



CHALMERS UNIVERSITY OF TECHNOLOGY
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MASTER THESIS

Metals and Metal Speciation in Waste Water from the
Nesjavellir Geothermal Power Plant, SW-Iceland and
Possible Effects on Lake Thingvallavatn

INGIBJÖRG E. BJÖRNSDÓTTIR

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Table of contents:

TABLE OF CONTENTS:	i
LIST OF FIGURES:	ii
LIST OF TABLES:	iii
ACKNOWLEDGEMENTS	iv
ABSTRACT	v
1. INTRODUCTION	1
2. DESCRIPTION OF THE STUDY AREA	2
3. PREVIOUS RESEARCH	6
3.1. RESEARCH AND PREPARATIONS FOR A POWER STATION	6
3.2. ENVIRONMENTAL RESEARCH	9
4. METAL SPECIATION AND METAL BIOAVAILABILITY	12
4.1. INTRODUCTION	12
4.2. MAIN METAL SPECIES IN FRESHWATER	13
4.3. COPPER, CADMIUM, LEAD AND ZINC.	20
4.4. BIOAVAILABILITY AND TOXICITY	26
4.5. UV-B RADIATION AND COPPER (I).	30
5. METHODOLOGY	31
5.1. INTRODUCTION	31
5.2. SAMPLING AND STORAGE	32
5.3. ANALYSIS	34
6. RESULTS	43
6.1. GENERAL CHEMICAL CHARACTERISTICS.	43
6.2. TRACE METALS	43
7 DISCUSSION	45
7.1. THE SPECIATION OF ZINC, LEAD, CADMIUM AND COPPER.	45
8. CONCLUSIONS AND RECOMMENDATIONS	53
8.1. CONCLUSIONS	53
8.2. RECOMMENDATIONS	53
9. REFERENCES:	54
10. APPENDIX	58

List of figures:

Figure 1 Position of the Mid-Atlantic Rift zone (Jónasson, 1992).	2
Figure 2. The volcanic zones of Iceland. The spreading zones are shaded dark (Jónasson, 1992).	3
Figure 3. Tectonic map of the Hengill volcanic system. Black circles indicate warm springs and the black box shows the Nesjavellir area (Gunnarsson, et.al, 1991).	4
Figure 4. Map of the Thingvallavatn area (Magnússon, 1992).	5
Figure 5. Temperature cross-section through the area from Kýrdalur in the west to Nesjavalladalur in the east (Gunnarsson et.al 1991).	6
Figure 6. Three dimensional flow model of the Nesjavellir geothermal area (Gunnarsson et.al, 1991).	7
Figure 7. Map of the Nesjavellir area, SW-Iceland (Egilson and Kjaran, 1986).	8
Figure 8. Results of flow measurements at Nesjavallalaekur 22nd august 1996. Graph a) shows depth (cm) and width (m) of the stream channel. Graph b) shows the velocity (m/s) along the width of the stream channel. Q was found to be $155 \pm 5 \text{ m}^3/\text{sec}$.	9
Figure 9 Model of an aquatic fulvic acid (Buffle, 1994).	16
Figure 10. The structure of clays (Buffle, 1994).	19
Figure 11. Eh-pH diagram for Cu in the presence of sulphur and CO_2 . Stability fields of chalcocite and covellite are calculated for a system where $\Sigma S = 1 \times 10^{-1} \text{ mol/L}$ and the fugacity of $\text{CO}_2 > 1 \times 10^{-3} \text{ atm}$ (Faure, 1992).	21
Figure 12. Distribution diagram for the cadmium hydroxide system (Fergusson, 1990).	22
Figure 13. Eh-pH diagram for the system $\text{Cd}^{2+}/\text{H}_2\text{S}/\text{CO}_2/\text{H}_2\text{O}$.	23
Figure 14. Distribution diagram for lead-hydroxy species (Fergusson, 1990).	24
Figure 15. Eh-pH diagram for the Pb- H_2O - CO_2 system (Fergusson, 1990).	25
Figure 16 Eh-pH diagram for the system $\text{Zn} + \text{CO}_2 + \text{H}_2\text{O}$ in freshwaters at 25 degrees C and 1 atm. (Salomons and Förstner, 1987).	26
Figure 17. The relationship between measured DOC concentration and the depth of the UV-B isopleth. The dotted line represents the equation: $1\% \text{ UV-B} = 5,173(\text{DOC})^{0.706} - 1.029$. $r^2 = 0,98$.	31
Figure 18. Map showing sampling locations in the Nesjavellir area (Ólafsson, 1992).	33
Figure 19 Bathocuproine disulfonic acid ($\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}_6\text{S}_2\text{Na}_2$). (www.dojindo.co.jp/products/info/202/TEXT/BATHOCUS.html)	35
Figure 20. A typical dropping mercury electrode (Skoog and Leary, 1990).	38
Figure 21. A typical anodic stripping voltammogram for Zn, Cu, Pb and Cd (Reeve, 1994).	40
Figure 22. Interrelationships between various metal species in water and their relationship to electroanalytical methods (Salomons and Förstner, 1984).	40
Figure 23 The speciation of zinc. Some of the values are averages representing more than one measurement.	45
Figure 24 The speciation of cadmium.	46
Figure 25 The speciation of lead.	47
Figure 26 The speciation of copper. Values for total copper are averages of bathocuproine total copper and DPASV total copper.	49
Figure 27 Graph comparing the results from the bathocuproine spectrophotometric method for copper with the results from the differential pulse anodic stripping voltammetry method.	51
Figure 28 An example from a DPASV voltammogram where the copper peak is subject to interferences.	52



List of tables:

Table 1. Emission of carbon dioxide (CO ₂) and sulphurs from diverse types of power plants (National Energy Authority of Iceland, Factsheet).	1
Table 2 Mean chemical composition of water that flows into lake Thingvallavatn (Ólafsson, 1992).	10
Table 3 Trace constituents in spring water by Nesjahraun (Ólafsson, 1992).	10
Table 4 Levels of the Heavy Elements in Freshwater (µg/L) (Fergusson, 1990).	10
Table 5. Trace metals in liver of arctic charr <i>Salvelinus alpinus</i> (Jónsson et.al. 1995)	11
Table 6. Trace metals in tissue and shell of the gastropod <i>Lymnaea peregra</i> (Jónsson et.al, 1995)	11
Table 7 Inorganic Lead Species in Freshwater (Fergusson, 1990).	25
Table 8 Absolute Detection Limits (ng) (Fergusson,1990).	35
Table 9 . Reagents added to samples.	36
Table 10 Ce2020 spectrophotometer specifications.	38
Table 11 Temperature, pH, H ₂ S, CO ₂ , TOC and DOC.	43
Table 12 Results from zinc speciation analysis (µg/L).	43
Table 13 Results from copper speciation analysis (µg/L).	43
Table 14. Results from lead speciation analysis (µg/L).	44
Table 15. Results from cadmium speciation analysis (µg/L).	44

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Abstract

This study examines metals and metal speciation in geothermal wastewater from the *Nesjavellir* geothermal power station, SW-Iceland. Metal speciation was also measured at the south coast of lake *Thingvallavatn*, where geothermal wastewater enters the lake in warm springs.

The bathocuproine spectrophotometric analytical method for copper was used along with Differential Pulse Anodic Stripping Voltammetry to measure both total copper and copper (I). It thus became possible to compare these two methods with each other.

Cu (I) was found to be of particular interest because of the low DOC concentrations of lake *Thingvallavatn*. Thus Cu(I) concentrations in the lake were found to be high, most likely because UV-B radiation reaches deep into the lake, causing photolytic reduction of Cu(II) to Cu(I).

Zinc, copper and cadmium concentrations both in lake *Thingvallavatn* and in the geothermal wastewater were low. Cadmium however, was slightly higher in the geothermal water than in the unaffected lake water.

Lead was found to be very low in unaffected lake water. However, everywhere where geothermal water enters the lake, lead concentrations were significantly higher. Total lead concentrations in geothermal wastewater leaving the power station were also found to be comparatively high.

1. Introduction

Geothermal energy is known to be an environmentally benign energy source compared to sources such as coal, oil and natural gas (see table 1). Although too small to be a global energy option, geothermal energy is nevertheless vital in such countries as Iceland and New Zealand. Generally speaking, the use of geothermal energy, where available, has been increasing worldwide. Along with this increase, more attention is being paid to the environmental effects of geothermal power utilization.

The principal changes brought about by the use of geothermal energy are: visual effects such as wellheads and pipelines, chemical discharge (geothermal wastewater), thermal effects and physical changes such as subsidence (Iceland National Energy Authority, Fact sheet).

Table 1. Emission of carbon dioxide (CO₂) and sulphur from diverse types of power plants (National Energy Authority of Iceland, Fact sheet).

Type of energy source	CO ₂ kg/MWh	S kg/MWh
Fossil fuels:		
Coal	1000	11
Oil	850	11
Natural gas	550	0.005
Geothermal:		
Flash type	96	6
Hot dry rock	11	0
Hydropower	0	0
Nuclear	<1	0

Of major environmental concern is geothermal wastewater as it contains heavy metals such as lead, cadmium, arsenic and mercury. Both mercury and cadmium are known to exhibit toxicity to living organisms at extremely low concentrations. The elements silver, chromium, lead, copper, and zinc also exhibit toxicity to organisms although the concentrations are orders of magnitude higher than that required for Cd or Hg toxicity (Peters and Ku, 1987). It is therefore not without reason that careful monitoring of geothermal wastewater is recommended.

Therefore the objective of this study was to examine metal content and metal speciation in geothermal wastewater from the *Nesjavellir* geothermal power plant, SW-Iceland. The power plant, which supplies warm water for household heating, utilizes the energy of the geothermal liquid to warm up cold groundwater, the geothermal liquid being discarded in the process. This geothermal wastewater then falls into a small stream, *Nesjavallalaekur* which eventually mixes with groundwater that flows into a large lake, called lake *Thingvallavatn*.

It so happens that the north coast of lake *Thingvallavatn* is part of a National Park, while the whole area is extremely popular for recreational purposes. It is therefore considered important to preserve the lake in its pristine state.

It is also an objective of this study to examine metal speciation in an area where the natural environment is, as yet, relatively unpolluted. Lake *Thingvallavatn* can thus be said to represent clear oligotrophic lakes at high latitudes where the effects of acid rain are, as yet, absent, inflow of nutrients is low and where sunlight penetrates the water column.

2. Description of the study area

The surface of our planet is composed of crustal plates which move in different directions. At places where the plates diverge, new crustal material is constantly being formed through volcanic activity. One such zone of plate divergence is the Mid-Atlantic Ridge (see figure 1).

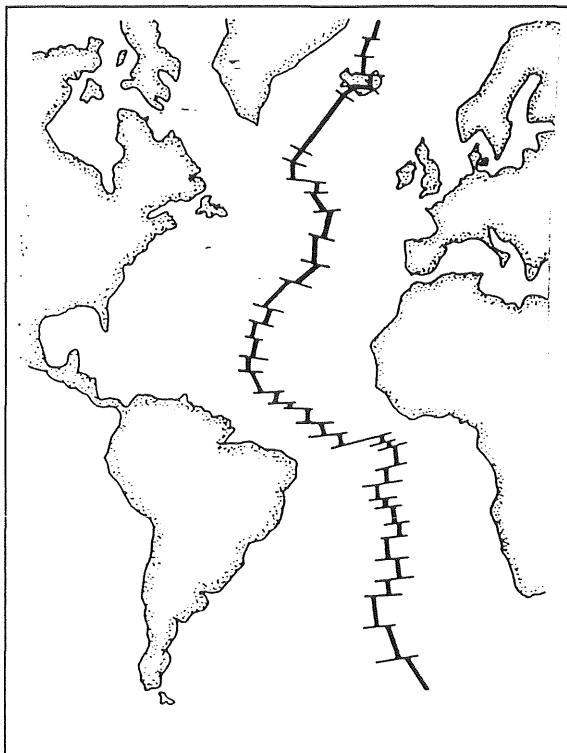


Figure 1 Position of the Mid-Atlantic Rift zone (Jónasson,1992).

The Mid-Atlantic Ridge forms a submerged mountain chain 500 km wide which stretches from the Arctic into the South Atlantic. Islands such as The Azores, Tristan da Cunha and Jan Mayen form a part of this ridge, but only in Iceland does the spreading axis itself rise above the surface of the ocean creating a complicated pattern of neovolcanic zones on land (see figure 2). Within these zones rifting, volcanism and geothermal activity continuously shape the natural environment.



Figure 2. The volcanic zones of Iceland. The spreading zones are shaded (Jónasson, 1992).

In Iceland there are at least 28 high temperature geothermal fields where the temperature at 1 km depth is higher than 200 °C. Such high temperature areas are ideal sites for geothermal power stations and the study area of this research is located at one such power station, *Nesjavellir* on the south coast of lake *Thingvallavatn*, 27 km east of *Reykjavík*, Iceland (see figure 3).

South of the *Nesjavellir* power station lies an active central volcano, *Hengill* (803 m), composed mainly of hyaloclastite and olivine tholeiitic lavas (see figure 3). Large fissures with a direction NE-SW extend from the volcano through the *Nesjavellir* area and one of them, *Kýrdalshryggur* constitutes a main upflow zone for the geothermal field (Jónasson, 1992). The natural geothermal flow in the area is estimated to be 15 MWv (Gunnarsson et.al. , 1991).

There have been three or possibly four eruptions within the *Nesjavellir* fissure swarm in postglacial times. The latest was around 2000 years ago forming an 11 km² lava field called *Nesjahraun* (see figure 3).

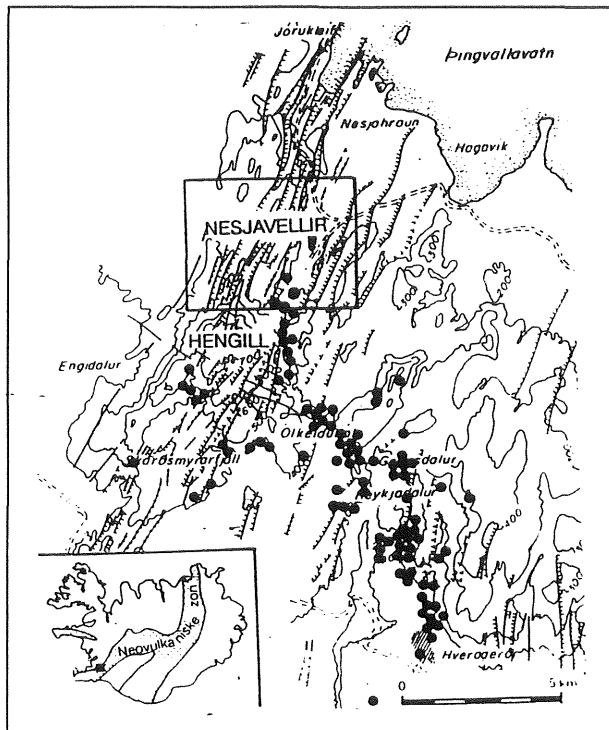


Figure 3. Tectonic map of the *Hengill* volcanic system showing fault-lines. Black circles indicate warm springs and the black box shows the *Nesjavellir* area (Gunnarsson, et.al, 1991).

North of the *Nesjavellir* geothermal field at 101 meters above sea level, is lake *Thingvallavatn*^{*}, a 114 m deep, 83 km², oligotrophic subarctic lake (see figure 3 and 4). The lake resides in a basin or graben formed by tectonic subsidence and glacial erosion, but has since then been strongly modified by volcanic activity. The graben is over 25 km wide in the NE but narrows towards the SW (Saemundsson, 1992).

Thingvallavatn is largely fed by subterranean groundwater flow and springs, but three small rivers drain into it. A single outflow, lies at the southern end of the lake (Jónasson, 1992). The catchment area has been estimated at 1000 km² from the *Hengill* mountain in the SW to the *Langjökull* glacier in the northeast, a distance of 73 km (Adalsteinsson et. al., 1992). The basaltic lavas and breccias of the catchment produce chemically neutral or alkaline water, pH in the groundwater entering *Thingvallavatn* being 7.5-8.5. The retention time of the lake is 330 days. Primary production is relatively high, nitrogen being the limiting factor. The plant communities in *Thingvallavatn* are also rich with high phytoplankton productivity (Jónasson, 1992).

In terms of species diversity *Thingvallavatn* is similar to other subarctic lakes. There are three fish species in the lake, arctic charr (*Salvelinus alpinus* (L.)), brown trout (*Salmo trutta* L.) and the three spined stickleback (*Gasterosteus aculeatus* L.). There are also four different polymorphs of arctic charr in the lake, something which is unique (Jónasson, 1992).

^{*} The name of the lake in Icelandic is Þingvallavatn, but as the letter Þ does not exist in the common Latin alphabet, Th is used here instead of Þ. The pronunciation of Þ is similar to th- in the English language, i.e. thorough.

Among birds found in the area are some unusual species such as the great northern diver (*Gavia immer*), Barrow's goldeneye (*Bucephala islandica*) and Gyrfalcon (*Falco rusticolus*). The most common birds however are mallards (*Anas platyrhynchos* L.), merganser (*Mergus serrator* (L.)) ,tufted duck (*Aythia fuligula* (L.)) and grey-lag geese (*Anser anser* (L.)) (Magnússon, 1992).

Vegetation is characterized by the absence of trees. Thus the most extensive plant communities are moss heath, dwarf scrub heath, graminoid heath and wetlands. Only a small part of arable land is cultivated (Thorsteinsson and Arnalds,1992).

