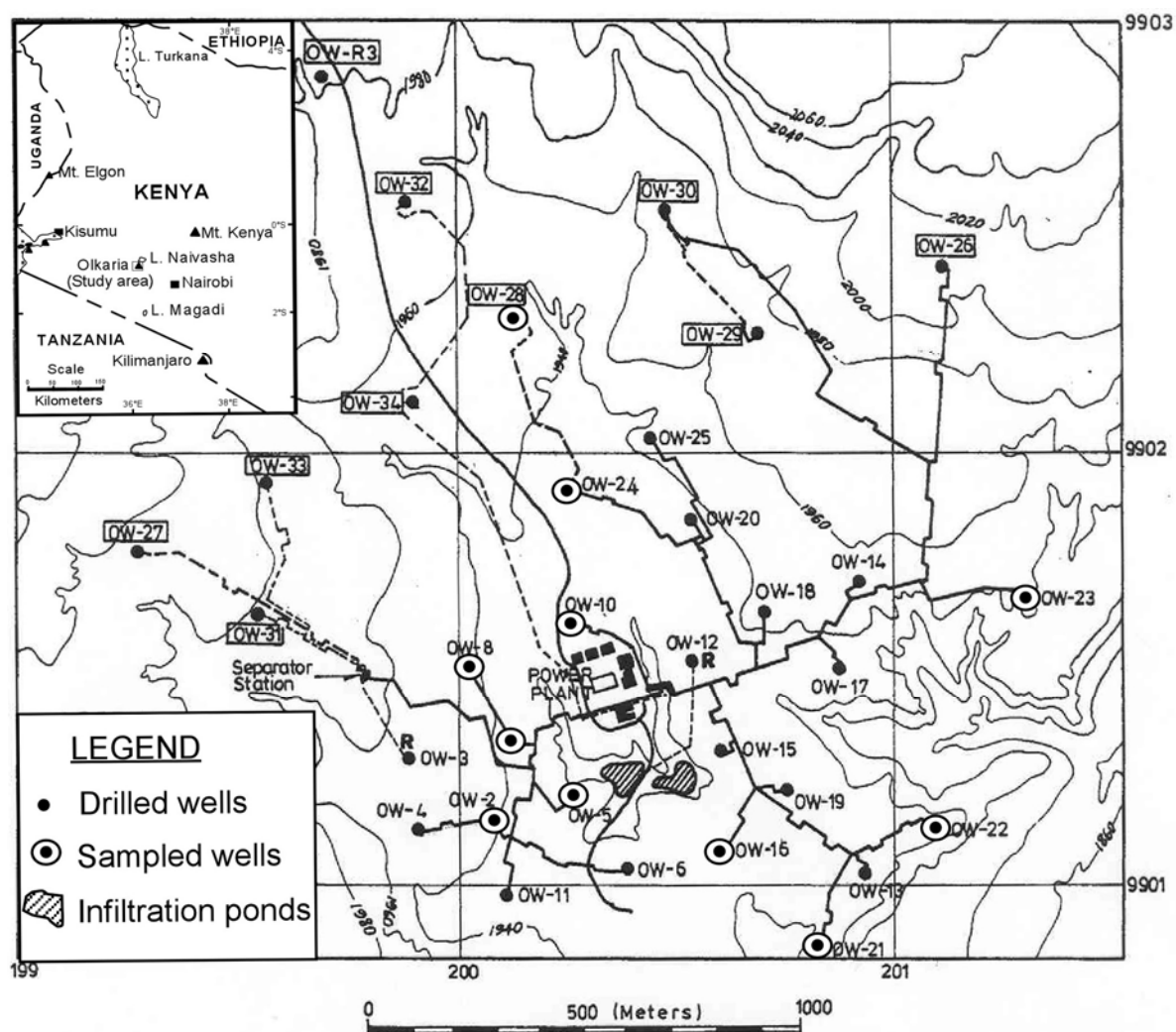


FIGURE 24: Location of Olkaria field and sampling points of the wastewater in the East field

