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THE SPECIATION OF TRACE ELEMENTS IN SPENT GEOTHERMAL FLUIDS AND IMPLICATIONS FOR ENVIRONMENTAL HEALTH AROUND OLKARIA, KENYA

**MSc Thesis
Department of Earth Sciences
Faculty of Science
University of Iceland**

by

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**United Nations University
Geothermal Training Programme
Report 1
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INTRODUCTION

The Geothermal Training Programme of the United Nations University (UNU) has operated in Iceland since 1979 with six month annual courses for professionals from developing countries. The aim is to assist developing countries with significant geothermal potential to build up groups of specialists that cover most aspects of geothermal exploration and development. During 1979-2006, 359 scientists and engineers from 40 countries have completed the six month courses. They have come from Asia (44%), Africa (26%), Central America (14%), and Central and Eastern Europe (16%). There is a steady flow of requests from all over the world for the six month training and we can only meet a portion of the requests. Most of the trainees are awarded UNU Fellowships financed by the UNU and the Government of Iceland.

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

It is a pleasure to introduce the tenth UNU Fellow to complete the MSc studies at the University of Iceland under the co-operation agreement. Mr. Joshua Ochieng´ Were, BSc in Chemistry, of the Kenya Electricity Generating Co., Ltd. - KenGen, completed the six month specialized training in Environmental Studies at the UNU Geothermal Training Programme in October 1998. His research report was entitled “Aspects of waste management and pollution control in Olkaria geothermal field, Kenya”. After six years of geothermal research work in Kenya, he came back to Iceland for MSc studies at the Faculty of Science of the University of Iceland in September 2005. In March 2007, he defended his MSc thesis presented here, entitled “The speciation of trace elements in spent geothermal fluids and implications for environmental health around Olkaria geothermal field, Kenya”. His studies in Iceland were financed by a fellowship from the Government of Iceland through the UNU Geothermal Training Programme. We congratulate him on his achievements and wish him all the best for the future. We thank the Faculty of Science of the University of Iceland for the co-operation, and his supervisors for the dedication.

Finally, I would like to mention that Joshua´s MSc thesis with the figures in colour is available for downloading on our website at page www.os.is/unugtp/yearbook/2007.

With warmest wishes from Iceland,

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

DEDICATION

I dedicate this work to my mother, Yucabeth Ogwang' Were and late father, Eshmael Were Ouma, who invested their scarce resources on my education, instructed me to cherish hard work and above all love and serve God and other people with humility.

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I am indebted to my wife, Janet for her support and encouragement and children, Linda, Marianne, Emmanuel, and Philip for enduring my long absence. Finally, I give honour and glory to the Almighty God for his gift of spiritual, physical and mental health while in Iceland.

ABSTRACT

The greatest environmental challenge in the Olkaria, Kenya, has been the large volume of spent geothermal fluids and the constituent chemicals generated during geothermal development. The potential environmental health risks of trace elements in spent geothermal fluids from Olkaria have been studied fairly intensively but based on the total recoverable and dissolved concentrations. However, there has been extensive evidence that neither total nor dissolved aqueous metal concentrations are good predictors of metal mobility, bioavailability, and toxicity. The current study is, therefore, an attempt to investigate the distribution of the chemical species of selected toxic trace elements in spent geothermal fluids and assess the environmental health risks posed on the ecosystems around Olkaria. The study involved sampling and analysis of the major ions and trace elements in spent geothermal fluids from 4 discharging and 2 shut-in geothermal wells, outfall fluids from the Olkaria I geothermal power station, and the Infiltration Lagoons located in the Eastern sector of the Olkaria. The Ol’Njorowa Gorge thermal spring fluids and Lake Naivasha were used as control samples. A chemical equilibrium model, EQ3/6 solubility-speciation code, was applied to predict the probable distribution of the aqueous Al, As, Cd, Pb, Hg, and Zn with inorganic ligands at in-situ pH and temperatures with the results of analysis of the sampled fluids as input data. The analytical results reveal that the dissolved toxic trace element concentrations are significantly low (in $\mu\text{g/L}$) and in compliance with the Kenyan maximum permissible limits for recreational water and effluent discharge to terrestrial environment and the Canadian maximum acceptable concentrations for livestock watering and protection of plants, except for As, Hg, Mo, and F. The speciation modelling with inorganic ligands predicts occurrence of labile and toxic Cd in all the fluids sampled, Cu, Pb, and Zn species in acidic to neutral fluids from Olkaria I outfall, shut-in geothermal wells, and the Infiltration Lagoons and non-toxic aqueous Al, As, and Hg species in all the sampled fluids. The aqueous Cd concentrations in all fluids were below the detection levels and in all probability low. Therefore, the model predicted toxic Cd species is of relatively small environmental health concern. The speciation modelling results confirm that the total or dissolved trace element concentrations adopted in the national standards and international criteria or guidelines for environmental health quality are not reliable predictors of trace element toxicity. The results also indicate that the fluids from discharging geothermal wells are chemically benign. With increased hot fluid re-injection and incorporation of detoxification and recovery procedures (fluid pH adjustment and use of appropriate organic complexes or chelating chemicals) and use of constructed wetlands for acidic to neutral fluids from Olkaria I outfall, shut-in geothermal wells, and the Infiltration Lagoons, the environmental health risks of the model predicted toxic Cu, Pb, and Zn species and other elements Al, As, Cd, Hg, and Mo in spent geothermal fluids are made negligible.

TABLE OF CONTENTS

	Page
1. INTRODUCTION	1
1.1 Geothermal energy and associated environmental issues	1
1.2 Environmental chemistry of some selected trace elements	2
1.3 Justification for the speciation study of trace elements in spent geothermal fluids from Olkaria geothermal field	4
1.3.1 Environmental settings	4
1.3.2 Environmental challenges and mitigation options	5
1.3.3 Previous environmental studies	7
1.4 The study objectives	7
2. MATERIALS AND METHODS	8
2.1 Sampling locations	8
2.2 Sampling	10
2.3 Treatment and storage of samples	10
2.4 Analysis of samples	11
2.4.1 Analysis of physico-chemical parameters	11
2.4.2 Analysis of trace elements and major cations	11
2.4.3 Analysis of CO ₂ , DOC, and major anions	12
2.4.4 Reagent blanks	12
2.5 Analytical data	12
2.6 Speciation modelling of selected trace elements using the EQ3/6 speciation–solubility code	12
2.6.1 An overview of the chemical speciation modelling concept	12
2.6.2 Theoretical assumptions and limitations of speciation model calculations	13
2.6.3 Speciation modelling of selected trace elements in spent geothermal fluids from the Olkaria geothermal field, Ol’Njorowa thermal springs, and Lake Naivasha water using EQ3/6 code	14
3. RESULTS	15
3.1 Temperature, pH, and DOC	15
3.2 Conductivity and Total Dissolved Solids	15
3.3 Dissolved major cation and anion concentrations	15
3.4 Dissolved trace element concentrations	19
3.5 The probable speciation of selected trace elements in spent geothermal fluids from the Olkaria geothermal field, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, Kenya using the EQ3/6 code	21
3.5.1 Aluminium	21
3.5.2 Arsenic	25
3.5.3 Cadmium	30
3.5.4 Copper	34
3.5.5 Lead	39
3.5.6 Mercury	43
3.5.7 Zinc	47
4. DISCUSSION	53
4.1 Omissions, errors and uncertainties	53
4.2 Comparison with reported data from previous studies in Olkaria	53
4.3 Comparison with reported data from other geothermal fields	54
4.4 Evaluation of compliance with the Kenyan standards and some relevant international environmental guidelines	54
4.4.1 Physical parameters	54
4.4.2 Major ion species	55

	Page
4.4.3 Trace element species	56
4.5 Variations in pH, temperature, DOC, TDS, and conductivity values	57
4.6 Correlations between the major ion species.....	57
4.7 Spatial variations in the concentrations of selected trace elements and correlations with the major ion species	58
4.8 Assessment of the potential environmental and health risks of the predicted species of selected trace elements	61
4.9 Alternative environmental pollution control options	64
4.9.1 Detoxification through pH adjustment	64
4.9.2 Detoxification with inorganic or organic ligands and chelating chemicals.....	64
4.9.3 Reconstruction and use of the Infiltration Lagoons as “wetlands”	65
4.10 Critical environmental data gaps, future monitoring, and research needs	65
5. SUMMARY	66
6. CONCLUSIONS AND RECOMMENDATIONS	68
6.1 Conclusions.....	68
6.2 Recommendations.....	68
REFERENCES.....	69