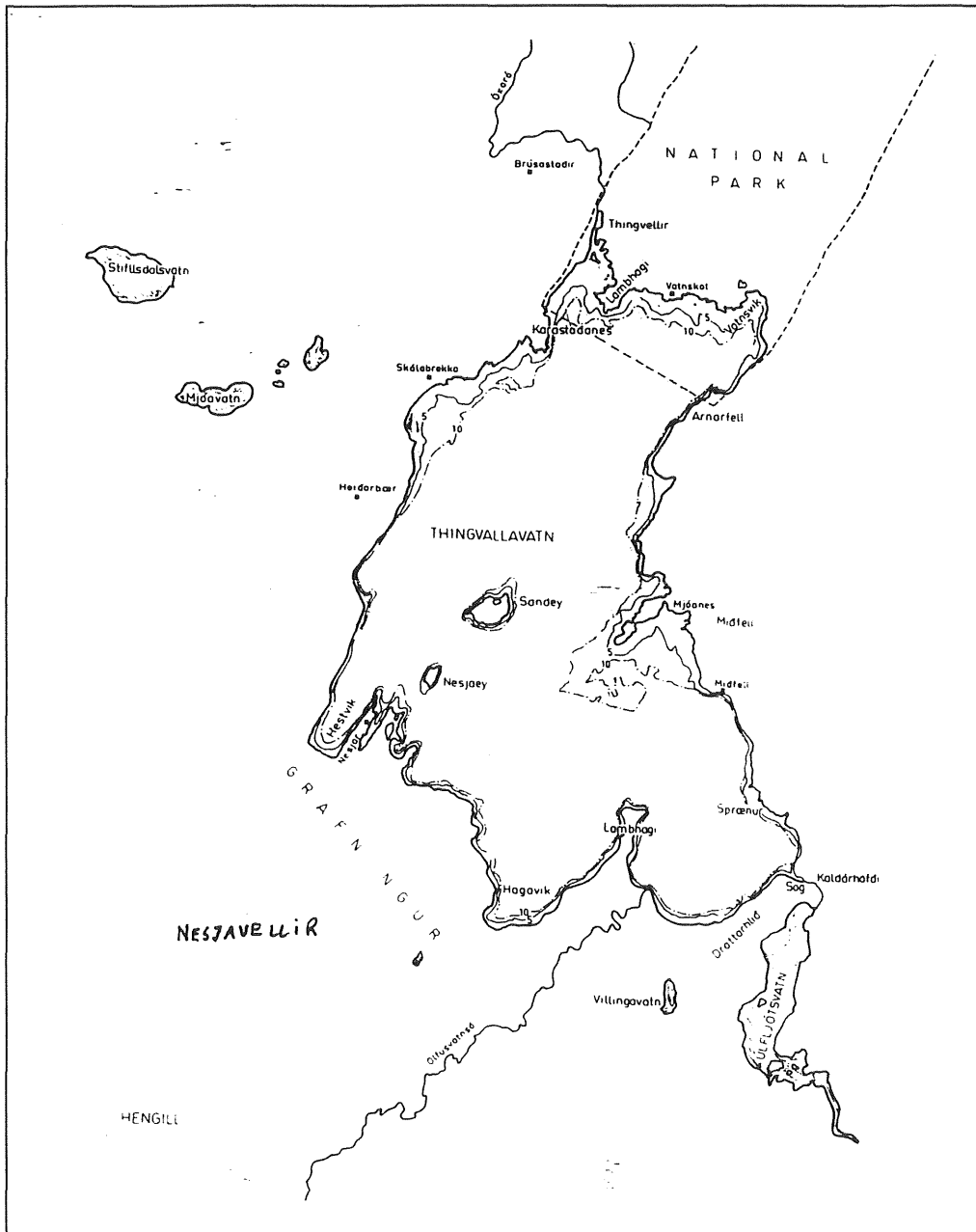


Figure 4. Map of the Thingvallavatn area (Magnússon, 1992).

The weather around *Nesjavellir* shows irregular variations (Einarsson,1992). Cyclones are frequent during wintertime bringing precipitation and strong winds. Thus precipitation at *Nesjavellir* has been estimated to be 2800-3000 mm/year. The annual mean temperature from 1961-1980 was 12.5 °C and the annual mean solar radiation from 1974-1988 was 74.7 kcal/cm² or 313 × 10⁷ kJ/m² (Adalsteinsson et.al, 1992)

3. Previous research

3.1. Research and preparations for a power station

Research and preparations for the power station at *Nesjavellir* began in 1964. The first drillhole was drilled in 1965 and the last one, nr. 18 in 1986. During this drilling stage the highest temperatures were recorded along the *Kýrdalur* fissure in boreholes 3 and 11 (>380°C , see figure 5) (Gunnarsson et. al, 1991). This, incidentally, is the highest temperature recorded so far in any geothermal borehole in Iceland.

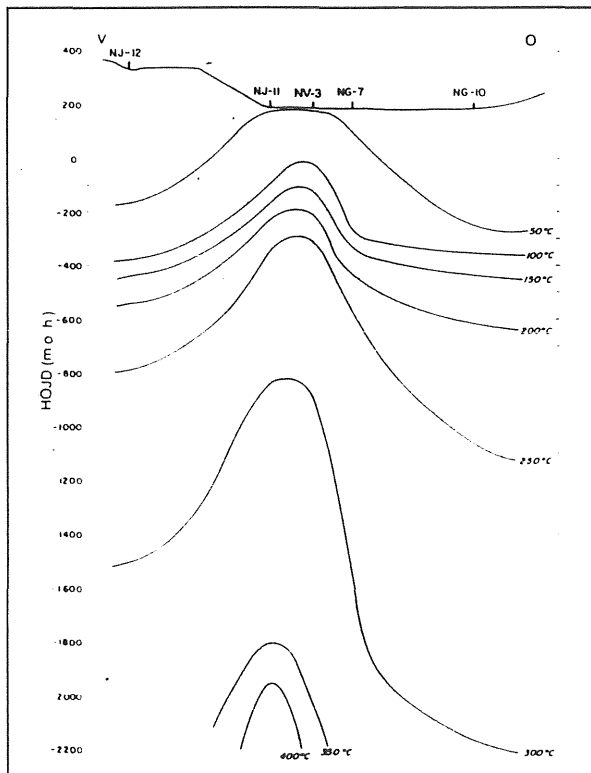


Figure 5. Temperature cross-section through the area from *Kýrdalur* in the west to *Nesjavalladalur* in the east (Gunnarsson et.al 1991).

Research has shown that there are both one phase (liquid) and two phase (gas-liquid) systems present at *Nesjavellir*. Most probably the steam at the bottom of the geothermal reservoir is in a supercritical state.

A computer model of the geothermal field has been constructed which explains how the two-phase geothermal liquid flows along the system. The water which is originally rainwater from the area north of lake *Thingvallavatn*, warms and rises close to the *Hengill* volcano and then flows north along the *Kýrdalur* fissure.

Rain that falls around *Nesjavellir* however, flows as cold groundwater from *Hengill* north to lake *Thingvallavatn* (see figure 6) (Gunnarsson et.al, 1991). Tracer measurements have been used to quantify this groundwater flow, giving a value of 1600 L/sec (Egilson and Kjaran 1986).

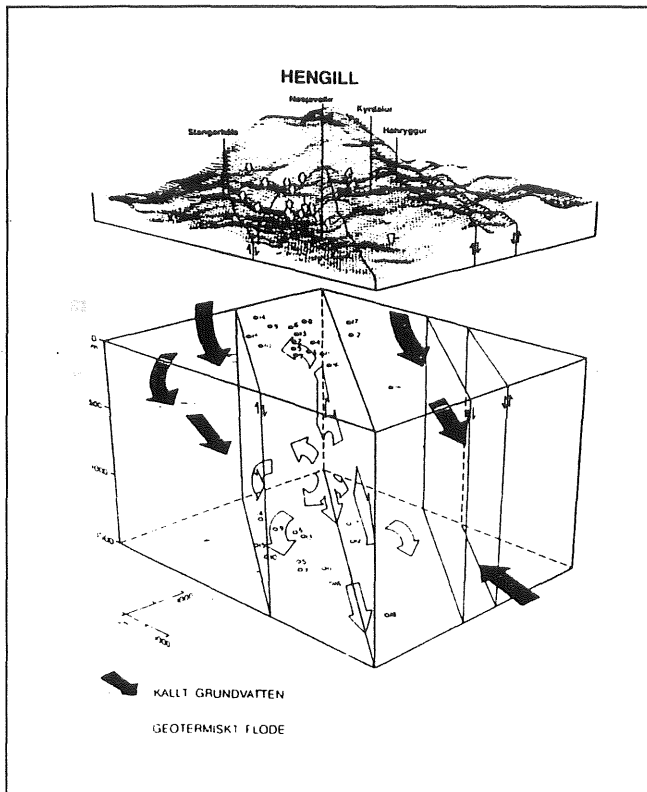


Figure 6. Three dimensional flow model of the Nesjavellir geothermal area (Gunnarsson et.al, 1991).

Based on the above research the *Nesjavellir* power plant started operation in 1990. The 18 boreholes currently give a capacity of 150 MW with a maximum possibility of 400 MW. They discharge a high pressure mixture of water, steam and uncondensable gases. The drillhole discharge is collected with a system of collection pipes running to the geothermal power plant where liquid and steam are separated. Cold groundwater from wells at *Grámelur* (see figure 7) is also pumped into the power station, heated and piped to *Reykjavík* (Ólafsson, 1992).

The power plant uses only the energy of the geothermal liquid. Consequently, geothermal wastewater oversaturated with sulfur and carbon dioxide is disposed of into a small stream *Nesjavallalaekur* (see figure 7). The stream eventually disappears under the small lava field, *Nesjahraun* where it mixes with groundwater that flows 3.8 km into lake *Thingvallavatn*. The stream then resurfaces in hot springs which flow into lake *Thingvallavatn* around *Thorsteinsvík* (see figure 7).

The flow in *Nesjavallalaekur* has been found to be highly variable with a minimum around 70 L/sec and a maximum of 1000 L/sec (Egilson and Kjaran, 1986). Flow measurements done on 22nd August 1996 yielded a discharge of 155 ± 5 L/sec (see figure 8). As the groundwater flow towards *Thingvallavatn* is 1600 L/sec a considerable dilution takes place when the stream disappears underground and mixes with groundwater (Egilson and Kjaran,1986).

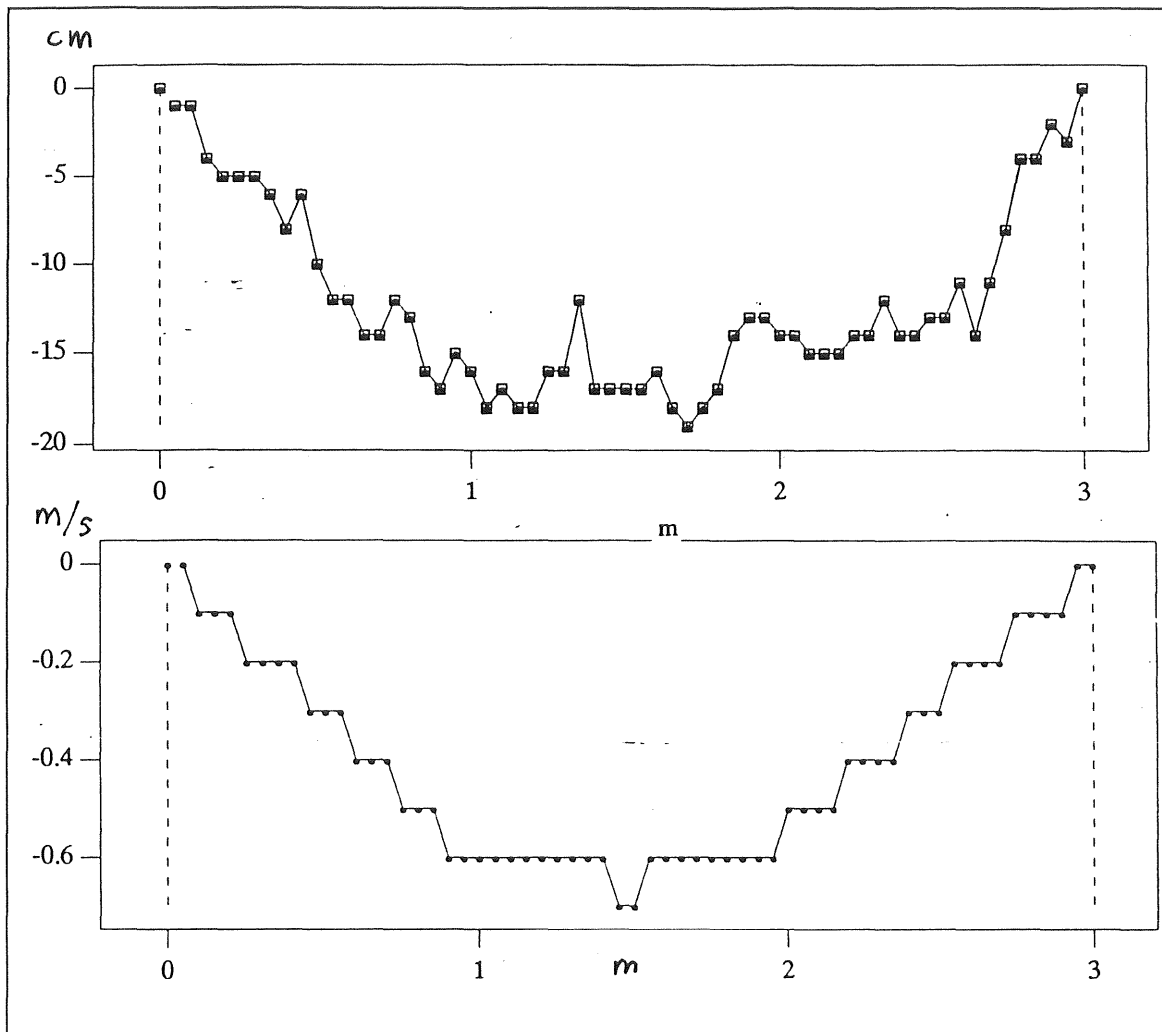


Figure 8. Results of flow measurements at Nesjavallalaekur 22nd August 1996. Graph a) shows depth (cm) and width (m) of the stream channel. Graph b) shows the velocity (m/s) along the width of the stream channel. Q was found to be 155 ± 5 m³/sec.

3.2. Environmental research

3.2.1. Analyses of trace metals in water

During the years 1984 and 1991 Ólafsson (1992) measured trace metals both in condensed steam, cooled geothermal water and in hot springs near *Thorsteinsvík* at the south coast of *Thingvallavatn*. His results are presented in Tables 2 and 3.

Table 2 Mean chemical composition of water that flows into lake Thingvallavatn (Ólafsson, 1992).

Meas. site	T(°C)	pH	Alk. meq / L	Cl mg/L	Mg mg/L	Ca mg/L
Varmagjá	6.8	7.8	1.17	7.8	5.6	9.6
Eldgjá	9.6	x	x	x	x	x
Markagjá	3.6	x	x	x	x	x

x = not measured

Markagjá in lake *Thingvallavatn* is unaffected by geothermal water which is reflected in low water temperature. In both *Varmagjá* and *Eldvík* however, geothermal springs flow into the lake. In *Varmagjá* pH is high (7.8) and alkalinity low (1.17 meq/L). The chloride value of 7.8 mg/L is not high, neither are the magnesium and calcium contents.

Table 3 Trace constituents in spring water by Nesjahraun (Ólafsson, 1992).

Meas. site	Zn µg/L (1984/1991)	Pb µg/L (1984/1991)	Cd µg/L (1984/1991)	Cu µg/L (1984/1991)
Varmagjá	0.2/1.1	0.06/0.03	0.006/0.04	1.2/1.2
Markagjá	0.2/2.9	0.07/0.07	0.005/0.11	0.4/1.0
Eldvík	0.3/0.3	0.05/0.10	0.004/0.06	0.7/1.5

3.2.1.1. Lead

The lead concentration in *Varmagjá* and *Eldvík* was found to be between 0.03 and 0.1 µg/L (Ólafsson, 1992). In comparison, natural concentrations of lead in unpolluted Antarctic ice have been found to be 1.7-1.8 ng/L (Fergusson, 1990). The Antarctic is considered the most remote and unpolluted place on earth with respect to heavy metals, levels in other places such as the Arctic corresponding to some global contamination (Fergusson, 1990). In freshwaters, however the most probable background concentration for lead is 5-50 ng/L or less than 10 µg/L (see table 4).

Table 4 Typical levels of Heavy Elements in Freshwater (µg/L) (Fergusson, 1990).

Elements	Fresh water	Rivers non-polluted	Rivers polluted	Lakes	Rivers mining areas	Geothermal water
Cd ^a	< 1	0.01-1	1- > 10	0.01-20	100-700	0.01-0.5
Hg ^b	0.02-0.1	0.0001-1	> 1	0.02		0.05-60
Pb ^c	< 10	< 1-10	20-100	0.1-30	100-1000	1-10
As ^d	< 1-5	< 1-10	10-1000	1-70	100-5000	1000-5000
Se ^e	< 0.1	0.1-0.3				
Sb ^e	< 0.3	0.3-5				
Bi ^e		0.02				
Tl ^e	0.004					

In general Pb reference values for the protection of ecosystems depend on the hardness of the water. Thus in Canada for example, the Pb reference value for soft water is 1 µg/L. In Iceland however, the Pb limiting value for drinking water is 50 µg/L (Jónsson,1995).

3.2.1.2. Cadmium

Ólafsson (1992) also measured a Cd concentration of 0.04 µg/L in *Varmagjá* in 1991. In comparison, cadmium in rain and ice in the Arctic/Antarctic has been found to be 0.008/0.004-0.639 µg/L (Ferguson,1990). In freshwaters probable background concentrations for cadmium are 10-100 ng/L. In Iceland the limiting value for cadmium in drinking water however, is 5 µg/L (Jónsson, 1995).

3.2.1.3. Zinc

Zinc in *Varmagjá* was 0.2 µg/L in 1984 and 1.1 µg/L in 1991. In lakes in Canada zinc ranges from 1-50 µg/L and Canadian reference values for soft water are 30 µg/L. Icelandic Zn limiting values for drinking water however, are 3 mg/L (Jónsson,1995).

3.2.1.4. Copper

Copper was 1.2 µg/L in *Varmagjá* and 0.7-1.5 µg/L in *Eldvík*. Background values for copper in freshwater have been found to be 0.43 µg/L in northern Finland and 0.51 µg/L in the north of Sweden. Reference values in Canada for soft water are 2.0 µg/L and in USA 3.0 µg/L (Notter, 1993).

3.2.2. Analyses of trace metals in fish and gastropod tissue

From 1994-1995 trace metals were measured both in the tissue and liver of small benthivorous arctic charr (*Salvelinus alpinus*) and in the tissue/shell of the gastropod *Lymnaea peregra* (see tables 5 and 6). The gastropods are benthic organisms which feed on sediments and approximately 80-90% of the diet of small benthivorous charr consists of *Lymnaea peregra* (Jónasson, 1991). Any bioaccumulation taking place from metals in the sediments and water should thus be detectable in either or both of these organisms.