10.0 RESULTS

Geothermal wastewater from infiltration ponds of selected wells (OW-2, OW-5, OW-7/8, OW-10, OW-16, OW-21, OW-22, OW-23, OW-24/28 and OW-32) in Olkaria East field were analysed for the following trace elements: aluminium, arsenic, boron, barium, cadmium, cobalt, chromium, copper, mercury, manganese, molybdenum, nickel, lead and zinc in August 2002 and August 2003 (Table 18). Also presented is trace element analysis data from the ongoing KenGen environmental monitoring program of significant environmental chemical elements; and other published literature on Olkaria

◆ OW-2 ■ OW-5 ▲ OW-7/8 △ OW-10 □ OW-16 ◆ OW-21 + OW-22 × OW-23
◇ OW-24/28 - OW-32

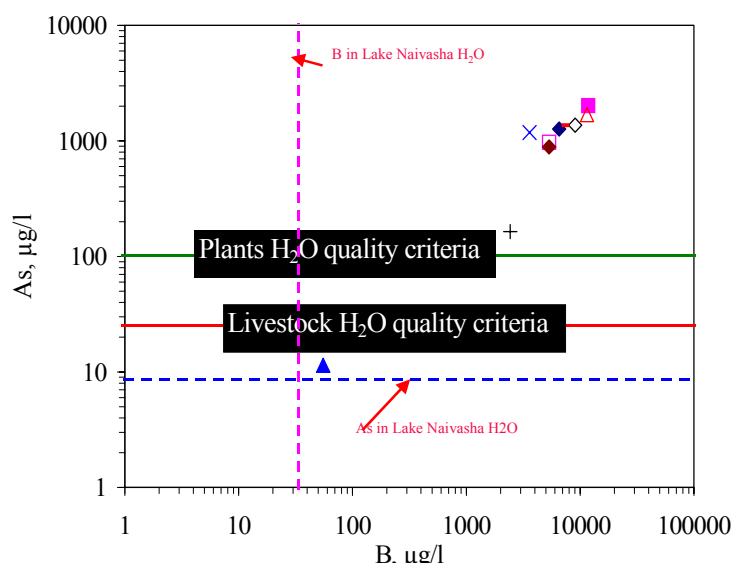


FIGURE 25: Relationship between As and B in wastewater from selected wells in Olkaria East field

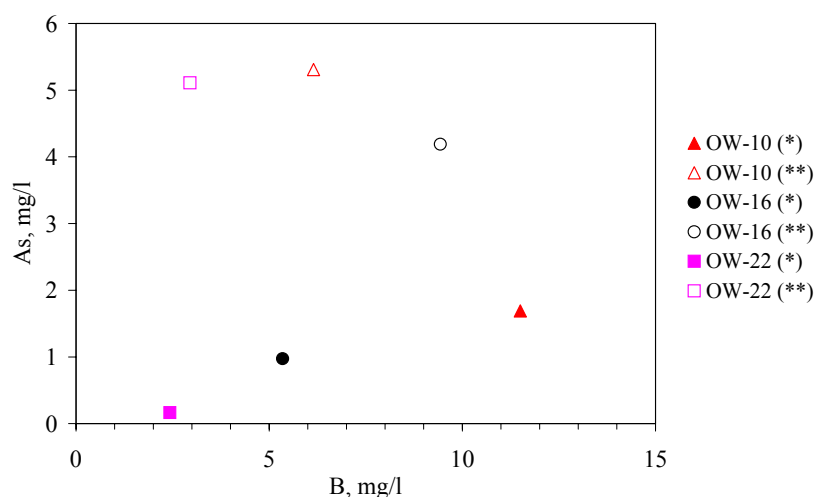


FIGURE 26: Arsenic and boron concentrations at wells OW-10, OW-16 and OW-22 based on different data sources.
[(*) = current study, (**) = Simiyu, 1995]

of 0.577 to 8.39 ppm in wells OW-22 and OW-7/8 respectively. The Al concentration of wastewater from wells OW-5, OW-10 and OW-32 were 1 ppm. Al has not been among the key elements being monitored in the ongoing KenGen environmental monitoring program. The Al-B relationship (Figure 27) shows that Al is removed from the wastewater of most wells preferentially to B by $\text{Al}(\text{OH})_3$ precipitation. The behaviour of Al could also be quantitatively interpreted by calculation of saturation of amorphous $\text{Al}(\text{OH})_3$ which was not however done in this study.