LIST OF FIGURES

1. Location map of the Olkaria and other geothermal prospects in Kenya.....	4
2. Map of the major industries in the vicinity of Olkaria, Kenya	5
3. Map of sampling locations in the Olkaria East geothermal field, Kenya.....	8
4. The Infiltration Lagoons in the vicinity of Olkaria I power station	9
5. Selected ion concentrations in spent geothermal fluids from Olkaria, Ol’Njorowa Gorge thermal spring, and Lake Naivasha.....	18
6. Selected trace element concentrations in spent geothermal fluids from Olkaria, Ol’Njorowa Gorge thermal springs, and Lake Naivasha	20
7a. Distribution curves for aluminium species in spent geothermal fluids from discharging geothermal wells.....	22
7b. Distribution curves for aluminium species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoon 1 and 2 outfalls	23
7c. Distribution curves for aluminium species in spent geothermal fluids from the Infiltration Lagoons 1 and 2, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha	24
8a. Distribution curves for arsenic species in spent geothermal fluids from discharging geothermal wells.....	27
8b. Distribution curves for arsenic species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoons 1 and 2 outfalls	28
8c. Distribution curves for arsenic species in spent geothermal fluids from the Infiltration Lagoons 1 and 2, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha	29
9a. Distribution curves for cadmium species in spent geothermal fluids from discharging geothermal wells.....	31
9b. Distribution curves for cadmium species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoons 1 and 2 outfalls	32
9c. Distribution curves for cadmium species in spent geothermal fluids from the Infiltration Lagoons 1 and 2, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha	33
10a. Distribution curves for copper species in spent geothermal fluids from discharging geothermal wells.....	35
10b. Distribution curves for copper species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoons 1 and 2 outfalls	36

	Page
10c. Distribution curves for copper species in spent geothermal fluids from the Olkaria I outfall, Infiltration Lagoons, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha	37
11a. Distribution curves for lead species in spent geothermal fluids from discharging geothermal wells.....	40
11b. Distribution curves for lead species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoons 1 and 2 outfalls	41
11c. Distribution curves for lead species in spent geothermal fluids from the Infiltration Lagoons 1 and 2, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha	42
12a. Distribution curves for mercury species in spent geothermal fluids from discharging geothermal wells.....	44
12b. Distribution curves for mercury species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoons 1 and 2 outfalls	45
12c. Distribution curves for mercury species in spent geothermal fluids from the Infiltration Lagoons 1 and 2, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha	46
13a. Distribution curves for zinc species in spent geothermal fluids from discharging geothermal wells.....	48
13b. Distribution curves for zinc species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoons 1 and 2 outfalls	49
13c. Distribution curves for zinc species in spent geothermal fluids from the Infiltration Lagoons 1 and 2, Ol’Njorowa Gorge thermal springs, and Lake Naivasha	50
14. The correlations of aqueous Al with pH, F, SiO ₂ (aq), and Na ⁺	59
15. The correlations of aqueous As with pH, Cl ⁻ , and SiO ₂ (aq).....	60
16. The correlations of aqueous Cd, Cu, Pb and Zn with pH.....	62

LIST OF TABLES

1. Physico-chemical parameters and major cation and anion concentrations in spent geothermal fluids from the Olkaria East geothermal field, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha.....	16
2. Trace element concentrations (in µg/L) in spent geothermal fluids from the Olkaria, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha.....	17
3. Composition of aluminium species at in-situ pH and temperatures within sampling locations ..	25
4. Range of aluminium species in spent geothermal fluids from the Olkaria, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha.....	25
5. Composition of arsenic species at in-situ pH and temperatures within the sampling locations...	26
6. Range of arsenic species in spent geothermal fluids from the Olkaria, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha.....	26
7. Composition of cadmium species at in-situ pH and temperatures within sampling locations	30
8. Range of cadmium species in spent geothermal fluids from the Olkaria, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha.....	34
9. Composition of copper species at in-situ pH and temperatures within the sampling locations ...	38
10. Range of copper species in spent geothermal fluids from the Olkaria, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha.....	38
11. Composition of lead species at in-situ pH and temperatures within the sampling locations	43
12. Range of lead species in spent geothermal fluids from the Olkaria, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha.....	43
13. Percentage composition of mercury species at in-situ pH and temperatures within sampling locations.....	47
14. Range of mercury species in spent geothermal fluids from the Olkaria, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha.....	47
15. Composition of zinc species at in-situ pH and temperatures within the sampling locations	51
16. Range of zinc species in spent geothermal fluids from the Olkaria, Ol’Njorowa Gorge thermal springs, and Lake Naivasha	51
17. Concentrations of chemical constituents of spent geothermal fluids from some selected geothermal fields.....	55

1. INTRODUCTION

The main source of energy in the world has been fossil fuels constituting about 80% of the world primary energy consumption (Fridleifsson, 2005). Over the years, there has been an increasing awareness of the detrimental effects of excessive burning of fossil fuels on the environment due to emission of greenhouse gases (GHGs). This has led to an increasing interest worldwide in the use of alternative energy sources that are renewable and less damaging to the environment. Geothermal energy, a favourite alternative, was considered to be a relatively clean and non-polluting “new renewable” source of energy (El Hinnawi and Biswas, 1981). However, studies on environmental impacts of geothermal energy development have revealed a number of potential bio-physical, social and economic impacts. Utilization of geothermal energy sources is also increasing worldwide. Of the main sources of electricity and renewable energy installed in the world by 2002, geothermal had a share of 0.31% and 8356 MW, respectively, and an annual growth rate of 1.2% (Popovski, 2005). These scenarios underscore the need for further research on the potential impacts of geothermal exploration and utilization to ensure sustainability of geothermal energy development.

1.1 Geothermal energy and associated environmental issues

Geothermal energy originates in the interior of the earth, which is considered as a heat engine due to the vast amount of energy generated by processes such as the decay of radioactive elements present within rocks of the earth’s crust and mantle, mainly in the isotope of Potassium (^{40}K) and certain isotopes of Uranium and Thorium. The energy can be exploited in regions where it occurs at reasonable depths and quantity within the earth’s crust. Examples of such regions are the tectonic plate boundaries where due to instability within the earth’s crust, surface derived water circulates to great depths, gets heated up and flows back to the earth’s surface. It is also possible for hot rocks to occur at fairly shallow depths within the earth’s crust. These heat up underground water, which in turn up-flows to the earth’s surface and is visibly manifested as hot springs, geysers, and fumaroles (steam vents). They also occur as lava and ash from volcanic eruptions. In addition, sub-surface temperatures increase everywhere with depth below the upper several meters that are affected by solar radiation and infiltration of surface water.

During circulation at depth, the surface derived waters interact with the sub-surface rocks through which they pass. High temperatures, pressures, and possibly long contact periods with the sub-surface rocks enhance the water-rock interactions. The water dissolves some of the chemical elements constituting the sub-surface rocks. This is dependent on the nature and rates of dissolution reactions of the sub-surface rocks. The geothermal fluids (water and steam) acquire a chemical composition very different from the normal underground and surface waters (El Hinnawi and Biswas, 1981). Typical geothermal fluids from high temperature fields may, however, contain high concentrations of at least one of the following toxic chemical elements Al, As, B, Cd, Cu, F, Pb, and Hg, and insignificant to major (> 10%) concentrations of non-condensable gases (principally CO_2 , with H_2S , N_2 , CH_4 , NH_3 , etc.) Other chemical constituents, $\text{SiO}_2(\text{aq})$, Na^+ and Cl^- ions occur in abundance, and Ca^{2+} , K^+ , HCO_3^- , and SO_4^{2-} in lesser quantities (Skinner, 1967; Weissberg and Zobel, 1973; Nakahava, 1978; Webster, 1998; Sanyal, 2005). The concentrations of these chemical constituents are largely controlled by their influx to the deep circulating geothermal fluids, which extract them from either enclosing rocks or degassing magma.

To maximise the utilization of geothermal energy, geothermal wells are drilled to economical depths of up to or less than 3 km to enable tapping of the thermal water or steam concentrated at depths in restricted volumes, analogous to oil in commercial oil reservoirs. The resulting geothermal fluids are harnessed for either direct (space heating and other industrial applications) or indirect (generation of electricity) uses, depending on the fluid temperature. However, the use of ground source heat pumps has changed this scenario. In this case, the earth is the heat source for heating and/or the heat sink for cooling, depending on the season and can be used basically everywhere around the world.

Geothermal energy development, therefore, increases the volume of the spent geothermal fluid discharges over and above those, which would be obtained from normal surface discharges. Thus, substantial amounts of the chemicals constituting the sub-surface rocks are brought to the surface with a potential for causing adverse environmental and health impacts on vital ecosystems. Once geothermal energy has been extracted, the spent geothermal fluids are either disposed of into the surface environment in ponds or sumps before re-injection or immediately re-injected back into the geothermal reservoir to avoid pollution of surface waters, as well as to maintain reservoir pressure. In cases of surface discharges, the spent geothermal fluids, may subsequently join regional underground and surface natural water bodies such as lakes, rivers, and estuaries, and become sources of trace metal contamination or pollution in these ecosystems.

1.2 Environmental chemistry of some selected trace elements

In environmental chemistry, a contaminant is defined as a chemical substance that causes a deviation from the existing environment. It is not necessarily a pollutant. The term pollution, however, only applies when a contaminant has some detrimental effects. A pollutant in the environment may therefore be defined as a substance present in greater than natural concentrations as a result of human activity and having a net detrimental effect upon the environment or something of value in the environment (Manahan, 1990).