Table 5. Trace metals in liver of arctic charr *Salvelinus alpinus* (Jónsson et.al. 1995)

Measuring site	Zn(µg/g)	Pb(µg/g)	Cd(ng/g)
Vatnsskot*	37.3	≤ 0.3	76.8
Varmagjá	47.8	≤ 0.3	88.1
Varmagjá	46.8	≤ 0.3	89.2
Thorsteinsvík	42.2	≤ 0.3	88.7

* The site Vatnsskot is unaffected by geothermal wastewater

Table 6. Trace metals in tissue and shell of the gastropod *Lymnaea peregra* (Jónsson et.al, 1995)

Measuring site	Zn ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Cd (ng/g)
Vatnsskot	53.9	≤ 0.3	0.24
Varmagjá	62.4	1.8	0.41

Lead background concentrations in fish (marine muscle and tuna) have been found to be 0.3-0.4 ng/g (Fergusson,1990). The results here show high lead content, 1.8 $\mu\text{g/g}$ in *Lymnaea Peregra* in *Varmagjá*. Lead in arctic charr, however, was below detection limits in all cases. It therefore seems that the gastropods are affected by lead in sediments and water, while the fish are not (Jónsson et.al, 1995).

In general it can be said that the metal values were found to be higher in *Varmagjá* than in *Vatnsskot*, especially in *Lymnaea peregra*.

4. Metal speciation and metal bioavailability

4.1. Introduction

Natural waters are extremely complex chemical environments. They contain various elements, dissolved organic matter and colloidal and particulate material both inanimate and living.

Metal ions in freshwaters interact with this complex environment forming many different physicochemical forms.

The distribution of a metal ion between different chemical species and forms is called metal speciation. A better understanding of metal speciation is important because it gives information both about the geochemistry and about the bioavailability of the metal in question to living organisms.

The main factors that influence the speciation of trace metals in water have been found to be: the solubility of compounds of the metals, the oxidation state of the metals, availability of complexing agents, complex formation, ion-pair formation, adsorption or desorption to particulate material, redox and pH conditions of the environment and biochemical processes (Fergusson, 1990).

The first metal speciation scheme was devised by Batley and Florence (1976). The scheme divided metals into dissolved and particulate by passing the samples through a 0.45 μm filter. The dissolved fraction was then measured with ASV and distinguished into ASV-labile and non-ASV labile fractions. Samples were also irradiated with UV radiation and passed through chelating resins. Many different speciation schemes have since been devised (Salomons and Förstner, 1988).

4.2. Main metal species in freshwater

The main metal species in freshwater are:

1. Simple ionic species and weak complexes
2. Inorganic complexes
3. Differing valency states
4. Lipid soluble complexes
5. Organometallic complexes
6. Metals adsorbed on colloidal particles
7. Particulate metal adsorbed onto or contained within clay particles

4.2.1. Simple ionic species and weak complexes

Some metals such as cadmium exist in natural waters mainly as free ions, while other metals are bound to carbonates, colloids and humics.

In the past toxicity was measured by adding metal ions directly to laboratory test organisms (Morrison, 1989). Then metal toxicity was taken to be directly related to the concentration of the ionic metal species in water. It is now known however, that the toxicity of a metal depends highly on its form. For instance, both the carbonate and ionic forms of Pb have been reported as toxic to rainbow trout (Morrison, 1989). In order to estimate the toxicity of a particular metal for living organisms it is thus necessary to measure not only the concentration of the free metal ion but also to consider the partitioning of the metal into different species.

4.2.2. Inorganic complexes

If the concentration of metals is high then the solubility product constant, K_{sp} may be exceeded and precipitation of hydroxides, sulphides, carbonates and phosphates may occur (Fergusson, 1990).

For instance metal ions are adsorbed onto hydrous oxides of manganese and iron. The main iron compounds involved are $\text{Fe}(\text{OH})_3$, Fe_3O_4 (magnetite), amorphous $\text{FeO}(\text{OH})$ and goethite. Manganese compounds are birnessite, manganite and mango-manganite.

The metals adsorb to the surface of the hydrous oxides, and exchange between protons and metal ions occurs (Fergusson, 1990):



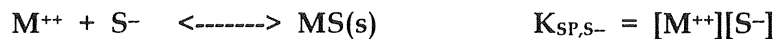
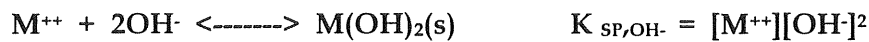
The resulting oxide then precipitates, and the metal is incorporated into sediments.

Under high pH conditions hydrous Fe and Mn oxides constitute significant sinks for heavy metals through the effects of sorption/coprecipitation. The importance of metal-carbonates however, depends both on alkalinity and pH.

Sulphate is an important ion in natural waters. In an anaerobic environment sulphate is reduced to sulphide which can either be transformed to hydrogen sulphide gas or iron sulphide (Morrison and Johansson, 1992). Hydrogen sulphide is also a significant component of geothermal waters. Under such circumstances, the bioavailability and toxicity of cationic metals can be influenced by the presence of insoluble metal sulfides.

Whereas the presence of chelating agents greatly inhibits metal hydroxide precipitation the extent of metal sulfide precipitation is influenced by chelating agents due to competition between the formation of metal sulfide and metal chelates (Peters and Ku, 1987).

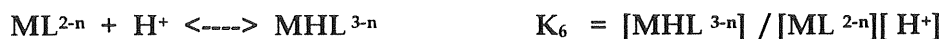
Precipitation of metal hydroxide or metal sulfide takes place through the following reactions (Peters and Ku, 1987):



Complexation of metal ion with hydroxide ion:



Complexation of metal ion with a chelating agent (L) (Peters and Ku, 1987):



Protonation of sulfide ion:



Total metal in solution (Peters and Ku, 1987):

$$M_T = C_M + M_S + M_{OH}$$

where M_S and M_{OH} are the metal sulfide and metal hydroxide precipitate respectively.

$$\text{Total sulfide ion: } S_T = [S^{2-}] + [HS^-] + [H_2S] + M_S$$

The precipitation of metal hydroxides, metal sulfides and even metal carbonates has to be taken into account when describing metal speciation in reducing environments or close to geothermal areas.

Thermodynamic models have been used to describe inorganic complexation in natural waters. A thermodynamic equilibrium constant K^θ based on ion activities or a conditional constant K^* based on ion concentrations is used. Activities are important in water systems and cannot always be ignored. This is especially true for seawater where several models already exist (Harrison, 1990). Devising thermodynamical models for natural waters has been found to be difficult however, because there the main inorganic complexes are hydroxides and carbonates (Harrison, 1990). Also most thermodynamic data available today come from measurements in acid solutions, so accurate thermodynamic/conditional constants for freshwaters do not as yet exist.

4.2.3. Differing valency states

Ions exist in different valency states. This is important with respect to bioavailability, for instance chromium VI ion is highly toxic to living organisms while chromium III ion is relatively harmless. This is because the small chromium VI ion ($Cr_2O_7^{2-}$), which is similar in size to SO_4^{2-} easily goes through ion channels in biomembranes, while the larger chromium III ion does not (Morrison, 1989).

4.2.4. Lipid soluble complexes

Lipid solubility can be estimated by solvent extraction using a solvent mixture with similar dielectric properties to the lipid bilayer. Lipid solubility of metals is often directly related to their toxicity. For instance some lipid-soluble Cu complexes have been found to be highly toxic because it seems that certain lipid-soluble ligands facilitate passive diffusion of metals through cell membranes (Morrison, 1989).

4.2.5. Organometallic species

Organic ligands play an important role in metal speciation in freshwaters. They can arise in three possible ways: (i) from organisms such as bacteria and algae, (ii) from the breakdown of plants and animal material or (iii) when lower-molecular weight organic matter is sorbed onto clay or metal oxide substrates. Organic ligands include humic, fulvic and tannic acids which are complex aromatic polymer molecules (see figure 9). Because of their sheer size humic substances are insoluble in water. Fulvic acids are smaller, they remain in solution and hence metal ions coordinated to them are solubilized.

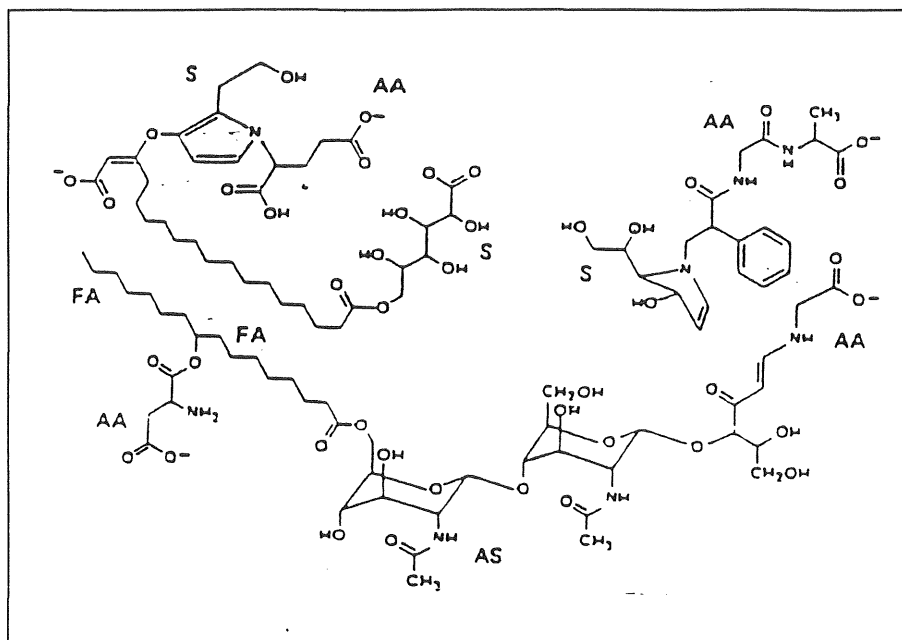


Figure 9 Model of an aquatic fulvic acid (Buffle, 1994).

Humics have a great affinity for metal cations, and extract them from the water that passes through them. The binding of metal cations occurs largely because of the formation of complexes with the metal ions by carboxyl groups in the humic and fulvic acids. However, for macromolecules such as humic acid and fulvic acid not only covalent and electrostatic binding may be important but in addition, macromolecules may entrap ions in their gel-like structure.

Macromolecules are considered to be polyfunctional, that is they include several to many types of complexing (binding) sites and their complexation properties for a given metal result from a combination of many individual complexation reactions (Buffle, 1994).

The major ions compete for the binding sites on the macromolecules. Laboratory studies on complexation by fulvic acid have concentrated mainly on copper and have been conducted at fixed pH and fixed ionic strength. Under these conditions competition by the hydrogen ion and the major salt cations for binding sites is constant (Harrison, 1990).

However, if the pH is changed the competition between the proton and major cations totally changes. At low pH, hydrogen ion saturates the metal binding sites on the humic substances whereas at high pH values free metal ion is not an important species. A relatively neutral pH is thus favoured for metal complexation of humics (Morrison, 1989).

Of the metals considered here, Cu is easily complexed and seems to have a higher affinity for humic acid than for instance, cadmium (Salomons and Förstner, 1988). The presence of soluble humic substances has thus been found to enhance Cd, Pb and Ni adsorption to sediments while retaining copper in solution. This behaviour is consistent with the formation of soluble copper-humic complexes.

In metal speciation analysis it is possible to measure the complexing capacity of water samples. Complexing capacity of a sample is determined by adding a specified ionic metal to a natural water sample. After addition, and when equilibrium has been reached, the total metal concentration is given by:

$$[M] = [M^{n+}] + [MI] + [ML]$$

where $[M^{n+}]$ is the concentration of free metal ion; $[MI]$ is the total concentration of the inorganic complexes, and $[ML]$ is the total concentration of the metal-ligand complexes.

and $[ML]$ is in equilibrium with the free metal ion:

$$ML = *K [M^{n+}][L_t]/1 + *K[M^{n+}]$$

where $*K$ is the conditional equilibrium constant ($*K = [ML]/[M^{n+}][L]$) and L_t is the metal complexing capacity of the sample.

In order to know the value of the equilibrium constant it is necessary to titrate the sample with a suitable metal ion. The $*K$ value can then be used in calculations.

A related concept used is binding capacity which depends on how many binding sites are available for complexing the added metal ion per unit weight. The relationship between complexing capacity and binding capacity is expressed in the following equation:

$$L_t = BC \times OM$$

where BC is the total amount of binding sites per unit weight of the complexing material and OM is the concentration of the complexing material (Salomons and Förstner, 1988).

One of the most common analytical methods used to determine free metal ion in a complexing capacity titration is ASV.

4.2.6. Metals adsorbed on colloidal particles

On the surface of solid colloidal particles there is a large number of densely packed complexing sites. When these sites are deprotonated, an intense negative electric field is produced that creates electrostatic attraction for metals which adsorb onto the particles.

Adsorption can be characterized in terms of a partition coefficient, K_D defined by:

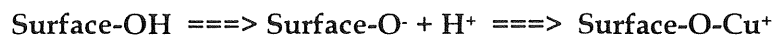
$$K_D = \frac{\text{adsorbed metal/mol/kg}}{\text{dissolved metal/mol/L}}$$

K_D values are by no means constants. They are a function of variables such as pH, salinity and particle surface.

Adsorption is very much dependent on pH. Thus a shift in pH in waters such as lakes will change the dissolved metal concentrations. A metal will generally be more competitive with H^+ at low pH, even though all metals have distinctive adsorption characteristics. It has thus been proven that lead and copper adsorb more easily at low pH than zinc and cadmium (Salomons and Förstner, 1988).

Inorganic ligands which form dissolved complexes with metal ions can either increase or decrease metal adsorption. Benjamin and Leckie (1982) showed that chloride and sulfide generally decrease the fractional adsorption of cadmium at a given pH (Salomons and Förstner, 1988). Thus metal complexation may reduce the tendency of metal ions to adsorb, as apparently is the case when cadmium ions form complexes with chloride or sulfate.

Adsorption models exist which assume the particle surface to consist of an array of immobilized hydroxyl groups (Harrison, 1990). These groups gain or lose protons:



These models are simplified because real particles in natural waters are rarely pure phases and the particles are often coated with organic matter. Detailed adsorption models for particles in natural waters do not as yet exist.

Metals bound to particles are not usually considered bioavailable. However, solubility, mobility and bioavailability of particle-bound metals can be realised either through lowering of pH, changing redox conditions, increasing occurrence of natural and synthetic complexing agents or by the formation of soluble chloro-complexes with some trace metals (Förstner, 1987).

4.2.7. Particulate metal adsorbed onto or contained within particles

Ion exchangers have a structure containing an excess of fixed negative or positive charge and take up ions from solution as needed to neutralize the charge. They can preferentially adsorb some types of ions relative to other ions; therefore the ratio between different counterions on an ion exchanger is usually not the same as the ratio between those ions in solution (Hemond and Fechner, 1994).

Clays consist of composite layers of tetrahedrally and octahedrally coordinated cations. Layers of silica-oxygen tetrahedra are connected by cation-hydroxyl layers, the most common cations being aluminium ion and magnesium ion (see figure 10). Water molecules are also often found in between layers.

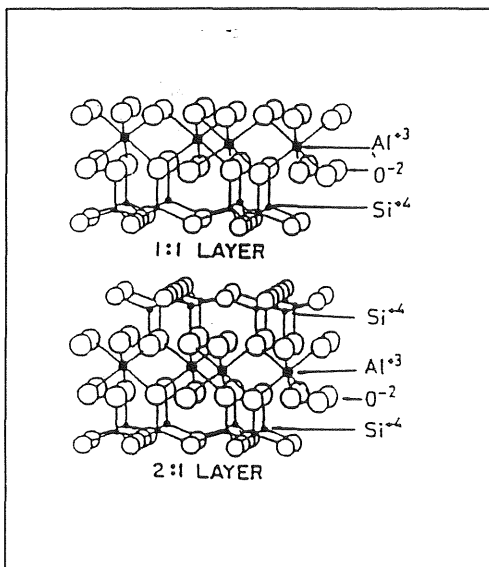


Figure 10. The structure of clays (Buffle, 1994).

The clay minerals differ in their cation exchange properties according to the nature of their interlayer cations and residual surface charges (Deer et. al, 1992). In clays, Si, Mg and Al are often replaced by other cations with similar sizes but different charges. Thus, the surface of the clay can become negatively charged which attracts more metal ions.

Adsorption of metals onto clays is influenced both by the number of free bonding sites on the clay surface, and by the proportion of atoms replaced with others of different valencies in the clay. The pH, the charge and the hydration of the metal species also influence adsorption.

The type of clay is significant as may be seen by how the ability of clay to accumulate metals decreases, in the following order: montmorillonite > vermiculite > illite > chlorite > kaolinite > (Fergusson, 1990). In general it may be said that the greater the ability of clay to expand, and effectively increase its surface area, the more metals it can accumulate. Clays can therefore contain considerable quantities of metals both on the surface and in between layers.

4.3. Copper, Cadmium, Lead and Zinc.

4.3.1. Copper

Copper is found mainly in the two oxidation states Cu(II) and Cu(I). The usual form is Cu(II) and it is known to form relatively stable complexes with many ligands, including humic and fulvic acids. Thus in some freshwaters more than 90% of the copper has been found to be bound to humic acids (Moore, 1991).

In freshwaters with pH around 7.0 copper ion is present in complexes with carbonate, nitrate, sulfate and chloride but not in the hydrated ionic form (Moore, 1991). At higher pH carbonate and hydroxide species are dominant, however, below a water pH of 7 the amount of free Cu ions rapidly increases thereby enhancing toxicity (Stouthart et.al.,1996).

Copper binds strongly to sulfides, and to complexing ligands such as ammonia, ethylenediamine and pyridine. It also forms stable complexes with Fe(OH)_x , manganese oxides, clays and organic matter in bottom sediments. Binding to particulates such as clay can result in significant downstream transport of copper in river environments.

The adsorption maximum for copper has been found to be in the vicinity of pH 8. In this case it has to be kept in mind that copper speciation above pH 7 is strongly influenced by the formation of the soluble Cu(OH)_2 complex (Salomons and Förstner,1988).