The boron concentrations varied from 0.0553 ppm in the wastewater of well OW-7/8 to 11.5 ppm and 11.8 ppm in well OW-10 and OW-5 wastewater respectively. From As-Al-Mo-B relationships much of the B in wastewater from half of wells remains in solution compared to As, Al and Mo (Figures 25, 27 & 28). The boron concentration was however within the levels observed in the on going monitoring program and that documented in past studies (Simiyu, 1995; Simiyu and Tole, 2000; Figure 26).

geothermal field (e.g. Simiyu, 1995, 2000; Simiyu and Tole, 2000). From the current study results Al, As, B, and Mo are the only trace constituents slightly elevated in wastewater of some wells.

The lowest and highest arsenic concentrations were 0.0114 ppm and 2.02 ppm in wells OW-7/8 and OW-5 respectively (Figure 25). Arsenic concentrations in wells OW-10, OW-16 and OW-22 were 1.69 ppm, 0.973 ppm, and 0.164 ppm respectively. These concentrations were however much lower than to the 1994 arsenic concentration of 5.31, 4.19 and 5.11 ppm (Simiyu, 1995; Simiyu and Tole, 2000; Figure 26) observed in the respective well waters. There is no sufficient arsenic data from the ongoing monitoring program to establish the mean As levels over the years. These levels were however high compared to geothermal waters in Nesjavellir geothermal field, Iceland.

For the period of August 2002/2003 Al was in the range

Mercury concentration was in the range of 0.000016 ppm to 0.00931 ppm. Mercury concentration in the wastewater from wells OW-10, OW-16 and OW-22 was 0.00013 ppm, 0.002942 ppm and 0.0000512 ppm respectively. This was however lower than the 0.94 ppm, 0.52 ppm and 5.41 ppm (Simiyu, 1995; Simiyu and Tole, 2000) for same wells respectively during the 1994 analysis.

The lowest and highest molybdenum concentrations were 0.00593 ppm and 0.7 ppm in wastewater from wells OW-7/8 and OW-5 respectively (Figure 28). Molybdenum concentrations in most well fluids were higher than levels reported in past studies. Cadmium, cobalt, copper, lead and zinc concentration levels in wastewater from most wells were low. The concentrations of Cd, Co and Pb were low compared to the 1994 levels (see Simiyu, 1995; Simiyu and Tole, 2000) while other trace elements were within the same concentration range in this study and previous studies (Table 18). Chromium and nickel concentration which have not been determined before were 0.518 ppm and 0.287 ppm respectively in wastewater from OW-7/8.

An evaluation of fluoride in the wastewater based on the KenGen trace element environmental monitoring program data (1997- 2003) show that fluoride concentration levels have been high all through compared to other elements. Its concentration has been variable over time with a mean fluoride concentration of around 70 mg/L (Figure 29).