Trace elements are widespread in aquatic and terrestrial ecosystems. They may exist in natural water (river, stream, spring, swamp, pond, lake, sea, hydrothermal fluids or other water source flowing in a natural water course) irreversibly bound to inorganic anions or to organic compounds, or they may, in a few cases, be present as organometallic compounds containing carbon to metal bonds. These species of trace metals will often have vastly different solubility, transport properties, and biological effects compared to the aquo-metal ions themselves. The protection of the ecosystems, upon which our health and lives depend, requires that we understand natural processes to develop an ability to predict the effect of anthropological changes e.g. the addition of chemical contaminants to these ecosystems.

Until recently most environmental research on metals was based on an assessment of total recoverable or dissolved metal concentrations but it has become increasingly evident that environmental concerns for a particular metal species may be more important in addition to knowledge of the total concentration. The equilibrium between various metal species becomes essential in the evaluation of environmental and health effects, in addition to other bio-physical environmental factors. Studies involving metal speciation in dilute solutions require the values of stability constants of complexes with a number of inorganic and organic ligands. Many of these data are already available from published compilations (Martell and Smith, 1976; Sillen and Martell, 1964, 1971) but there are still gaps and inaccuracies in the data. Experimental data on mixed ligand complexes are also rather sparse.

Below differing threshold levels many metal ions have essential functions for all sorts of biological organisms, including man. Among hazardous environmental chemicals certain trace metals and metalloids have gained particular significance and priority due to their toxicity. In primary focus are the non-essential toxic trace metals Cd, Pb, and Hg, but also a number of others e.g. Cu, Zn, and Ni, which have essential functions of growth and development of living organisms at low concentrations, and exert toxicity above their respective threshold limit values. These values will, among other parameters, depend on the type of the exposed organism (Venugopal and Luckey, 1978). Metals are non-biodegradable and can, as a result, be persistent and insidious poisons. They tend to accumulate in various vital organs of man and mammals, e.g. kidneys, liver, intestinal tract, lungs, and brain, and some metals, e.g. Pb and Cd, may be deposited in bones. From these deposits, the toxic metals may also be re-mobilised under certain metabolic conditions. When in the above organs, and also in other parts of the body, toxic metals probably act as poisons at even lower doses than those normally considered. This toxic action is of a progressive character as it persists over a long period of time.

Metals in natural waters will seldom exist as the free, solvated aqueous ions. If it is assumed that the pH of the water is between 5 and 8 (most natural waters will fall within this range) then the only ions which can exist in appreciable concentrations as aqueous ions are mono-valent ions e.g. alkali metal ions Na^+ , K^+ , etc., and a few divalent metal ions e.g. Mg^{2+} . Aquo-complexes of all other metals hydrolyse at these pH values to form hydroxy and polynuclear complexes, which are generally insoluble, resulting in precipitation. As a result transition and heavy metal ions are only likely to be found in solution in appreciable quantities in the presence of other ligands. Monodentate ligands are not normally effective competitors for naturally occurring multidentate ligands unless they form exceedingly stable complexes with particular metal ions e.g. some sulphur ligands which co-ordinate strongly to Hg^{2+} , hence the most likely ligands to solubilise metal ions are polydentate weak acids which can bond simultaneously to a central metal ion, forming a ring structure which is generally considerably more stable than comparable complexes with unidentate ligands. With divalent transition and heavy metal ions, nitrogen donors are frequently more effective ligands with the result that a combined O, N polydentate chelating ligands e.g. EDTA, would be expected to solubilise the metal ions particularly well. Once solubilised, the metal ions may be held in solution as either a binary complex with the solubilised ligand, L e.g. ML_2 (charges omitted) or as a ternary complex with the solubilising ligand and a naturally occurring ligand such as OH^- or HCO_3^- e.g. $\text{M}(\text{HCO}_3)_2$.

It has been increasingly recognised that proper understanding of the transport and behaviour effects on the fate of many trace metals and other chemical substances in water will usually require more than the knowledge of their total or dissolved concentrations alone. Depending on the chemical speciation of a metal, a particular water system with a high total or dissolved metal concentration may be less toxic than another with a lower metal concentration (Allen, 1976). For example ionic aqueous copper is far more toxic towards aquatic organisms than complexed copper and, as a general rule, the more stable the copper complex, the lower is its toxicity (Pagenkopf and Thurton, 1974; Steeman and Anderson-Wium, 1970).

In environmental sciences, the term speciation means the identity of inorganic, organometallic or organic compounds actually present in the environment (David and Phillip, 1983). The term distinguishes between the measurement of the total concentration of an element and the determination of the concentration of each of its chemical forms. Nriagu (1983) defines the term metal speciation in its broadest sense as all possible chemical forms of a metal that may occur in different environments, while Florence (1983) uses the term chemical speciation to refer to the determination of individual physico-chemical forms of an element, which together make up its total concentration in a sample. Particular attention is now being paid to the aqueous speciation of trace metals and metalloids (Nurnberg, 1982). This reflects the importance of these elements as common pollutants, the potential toxic effects which they may exert upon aquatic and other ecosystems, the complexity of their speciation, and therefore their behaviour and properties in water (Hunt and Wilson, 1986).

An investigation of the speciation of metals relies on three different basic approaches (Laxen and Harrison, 1981);

- The study of the behaviour and reactions of metal ions in a model water system, usually at a constant ionic strength and temperature. Stability constant data for a wide range of metal complexes have been calculated from such studies. Knowledge of exact speciation composition, based on complex formation, is widely applied in research.
- The prediction of species distribution using thermodynamic modelling. The use of thermodynamic data to predict trace metal speciation is an important facet of the study of trace elements. Despite a number of problems (notably inaccuracies of, and gaps in, stability constant data), thermodynamic calculations of equilibrium species distribution provide an essential theoretical basis for speciation analysis (Jenne, 1979; Stumm and Morgan, 1981)
- The determination of species, or groups of species, in real samples using analytical techniques such as anodic stripping voltammetry. The speciation of trace elements in water has been reviewed by Florence and Batley (1980).

1.3 Justification for the speciation study of trace elements in spent geothermal fluids from Olkaria geothermal field

1.3.1 Environmental settings

The Olkaria geothermal field is located in a multi-centered volcanic complex comprising of at least 80 small centres covering an area of approximately 240 km². It is located in the Eastern branch of the African rift system in Kenya about 120 km to the Northwest of the capital city of Nairobi (Figure 1). In the precincts of the Olkaria geothermal field, there are areas of environmental, social, and economic significance (Figure 2).

The Olkaria I geothermal power station with an installed capacity of 45 MW of electricity, which was the first geothermal power station in Africa, has been operating in the Olkaria East geothermal field for over 25 years. In the Olkaria Northeast field, there is the 70 MW Olkaria II power station commissioned in 2003. The Olkaria I and II power stations are owned and operated by KenGen. In the Olkaria West and Central fields, there are 12 and 2 MW binary power plants operated by OrPower4 Inc. and Oserian Development Company respectively, which are Independent Power Producers.

A large part of the field is within Hell's Gate National Park, which is a protected area for wildlife conservation. The Park attracts large numbers of both local and foreign tourists. Other social and economic activities include private commercial livestock ranches, horticultural and flower farms, wildlife sanctuaries, and domestic livestock keeping by the native Maasai community. The southern shoreline of Lake Naivasha, which is the main source of water for both domestic and commercial uses in this semi-arid region besides being a Ramsar site, is located approximately 5 km from the recently commissioned 70 MW Olkaria II power station. The geothermal resource field is also about 27 km south of Naivasha Town with a population of about 150,000 people and therefore, considered to be one of the few geothermal fields in the world not very far from large urban centres. The commercially vital floricultural farms that grow high quality cut flowers (Roses, Carnations, Statice and Gypsophila, and Lisianthus) for export to Europe are located northwest of the geothermal field. Apart from being vital sources of foreign exchange earnings for Kenya, the industrial activities offer employment opportunities for both the local communities inhabiting the surrounding areas and immigrant populations from other regions of Kenya. As a result, the areas in the precincts of Olkaria are inhabited by populations of diverse ethnic and social classes,