Cu(I) has been found to a significant extent in river water and is believed to be formed by photoreduction caused by ultraviolet radiation (Morrison, 1995). Cu(I) can also be reoxidized under natural conditions, but is hindered under low O_2 or high chloride (e.g. seawater) concentrations (Morrison, 1995).

4.3.2. Copper and H_2S

Copper is commonly associated with Fe in mineral deposits where it occurs either as the pure sulfides chalcocite (Cu_2S) or covellite (CuS) and as mixed sulfides such as chalcopyrite (CuFeS_2). In addition, Cu sulfides may coexist with sulfides of other metals, including Ni, Co, Zn, Pb, Mo, Ag, As and Sb (Faure, 1992).

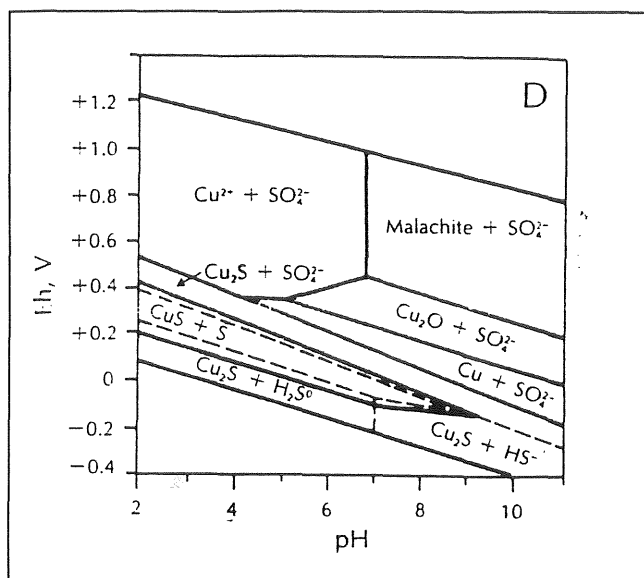
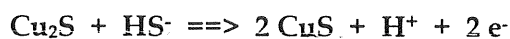


Figure 11. Eh-pH diagram for Cu in the presence of sulphur and CO₂. Stability fields of chalcocite and covellite are calculated for a system where $\Sigma S = 1 \times 10^{-1}$ mol/L and the fugacity of CO₂ > 1×10^{-3} atm (Faure, 1992). Higher Eh values indicate a more oxidizing environment.

The reaction between metallic Cu and HS⁻ in aqueous solution follows the equation:



And at pH > 7.0 where HS⁻ is the dominant S species, chalcocite will convert to covellite:



Copper sulfates are quite soluble and occur naturally only under arid climatic conditions. Therefore, the oxides of Cu are stable in the presence of water under oxidizing conditions in systems containing insufficient carbonate ions to precipitate the Cu carbonates malachite (CuCO₃ × Cu(OH)₂) and azurite (2CuCO₃ × Cu(OH)₂). Both oxides and carbonates of copper become increasingly soluble with increasing acidity. Thus, Cu is generally mobilized in environments where pH < 6.8 (Faure, 1992).

4.3.3. Cadmium.

Cadmium has the oxidation state Cd(II) (Fergusson, 1990). In freshwaters it is generally found in the ionic form or complexed to humic substances.

The speciation of Cd in freshwater is determined by the oxidation state and pH, as well as by the concentrations of numerous organic and inorganic anions/cations.

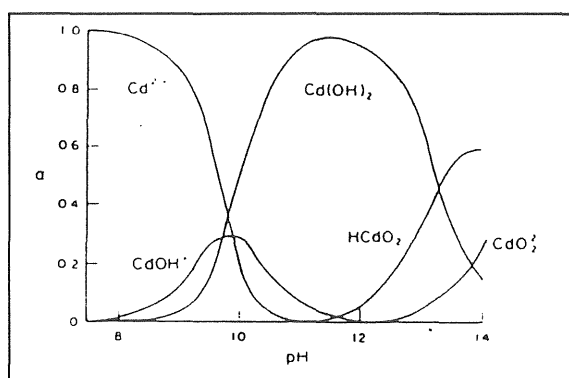


Figure 12. Distribution diagram for the cadmium hydroxide system (Fergusson, 1990).

Free cadmium ion is a major component of inorganic species in freshwaters with pH under 7 (see figure 12). The hydroxy species only persist down to a pH of 8-9, below which the Cd^{2+} ion occurs.

At higher pH values, CdCO_3 can be said to control the cadmium ion concentration under oxidizing and slightly reducing conditions, whereas CdS(s) is the controlling species in more strongly reducing environments (Ferguson, 1990). The amount of CdCO_3 formed will depend on the pH of the water and the alkalinity, the higher the alkalinity the greater the amount of CdCO_3 expected.

Under oxidizing conditions cadmium is mobile and present as the aquated Cd(II) cation, hence under normal environmental conditions the major species of cadmium in fresh water is the hydrated ion.



Under reducing conditions however, the soluble species of cadmium is probably the bisulphite ion, CdHS^- (Fergusson, 1990).

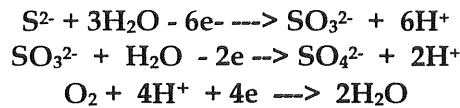
In contaminated environments other species of cadmium occur such as CdSO_4 and Cd-organic ligand complexes. Cadmium binds well to sulphur donors, aminoacids, carboxylic acids, polysaccharides and organic pollutants such as NTA (nitrilotriacetic acid). Whether or not organic-Cd complexes are present depends on the availability of organic material and the presence of competing cations. Unless the organic content of freshwater is very high, cadmium organic complexes are of less importance than the free ion, and inorganic species. In river water, dominant inorganic forms are Cd^{2+} and CdCO_3 , depending on pH (see figure 12). Cadmium hydroxide, however, is found only in very alkaline solutions and cadmium halides are significant mainly in seawater. A high proportion (> 70%) of cadmium is labile both in seawater and freshwaters depending on pH. Cadmium ions are adsorbed onto colloidal particles only at very high pH values.

The sorption of cadmium to sediments, and to the clay content, increases with pH, and the release of Cd from sediments is affected by pH, redox conditions and complexing agents in the water. The affinity of materials for cadmium

follows the order: Mn > Fe amorphous > chlorite (montmorillonite) > Fe crystalline = illite = humics > kaolinite > silica (Fergusson, 1990).

4.3.4. Cadmium and H₂S

Solid cadmium sulphide is produced when Cd(II) comes into contact with H₂S. Two structural forms exist, a cubic (zinc blende) structure and a hexagonal (wurtzite) structure. Cadmium has a strong affinity for sulphur. However in contact with atmospheric O₂ cadmium sulphide is unstable because of the oxidation of the sulphide ion (Fergusson, 1990):



Both CdS and CdCO₃ can occur together in the environment, where the following reactions may take place:

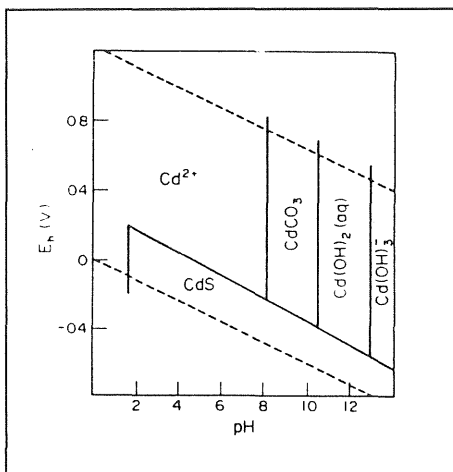
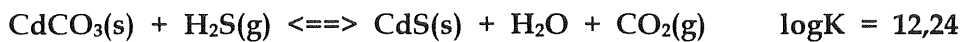
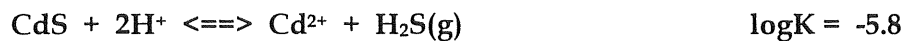


Figure 13. Eh-pH diagram for the system Cd²⁺/H₂S/CO₂/H₂O (Fergusson, 1990).

From figure 13 it can be seen that the important species up to a pH of 7-8 is the cadmium ion. At higher pH values, CdCO₃ (s) controls the cadmium concentration in solution in oxidizing and slightly reducing conditions, whereas CdS(s) is the controlling species in more strongly reducing environments (Fergusson, 1990).

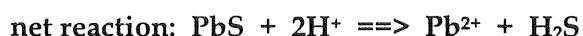
4.3.5. Lead

Lead has two oxidation states Pb(II) and Pb(IV) as well as the elemental state Pb(0). The major environmental inorganic forms of lead are divalent, whereas the organic forms are tetravalent.

The presence of significant concentrations of the Pb²⁺ ion in unpolluted natural waters is highly unusual. Instead the dominant lead species are found to be lead carbonates, up to 90% PbCO₃ and Pb₂(OH)₂CO₃, (see figure 15) or under more reducing conditions, lead sulphides. The reason for this is that lead sulphide, PbS_(s) and its carbonate PbCO₃ are both highly insoluble in water.



In highly acidic waters lead salts such as PbS dissolve to a much greater extent than in neutral waters, producing Pb²⁺ in the process (Baird, 1995).



Pb(II) hydrolyzes in water to give PbOH⁺, Pb(OH)₂ and other hydroxy forms (see figure 14). Pb(II) also forms halides in freshwater but only if chloride concentrations exceed 0.1 M (Fergusson, 1990).

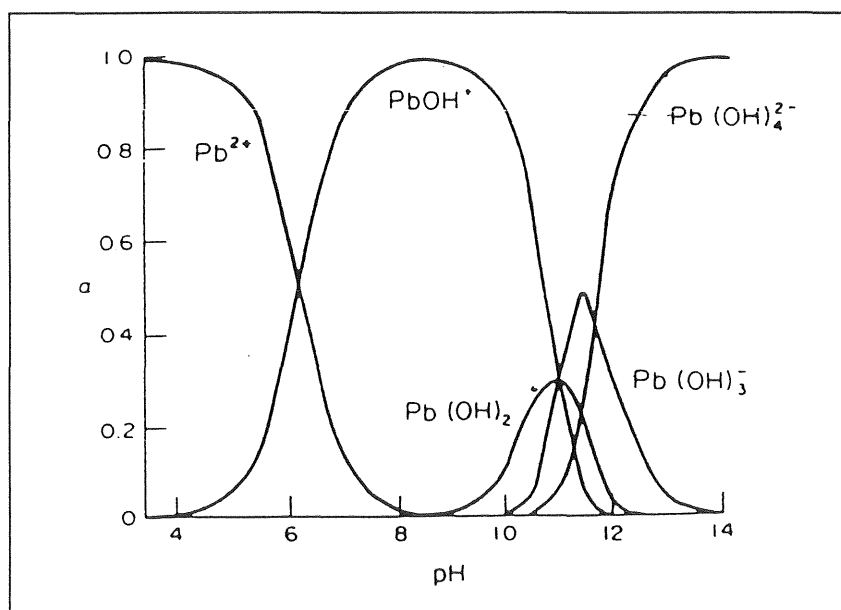


Figure 14. Distribution diagram for lead-hydroxy species (Fergusson, 1990).

In highly oxidizing environments, lead forms the Pb⁴⁺ ion and oxides such as PbO₂ and Pb₂O₃ are formed (see figure 15). Pb⁴⁺ compounds are usually covalent compounds. Organic ligands can form complexes with tetravalent lead. For instance, lead binds well to S, N and O, particularly to S which is a soft acid. Ligands, such as amino acids, fulvic acid, humic substances, citrate, acetate, glycolate and NTA can all coordinate to lead. The limiting factors for

lead complexation are the amount of ligands present, and competing metals (Fergusson, 1990). For instance, if calcium ions are present they will compete with tetravalent lead for NTA.

Lead also has a strong affinity for some inorganic adsorbents such as Fe/Mn oxides and in natural waters with pH > 7.0 a significant fraction of lead is bound to hydrated Fe₂O₃ (hematite). This association is said to be more important than association with organic material. Lead correlates best with iron when manganese levels are low and *vice versa* (Fergusson, 1990).

Montmorillonite adsorbs lead over a broad pH range, and the sorption is dependent on the amount of calcium present owing to competition.

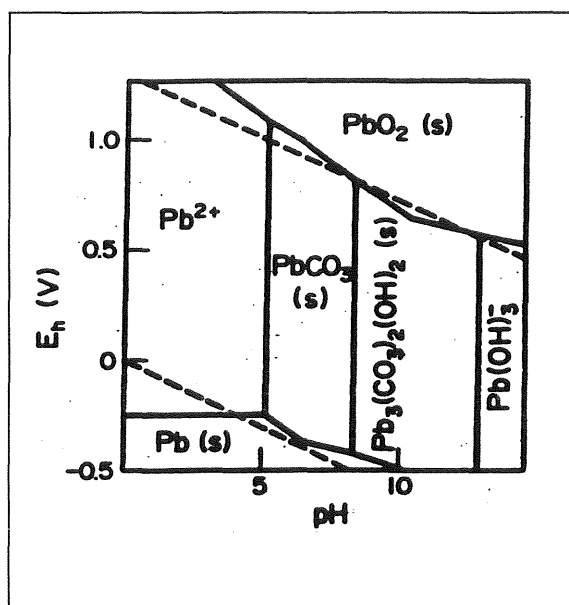


Figure 15. Eh-pH diagram for the Pb-H₂O-CO₂ system (Fergusson, 1990).

It follows from the above discussion that the main species of lead in freshwaters are PbCO₃, Pb(CO₃)₂²⁻, PbCl⁺, PbCl₂, PbOH⁺ and Pb(OH)₂. Only under acid conditions, or low chloride concentration is the Pb²⁺ ion likely to occur in reasonable amounts (Fergusson, 1990).

Table 7 Inorganic Lead Species in Freshwater (Fergusson, 1990).

Species	a	b	c	d	e	f
PbCO ₃			main			91
Carbonate species	90				main	
PbOH ⁺		main	main			
Pb ²⁺		main		38, 71		
PbCl ⁺				60, 24		
PbCl ₂				2, 5		

References: a 75, b 59 low alkalinity, c 59, high alkalinity, d 39, thermal waters, e 175, 187, f 76.

4.3.6. Zinc

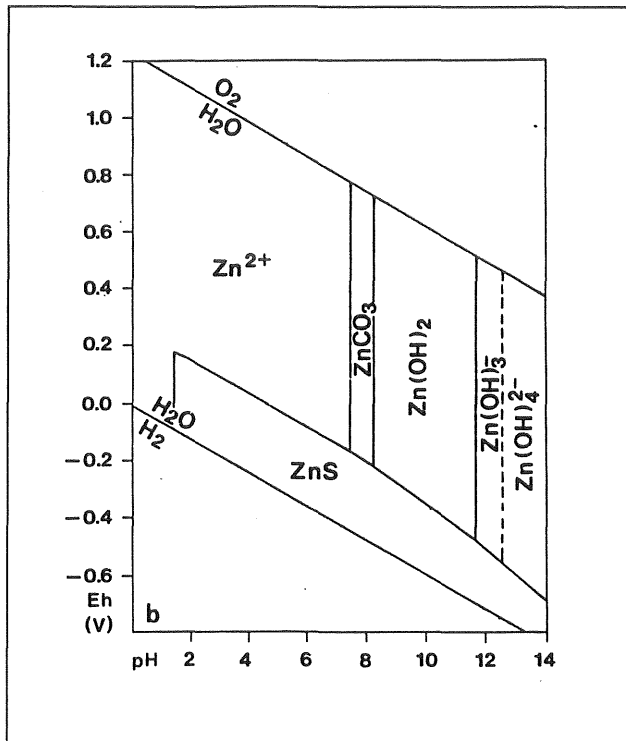


Figure 16 Eh-pH diagram for the system Zn + CO₂ + H₂O in freshwaters at 25 degrees C and 1 atm. (Salomons and Förstner, 1987).

Zinc has the electronic configuration [Ar] 3d¹⁰ 4s² and the principal oxidation state +2 (Petrucci and Harwood, 1993).

Figure 16 shows an Eh-pH diagram for zinc. Under oxidizing conditions the Zn²⁺ ion persists up to a pH of 7-8. Above that, zinc hydroxides and zinc carbonates become dominant. Under more reducing circumstances, ZnS is the preferred zinc species.

4.4. Bioavailability and toxicity

4.4.1. Introduction

The toxicity of metals depends on whether they are present in a form that can easily enter cells or be taken up by organisms (biological availability or bioavailability). Metals are bioavailable either as simple metal ions, bound in weak complexes or as lipid-soluble metal (Morrison, 1989). On the other hand organic complexes are relatively harmless and complexation by humics has been found to reduce metal bioavailability and hence metal toxicity to a considerable extent.

Metals can enter cells in various ways. Some metal species passively diffuse through aqueous pores in the cell membrane, the smaller the ion the faster the

rate of molecular diffusion (Morrison, 1989). Lipid-soluble metals are known to diffuse quickly across membranes, and this in part explains their high toxicity.

Sometimes a metal is carried across a membrane as a lipid soluble complex which binds metal at the lipophobic end and enters the cell at the lipophilic end, thus effectively "dragging" the metal into the cell (Morrison, 1989). Or in other cases metal uptake into the cell may be facilitated *via* the "nutrient/ATPase membrane transfer system" (Morrison, 1989).

The surface area of an organism is important as regards diffusion of metals into cells. Thus bacteria which have a large surface area/body weight ratio have been found to contain the highest metal concentrations.

Generally speaking, aquatic organisms are known to accumulate metals, and certainly lipid-soluble complexes are bioconcentrated to a much greater extent than simple ionic species due to the fact that they rapidly diffuse through biological membranes.

Cells can prevent toxic metal action by inducing the formation of metal binding granules or proteins. One such protein is metallothionein found in the liver and kidneys of vertebrates. Metallothionein binds metals and although its half life is only 4-5 days it can be continually synthesized in the liver allowing long term metal retention. This kind of retention prevents metal ion diffusion which could cause damage to various enzyme and protein systems (Morrison, 1989).

When however, the capacity of a cell to detoxify accumulated metal is exceeded, damage to the cell will occur. Signs of intracellular metal toxicity may include ultrastructural deformities as well as reductions in cell division rate, respiration, photosynthesis and ATP production (Morrison, 1989).

From the above it may be concluded that the toxicity of a metal species depends to a large extent on how well it passes through biological membranes/cell membranes.

4.4.2. Copper

Copper is an essential trace element needed in small quantities by most organisms, but toxic when present in excess. Many studies exist on the bioavailability and toxicity of copper to living organisms.