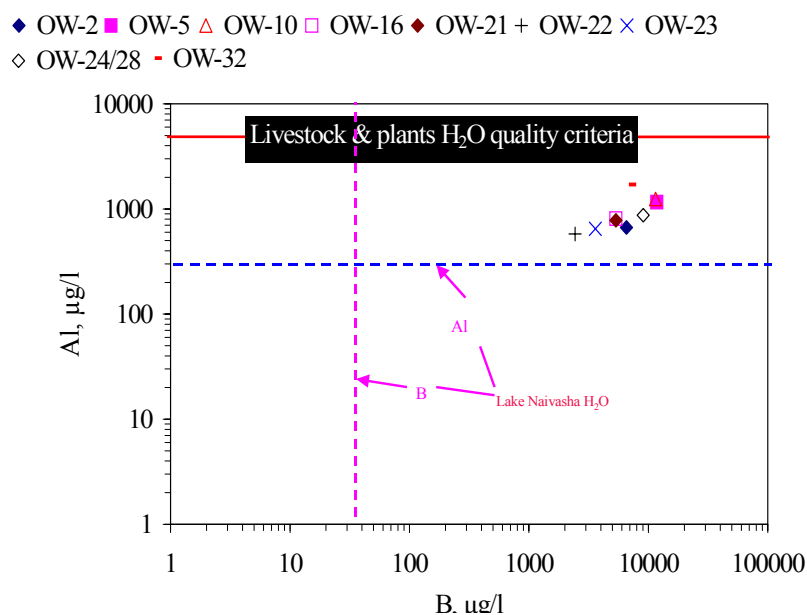


FIGURE 27: Relationship between Al and B in wastewater from selected well in Olkaria East field

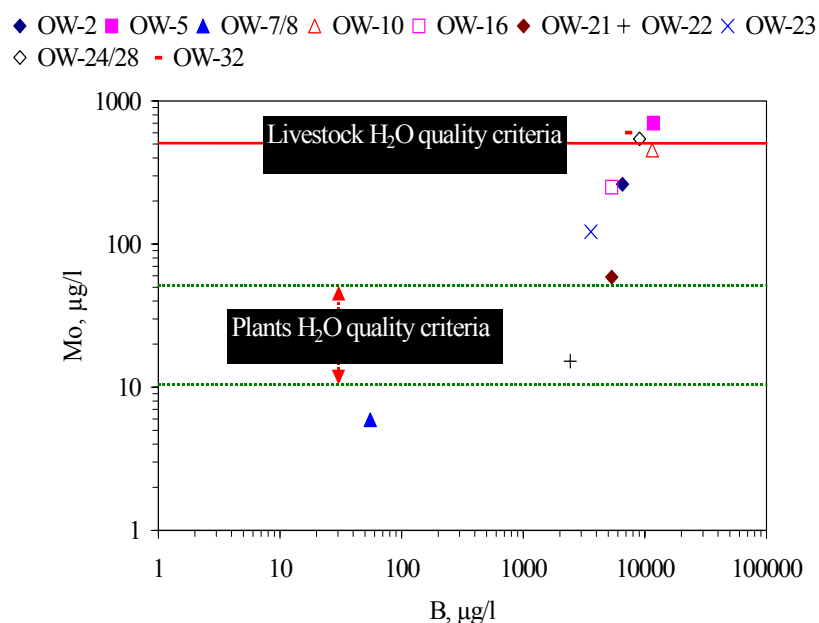


FIGURE 28: Relationship between Mo and B in wastewater from selected well in Olkaria East field

TABLE 18: Trace elements levels in wastewater of selected Olkaria East field wells from different data sources