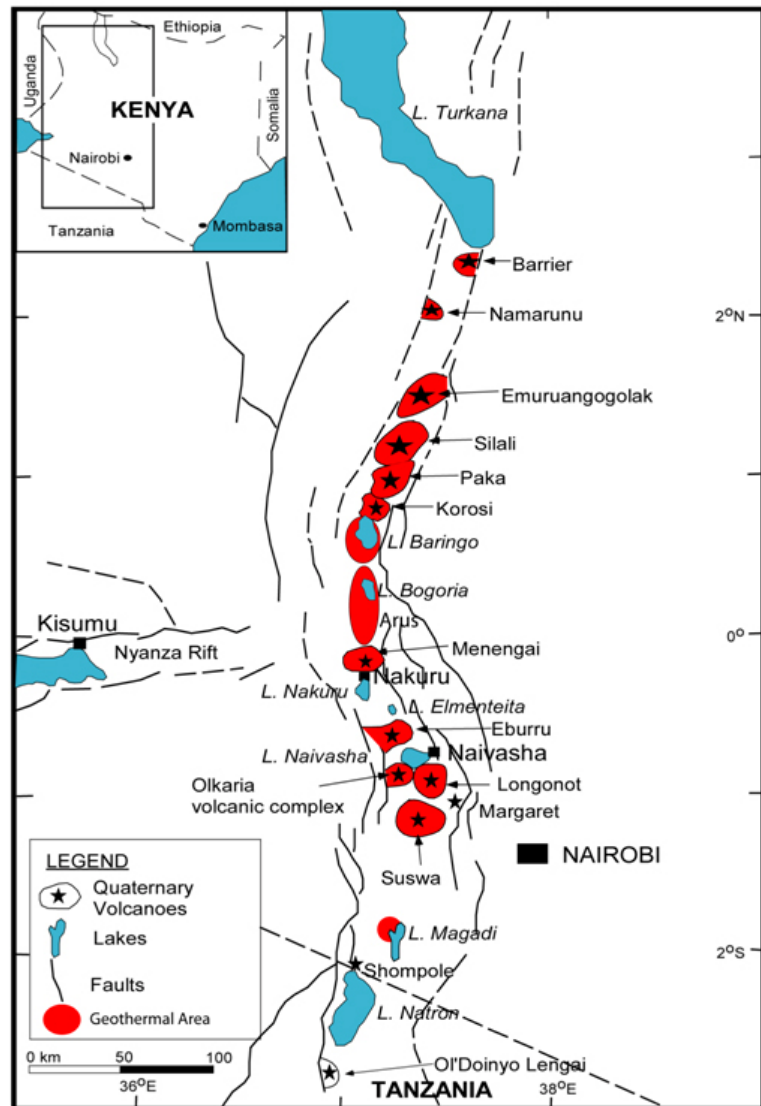


FIGURE 1: Location map of the Olkaria geothermal field and other geothermal prospects in Kenya

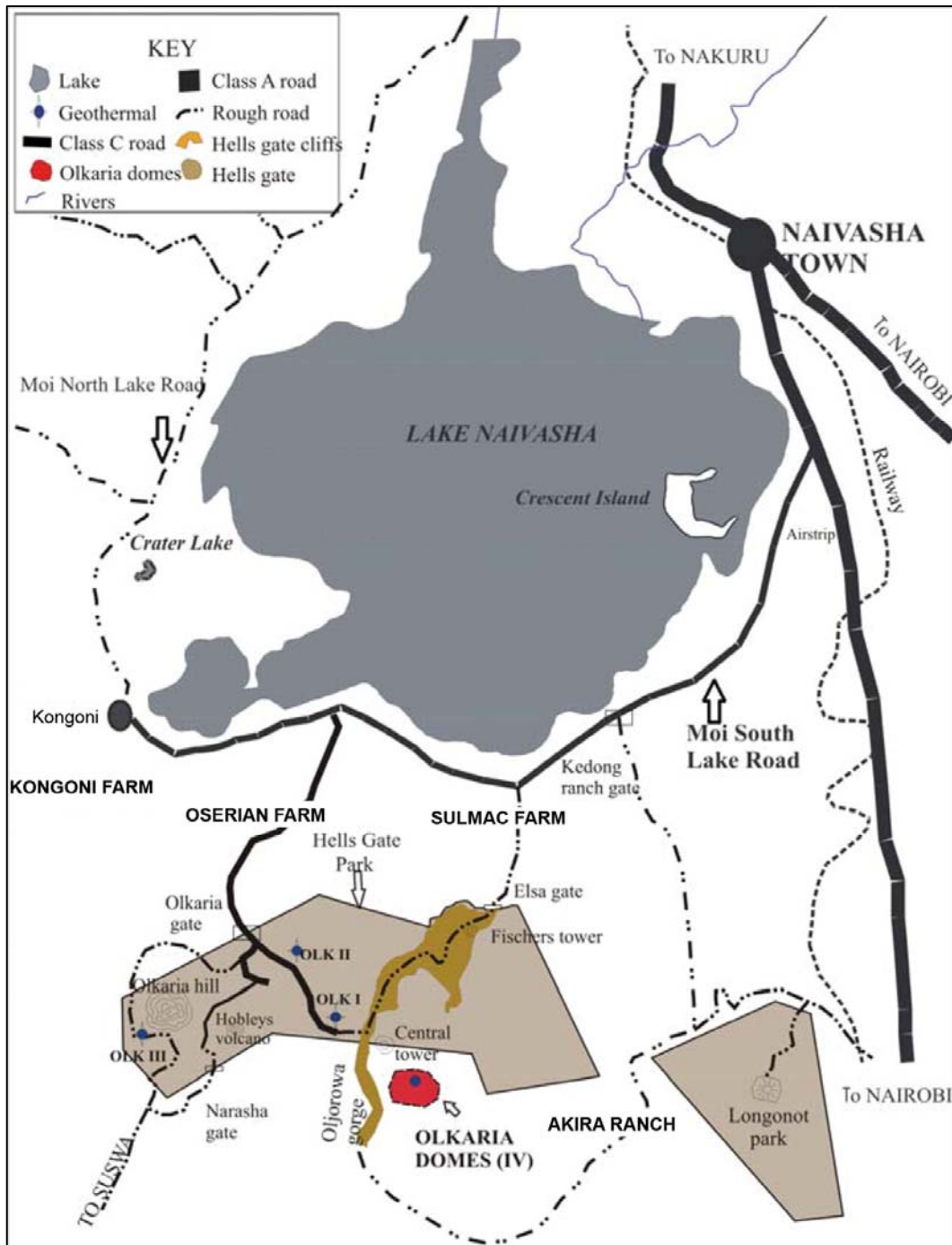


FIGURE 2: Map of the major industries in the vicinity of Olkaria geothermal field, Kenya ranging from affluent horticultural and floricultural farmers of European descent to the local Maasai communities, who are pastoralists.

Due to the sensitive setting of the Olkaria geothermal field, it is essential to take environmental and social issues into account in power development plans, implementation, and operations to ensure sustainability of geothermal energy development within the resource area.

1.3.2 Environmental challenges and mitigation options

The large volume of spent geothermal fluids generated during geothermal energy development in the Olkaria geothermal field, is of major environmental concern. Virkir Mertz and McLellan (1977)

estimated that about 120 t/hr of spent geothermal brine is discharged from the 45 MW Olkaria I power station out of a total flow rate of 570 t/hr of the geothermal fluids in the Olkaria East field. Geothermal steam constitutes the remaining 450 t/hr of the geothermal fluid flow from the Olkaria East field. Moreover, the volume of spent geothermal fluid output has increased in Olkaria after the commissioning of the 70 MW Olkaria II in 2003. Further increase in spent geothermal fluids output is envisaged, when other geothermal prospect areas within the Kenyan rift system are harnessed under the African Region Geothermal (ArGeo) development initiative. The ArGeo objective is to accelerate geothermal power development in African countries within the African rift system through the Global Environmental Fund of The United Nations Environmental Programme and other bilateral organizations e.g. The Icelandic International Development Agency (ICEIDA).

In the Olkaria East field, which has been in production for the last 25 years, each geothermal well is equipped with a wellhead separator and concrete-lined conditioning ponds, for containment of separated geothermal brine to allow for the precipitation of chemical residues. Most of the separated brine drains through open concrete channels into natural depressions referred to as Infiltration Lagoons for temporary containment prior to disposal through cold water re-injection into Olkaria well (OW) OW-12. A small fraction of separated geothermal brine from wells OW-27/31/33 is re-injected hot into well OW-3. The ponds and lagoons allow for evaporation of hot geothermal fluids in the form of aerosols. Separated dry geothermal steam is piped to the power station for electricity generation. In the process, spent geothermal steam condenses forming excess liquid condensates or blow-downs, which are channelled to the Infiltration Lagoons for disposal.

In the Olkaria Northeast field, two-phase fluid from geothermal production wells is combined in a few wellhead separator systems. The temporary brine holding ponds are lined with High Density Polyethylene (HDPE) material to prevent direct soil contamination prior to piping together with excess blow-downs for re-injection into wells OW-201, OW-202, and R3.

In the Olkaria East and Northeast fields, re-injection systems are installed both as a disposal mechanism for the separated brine and excess condensates from the geothermal power stations for environmental reasons and for managing decline in steam production and falling reservoir pressures. Based on the results of injection and tracer tests for thermal efficiency of re-injection in the Olkaria East field, Ofwona (1996) observed that re-injection of hot water ($T > 100\text{ }^{\circ}\text{C}$) at the rate of $< 50\text{ t/hr}$ is feasible and preferable for the dipole around wells OW-3 and OW-4 (Figure 3). The results of the injection study coupled with low rates of re-injection imply that some spent geothermal fluids would still be left in the surface environment in the Olkaria East geothermal field during operations of Olkaria I power station, unless hot water re-injection is increased. In addition, re-injection of spent geothermal fluids from the Olkaria East and Northeast fields only minimizes the magnitude of the potential chemical contamination from trace elements and does not eliminate it all (Tole, 1990; Simiyu, 1998). This is because some of the trace metals are released as aerosols with steam and the vegetation that flourishes, for example, adjacent to the ponds and within the Infiltration Lagoons, may become available to wild animals and domestic livestock that graze within Hell's Gate National Park.