Copper is known to inhibit several enzymes, reduce the assimilation of amino acids and sugars, inhibit respiration, induce leakage of K^+ and plasmolysis, and cause cell death in bacterial cells (Azenha et.al., 1996)

The intimate contact of fish gills with water makes fish generally very vulnerable to heavy metals, including Cu. Indeed Cu exposure has been shown to reduce plasma Na^+ and Ca^{2+} in rainbow trout (*Oncorhynchus mykiss*) and also decreases the whole body content of these ions in developing brown trout (*Salmo trutta* L.) (Stouthart et.al., 1996).

Furthermore Cu seriously interferes with branchial ion transport, plasma ion concentrations, hematologic parameters and enzyme activities. In addition Cu may cause immunosuppression, vertebral deformities, and neurological disorders (Stouthart et.al.,1996).

Strong ligands markedly reduce copper toxicity, suggesting that copper toxicity is a function mainly of the free ion concentration. Weak and moderate copper ligands (e.g. acetate, succinate, proline, and lysine) can also significantly reduce copper toxicity provided that sufficient ligand concentrations are present. Thus the availability and toxicity of copper to bacterial cells has been shown to be reduced markedly by the presence of weak and moderate ligands (Azenha, et al, 1996).

Protons and copper ions compete with each other for the available coordinating sites in dissolved ligands and on biological surfaces. This means that the efficacy of ligands to reduce copper toxicity is pH dependent (Azenha et. al.,1996).

Sunda and Gillespie (1979) studied the response of a marine bacterium to added copper and the influence of complexing agents like NTA, humic acids as well as salinity. The response of the bacterium, as measured by the uptake of C-14 labelled glucose did not depend on the total copper concentration but depended on the cupric ion activity. Growth rate and inhibition of the estuarine diatom *Thalassiosira pseudonana* was also found to be related to the cupric ion activity and not to the total copper concentration (Sunda and Guillard, 1976).

Results of studies on copper uptake by *Daphnia magna* (Andrew et.al. 1977) that were treated with multiple regression analysis showed that carbonate copper complexes are not toxic, the anionic hydroxy-Cu complexes have a toxicity of 15-18 % compared with free Cu ion and cationic/neutral hydroxy complexes are responsible for 60-70 % of the toxicity.

Stouthart et. al. (1996) investigated the toxicity of copper to the common carp (*Cyprinus carpio*). Their results showed that decreased water pH leads to an increased Cu toxicity which can be explained by higher concentrations of cupric ion. The results support the general view that Cu-carbonates and Cu-hydroxides (pH > 7) although potentially toxic, are hardly available for uptake by fish.

Copper toxicity to several aquatic species has been reported to be negatively correlated with hardness, but other reports indicate little or no effect (Erickson et. al., 1996). For instance, Lauren and McDonald (1986) found no effect of hardness on short-term lethality of copper to juvenile rainbow trout. The effects of hardness on copper toxicity might reflect competition between hardness ions (e.g. Ca^{2+} , Mg^{2+}) and copper for binding sites on the gill surfaces of fish (Erickson et.al., 1996).

Copper toxicity to rainbow trout has been found to decrease with increasing pH. However, other reports indicate that pH is not as important as alkalinity, because when alkalinity is increased, maintaining a constant pH, copper toxicity has been reported to decrease (Erickson et. al., 1996). Borgmann (1983) and French and Hunt (1987) concluded that copper toxicity increases with pH on the

basis of cupric ion toxicity, which may be due either to hydroxide complexes being toxic, or to antagonistic effects between copper and hydrogen ion (Erickson et. al., 1996). Lauren and McDonald (1986) however, concluded that cupric ion and copper hydroxy complexes, but not copper carbonates are toxic to fish (Erickson et. al., 1996).

In general the most toxic inorganic forms of copper are believed to be Cu^{2+} and CuOH^+ . Magnuson et al. (1979) reported that $[\text{Cu}_2(\text{OH})_2]^{2+}$ is also toxic in some cases. Furthermore Cowan et al. (1986) performed a statistical analysis of the copper toxicity literature and concluded that hydroxide species, but not carbonate species, contribute to the aquatic toxicity of copper (Allen and Hanson, 1996).

There is therefore no doubt about the toxicity of the cupric ion. Likewise copper-hydroxy complexes are generally reported to be toxic to fish. With few exceptions however, the presence of ligands will decrease copper toxicity. This also holds for increasing alkalinity but there is still some dispute whether the pH increase itself will decrease toxicity because of antagonistic effects between copper and hydroxide ion or because of the non-toxic nature of copper carbonates.

4.4.3. Zinc

Allen et.al (1980) studied the influence of Zn and complexing agents on algal growth and found a good correlation with free zinc ion (Allen et.al., 1980).

The toxicology of zinc has not been as thoroughly investigated as that of copper. However, zinc has, for instance, been known to induce premature hatching in common carp (*Cyprinus carpio*) (Stouthart et. al., 1996).

In hard or humus rich water , zinc toxicity is moderated and a greater concentration of zinc can be tolerated (Morrison and Johansson, 1992). Consequently rainbow trout survives longer in hard water.

4.4.4. Cadmium

In general cadmium toxicity is associated with the free cadmium ion. However, in studies on the uptake of cadmium by the mussel *Mytilus edulis* (George and Coombs, 1977) it was observed that the addition of ligands such as humic and alginic acids actually increased the metal content in the tissue. Apparently the metal was not transported across the cell membrane barriers as a simple ionic species but was first complexed to ligands either in the cell membranes or that the ligands carried the metal across the membranes (Salomons and Förstner, 1987).

The concentration of free cadmium ion has been found to decrease with increasing chlorinity with a resulting decrease in toxicity to the marine shrimp *Palaemonetes pugio* (Salomons and Förstner, 1987).

In fish cadmium is transferred through the gills and taken up by the olfactory system (Rouleau et al, 1995). Cadmium is known to induce premature hatching in common carp (Stouthart et. al., 1996).

4.5. UV-B radiation and copper (I).

4.5.1. Photolysis

For light to cause chemical reactions in surface waters, its energy must be absorbed by the chemicals in the water. Photolysis of chemicals in surface waters depends on both the intensity and wavelength spectrum of light. There are two types of photolysis, direct photolysis and indirect photolysis. In the former process a chemical absorbs light energy, becomes electronically excited and subsequently changes its form whereas in indirect photolysis excited molecules which act as chromophores transfer energy, electrons or hydrogen ions to another molecule. Photolysis in daylight is primarily due to the blue or ultraviolet fraction of the spectrum because of the higher energies associated with shorter wavelengths (Hemond and Fechner,1994).

Indirect photolysis occurs when highly reactive oxygen-containing species are formed in the presence of light, and subsequently attack and degrade chemical compounds. For example, the hydroxyl radical, OH^* , is formed in a two-step process; an organic chromophore absorbs light and reacts with water to form hydrogen peroxide (H_2O_2); H_2O_2 in turn can break into two hydroxyl radicals upon absorption of a photon of sufficient energy. OH^* is present at levels of about 10^{-17} M in many illuminated surface waters and it is an exceedingly powerful oxidant (Hemond and Fechner, 1994).

Dissolved organic carbon (DOC), is typically a complex yellow-brown mixture of organic chemicals originating primarily from decaying and exuded plant material. DOC is measured as the total concentration of organically bound carbon, and ranges from less than 1 mg/liter to several tens of milligrams per liter in natural waters DOC is significant as a source of organic carbon to bacteria, as an absorber of light, as a natural acid, and as a complexing agent that binds with metal ions to form metal-organic complexes (Hemond and Fechner, 1994).

Potentially harmful intensities of UV-B radiation can reach depths of several meters in clear freshwater lakes (Schindler et. al., 1996). The penetration of UV-B in boreal lakes is known to be a function of the concentration of dissolved organic carbon, DOC (see figure 17).

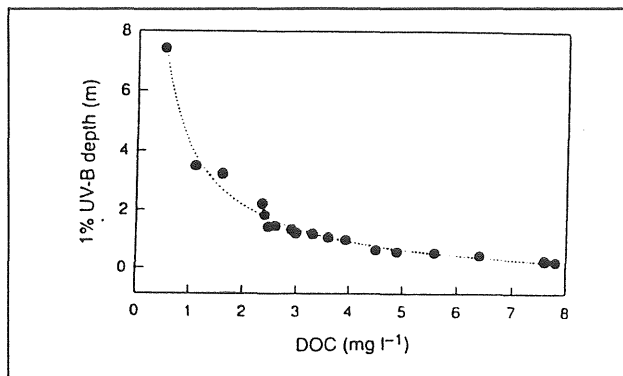


Figure 17. The relationship between measured DOC concentration and the depth of the UV-B isopleth. The dotted line represents the equation: $1\% \text{ UV-B} = 5,173(\text{DOC})^{-0.706} - 1.029$. $r^2 = 0,98$ (from Schindler et.al., 1996).

In most boreal lakes, DOC concentrations of several milligrams per litre are sufficient to provide an effective shield against ultraviolet radiation for aquatic organisms. But UV-B penetration increases exponentially as DOC declines (Schindler et. al., 1996). Low DOC lakes are common in arctic, alpine and subalpine regions, where concentrations less than 1 mg/L are common. In clear oligotrophic lakes, the possible decreases in DOC caused by climate warming should be of much more concern with respect to UV-B exposure than depletion of stratospheric ozone (Schindler et. al.,1996).

DOC reacts with UV-B radiation to form a number of chemically reactive and biologically toxic chemicals, including hydrogen peroxide, hydroxide radicals, carbon monoxide and superoxides, destroying and modifying DOC in the process.

Photoreduction has been suggested as a mechanism that transforms Cu(II) into Cu(I) (Morrison and Glazewski, 1996). Chloride and the amount of dissolved oxygen also significantly affect Cu (I) concentrations (Morrison and Glazewski, 1996). Thus, chloride binds strongly to Cu(I) which explains the presence of Cu(I) in seawater, while low dissolved oxygen concentrations in freshwater prevent Cu(I) from reoxidizing to Cu(II).

The reoxidation rate of Cu(I) to Cu(II) by peroxide is known to increase in the presence of HCO_3^- . Sharma and Millero (1989) provide half-lives for oxygen-mediated and peroxide-mediated oxidation of Cu(I) as 4 minutes and 525 minutes, respectively, in seawater. However, under typical freshwater chloride concentrations the oxygen-mediated reaction is very rapid.

5. Methodology

5.1. Introduction

The sampling and some of the measurements took place in Iceland during the summer of 1996. The objective of the study was, as stated before, both to examine total metal concentrations and metal speciation in geothermal wastewater from the *Nesjavellir* power plant and also to examine metal speciation in clear oligotrophic subarctic lake environment, particularly with regard to the influence of UV-B radiation on copper speciation.

Laboratory facilities were available at the Department of Food and Pollution Control in Reykjavík, Iceland and assistance during sampling was also given by the Reykjavík Space Heating Authorities. Trace metals had been measured at *Nesjavellir* and in lake *Thingvallavatn* before, but this was the first time any metal speciation analysis was attempted.

5.2. Sampling and storage

5.2.1. Sampling preparations

All sampling bottles and sampling equipment were thoroughly acid washed before sampling. Bottles were filled with 10% HNO₃, left to stand overnight and then rinsed carefully with nanopure water.

5.2.2. Collection and storage of samples

Sampling took place on 23rd July 1996 at *Nesjavellir*. The air temperature was 11° C. The weather was sunny with nearly cloudless skies.

Samples for bathocuproine analysis were taken directly into Pyrex 200 ml and 250 ml glass bottles with all reagents in them. 5 ml of methanol were also added to the bottles for stabilisation.

Samples for ASV and speciation analysis were collected directly into 250 ml polyethylene plastic bottles which were immediately put into a cooling box.

TOC samples were likewise collected directly into special polyethylene TOC bottles and put into a cooler. Samples for conductivity measurements were collected directly into 1 L polyethylene bottles.

Polyethylene gloves were used all the time in order to diminish the risk of sample contamination.

After collection the samples were taken directly to the laboratory at the Department of Food and Pollution Control, Reykjavík, Iceland. The ASV/speciation samples were frozen directly to be analysed later at Chalmers University of Technology. The TOC samples were filtered on the day after sampling through a Whatman GF/C filter and then frozen. The bathocuproine samples were also filtered through a GF/C Whatman filter and stored at 4°C until analysis. Samples for conductivity measurement were kept in the dark at 4°C until the day after sampling.

5.2.3. Description of sampling locations

Location 1. Markargjá

This is a small inlet on the south side of lake *Thingvallavatn* (see figure 18). There is a pier into the lake and a boathouse nearby. On the day of sampling there was visual evidence of green *Ulothrix* algae on the lake bottom. The water was otherwise clear. There are no warm springs here.

Samples taken: 960723-1a 960723-1b 960723-1c 960723-1d 960723-1e

Location 2. Eldvík

This is a small bay in lake *Thingvallavatn*. There is a summerhouse and a boathouse nearby. Warm springs flow into the lake. There is a lot of green *Ulothrix* algae present.

Samples taken: 960723-2a 960723-2b 960723-2c
960723-2d 960723-2e

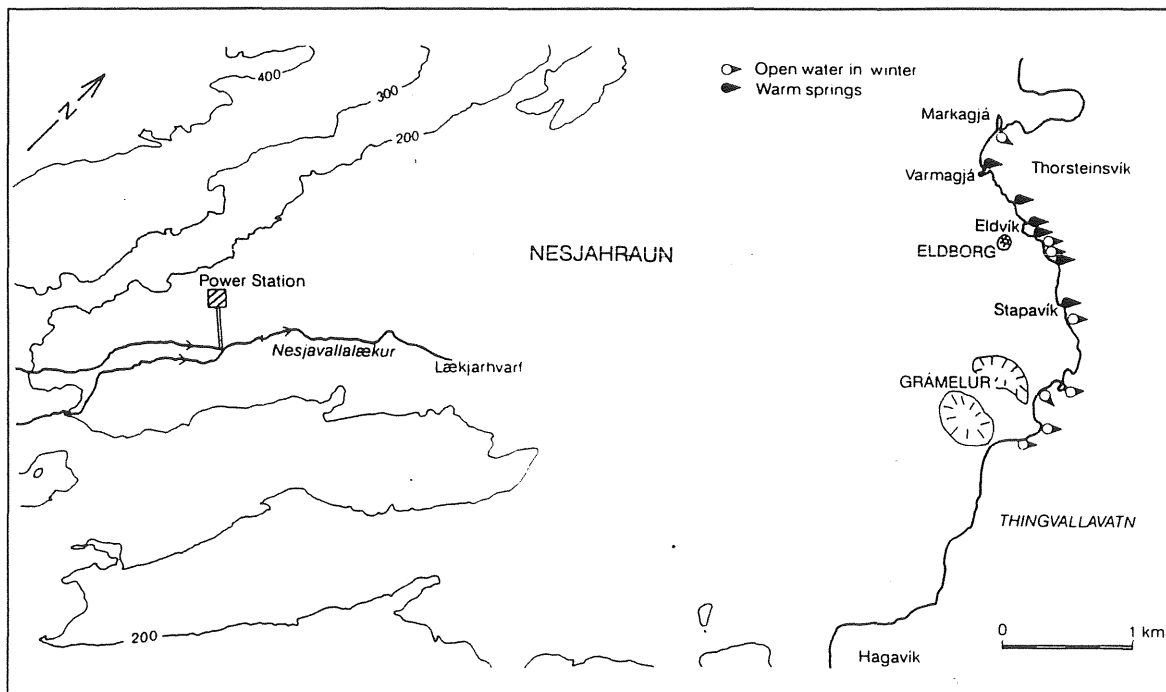


Figure 18. Map showing sampling locations in the Nesjavellir area (Ólafsson, 1992).

Location 3. Varmagjá

This is a small inlet where two plastic boats are situated during the summer months. The samples were taken where the warm springs enter the lake. *Ulothrix* algae were present.

Samples taken: 960723-3a 960723-3b 960723-3c
960723-3d 960723-3e

Table 8 Absolute Detection Limits (ng) (Fergusson,1990).

Method	Detection limit
X-ray fluorescence	1
Colorimetry	$1 - 10^{-2}$
Anodic stripping voltammetry	$1 - 10^{-2}$
D.C. Arc emission	$1 - 10^{-2}$
Fluorimetry	$0.1 - 10^{-2}$
AAS flame	$0.1 - 10^{-3}$
AAS electrothermal	$10^{-3} - 10^{-5}$
Mass spectrometry	$10^{-3} - 10^{-6}$
Neutron activation analysis	$10^{-6} - 10^{-8}$

5.3.1.2. The risk of contamination

Contamination of samples can occur at each stage in an analytical study, regardless of the analytical method used. This is especially relevant when analyte concentrations are as low as in this case. It is therefore necessary to acid wash carefully both sampling equipment and analytical apparatus used. The laboratory should be as clean as possible, especially with regard to aerosol or dust. Reagents used in metal analysis also have to be of the highest quality.

5.3.2. The bathocuproine spectrophotometric method for copper

The bathocuproine analysis method for copper involves a pre-concentration step on a *Varian Empore TM Octadecyl C18* extraction disc and selective elution into methanol:water (90:10). The resulting sample is then analysed in a spectrophotometer at $\lambda = 484$ nm.

This method has been found to be highly selective for Cu (I) (Morrison and Glazewski, 1996). Bathocuproine disulfonic acid (see figure 19) forms a water-soluble red chelate with copper (I), CuL_2^{3-} , in the pH range 3.5-8.0 with an optimum at pH 4.3-4.5 (West and Nürnberg, 1988). Ethylenediamine ($H_2NCH_2CH_2NH_2$) is usually added to the samples to stabilise Cu(II) and prevent overestimation of sample Cu (I) concentrations (Morrison and Glazewski, 1996).

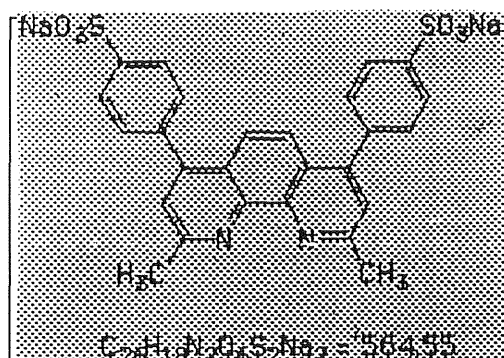


Figure 19 Bathocuproine disulfonic acid ($C_{25}H_{18}N_2O_6S_2Na_2$). (retrieved from: www.dojindo.co.jp/products/info/202/TEXT/BATHOCUS.html)

When measuring both Cu (I) and Cu (II) (bathocuproine total copper) it is first necessary to reduce Cu (II) to Cu (I) with hydroxylamine hydrochloride (H₄CINO). This reaction is highly selective in the presence of citrate (Morrison and Glazewski, 1996).