	Al	As	B	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Zn
<i>Present study (2002/2003 study)</i>												
OW-2	0.665	1.265	6.555	0.0002	0.0005	0.00035	0.00202	0.000454	0.262	0.0005	0.000204	0.00831
OW-5	1.16	2.02	11.8	<0.00006	<0.00005	0.000656	0.0035	0.000285	0.7	<0.0005	0.00186	0.0647
OW-7/8	8.39	0.0114	0.0553	0.0000966	0.00504	0.518	0.00486	0.00176	0.00593	0.287	0.00145	0.0564
OW-10	1.24	1.69	11.5	<0.00003	0.00008	0.00756	0.00176	0.00013	0.454	0.00308	0.000362	0.0105
OW-16	0.807	0.973	5.35	0.000035	0.00005	0.000614	0.00717	0.002942	0.25	0.00113	0.00132	0.05645
OW-21	0.778	0.885	5.35	<0.00002	0.00002	0.000563	0.00192	0.000016	0.0589	0.000297	0.000563	0.0185
OW-22	0.577	0.164	2.435	0.0000095	0.0000165	0.000288	0.00159	0.0000512	0.0152	0.000612	0.000190	0.0155
OW-23	0.646	1.18	3.6	<0.00002	<0.00005	0.000524	0.0075	0.00287	0.122	<0.0005	0.00029	0.0193
OW-24/28	0.869	1.37	9.06	<0.00004	<0.00005	0.000658	0.003	0.00931	0.544	<0.0005	0.000126	0.0177
OW-32	1.705	1.365	6.96	0.00005	0.00005	0.000539	0.0142	0.0068	0.601	0.00512	0.000687	0.0952
<i>August 2000 (Environmental monitoring program-Olkaria Geochemistry Laboratory)</i>												
OW-2			5.09	BDL							BDL	0.037
OW-5			2.65	0.011							BDL	0.458
OW-7/8			2.41	BDL							BDL	0.672
OW-10			3.48	30							30	1.74
OW-21			1.57	0.039							BDL	20
OW-22			1.7	BDL							BDL	0.091
OW-24/28			1.91	BDL							BDL	0.863
<i>March 1998 (Environmental monitoring program-Olkaria Geochemistry Laboratory)</i>												
OW-2				0			0.15				0.1	0.1
OW-10				0			0.02				0.1	0.03
OW-21				0			0.13				0.6	2.99
OW-22				0			0				0.1	0.01
<i>October 1997 (Environmental monitoring program-Olkaria Geochemistry Laboratory)</i>												
OW-10				0			0.02				0.1	0
OW-21				0			0.02				0.1	6.4
OW-22				0			0.03				0.3	0.2
OW-24/28				0			0.33				0.9	4.2
<i>September 1993-February 1994 (Simiyu, 1995; Simiyu & Tole, 2000)</i>												
OW-10		5.31	6.15	0.005			0.007	0.94			0.033	0.017
OW-16		4.19	9.43	0.008			0.007	0.52			0.037	0.015
OW-22		5.11	2.95	0.004			0.019	5.41			0.039	0.016
<i>October 1997-January 1999 (Simiyu, 2000)</i>												
OW-15				0.003	0.005		0.007		0.039		0.03	0.004
OW-25				0.001	0.002		0.005		0.011		0.007	0.015