The spent geothermal fluids from Olkaria, which is a high temperature field, contain high concentrations of the following chemical contaminants Al, As, B, F, and insignificant concentrations of non-condensable gases (principally CO_2 , with H_2S , N_2 , CH_4 , NH_3 , etc.) Other chemical constituents, $\text{SiO}_2(\text{aq})$ and Na^+ and Cl^- ions occur in abundance and Ca^{2+} , Mg^{2+} , K^+ , HCO_3^- , and SO_4^{2-} in lesser quantities (Tole, 1990). Most of the chemicals are toxic to flora, fauna, and humans depending on their levels of concentration and bioavailability. Thus, in cases of adverse chemical contamination of the underground and surface water bodies, soil, and vegetation, the trace elements, such as Hg, with capabilities to undergo bioaccumulation through the food chain will be incorporated into the bodies of the animals and humans through either consumption of the same or inhalation of dust particles. The trace elements could thus be passed on to higher feeders along the food chain at toxic concentration levels with adverse biological effects. Therefore, trace elements in spent geothermal fluids pose an environmental challenge to geothermal energy development.

In addition, there have been unsubstantiated claims of effects of geothermal chemical contaminants arising from waste geothermal fluids and residues discharged from the Olkaria geothermal wells and power stations on both human and livestock health. The complaints range from unconfirmed incidences of uncommon skin, respiratory, gastrointestinal ailments, and loss of both human lives and domestic livestock.

1.3.3 Previous environmental studies

The environmental impact of geothermal power development in Olkaria has been studied fairly extensively (Mertz and McLellan-Virkir, 1977; Ewbank Preece, 1989; Tole, 1990; Sinclair Knight and Partners, 1994; Simiyu, 1994, 1998; Were, 1998; Wetang'ula, 2004). The geothermal wastewater, in particular, has been found to contain high concentrations of dissolved chemical components. Although most of the dissolved components are below the Kenyan maximum permissible health limits and some relevant international guidelines for effluent discharge into the environment, the level of some elements e.g. fluoride is particularly high, as is the case in all the Kenyan rift waters. The studies have shown enrichment of trace elements in soil and vegetation in contact with spent geothermal fluids in the Olkaria area and high levels in blood samples from wild animals within Hell's Gate National Park compared to those in Amboseli National Park where there is no geothermal activity. High levels of concentrations of trace elements in soil, vegetation, and blood of wild animals indicated accumulation from spent geothermal fluids and other water sources within the Olkaria geothermal field. In these studies, the total recoverable concentrations of the trace elements and other chemical constituents in abiotic (spent geothermal fluid, soil, and sediment) and biotic (vegetation and blood from wild animals) environmental samples, were determined but not the specific ions or complexes of trace elements. However, there has been extensive evidence that neither total nor dissolved aqueous metal concentrations are good predictors of metal mobility, bioavailability, and toxicity (Janssen, 2003).

The current study is, therefore, an attempt to investigate the distribution of the chemical species of some selected trace elements in spent geothermal fluids and assess the environmental and health risks imposed on the terrestrial and aquatic ecosystems around Olkaria geothermal field.

1.4 The study objectives

The main objectives of the study are:

- To determine the total dissolved concentrations of trace elements and other chemical components of environmental significance in spent geothermal fluids from the Olkaria geothermal field, and Ol'Njorowa Gorge thermal springs and Lake Naivasha water as control samples. The specific aims are to: (1) confirm the results of previous studies in the Olkaria geothermal field; (2) provide a model of the internal economy of the fluid systems; and (3) vet compliance to the Kenyan water quality standards for sources of domestic water, effluent discharge to the environment, irrigation, and recreational water and some relevant international water quality guidelines for drinking, community use, agricultural (irrigation and livestock watering) use, and protection of aquatic life;
- To model the probable species distribution of some selected trace elements (Al, As, Cd, Cu, Pb, Hg, and Zn) in spent geothermal fluids from the Olkaria geothermal field, Ol'Njorowa Gorge thermal springs, and Lake Naivasha water;
- To assess the potential environmental health risks of discharge of spent geothermal fluids on the existing terrestrial and aquatic ecosystems around the Olkaria geothermal field based on the levels of concentrations, predicted species distribution, and available information on the mobility, bioavailability, and ecotoxicity of selected trace elements;
- To recommend alternative cost-effective environmental pollution surveillance and control options to supplement re-injection of spent geothermal fluid in the Olkaria East geothermal field; and
- To identify critical environmental data gaps, future monitoring, and research needs to ensure sustainability of geothermal energy development in the Olkaria geothermal field, Kenya.

2. MATERIALS AND METHODS

2.1 Sampling locations

Ten sampling locations shown in Figure 3 were sited within the Olkaria East geothermal field, Kenya, to assess the levels of concentrations and species distribution of trace elements in spent geothermal fluids. Two sampling locations, Ol’Njorowa Gorge thermal springs, with hydrothermal fluids input, and Lake Naivasha, one of the few freshwater lakes within the Kenyan rift system, were designated as control sampling locations.

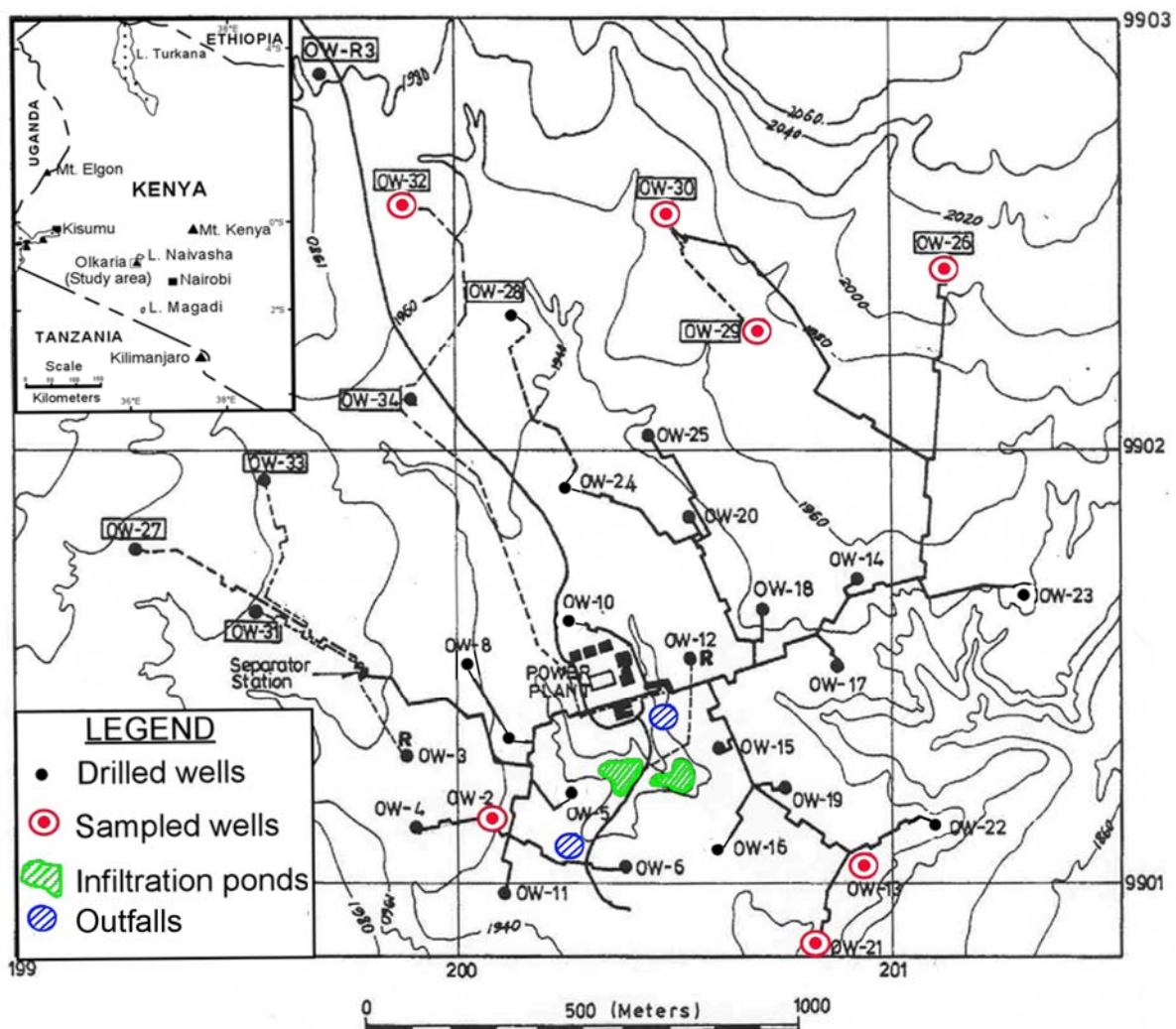


FIGURE 3: Map of sampling locations in the Olkaria East geothermal field, Kenya

In the Olkaria East geothermal field, about 25% of the spent geothermal fluids are disposed of back into the geothermal reservoir through both cold and hot re-injection systems. A substantial (about 75%) amount of the spent geothermal fluids is discharged into the surface environment. In the Olkaria Northeast geothermal field, about 100% of the spent geothermal fluids are re-injected back into the reservoir without any surface discharges. Based on the re-injection status in the Olkaria geothermal field all the sampling locations were sited in the Olkaria East geothermal field and none in the Olkaria Northeast field.