In general, interferences in copper analysis with bathocuproine can occur if large amounts of substances such as Co (II), Cr (III), Ag, Cd, Hg, Sn, Sb ,CN⁻, SCN⁻, EDTA, oxalate and persulfate are present (West and Nürnberg,1988).

5.3.2.1. Procedure

5.3.2.1.1. Sampling

The samples were collected directly into 200 and 250 ml Pyrex glass bottles containing the reagents shown in table 9.

Table 9 . Reagents added to samples.

	Cu (I) 250 ml sample	Cu (I) and Cu (II) 200 ml sample
Bathocuproinedisulfonic acid (1.8×10^{-3} M)	2.5 ml	2 ml
Sodium citrate buffer (1.0 M)	2.5 ml	2 ml
Ethylenediamine (10 ⁻² M)	5 ml	
Hydroxylamine hydrochloride (1.4 M)		15 ml
Methanol (100%)	5 ml	5 ml

5.3.2.1.2. Analysis

First the C18 disk was placed in a Millipore filter apparatus and conditioned with 5 ml of 100% methanol. This activated the C18 chains. Then 200/250 ml of sample were with added reagents was filtered through. After that the C18 disk was eluted three times with 4 ml of 90% methanol and the eluate diluted to 15 ml. Between samples the disk was cleaned with 20% methanol and nanopure water.

Finally, all samples were measured for absorbance at 484 nm in a 1 cm cell in a Cecil Ce2020 spectrophotometer (see table 10). Pure 90% methanol was used to zero the spectrophotometer.

5.3.3. Visible Absorption Spectroscopy

Visible spectroscopic methods measure light absorption in accordance with Beer's law (Skoog and Leary, 1992):

Beer's law:

$$\log P_0/P = \epsilon bc = A$$

where P_0 = power of incoming radiation (Joules),
 P = power of radiation after absorption has taken place (Joules),
 ϵ = molar absorptivity (L/mol/cm)
 b = length of cell (in centimeters)
 c = concentration (moles/L)
 A = absorbance

Sometimes the light transmittance is measured instead of absorbance where transmittance is defined as the fraction of incident radiation transmitted by the solution ($T = P/P_0$).

Beer's law is successful in the describing adsorption behaviour of dilute solutions only ($c < 0.01$ M). At higher concentrations the relationship between absorption and concentration ceases to be linear.

When measuring absorbance in the visible region the beam from a light source (usually a tungsten lamp) passes through the sample directly into the wavelength selector. Ideally the output would be radiation of a single wavelength or frequency. However, no existing wavelength selectors can achieve this (Skoog and Leary, 1992).

For visible spectroscopy the wavelength selector most commonly used is an absorption filter, which functions by absorbing certain portions of the spectrum. Filters that provide the narrowest bandwidths absorb a significant fraction of the desired radiation, and may have a transmittance of 10% or less at their band peaks (Skoog and Leary, 1992).

For many spectroscopic methods it is desirable to scan the spectrum. This can be achieved with monochromators. Most of them are based on reflection gratings instead of prisms as they provide better wavelength separation.

Photoelectric detectors have an active surface, which is capable of absorbing radiation. Many detectors exhibit a small, constant response, known as dark current, in the absence of radiation:

$$S = kP + k_d$$

where S = electrical response, P is radiant power and k_d is dark current.

Because of this, spectrophotometric instruments are usually equipped with a compensating circuit which reduces k_d to zero.

Table 10 Ce2020 spectrophotometer specifications.

Optical system	Littrow monochromator with 200L/m holographic grating
Wavelength range	190-1000 nm
Optical bandwidth	4 nm
Photometric accuracy	+/- 1% or 0.005A whichever is greater

The accuracy and precision of spectrophotometric analyses are often limited by the uncertainties or noise associated with the instruments (see table 10). The three steps of spectrophotometric analysis, 0%T adjustment, 100% T adjustment and measurement of %T with the sample in the radiation path all contribute to this net uncertainty. An indeterminate uncertainty of 0.3% T is typical of many spectrophotometers. Concentration error of the bathocuproine spectrophotometric method for copper can therefore be expected to be 1-2%.

5.3.4. Voltammetric techniques

In voltammetry, information about the analyte is derived from the measurement of current as a function of applied potential obtained under conditions that encourage polarisation of an indicator, or a working electrode. Historically the field of voltammetry developed from polarography, which was discovered by the Czech chemist Jaroslav Heyrovsky in the early 1920's (Skoog and Leary, 1992).

In voltammetric analysis a dropping mercury electrode (DME) is most frequently used (see figure 20). This electrode has the advantage of the drops being reproducibly formed so that currents are also reproducible. In addition many metal ions are reversibly reduced to amalgams at the surface of the electrode, which simplifies the chemistry (Skoog and Leary, 1992). Solutions can thus be partially electrolysed many times without measureable reduction in concentration (Bagotzky, 1993).

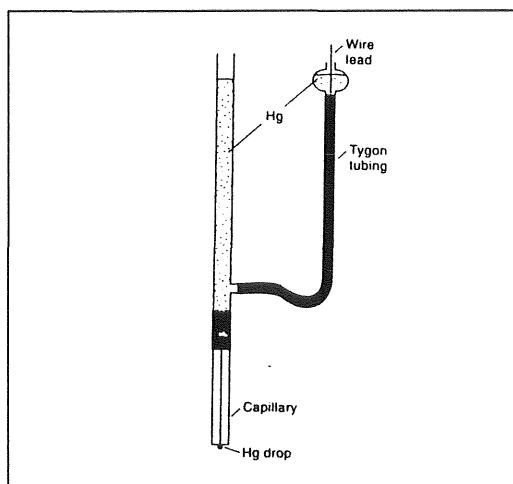


Figure 20. A typical dropping mercury electrode (Skoog and Leary, 1990).

There are however, some disadvantages. They include interference from oxygen, a non-faradaic residual current and the fact that at potentials greater than +0.4 V, formation of Hg (I) occurs, producing a wave that masks the curves of other species (Skoog and Leary,1992).

Polarographic waves show development of a faradaic current signal superimposed on the residual non-faradaic current. Mean diffusion currents are expressed in the Ilkovic' equation:

$$I_d = 607 n D^{1/2} m^{2/3} t^{1/6} C$$

where

n =	number of electrons transferred in the electrode reaction,
D =	diffusion coefficient of the metal in question (cm ² /sec),
m =	rate of flow of Hg (mg/sec)
t =	drop time (sec)
C =	the metal concentration (mmol/dm ³)

It is therefore possible to use diffusion controlled polarographic waves for quantitative analysis. However, in order to minimize the effect of other mass transfer processes, such as migration, a supporting electrolyte has to be used. Furthermore the diffusion layer, δ , at the electrode surface, where mass transfer takes place by diffusion alone, is made as thin as possible by stirring the solution rapidly. In this way diffusion-controlled currents can be realized shortly after application of voltage (Skoog and Leary,1991).

5.3.5. Differential Pulse Anodic Stripping Voltammetry (DPASV)

This method differs from the other voltammetric methods in the principle of analysis. The analysis is performed in a cell which contains a mercury drop or film electrode. A negative voltage is applied and the metals are reduced with the formation of an amalgam at the electrode. In this way the metals are concentrated in the mercury electrode. The amount of metal removed from the solution by this step is about 0.25% of the total content (Salomons and Förstner, 1984). After this the voltage is increased gradually and as the voltage approaches the oxidation potential of one of the metals present, the ions of the metal pass into solution and the current increases. When this happens it is possible to construct an anodic stripping voltammogram (see figure 21).

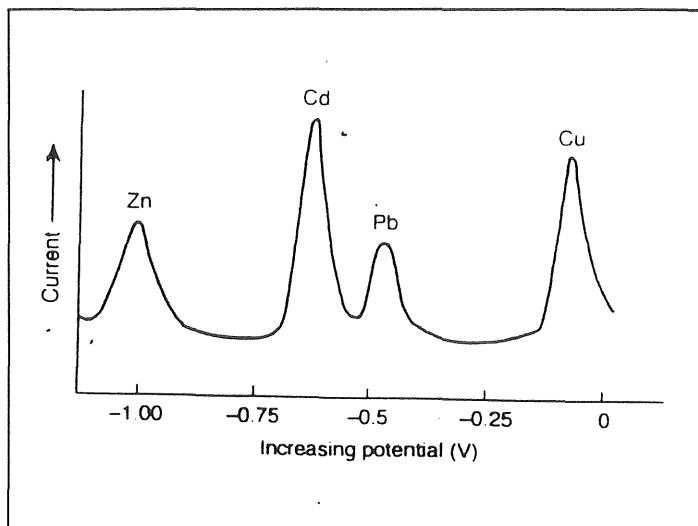


Figure 21. A typical anodic stripping voltammogram for Zn, Cu, Pb and Cd (Reeve, 1994).

The position and height of the current maximum in the voltammogram characterize the nature and total amount of the metal in question. The concentration measured by ASV corresponds to the electroreducible metal species, the aquo ion and those metal complexes which are in sufficiently labile equilibrium during the time scale of the measurement (See figure 22) (Salomons and Förstner, 1984).

Batley (1983) found that at a pH around 5 all simple ionic species can be detected by ASV (Salomons and Förstner, 1984), whereas at higher pH values ionic species like hydroxy carbonates of lead and cadmium are electrochemically inactive. At very low pH, on the other hand, organic complexes may dissociate.

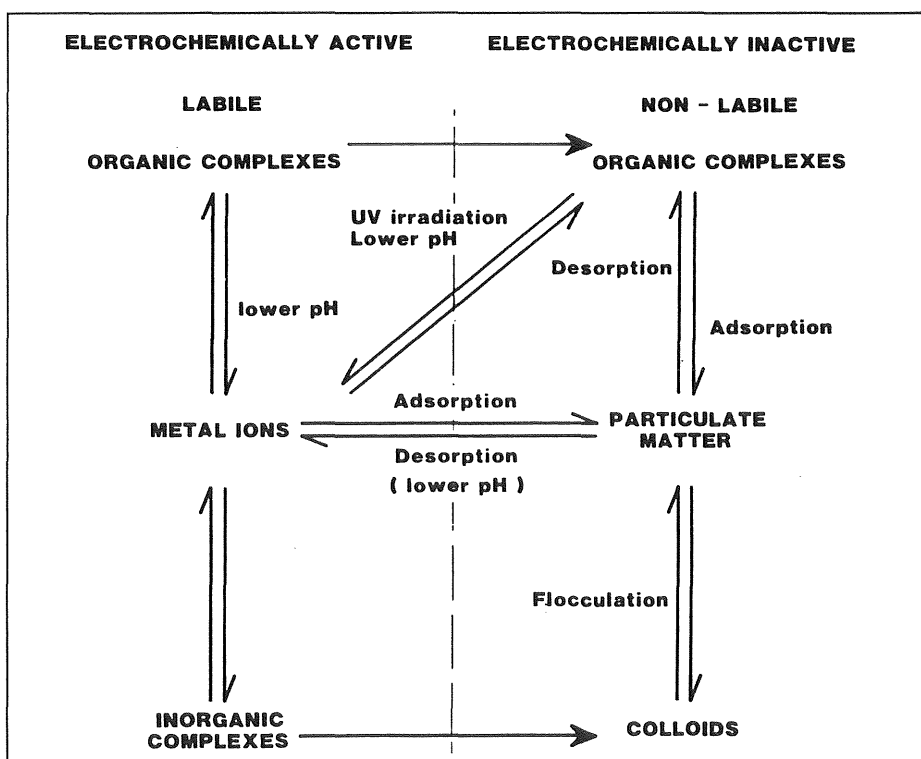


Figure 22. Interrelationships between various metal species in water and their relationship to electroanalytical methods (Salomons and Förstner, 1984).

Anodic stripping voltammetry is an extremely sensitive technique; in some cases metal concentrations can be detected to concentrations of 10^{-9} M or even less (Bagotzky, 1993).

Small amounts of humic substances however, can adsorb to the Hg electrode and create interference. Thus DPASV can give rise to organic adsorption-desorption peaks, which can be misinterpreted as metal ion peaks, especially in the case of lead and cadmium. This kind of trouble can be avoided by UV-irradiating the samples (Cleven et.al.,1987).

Stripping analysis can also be complicated by the formation of intermetallic compounds at the electrode surface. The formation of an intermetallic compound results in a decrease or an increase of the height of the metal stripping peak. This kind of interference can be minimized by using Differential Pulse ASV, because there the deposition periods can be kept as short as possible (Cleven et.al.,1987).

Finally it must be kept in mind that the ASV method is a dynamic method which disturbs the natural ion equilibria in the sample while measuring. Thus it cannot directly measure the "natural" metal speciation. It can however be used to estimate the bioavailable fraction of metal which can then be correlated with metal toxicity (Florence, 1989).

5.3.5.1. Procedure

Electrochemically available metals were measured at a mercury drop electrode (DME) through differential pulse anodic stripping voltammetry (DPASV) in 0.03 M sodium acetate at pH 4.7. Measurements were made on a Metrohm 646 VA processor. Deposition time and initial potential were 180-1200 sec and -1.2 V (vs. Ag/AgCl), respectively. The samples were deaerated for 5 minutes before DPASV.

Total metal content was measured by DPASV after photolytic oxidation for 3 hours of 20 ml sample in a Metrohm UV-digester. 50 μ l of H_2O_2 and 20 μ l of concentrated suprapur HNO_3 were added before digestion in order to dissolve all metal-organic complexes in the sample.

5.3.6. The Chelex ion-exchange resin

Samples 1-6d were passed through an iminodiacetate chelating resin (Chelex-100[®]) and then analysed with ASV. Chelex-100[®] has been used successfully in metal speciation studies (Batley and Florence, 1976). It distinguishes between exchangeable (labile) and non-exchangeable metal forms. The exchangeable metal includes the free aquo ion, exchangeable complexes, metal bound in kinetically labile monomeric complexes weaker than the metal-Chelex complex, plus any cationic polynuclear species which have an ionic diameter less than the resin pore-size. Non-exchangeable forms will include: strong or kinetically inert complexes, colloidal metal species, and metal absorbed on, or occluded within inorganic or organic colloidal material (Cleven et.al., 1987).

In the ion-exchange method the sample is passed through a column packed with ion-exchange medium. The fraction not removed by the Chelex resin is called the "bound fraction" and the fraction removed by the resin the "exchangeable fraction". Calculations have shown that all ligands with formation constants ($\log K$) less than about 11 are stripped off their metals. Those substances which keep the metals bound to them are probably non-ion-exchangeable fractions, which exist as colloids and inorganic forms (Salomons and Förstner, 1984).

Figura et al. (1979) compared the lability of trace metal ions (Cu^{2+} , Cd^{2+} and Pb^{2+}) measured by ASV with those by the Chelex-100 resin method. In this study, the labile fractions determined by the Chelex-100 were larger than the fractions determined by ASV. As iminodiacetate groups have a very strong affinity for divalent heavy-metal ions a dissolution of certain metal complexes may take place (Fukushima and Taga, 1993).

6. Results

6.1. General chemical characteristics.

Temperature was measured in the field. pH, CO₂ and H₂S were measured by the Reykjavík Space Heating Authorities (Hitaveita Reykjavíkur). Conductivity was measured with an Orion Model 120 Conductivity Meter at the laboratory of the Department of Pollution Control (Hollustuvernd Ríkisins). Both TOC and DOC were analysed at Chalmers University of Technology (see table 11).

Table 11 Temperature, pH, H₂S, CO₂, TOC and DOC.

Location	Temp °C	pH	CO ₂ mg/L	H ₂ S mg/L	Cond. µS/cm	TOC mg/L	DOC mg/L
Markagjá	4.5	8.01	9.1	x	83.2	6.23	0.72
Eldvík	14	7.72	51.7	x	239	13.52	1.36
Varmagjá	12.3	8.93	38.8	x	220	17.06	3.98
Laekjarhvarf	32.4	9.40	31.9	x	523	14.78	4.44
Separated w.	x	8.74	30.3	61.3	115	x	x
Cooled gth.w.	x	4.44	253	265	802	x	x

X = not measured

6.2. Trace metals

Zinc, lead and cadmium were analysed with ASV at Chalmers University of Technology. Copper was measured both with ASV at Chalmers and also with C18 bathocuproine method at the Department of Pollution Control, Reykjavík (see tables 12-15).

Table 12 Results from zinc speciation analysis (µg/L).

Location	ASV-Zn	Chelex Zn	Total Zn
Markagjá	2.10	4.10	4.2
Eldvík	0.71	1.54	1.7
Varmagjá	1.75	2.77	3.0
Laekjarhvarf	0.23	2.51	2.9
Separated w.	0.48	2.21	2.8
Cooled gth.w.	0.02	1.01	1.2

BDL = below detection limit. Total zinc was measured with DPASV.

Table 13 Results from copper speciation analysis (µg/L).

Location	Cu (I)	ASV-Cu	Chelex Cu	Total Cu
Markagjá	0.54	0.09	0.99	1.0
Eldvík	1.52	0.19	0.19	0.8
Varmagjá	0.54	0.15	0.81	0.6
Laekjarhvarf	0.89	2.02	BDL	1.8
Separated w.	0.36	0.02	BDL	0.4
Cooled gth.w.	0.27	BDL	BDL	0.5

BDL = below detection limit. Total Cu represents an average value from both DPASV and the bathocuproine analytical method for copper.

Table 14. Results from lead speciation analysis ($\mu\text{g/L}$).

Location	ASV-Pb	Chelex Pb	Total Pb
Markagjá	0.01	0.02	0.4
Eldvík	0.18	0.02	0.8
Varmagjá	0.01	0.69	1.0
Laekjarhvarf	0.32	0.19	0.5
Separated w.	0.51	BDL	0.6
Cooled gth.w.	0.73	BDL	4.2

BDL = below detection limit. Total Pb was measured with DPASV.