Units: mg/l (ppm); BDL = below detection limit; Blank cell = Not determined

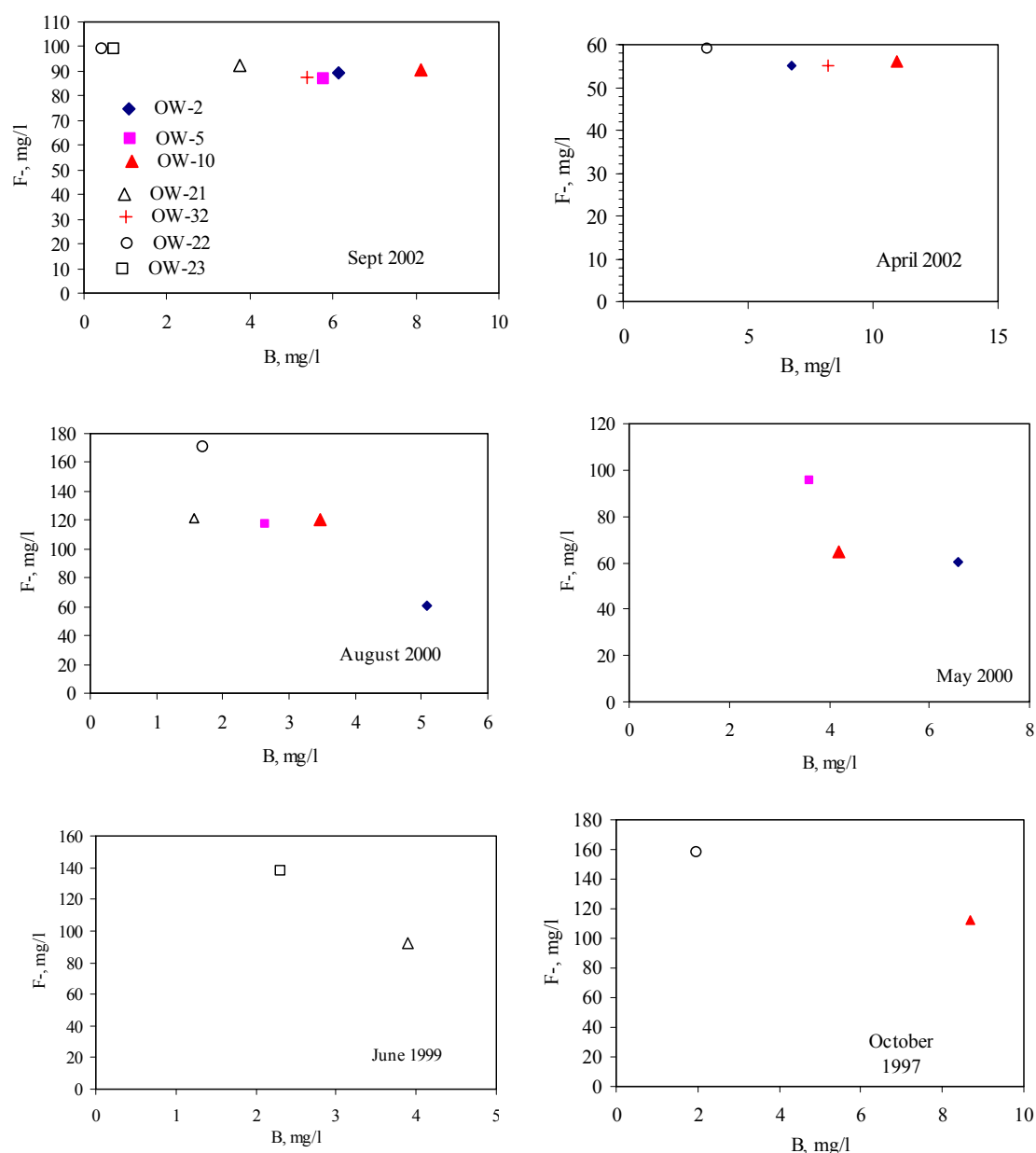


Figure 29: Concentration of boron and fluoride in selected wells of Olkaria East field (1997-2003)

11.0 DISCUSSION

Evaluation of trace element concentrations (Al, As, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb and Zn) in the wastewater of 10 geothermal wells in the Olkaria East field in relation to plants and livestock/wildlife (mammals) water quality criteria (Table 19) show Al, As, B and Mo as the only trace elements that could pose a potential ecotoxicological hazard if the wastewater disposal option is not environmentally sound. The standards referred to are for protection of livestock thus once the water quality standards for livestock are attained, then all the wildlife in the Hells Gate National Park would have been protected. Utilisation of livestock water quality criteria is also of relevance bearing in mind that livestock ranching is one of major land uses around the Olkaria area. The area around the Park has

TABLE 19: Average concentration of trace elements in wastewaters of selected Olkaria East field wells for the sampling period August 2002 and 2003 in relation to water quality criteria for livestock and plants

Element	Livestock water Quality criteria (CCME, 1999)	Plants water quality criteria (CCME, 1999)	OW-2	OW-5	OW-7/8	OW-10	OW-16	OW-21	OW-22	OW-23	OW-24/28	OW-32
Al	5000	5000	665	1160	8390	1240	807	778	577	646	869	1705
As	25	100	1265	2020	11.4	1690	973	885	164	1180	1370	1365
B	5000	500 - 6000	6555	11800	55.3	11500	5350	5350	2435	3600	9060	6960
Cd	80	5.1	0.02	<0.06	0.0966	<0.03	0.035	<0.002	0.0095	<0.02	<0.04	0.05
Co	1000	50	0.05	<0.05	5.04	0.08	0.05	0.02	0.0165	<0.05	<0.05	0.05
Cr	50	4.9 - 8	0.35	0.656	518	7.56	0.614	0.563	0.288	0.524	0.658	0.539
Cu	500-1000	200 - 1000	2.02	3.5	4.86	1.76	7.17	1.92	1.59	7.5	3	14.24
Hg	3		0.454	0.285	1.76	0.13	2.9423	0.016	0.05115	2.87	9.31	6.8129
Mo	500	10-50	262	700	5.93	454	250	58.9	15.2	122	544	601
Ni	1000	200	0.5	<0.5	287	3.08	1.13	0.297	0.6115	<0.5	<0.5	5.105
Pb	100	200	0.204	1.86	1.45	0.362	1.32	0.563	0.1895	0.29	0.126	0.687
Zn	50,000	1000 - 5000	8.31	64.7	56.4	10.5	56.45	18.5	15.5	19.3	17.7	95.35

Units: µg/L (ppb)

also been frequently utilized by a nomadic pastoralist community (the Maasai) as grazing grounds for their livestock especially in dry season when grass is scarce elsewhere. An evaluation in relation to such standards will thus protect such livestock through containment of the wastewater.