The 12 sampling locations were divided into 7 distinct categories. In the first category, there were discharging geothermal wells OW-2, OW-26, OW-29/30, and OW-32, which were on-line for steam production for Olkaria I power station. In the second category, there were geothermal wells OW-13

and OW-21, which were shut-in for routine maintenance. The aim of sampling spent geothermal fluids from both discharging and shut-in geothermal wells was to assess the effect, if any, of well discharge status on the composition and distribution of dissolved trace elements in spent geothermal fluids as potential point sources of trace metal contamination.

In the third category was Olkaria I outfall encompassing excess condensates and blow-downs from the 45 MW Olkaria I power station.

In the immediate vicinity of Olkaria I station there are two natural depressions, often referred to as Infiltration Lagoons (Figure 4). The two lagoons are separated by an access road but connected to each other through a culvert.



FIGURE 4: The Infiltration Lagoons in the vicinity of Olkaria I power station

Infiltration Lagoon 1 (IL-1) and Infiltration Lagoon 2 (IL-2) comprised the fourth category of sampling locations. The IL-1 and 2 outfalls are designated as the fifth category of sampling locations. Spent geothermal fluids from the geothermal wells in the steam production field and excess condensates and blow-downs from Olkaria I power station, are discharged into surface conditioning ponds to allow for cooling and precipitation of dissolved chemical constituents e.g. silica. The cold spent geothermal fluids then flow from the ponds through concrete-lined drainage channels into the Infiltration Lagoons. The Infiltration Lagoons allow for some unquantified evaporative losses and underground leakage of the spent geothermal fluids prior to cold re-injection back into the geothermal reservoir. According to the available literature (Murray-Gulde et al., 2005), lagoons or wetlands with flourishing aquatic plants such as is in the Olkaria East geothermal field, are effective sinks and filters for toxic trace metals in contaminated environments. Therefore, these sampling locations were selected in an attempt to evaluate the effectiveness of the natural lagoons in removal of trace metal ions from spent geothermal fluids.

In the sixth category of sampling locations, there were Ol’Njorowa Gorge thermal springs situated close to the Olkaria East geothermal field. The thermal springs are typical surface manifestations of outflows of geothermal systems at depth. Therefore, Ol’Njorowa Gorge thermal springs were selected as control sampling locations representative of aquatic ecosystems with input of natural discharge of hydrothermal fluids and associated geothermal chemical constituents. The analysis of Ol’Njorowa Gorge thermal spring fluids was expected to give an indication of levels of concentration and speciation of trace metal ions in aqueous systems with natural inputs of geothermal fluids.

The seventh and last category of sampling location was Lake Naivasha, a freshwater body, devoid of influence of both natural and anthropogenic discharges of geothermal fluids and associated chemical contaminants. This was based on the observations of the previous hydro-geological studies of the Lake and its catchment basins that indicated no hydro-geological connection between it and the deep-seated geothermal reservoir under exploitation in Olkaria geothermal field (Darling et al., 1990, Omenda, 2000; Arusei, 2001).

2.2 Sampling

The samples of spent geothermal fluids, Ol’Njorowa Gorge thermal springs, and Lake Naivasha water, were collected in August 2005. The procedures for collection and handling of the natural water and geothermal fluid samples were adopted from those used by Onindo (1995) with some modifications.

New 250 ml polythene bottles were used in the sampling process. The bottles were first washed with hot soapy water to remove grease then soaked in dilute 0.1 N HNO₃ acid of analytical grade for a minimum of 4 days. This was followed by further soaking for 24 hours in distilled deionised water. Finally, the bottles were rinsed thoroughly in distilled deionised water and filled with leaching solution of 0.1 N HNO₃. Each bottle was then placed in separate plastic bags and sealed. The leaching solution remained in the bottles for at least one week before sampling.

The sampling bottles were transported in sealed plastic bags taking care to avoid exposure to and contamination with dust particles. On reaching the sampling locations, the bottles were filled partially at least twice with the fluid samples and shaken before emptying. The bottles were subsequently filled by hand-dipping beneath the fluid surface while wearing plastic hand gloves to prevent contamination from greasy or dusty hands. After sampling, the bottles were capped and immediately wrapped in plastic bags and transported to the Olkaria Environmental Laboratory for treatment and storage.

Four aliquots of 250 ml each of representative samples of spent geothermal fluids were withdrawn from each of the sampling locations.

2.3 Treatment and storage of samples

Four aliquots of the 250 ml spent geothermal fluid samples from each of the sampling locations were filtered using 0.45 µm Nuclepore cellulose fibre filters to remove suspended particulates as soon as they were taken to the laboratory. The filters were first leached with distilled deionised water and the samples then filtered directly into the acid pre-washed polythene bottles. By convention, whatever passes through the filters is considered dissolved.

After filtration, two of the 250 ml fluid samples from each location were preserved at pH in the range 1.5 – 2.0 by adding 2.0 mls of concentrated Ultrex Supra pure HNO₃ acid for later analysis of dissolved major and trace elements. The acidification of the samples prevents loss of trace elements by adsorption onto the walls of the polythene sampling bottles. The remaining two aliquots of the filtered samples were left unacidified for analysis of Dissolved Organic Carbon, carbon dioxide, and major anions.

All filtered, acidified and unacidified samples were stored frozen during transport through International Courier Services (DHL) from Kenya to The University of Iceland's Geochemistry and Iceland GeoSurvey (ISOR) Laboratories, Iceland, for analysis of DOC, CO₂, and major anions, and through International Airlines from Iceland to Analytica AB Laboratory, Sweden, for analysis of dissolved major and trace elements.

2.4 Analysis of samples

A variety of chemical analytical methods and procedures routinely used in the analysis of geothermal fluids and natural water samples were adopted. The Atomic Optical (or Emission) Spectrometry with Inductively Coupled Plasma (ICP-AES) analyses for DOC, CO₂, and major elements (Al, As, Ca, Fe, Mg, Mo, K, Si, Na, S, and Sr) were carried out using the United States Environmental Protection Agency (USEPA) Method No. 200.7, with some modifications. The Sector Field Mass Spectrometry with Inductively Coupled Plasma (ICP-SFMS) analysis for trace elements (Ba, Cd, Cr, Co, Cu, P, Pb, Mn, Ni, and Zn) was carried out using USEPA Method No. 200.8, also with some modifications. The Atomic Fluorescence Spectrometry (AFS) analysis for Hg was carried out according to Swedish Standard – European Norm (SS-EN) 13506 (modified). Ion Chromatography (IC) analysis for chloride and sulphate and the Ion Selective Electrode method for the determination of fluoride were also used according to USEPA recommended methods.

The detection limits for the elements analysed using ICP-AES, ICP-SFMS, and AFS were: Ca (100 µg/L), K (400 µg/L), Mg (90 µg/L), Na (100 µg/L), S (160 µg/L), Si (30 µg/L), Sr (2.0 µg/L), Al (0.2 µg/L), As (0.2 µg/L), Ba (0.01 µg/L), Cd (0.002 µg/L), Co (0.005 µg/L), Cr (0.01 µg/L), Cu (0.1 µg/L), Fe (0.4 µg/L), Hg (0.002 µg/L), Mn (0.03 µg/L), Mo (0.05 µg/L), Ni (0.05 µg/L), P (1.0 µg/L), Pb (0.01 µg/L), and Zn (0.2 µg/L). Higher detection limits for the quantification of Cd apply to samples with high Mo levels. The detection limits for the anions analysed using IC were: Cl⁻ (0.1 mg/L) and SO₄²⁻ (0.2 mg/L). The detection limit for the F⁻ determination using the Selective Ion Electrode method was 0.002 mg/L. Analytical concentration values lower than these, were reported as < detection limit for the elements analysed and not as zero. The concentration values obtained for diluted sample solutions were corrected by multiplying with the respective dilution factors (Colterman, 1978).