Table 15. Results from cadmium speciation analysis ($\mu\text{g/L}$).

Location	ASV-Cd	Chelex Cd	Total Cd
Markagjá	0.07	0.06	0.2
Eldvík	BDL	BDL	BDL
Varmagjá	0.32	BDL	0.04
Laekjarhvarf	0.11	0.23	0.4
Separated w.	BDL	BDL	BDL
Cooled gth.w.	0.88	BDL	0.11

BDL = below detection limit. Total Cd was measured with DPASV.

7 Discussion

7.1. The speciation of zinc, lead, cadmium and copper.

7.1.1. Zinc

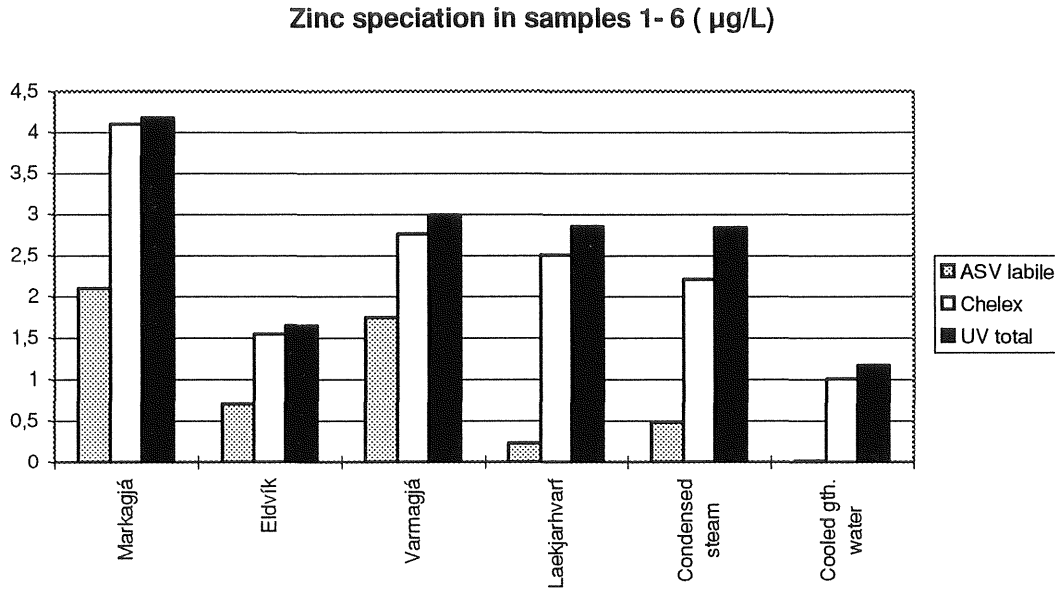


Figure 23 The speciation of zinc. Some of the values are averages representing more than one measurement.

In samples 1-5 where alkalinity is low and pH 7.72 - 9.40, zinc will be present in the form of zinc hydroxides such as $Zn(OH)_2$, zinc carbonate ($ZnCO_3$) or as ZnS depending on the alkalinity and sulfur content of the sample. In sample 6 (cooled geothermal water) where pH is 4.4, ZnS is the most probable metal species.

The highest total zinc values were found in *Markargjá*, 4.2 µg/L. *Markagjá* is totally unaffected by geothermal water from the power plant. The highest Chelex and ASV labile values are also found in *Markagjá* indicating that the geothermal water in fact lowers the amount of bioavailable zinc.

There is much more CO_2 in the geothermally affected water than in the natural lake water (see table 11). The TOC and DOC is also higher indicating the presence of humic substances. Therefore zinc will more readily bind to humics and form zinc carbonates in the geothermally affected water. The presence of excess sulfide in the geothermal water entering the lake could also lead to some local zinc sulfide precipitation, even though zinc sulfides are not stable under oxidizing conditions.

In the cooled geothermal water however, the pH is 4.4, H₂S is 265 mg/L, and CO₂ is 253 mg/L. Under those conditions zinc sulfides will certainly form which probably explains the absence of ASV-labile zinc.

Ólafsson (1992) measured a zinc concentration of 1.1 µg/L at *Varmagjá*, 2.9 µg/L at *Markagjá* and 0.3 µg/L at *Eldvík* in 1991. He used solvent extraction followed by atomic absorption spectrometry (Ólafsson, 1992). The values measured now with DPASV are higher, 3.0 µg/L at *Varmagjá*, 4.2 µg/L at *Markagjá* and 1.7 µg/L at *Eldvík*. In both cases however, *Markagjá* has the highest zinc level, followed by *Varmagjá* and then *Eldvík*.

7.1.2. Cadmium

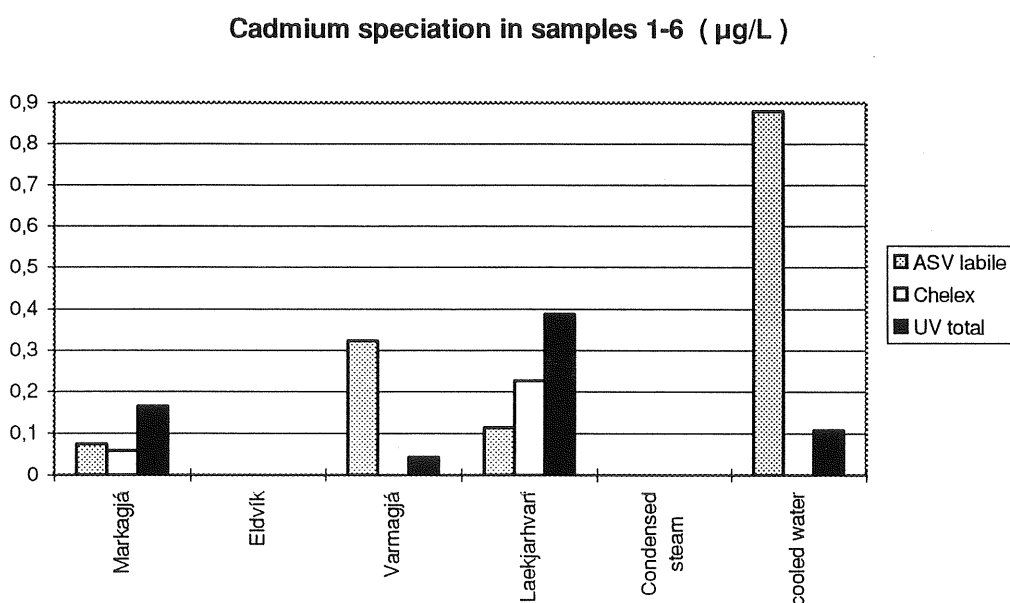


Figure 24 The speciation of cadmium.

Cadmium is present in very low concentrations, making its detection both difficult and subject to uncertainties. The total cadmium concentration is highest at *Laekjarhvarf*, while a disproportionately high ASV-labile cadmium peak appears in the geothermal cooled water. This large ASV-labile peak is probably a ghost-peak and not representative of the real cadmium content of the sample. A similar problem was encountered in *Varmagjá*.

The pH of all the samples ranges from 7.7 to 9.4 (excluding the cooled geothermal water - see table 11). At pH above 8 cadmium is in the form of cadmium carbonate except in very alkaline solutions (see figure 12). This means that cadmium carbonate should be the dominant cadmium species in samples 1-5. Below pH 8 however, cadmium will be present either in the form of the free cadmium ion or in the form of cadmium sulfide. In the cooled geothermal water (sample 6) cadmium sulfide (CdS) is likely to form and as it is very insoluble, cadmium will be precipitated out of the water.

There seems to be a slight tendency for cadmium to be higher in the geothermally affected water compared to *Markagjá*. However, in this case concentrations are too low for any certain conclusions to be reached.

Ólafsson (1992) measured 0.04 µg/L Cd at *Varmagjá*, 0.11 µg/L Cd at *Markagjá* and 0.06 µg/L Cd at *Eldvík* in 1991. In the present study, ASV-total cadmium was found to be 0.17 µg/L at *Markagjá* and 0.04 µg/L at *Varmagjá*. This is similar and does not indicate any change.

7.1.3. Lead

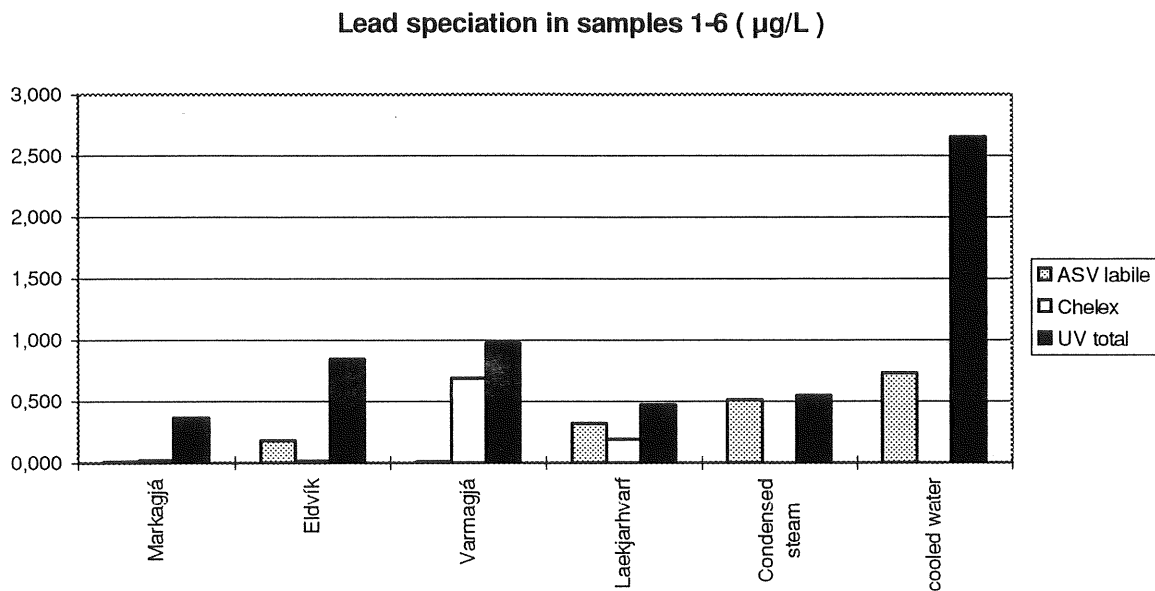


Figure 25 The speciation of lead.

In samples 1-5 where alkalinity is low and pH 7.72 - 9.40 lead will be present mainly in the forms of $PbOH^+$ and $Pb(OH)_2$ along with some $PbCO_3$. However, where sulfur content is high, insoluble $PbS(s)$ will precipitate. Thus in sample 6 (cooled geothermal water), where pH is 4.4 and sulfur high the Pb^{2+} ion may be present along with PbS .

Total lead was found to be lowest in *Markagjá*. Furthermore almost no ASV-labile and Chelex lead was detected in *Markagjá*. This means that the lead concentrations in unaffected lake water are very low. However, in the geothermally affected water, total lead contents are higher, especially in *Eldvík* and *Varmagjá*. Total lead in the geothermal cooled water is also high. Furthermore the proportion of ASV-labile lead in condensed steam from the separation station is extremely high, 93 %, which could indicate the presence of free lead ion and soluble lead complexes. However, as the Chelex-exchangeable fraction is low it is possible that the ASV-labile peak represents a colloidal but labile PbS species.

The results therefore show some lead pollution in all locations affected by geothermal water. The high amount of total lead present in the cooled geothermal water from the separation station is a matter of some concern.

Ólafsson (1992) found lead to be 0.03 µg/L at *Varmagjá*, 0.07 µg/L at *Markagjá* and 0.10 µg/L at *Eldvík* in 1991. The values obtained with DPASV are significantly higher, with 0.97 µg/L at *Varmagjá*, 0.37 µg/L at *Markagjá* and 0.84 µg/L at *Eldvík*. Furthermore the lead concentrations are now clearly lowest in *Markagjá*.

Lead in drillhole liquid discharge from the power station was low in 1991, measured at 0.09 µg/L. The values determined in the present study in the condensed steam and cooled geothermal water from the separation station are much higher, 0.55 µg/L and 2.66 µg/L respectively. Therefore lead seems to have increased significantly since 1991 both in water coming from the separation station and in *Varmagjá* and *Eldvík*.

Jónsson (1995) measured trace metals in both benthivorous arctic charr and in the gastropod *Lymnaea peregra*. Unusually high lead content 1.8 µg/g was found in *Lymnaea peregra* at *Varmagjá*.

This is in agreement with the DPASV results, which show higher total lead content at *Varmagjá* than at *Markagjá*, *Eldvík* and *Laekjarhvarf*. Chelex exchangeable lead is also high at *Varmagjá* while ASV-labile lead is low. It is therefore quite possible that the high lead contents of *Lymnaea peregra* at *Varmagjá* reflect high lead concentrations in the water, although as *Lymnaea peregra* is a sediment feeding organism it would be better to measure lead concentrations directly in the sediment pore water.

7.1.4. Copper

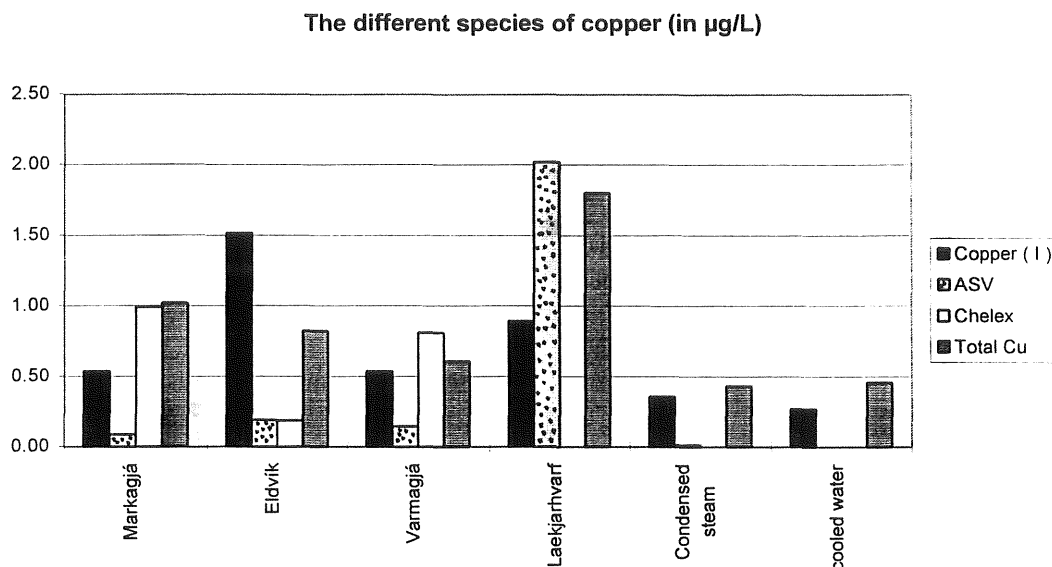


Figure 26 The speciation of copper. Values for total copper are averages of bathocuproine total copper and DPASV total copper. CuI values were obtained with bathocuproine method.

In samples 1-5 where alkalinity is low and pH 7.72 - 9.40 copper will be present in the form of copper hydroxides, such as $\text{Cu}(\text{OH})_2$, or copper carbonates, rather than in the form of the free metal ion. In sample 6, however, where the pH is 4.4 and the sulfur content is high, CuS or Cu_2S may be formed.

Both total copper and ASV-labile copper are notably highest in *Laekjarhvarf*. The pH there is 9.4, CO_2 31.9 mg/L and DOC 4.44 mg/L. At this pH carbonate and hydroxide copper complexes will be present. Also when DOC is high, copper will form copper-humic complexes. Even so, ASV-labile copper in *Laekjarhvarf* is very high.

There seems to be little copper coming from the separation station, the values in the condensed steam and cooled geothermal water are low. Furthermore copper values at *Markagjá* are higher than those at *Eldvík* and *Varmagjá*. This indicates that the copper content in the water has a natural origin, and is not influenced by the discharge of geothermal wastewater.

Ólafsson (1992) measured 1.2 µg/L copper at *Varmagjá*, 1.0 µg/L at *Markagjá* and 1.5 µg/L at *Eldvík* in 1991. The corresponding values now are 0.61 µg/L at *Varmagjá*, 1.02 µg/L at *Markagjá* and 0.82 µg/L at *Eldvík*. In this case the copper values are lower in 1996, indicating no significant change.

7.1.5. UV-B radiation, DOC and copper (I).

Schindler et. al. (1996) found a clear relationship between measured DOC concentration and the depth of the UV-B isopleth in clear freshwater lakes (see

figure 17). DOC reacts with UV-B radiation to form a number of chemically reactive chemicals such as hydrogen peroxide. Photoreduction caused by radicals created by UV-B radiation has been suggested as a mechanism that transforms Cu (II) into Cu (I) (Morrison and Glazewski, 1996). Thus high levels of UV-B radiation are believed to cause photoreduction of Cu(II) to Cu(I).

The depth to which 1% of surface light penetrates into lake *Thingvallavatn* is considered to indicate the thickness of the photic layer. Measurements in May, June, July and September 1982 showed that the photic layer varied from 22 to 30 meters. It had its minimum in spring and maximum in early summer. In late September 1976 1% of surface light could penetrate to ca. 33 m, corresponding to the epilimnic zone. These measurements show that in May the photic zone is ca. 20 m thick or between 30 and 40 m in July and 20 to 30 m in September.

In *Markagjá* where DOC is 0.72 mg/L, the depth of the UV-B isopleth according to Schindler et.al. (1996) is 5.49 meters. As *Markargjá* is not that deep it actually means that light reaches the lake bottom. In *Laekjarhvarf* however where DOC is 4.44 mg/L the UV-B depth should be 0.78 m. Considering the shallowness of the *Nesjavallalaekur* stream, light will also reach the bottom there.

Markagjá represents the unpolluted clear water of lake *Thingvallavatn*. There DOC is only 0.72 mg/L and % Cu(I) is 53%. This proportion of Cu(I) is high compared with Cu(I) measured by Morrison and Glazewski in an urban river (Morrison and Glazewski, 1996).