Aluminium concentration levels in the wastewater were generally low at all wells evaluated with exception at well OW-7/8 where the level was higher than the Al water quality criteria for protection of plants and livestock. The arsenic concentration level in the wastewater was above the 25µg/L and 100 µg/L (CCME, 1999) water quality criteria levels for livestock and plants respectively. Concentrations in most well wastewater was higher than 0.164 ppm with the highest being 2.02 ppm. Though the levels are above the plant and livestock water quality criteria levels, studies elsewhere have shown that toxicity of arsenic to plants or animals is dependent on the arsenic species present. Thus the potential toxicity of arsenic to plants around the geothermal wastewaters will be governed by its speciation and not the total arsenic concentration. It has been shown that some forms of arsenic such as sodium arsenate and arsenic trioxide are extremely toxic to plants. For example arsenic concentration in water as low as 1-15.2 µg/L of As(V) have been reported to inhibit growth in certain aquatic plants resulting in noticeable changes in plant community (Sanders and Cibik, 1985). For animals that might be exposed arsenic, there is little evidence that arsenic is carcinogenic to mammals. However, it does cause teratogenic effects in many species (Eisler, 1988). Animals, both domestic and wildlife especially mammals in the study area may be exposed to arsenic mainly by ingestion of contaminated water or vegetation. With regard to mammals acute or sub-acute arsenic poisoning is much more common than chronic poisoning. The probability of chronic exposure of animals in the Olkaria area to arsenic is postulated to be rare because arsenic detoxification and excretion is very rapid in most mammalian species (Woolson, 1975). For example exposure of domestic sheep to a 58 mg/kg dietary concentration of arsenic showed no outward visible effects. The tissue arsenic increased after a 3-week exposure but then declined rapidly after return to low arsenic diet. It is however, worth to observe that beneficial effects of arsenic have also been reported in silkworms, rats, goats, and pigs at low dietary concentrations and low doses have been known to stimulate growth in plants and animals (Eisler, 1988, 1994).

The boron concentration was high in geothermal wastewater from most wells evaluated. Thus it also becomes of concern, as its environmental effects are most noticeable in plants. The concentration at wells OW-2, OW-5, OW-10, OW-24/28 and OW-32 was beyond the 500-6000 µg/L boron plant

tolerance ranges in water. Though boron is an essential trace element for the growth and development of higher plants, the range between insufficiency and excess is usually narrow. Gupta et al. (1985) for instance found that some plants show signs of deficiency when boron concentrations in the soil solution are <2 mg/L and show toxic effects at concentrations >5 mg/L. In another ecological risk assessment for a natural community of aquatic plants it was concluded that, with median concentrations of 3.6-5.9 mg/L, patterns of leaf tissue discoloration (yellowing) may indicate adverse ecological impacts of boron on vegetation (Powell et al., 1997).

Animals may also be exposed to high boron concentration in geothermal wastewater especially in dry season when surface drinking water in the areas becomes scarce. Boron concentration at some wells was above the 6 mg/L (CCME, 1999) boron water criteria level for animals with the highest boron concentration being 11.8 mg/L at well OW-5. This was still below the boron concentration levels that have been shown to cause deleterious growth effects in animals. For example, 150 mg/L of boron in drinking water has been reported to cause growth retardation in cattle (Eisler, 1990). For animals exposed to high boron concentration, potential ecotoxicological effects from the consumption of boron contaminated water are unlikely to be observed as several studies elsewhere have shown that animals to avoid boron contaminated drinking water. For example, rats and cattle rejected boron contaminated drinking water containing as little as 1 mg/L B (Dixon et al. 1976) and >29 mg/L B (Green and Weeth, 1977) respectively.