2.4.1 Analysis of physico-chemical parameters

The variable physico-chemical properties (pH, temperature, Total Dissolved Solids, conductivity and Dissolved Oxygen) of the fluid samples from Olkaria I outfall, Infiltration Lagoon 1, Infiltration Lagoon 2, Infiltration Lagoons 1 and 2 outfall, Ol'Njorowa Gorge thermal springs, Lake Naivasha water, and shut-in geothermal wells OW-13 and OW-21, were measured immediately upon sampling using Cyberscan Waterproof portable 4-in-1 pH/Temperature/TDS/Conductivity (Model: PC 300 Series) and 3-in-1 pH/Temperature/DO (Model: PD 300 Series) meters. The spent geothermal fluid samples from the geothermal wells in production: OW-2, OW-26, OW-29/30, and OW-32, were cooled to ambient temperature (25 – 30 °C) using a cold water bath and pH measured using the same portable instruments at Olkaria Environmental Laboratory, Kenya. The pH meters were calibrated using standard pH 4.00 and 7.00 buffer solutions before taking measurements.

2.4.2 Analysis of trace elements and major cations

The acidified samples were shipped from Iceland to Analytica Laboratory in Sweden for the analysis of total dissolved concentrations of major elements (Al, As, Ca, Fe, Mg, Mo, K, Si, Na, S, and Sr) using ICP-AES (Model: Perkin Elmer Optima 5300 DV), trace elements (Ba, Cd, Cr, Co, Cu, P, Pb, Mn, Ni, and Zn) using ICP-SFMS (Model: Thermo Finnigan Element), and Hg using AFS (Model: PSA Millennium).

2.4.3 Analysis of CO₂, DOC, and major anions

The total concentrations of DOC and CO₂ were analysed using ICP-AES (Model: Spectro Ciro Vision) at The University of Iceland's Geochemistry Laboratory. The HCO₃⁻ concentrations were estimated from CO₂ concentration values.

The SO₄²⁻ and Cl⁻ concentrations were determined using an Ion Chromatograph (Model: Dionex DX500; Column: AS15) at the Geochemistry Laboratory of Iceland GeoSurvey (ISOR).

The dissolved hydrogen sulphide concentrations were estimated from S and SO₄²⁻ concentrations. The estimation was based on the assumption that the difference between the analytical concentrations of H₂S and SO₄²⁻ was equivalent to dissolved HS⁻ concentrations. The dissolved concentrations of H₂AsO₄⁻, CrO₄⁻, SiO₂ (aq), MoO₄²⁻, and HPO₄²⁻ required for speciation model calculations were estimated from As, Cr, Si, Mo, and P concentrations, respectively.

Fluoride was analysed for using a Selective Ion Electrode (Model: Metroholm 6.0502.150 F⁻/0 – 80 °C) sensitive to dissolved F⁻ and a pH/mV meter (Model: 781 Metroholm). Metroholm 6.0726.100 Ag/AgCl/0 – 80 °C was used as the standard electrode. The F⁻ content of the samples was determined by directly comparing the sample response potential obtained in standard solutions of known F⁻ content. Comparisons were then made from automated computer plotting of readings. The standards and samples were diluted with an ionic strength adjustment buffer to maintain the pH of the samples at 5 - 6, to destroy complexes and adjust these to the fixed ionic strength.

2.4.4 Reagent blanks

The reagent blank solutions were treated and analyzed in a similar manner as the sample solutions.

2.5 Analytical data

The accuracy of the various analytical methods, data generated, and the quality of aqueous speciation model were tested through comparison of the model calculated electrical imbalance with the cation/anion subtotals for charge equivalents for all the fluid samples.

2.6 Speciation modelling of selected trace elements using the EQ3/6 speciation–solubility code

2.6.1 An overview of the chemical speciation modelling concept

Chemical equilibrium speciation codes provide an attractive alternative to the often difficult and tedious analytical experimental techniques in speciation studies. The most critical requirements are all the conceivable equilibrium stability constants for all possible metal-ligand and proton-ligand species of a system, at the correct fluid ionic strengths, temperatures, and pressures. The species considered are all the free metal ions, inorganic and organic complexes, organo-metallic compounds, and ion pairs derived from the aqueous system components.

In this study, EQ3/6 (Version 8) speciation-solubility code (Wolery, 1992) with an in-built thermodynamic database has been applied to compute the probable species distribution of selected trace elements Al, As, Cd, Cu, Pb, Hg, and Zn in samples of spent geothermal fluids from the Olkaria geothermal field, and Ol'Njorowa Gorge thermal springs, and Lake Naivasha water, as control samples.

2.6.2 Theoretical assumptions and limitations of speciation model calculations

The term natural water system refers to an actual system of some complexity, consisting of an aqueous solution phase, one or more solid phases, and most often a gas phase. The real system may be heterogeneous in its entirety, although it may be sufficiently well characterized as consisting of identifiable homogenous regions. Adequate characterisation of the real system requires caution if the pertinent physical, chemical, and thermal variables are to be adequately reflected in experimental or conceptual models. Local thermal equilibrium can be assumed for a part of the real system.

For an aqueous solution phase of a natural system, the actual composition is given by a set of concentrations of chemical constituents. The simplest thermodynamic model for a natural water system is an aqueous solution which is not subject to physico-chemical reactions with any solid or gaseous phase. Such a system is an idealisation in that water itself and all solutes have some finite escaping tendency, however small. An aqueous solution of an electrolyte in a laboratory maintained at constant temperature and exposed to atmospheric pressure represents a common arrangement for studying chemical equilibrium. Thermodynamic data obtained from such experiments can be used to interpret the behaviour of real or model systems of a more complex character such as a natural water system.

The objective of the calculations in the EQ3/6 code is to determine the most probable chemical model of the aqueous systems around the Olkaria geothermal field.

The concentration of the species in equilibrium is defined in terms of an equilibrium constant:

$$[M_p L_q H_r] = [M]^p [L]^q [H]^r \beta_{pqr}$$

Further, the concentrations of the species in equilibrium are constrained by the law of mass action. For a three component system of a metal ion, M, a ligand, L, and hydrogen ion, H⁺ with concentrations [M], [L], and [H], the expressions for the mass-balance equations are:

$$M_{\text{tot}} = [M] + p \sum \beta_{pqr} [M]^p [L]^q [H]^r$$

$$L_{\text{tot}} = [L] + q \sum \beta_{pqr} [M]^p [L]^q [H]^r$$

$$H_{\text{tot}} = [H] + r \sum \beta_{pqr} [M]^p [L]^q [H]^r$$

where M_{tot} , L_{tot} , and H_{tot} are the total concentrations of metals, ligands, and proton respectively.

The three component system would give three non-linear equations with [M], [L], and $[M_p L_q H_r]$ as the only unknowns if the hydrogen ion concentration obtained from the measurement of pH is known.

The total dissolved concentrations for each of the chemical constituents is used as input data for the EQ3/6 speciation-solubility code. In the calculations, the EQ3/6 code progressively estimates equilibrium concentrations until all the mass balance equations are satisfied. The EQ3/6 program provides an output file consisting of listing of both log of activities of all the probable species in the fluid and the percentage of the dominant species accounting for 99% or more of the aqueous metal species at various pH values.

The EQ3/6 solubility-speciation code has a few limitations similar to most speciation programs: (1) The model may not be inclusive of all significant trace element species due to scarce experimental data available on the stability constants; (2) The thermodynamic database may not be sufficiently correct; and (3) The species nomenclature system is different from other speciation programs e.g. PHREEQC. However, EQ3/6 code has an input file option which permits the user to temporarily modify equilibrium constants at run time. This makes it convenient to conduct sensitivity studies of the uncertainty in such estimated values.

2.6.3 Speciation modelling of selected trace elements in spent geothermal fluids of the Olkaria geothermal field, Ol’Njorowa thermal springs, and Lake Naivasha water using EQ3/6 code

In an attempt to model the predominant inorganic species in the aqueous systems around Olkaria geothermal field, the EQ3/6 (Version 8) which is an aqueous chemical equilibrium computer program, was applied. The EQ3/6 code was run for all the spent geothermal fluid samples, and analyses of Ol’Njorowa Gorge thermal spring fluids and Lake Naivasha water, which were used as control sample fluids. The in-situ pH (as H^+), temperatures ($^{\circ}C$), and total dissolved concentrations (in mg/L) of major ion species (Ca^{2+} , Fe^{2+} , K^+ , Mg^{2+} , Na^+ , $SiO_2(aq)$, HCO_3^- , Cl^- , F^- , HS^- , and SO_4^{2-}) and trace element species (Al^{3+} , $H_2AsO_4^-$, Ba^{2+} , Cd^{2+} , CrO_4^{2-} , Co^{2+} , Cu^{2+} , Pb^{2+} , Mn^{2+} , Hg^{2+} , MoO_4^{2-} , HPO_4^{2-} , Si^{2+} , and Zn^{2+}) determined for each of the sampled fluids (Tables 1 and 2) were entered into the EQ3 NR input file for the speciation calculations. The WATCH program of Arnórsson et al. (1982), version 2.1A (Bjarnason, 1994) was used to determine the in-situ pH values of the discharging geothermal wells OW-2, OW-26, OW-29/30, and OW-32. The pH in the WATCH version 2.1A is calculated taking into account all species of major components that can combine with H^+ . The pH values were varied with intervals of 0.2 from pH 2 to 10 for fluids of Olkaria I outfall and pH 4 to 10 for all the other fluids. The pH values were input into the EQ3/6 code to model the trace element species distribution with changes in pH of the fluids.