The high contents of Cu(I) in the urban river were caused by the inhibition of the oxidation of Cu(I) to Cu(II) through low dissolved oxygen content of the water. However, in lake *Thingvallavatn* Cu(II) is most likely constantly being reduced to Cu(I) through the impact of UV-B radiation which penetrates deeply into the clear subarctic lake. Thus Cu(I) values remain high, not because of low dissolved oxygen but because of constant exposure to UV-B radiation. The low DOC concentration in lake *Thingvallavatn* is also of interest considering the possible increase of UV-B radiation following global climatic changes foreseeable in the next century.

7.1.6. Comparison of the Bathocuproine and DPASV analytical methods for copper

The Bathocuproine spectrophotometric method for copper and the DPASV analytical method gave results for total copper which lie within the same range. However, the bathocuproine total copper is generally slightly higher than ASV total copper except in *Markagjá* where the difference is slight. It has to be kept in mind, that the bathocuproine samples were analysed immediately after sampling while the DPASV samples were frozen and stored for several weeks.

Total Copper measured with bathocuproine method and ASV respectively (in $\mu\text{g/L}$).

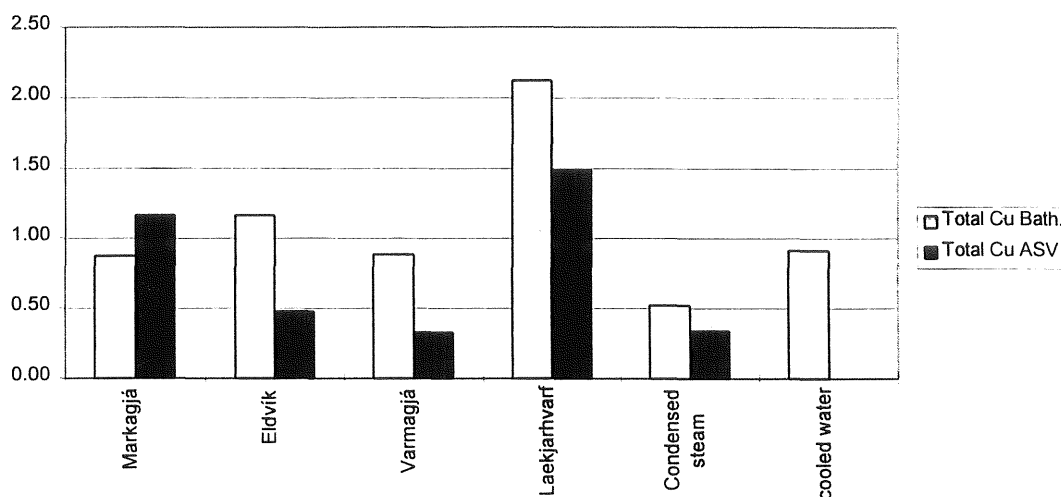


Figure 27 Graph comparing the results from the bathocuproine spectrophotometric method for copper with the results from the differential pulse anodic stripping voltammetry method.

The Bathocuproine spectrophotometric method for copper proved to be easy to use even under rather primitive circumstances. It has to be considered an advantage of this method that the only equipment really needed is a simple filter apparatus and a spectrophotometer. However, the accuracy of the method can be limited somewhat by the type of spectrophotometer available (see table 10). Also there is always a risk of contamination when working at such low metal concentrations, especially when the laboratory does not have a suitable air cleaning system (as was the case here). On the whole however, the bathocuproine method did not seem as susceptible to interferences as the DPASV method. Thus it was possible to measure a value for total copper in the cooled geothermal water, something which proved notoriously difficult with the DPASV.

DPASV is a sensitive technique and has the advantages of measuring many metals simultaneously. However, the copper peak being the last peak in the voltammogram is frequently subject to interferences which means that the peak can become skewed with a badly defined baseline (see figure 18). In some cases the peak does not appear at all. Sometimes the copper peak will become unclear because the ASV method is not able to distinguish between Cu(I) and Cu(II) which have slightly different oxidation potentials.

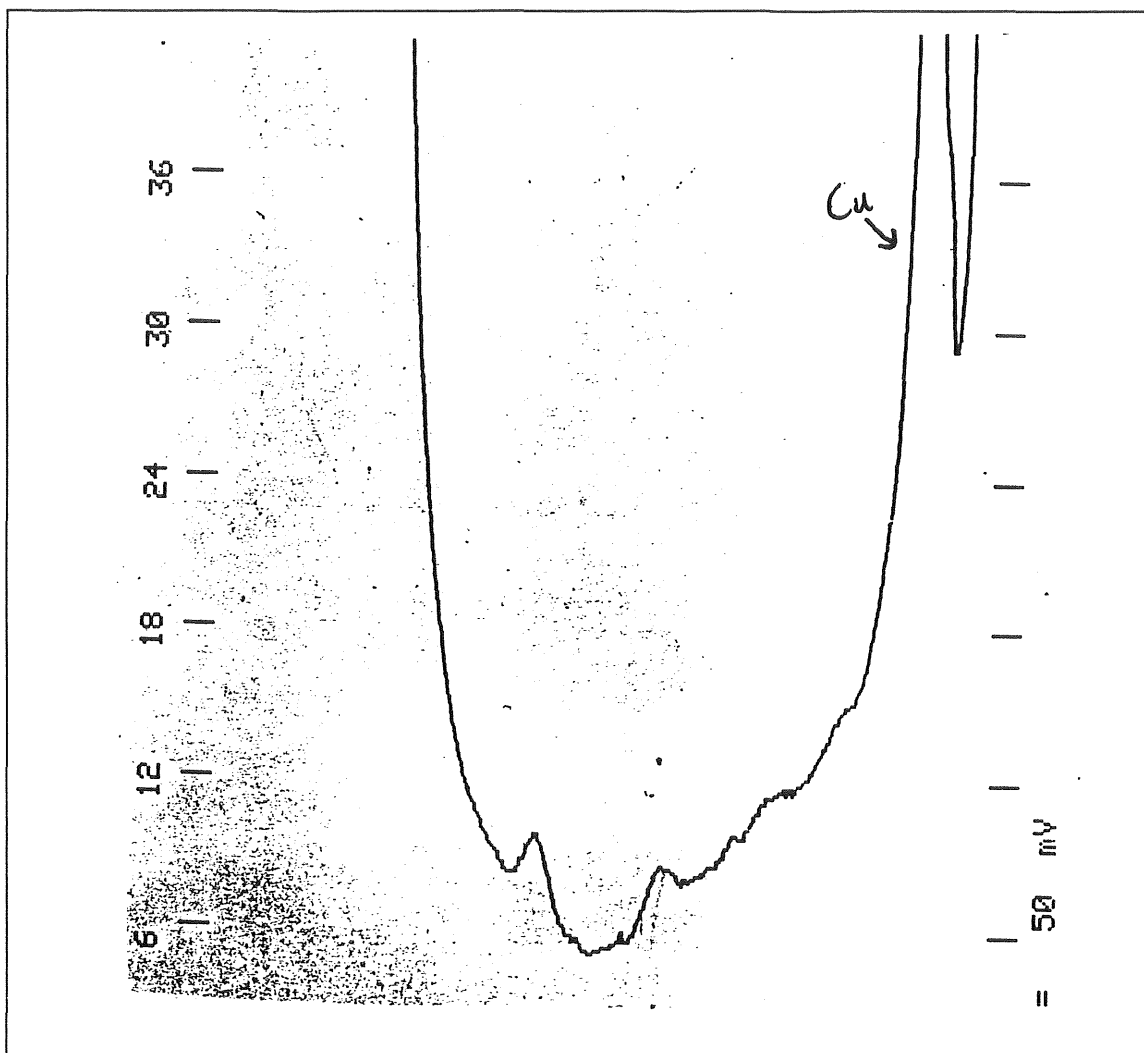


Figure 28 An example from a DPASV voltammogram where the copper peak is subject to interferences.

The sensitivity of DPASV to interferences was especially notable in condensed steam and cooled geothermal water from the separation station where the sulfur content of the sample was extremely high. Here interfering peaks representing labile sulfur species complicated the copper analysis.

In conclusion, both methods gave similar results and both methods are therefore viable options for analysing copper at such low concentrations. The bathocuproine method however, had the advantage of being less sensitive to interferences, especially in those samples which contained high amounts of sulfur and carbon dioxide. The bathocuproine method also requires less analytical equipment and can thus be used in laboratories where more high-technology methods are not available. When only analysing copper therefore, the bathocuproine spectrophotometric method for copper can be said to be of considerable interest. However, when analysing many trace metals, DPASV has the definitive advantage of analysing several metals at once.

8. Conclusions and recommendations

8.1. Conclusions

Metal concentrations in geothermal wastewater from the *Nesjavellir* power station and in warm springs entering lake *Thingvallavatn* were found to be low. However, lead concentrations were higher where geothermal water enters the lake. Lead was also higher in the condensed steam and cooled geothermal water from the separation station.

Cadmium also seems to be slightly higher where geothermal water enters the lake, but cadmium concentrations are nevertheless very low.

Copper(I) in *Markagjá* in *Thingvallavatn* was high (53% of total copper). As DOC concentrations are $< 1\text{mg/L}$, UV-B radiation is able to reach the lake bottom at *Markagjá*. Therefore Cu(II) is reduced photolytically to Cu(I). As the dissolved oxygen content of the surface water is high, reoxidation of Cu(I) to Cu(II) is able to take place. However, Cu(I) concentrations of the water remain high because of the continuous photolytic reduction of Cu(II) to Cu(I) due to high amounts of incoming UV-B radiation.

Comparison between the bathocuproine spectrophotometric method for copper and DPASV showed that both methods give similar results. Only in those samples where interference from sulphur was extremely high did the bathocuproine method yield better total copper values. One advantage of the bathocuproine method, however, is that it does not require expensive instruments and can thus be used close to the field or in a simple laboratory.

8.2. Recommendations

As metal concentrations in the geothermal wastewater from *Nesjavellir* are low there is no immediate necessity for changing the form of surface disposal of the water. However, because of possible lead pollution, and because of arsenic and mercury which were not measured in this study, but which are present in the geothermal wastewater, more regular monitoring of the metals both in the wastewater and in the warm springs on the south coast of lake *Thingvallavatn* is recommended.

The bathocuproine spectrophotometric method for copper proved quite useful in this study and should be developed further. Similar methods will hopefully be developed for other types of metals.

Finally, it may be of interest in the future to look more closely at the effects of UV-B radiation on the chemistry of lake *Thingvallavatn*. Furthermore, most aquatic organisms are sensitive to UV-B radiation something which may become a matter of concern if and when the projected global climate changes in the next century take place.

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10. Appendix

Presentation of the measurement-results

Zinc					
	Markagjá	Eldvík	Varmagjá	Laekjarhvarf	Condensed steam
ASV labile	2.097	0.709	1.749	0.2315	0.484
Chelex	4.102	1.544	2.765	2.5075	2.209
UV total	4.177	1.648	2.9885	2.852	2.836
Copper					
	Markagjá	Eldvík	Varmagjá	Laekjarhvarf	Condensed steam
ASV labile	0.088	0.191	0.147	2.022	0.015
Chelex	0.993	0.185	0.811	BDL	BDL
UV total	1.165	0.48	1.019	1.486	0.343
Cadmium					
	Markagjá	Eldvík	Varmagjá	Laekjarhvarf	Condensed steam
ASV labile	0.073	BDL	0.322	0.113	BDL
Chelex	0.058	BDL	BDL	0.226	BDL
UV total	0.165	BDL	0.043	0.387	BDL
Lead					
	Markagjá	Eldvík	Varmagjá	Laekjarhvarf	Condensed steam
ASV labile	0.008	0.184	0.012	0.321	0.511
Chelex	0.019	0.016	0.685	0.193	BDL
UV total	0.369	0.843	0.970	0.469	0.55

Final copper	Copper (I)	ASV	Chelex	Total Cu
Markagjá	0.54	0.088	0.993	1.02
Eldvík	1.52	0.191	0.185	0.82
Varmagjá	0.54	0.147	0.811	0.61
Laekjarhvarf	0.89	2.022	0	1.81
Condensed steam	0.36	0.015	0	0.43
cooled water	0.27	0	0	0.46

Bathocuproine standards

Total Cu	µg/L	abs			
	0.25	0.002	0.250233	Slope	208.2364
	0.5	0.0055	0.97906	Intercept	-0.16624
	1	0.0068	1.249768	Formula	208,2364x-0,16624
	2	0.0077	1.43718	Pearson	0.863415
	0	0	-0.16624		
					0.874942

Cu I	µg/L	abs			
	0.25	0.005		Slope	89.09445
	0.5	0.0075		Intercept	-0.08593
	1	0.011		Formula	89,09445x-0,08593
	0	0		Pearson	0.965232

STANDARDS:					
Zn 180 sec	Conc µg/L	abs	calc.conc	Regression	
	0.05	43.05	0.05	slope	0.001179565
	0.1	75.74	0.09	intercept	0.001869895
	0.15	129.2	0.15	Pearson	0.995750504
	0	0	0.00		
				Equation	0.00118x+0.00187
Zn 180 sec	Conc µg/L	abs	calc.conc	Regression	
Chelex	0.025	2.82	0.01	slope	0.001587451
	0.05	26.01	0.05	intercept	0.009707697
	0.075	41.2	0.08	Pearson	0.965446979
	0	0	0.01		
				Equation	0.001587x+0.009708
Zn 240 sec	Conc µg/L	abs	calc.conc	Regression	
	0.015	11.48	0.02	slope	0.001412125
	0.03	21.87	0.03	intercept	-0.000538826
	0.045	31.91	0.04	Pearson	0.999515708
	0	0	0.00		
				Equation	0.001412x-0.00054
Zn 240 sec	Conc µg/L	abs	calc.conc	Regression	
UV total	0.025	7.39	0.02	slope	0.001566907
	0.05	22.88	0.04	intercept	0.007826693
	0.075	45.48	0.08	Pearson	0.975828321
	0	0	0.01		
				Equation	0.001567x+0.007827
Zn 300 sec I	Conc µg/L	abs	calc.conc	Regression	
	0.025	30.07	0.03	slope	0.001244451

	0.05	47.14	0.05	intercept	-0.004553123
	0.075	57.96	0.07	Pearson	0.974942028
	0	0	0.00		
				Equation	0.001244x-0.00455
Zn 300 sec II	Conc µg/L	abs	calc.conc	Regression	
	0.015	12.75	0.02	slope	0.001213359
	0.03	24.82	0.03	intercept	-0.000174645
	0.045	37.18	0.04	Pearson	0.999944328
	0	0	0.00		
				Equation	0.001213x-0.00017
Cd 180 sec	Conc µg/L	abs	calc.conc	Regression	
	0.05	9.118	0.05	slope	0.005972288
	0.1	17.58	0.10	intercept	-0.002233624
	0.15	25.03	0.15	Pearson	0.998996072
	0	0	0.00		
				Equation	0.005972x-0.00223
Cd 240 sec	Conc µg/L	abs	calc.conc	Regression	
	0.015	3.838	0.02	slope	0.004356139
	0.03	6.959	0.03	intercept	-0.000606048
	0.045	10.42	0.04	Pearson	0.99922771
	0	0	0.00		
				Equation	0.004356x-0.00061
Cd 300 sec	Conc µg/L	abs	calc.conc	Regression	
	0.015	4.393	0.01	slope	0.003485003
	0.03	9.103	0.01	intercept	-0.000358134

	0.045	12.74	0.02	Pearson	0.998703065
	0	0	0.00		
				Equation	0.001213x-0.00017
Pb 180 sec	Conc µg/L	abs	calc.conc	Regression	
	0.05	3.229	0.06	slope	0.019085631
	0.1	5.617	0.10	intercept	-0.004754082
	0.15	7.869	0.15	Pearson	0.996123474
	0	0	0.00		
				Equation	0.019086x-0.00475
Pb 180 sec	Conc µg/L	abs	calc.conc	Regression	
Chelex	0.025	1.579	0.03	slope	0.015561616
	0.05	2.973	0.05	intercept	0.000844614
	0.075	4.87	0.08	Pearson	0.998094378
	0	0	0.00		
				Equation	0.015562x+0.000845
Pb 240 sec	Conc µg/L	abs	calc.conc	Regression	
	0.015	1.078	0.02	slope	0.019350929
	0.03	2.098	0.04	intercept	-0.002204434
	0.05	2.189	0.04	Pearson	0.929728204
	0	0	0.00		
				Equation	0.019351x-0.0022
Pb 300 sec	Conc µg/L	abs	calc.conc	Regression	
	0.03	2.723	0.03	slope	0.010541687
	0.05	5.334	0.06	intercept	-0.000299043
	0.075	6.76	0.07	Pearson	0.990999112

	0	0	0.00	Equation	0.010542x-0.0003
Pb 700 sec	Conc µg/L	abs	calc.conc	Regression	
	0.1	21.29	0.13	slope	0.006547879
	0.2	30.09	0.19	intercept	-0.010734064
	0.3	46.81	0.30	Pearson	0.988503924
	0	0	-0.01		
				Equation	0.006548x-0.01073
Cu 180 sec	Conc µg/L	abs	calc.conc	Regression	
	0.05	8.284	0.05	slope	0.001168122
	0.1	12.31	0.05	intercept	0.040086587
	0.15	98.96	0.16	Pearson	0.838444873
	0	0	0.04		
				Equation	0.001168x+0.040087
Cu 180 sec	Conc µg/L	abs	calc.conc	Regression	
Chelex	0.025	6.814	0.04	slope	0.005914096
	0.05	10.064	0.05	intercept	-0.005069663
	0.075	11.914	0.07	Pearson	0.960421637
	0	0	-0.01		
				Equation	0.005914x-0.00507
Cu 240 sec	Conc µg/L	abs	calc.conc	Regression	
	0.015	3.814	0.02	slope	0.003939656
	0.03	5.348	0.02	intercept	0.002159558
	0.045	11.49	0.05	Pearson	0.972431183

	0	0	0.00		
				Equation	0.00394x+0.00216
Cu 300 sec	Conc µg/L	abs	calc.conc	Regression	
	0.01	5.646	0.01	slope	0.000662251
	0.015	6.922	0.01	intercept	0.005109607
	0.025	32.07	0.03	Pearson	0.90739279
	0	0	0.01		
				Equation	0.000662x+0.00511
Cu 700 sec	Conc µg/L	abs	calc.conc	Regression	
	0.025	42.86	0.02	slope	0.000579163
	0.05	86.33	0.05	intercept	5.92977E-05
	0	0	0.00	Pearson	0.999991679
				Equation	0.000579x+0.0000593