The molybdenum concentration in the wastewater from most wells was above the 10-50 ppb (CCME, 1999) plant water quality criteria level. The concentration level was however far below the concentrations that have been observed to cause adverse effects in sensitive plant species i.e. 50 mg/L for reduced growth and 108 mg/L for abnormal development in *Euglena gracilis* and green algae (USDI, 1998). It should also be observed that molybdenum is considered essential for aquatic plant growth and may be beneficial in one way or another to plants growing in infiltration ponds though the concentration levels required are not known.

Currently available data for molybdenum's effects on wild mammals are inadequate and majority of toxicity effects of molybdenum on animals especially mammals reported have been observed in laboratory studies. From the present study, it seems that the molybdenum concentration in wastewater at wells OW-5, OW-24/28 and OW-32 was above the 0.5 ppm (CCME, 1999) molybdenum drinking water criteria for livestock. Ecotoxicological properties of molybdenum in animals (mammals) are governed by its interaction with copper and sulphur, as residues of molybdenum alone are not sufficient to diagnose molybdenum poisoning. A Cu:Mo ratio lower than 2:1 will result in copper deficiency, whereas a Cu:Mo above 10:1 increases the risk of developing copper toxicosis in animals (Osweiler et al., 1985). Thus the potential ecotoxicological effects of high molybdenum exposure to animals may not be molybdenum poisoning as such but molybdenosis which is a copper deficiency disease that is caused by the depressing effects of molybdenum on the physiological ability of copper when copper concentration is too low (Eisler, 1989).

The mercury concentration in the geothermal wastewater at most wells was low and does not constitute a potential ecotoxicological risk unless this element can bioaccumulate itself up the food chain in the study area. It worth observing that animals accumulate mercury from various environmental matrices, but those living in or near water tend to accumulate most, hence the need to isolate such contaminated wastewaters.

High fluoride wastewaters may contaminate vegetation and if fed on by animals will cause a condition known as fluorosis, which affects the bones and teeth of the animals. Plants can also be affected by fluoride toxicity and a synergistic effect of combined SO₂ and fluoride is recognized in plants in areas affected by atmospheric pollution (Alloway and Ayres, 1997). This high fluoride level in the geothermal wastewater is typical for most waters in the Kenyan rift, thus a proper disposal mechanism to preclude vegetation contamination is required to protect the animals.

12.0 CONCLUSIONS AND RECOMMENDATIONS

12.1 Conclusions

This study has shown that trace elements concentration levels in wastewater from most wells are within the international water quality criteria for protection of plants and animals (mammals) against any potential ecotoxicological risk except for As, B and Mo in wastewater from a few wells. Geothermal wastewater could be a potential ecotoxicological hazard due to these trace elements if proper disposal strategy is not in force. A review of the concentration levels of arsenic, cadmium, mercury, lead and cobalt in geothermal wastewater in previous studies show the current level to be low. The 1994 arsenic levels in wells OW-10, OW-16 and OW-22 are five times the present concentration levels. The fluoride level in the wastewater of all wells has been high which is typical of Kenyan rift waters.

12.2 Recommendations

From the results of this study, the following recommendations are made:

1. Arsenic and boron levels in geothermal wastewater in some wells is high and above the water quality criteria for protection of plants and animals (mammals), hence there is a need for closer monitoring of these elements.
2. The ongoing reinjection of the geothermal wastewater should be increased.
3. Plants growing in the geothermal wastewater infiltration ponds should be investigated for their phytoremediation qualities for these man-made “wetlands” to be used as geothermal wastewater treatment and disposal options.
4. There is a need to identify one given plant species as a biomonitor for trace elements arising from geothermal energy development and utilization in the Olkaria area.
5. Monitoring of trace elements concentrations for biological impacts on fauna should adopt the “biomarkers” concept. The use of biomarkers in trace element pollution monitoring has shown that even low concentration of a certain trace metal in the environment may constitute an ecotoxicological risk to certain species; while at the same time even high concentrations may not constitute a risk in other species.

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