The results of the speciation calculations were imported into Microsoft Excel Worksheets to obtain the graphical plots of the species distribution curves of the percentages of the total dissolved species of each of the selected trace elements Al, As, Cd, Cu, Pb, Hg, and Zn, as a function of pH for the spent geothermal fluids from the Olkaria geothermal field, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, Kenya.

3. RESULTS

The total dissolved concentrations of various water quality parameters of spent geothermal fluids from the Olkaria geothermal field, Ol’Njorowa Gorge thermal springs, and Lake Naivasha water, were analyzed in August 2005. The analytical results are presented in Tables 1 and 2.

3.1 Temperature, pH, and DOC

The measured temperatures of spent geothermal fluids from discharging geothermal wells were above 80.0 °C, with the highest temperature of 91.0 °C for spent geothermal fluids from wells OW-26 and OW-32. The Olkaria I outfall fluids had a temperature of 38.0 °C, which was intermediate between those of discharging geothermal wells and the rest of the fluids sampled. Temperatures of spent geothermal fluids from shut-in geothermal wells, Infiltration Lagoons and Infiltration Lagoons outfall were below 30.0 °C and in most cases comparable with temperatures recorded for the Ol’Njorowa Gorge thermal spring fluids (26.3 °C) and Lake Naivasha water (25.1 °C). The lowest recorded temperature was 16.0 °C for spent geothermal fluids of shut-in geothermal well OW-21.

The pH of the fluids sampled from discharging geothermal wells (measured after cooling to 25 – 30 °C) ranged from pH 8.1 – 8.9, shut-in geothermal wells (pH 6.9 – 8.7), for the Infiltration Lagoons (pH 8.4 - 8.6), and Infiltration Lagoons 1 and 2 outfall (pH 8.1). The highest pH value of 8.9 was recorded for spent geothermal fluids of OW-26, which was the most alkaline. The lowest pH value recorded was pH 2.7 for Olkaria I outfall fluids, which was very acidic. The pH of Ol’Njorowa Gorge thermal springs was 8.5, whereas that of Lake Naivasha water was 8.7.

The DOC concentration was highest in Lake Naivasha water (1.25 mg/L). All other fluids with a hydrothermal component sampled had low DOC concentrations ranging from < 0.3 mg/L in the Ol’Njorowa Gorge thermal spring fluids, < 0.02 – 0.31 mg/L in fluids from shut-in geothermal wells, 0.123 mg/L in Infiltration Lagoons outfall fluids, 0.05 – 0.11 mg/L in Infiltration Lagoons, 0.09 mg/L in Olkaria I outfall fluids, and 0.06 – 0.08 mg/L for fluids from the discharging geothermal wells.

3.2 Conductivity and Total Dissolved Solids

The range of conductivity values of spent geothermal fluids from both discharging (4260 – 6890 μScm^{-1}) and shut-in (978 - 5210 μScm^{-1}) geothermal wells were high compared to values determined for Ol’Njorowa Gorge thermal spring fluids (2070 μScm^{-1}) and Lake Naivasha water (325 μScm^{-1}).

The TDS values ranged from 2070 - 3550 mg/L for fluids from discharging geothermal wells, 480 - 2560 mg/L for shut-in geothermal wells, Infiltration Lagoons 1 and 2 outfall (813 - 992 mg/L), Infiltration Lagoons 1 and 2 outfall (1400 mg/L), and Olkaria I outfall (205 mg/L), in that order. The highest TDS value of 3550 mg/L was recorded for fluids of well OW-32. The TDS values for all the fluids were higher than that of Lake Naivasha water (162 mg/L). The spent geothermal fluids in Infiltration Lagoons 1 and 2 and Ol’Njorowa Gorge thermal springs (1030 mg/L) had comparable TDS values.

3.3 Dissolved major cation and anion concentrations

Selected water quality variables for spent geothermal fluids are graphically presented in Figure 5.

Na^+ was the major cation in the spent geothermal fluids and Ol’Njorowa Gorge thermal springs. The highest Na^+ concentrations was in the fluids from discharging geothermal well OW-32 (554.0 mg/L) and the lowest in Olkaria I outfall (31.8 mg/L).

TABLE 1: Physico-chemical parameters and major cation and anion concentrations (in mg/L) in spent geothermal fluids from the Olkaria East geothermal field, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, Kenya (August, 2005).

Location	Temp (°C)	pH@ 25 °C	Cond (µS _{cm} ⁻¹)	TDS	DOC	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	P	Si ⁴⁺	S	HS ⁻	SiO ₂ ^o	HCO ₃ ^{-s}	HPO ₄ ^{2-s}	Cl ⁻	F ⁻	SO ₄ ²⁻
OW-2	88.0	8.4	6820	3410	0.063	536	81.2	<0.09	0.585	0.004	317	9.86	0.22	679.3	21.98	0.013	788	66.9	28.9
OW-13	27.1	8.7	5210	2560	0.308	419	44.5	<0.09	0.674	0.026	227	17.8	0.15	486.4	171.38	0.083	350	101	52.9
OW-21	16.0	6.9	978	480	<0.02	67.3	13.7	0.148	4.58	0.006	45.6	28.3	0.14	97.7	8.94	0.02	46.1	12.2	84.4
OW-26	91.0	8.9	4260	2070	0.080	326	50.5	<0.09	0.244	0.002	335	7.28	2.48	717.9	68.31	0.007	355	69.0	14.6
OW-29/30	80.0	8.6	5060	2320	0.063	383	67.8	<0.09	0.315	0.002	391	9.51	1.34	837.9	12.15	0.007	534	52.6	24.6
OW-32	91.0	8.1	6890	3550	0.086	554	107	<0.09	0.396	0.006	461	15.5	0.19	987.9	11.25	0.019	822	57.9	45.9
Olkaria I outfall	38.0	2.7	412	205	0.090	31.8	6.44	0.113	0.732	0.012	24.5	18.8	0.00	52.5	2.21	0.039	45.1	3.99	57.3
IL-1	23.1	8.4	1621	813	0.058	289	50.8	0.092	0.663	0.008	189	17.0	0.32	405	38.31	0.026	417	38.0	50.0
IL-2	25.1	8.6	1979	992	0.118	379	63.7	<0.09	0.671	0.008	235	16.7	0.08	503.6	52.16	0.025	543	50.0	49.8
IL 1 and 2 outfall	24.1	8.1	2790	1400	0.123	534	86.9	<0.09	1.01	0.013	251	15.4	0.15	537.9	60.66	0.043	776	64.2	45.7
Ol’Njorowa Gorge	26.3	8.5	2070	1030	<0.3	466	16.7	0.237	2.28	0.064	62.5	51.3	0.24	133.9	371.00	0.198	338	65.4	153
Lake Naivasha	25.1	8.7	325	162	1.254	35.2	20.8	5.93	15.0	0.035	11.0	1.12	0.19	23.6	174.41	0.11	15.5	1.71	2.79
LN No. 120 (2006) ^a		6.5 -		1200															1.5
LN No. 120 (2006) ^b	± 3	8.5 -		1200									0.1				250	1.5	
LN No. 120 (2006) ^c		8.5 -		1200		SAR: 6										2.0	0.01	1.0	
LN No. 120 (2006) ^d	30	8.5 -																	
CCME (1999) ^e		6.0 -																	1.5
CCME (1999) ^f		9.0																	1 - 2
EC (1990) ^g		6.5 -				150 -										5.0	25	1.5 -	25
		8.5				175												1.7	
WHO (1990) ^h		6.5 -				200												1.5	400
		8.5																	

^aEstimated concentration values; Blanks: No set limit values; and SAR: Sodium Absorption Ratio; ^bKenyan Guide Value (Maximum Allowable) for Sources of Domestic Water; ^cKenyan Maximum Allowable Limits for Effluents Discharge to the Environment; ^dKenyan Permissible Level for Irrigation Water; ^eKenyan Maximum Permissible Level for Recreational Water; ^fCanadian Maximum Acceptable Concentrations in Water for Community Use; ^gCanadian Maximum Acceptable Concentrations in Water for Livestock Watering; ^hEuropean Community Maximum Allowable Concentrations for Drinking-Water Quality; and ⁱWorld Health Organisation Maximum Allowable Concentrations for Drinking-Water Quality

TABLE 2: Trace element concentrations (in µg/L) in spent geothermal fluids from the Olkaria East geothermal field, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, Kenya (August, 2005).

Location	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	Sr	Zn
OW-2	614	1210	3.28	<0.05	0.151	0.302	0.543	90.6	0.0931	6.52	266	0.436	0.247	5.66	4.15
OW-13	618	1150	2.33	<0.01	0.0304	0.472	1.66	92.1	0.185	13	96.2	0.692	0.795	2.97	7.46
OW-21	305	20.3	4.82	<0.007	0.872	3.84	3.1	2640	0.0305	426	22.4	42.5	2.58	12.8	22.3
OW-26	988	934	1.99	<0.02	0.0082	0.141	0.484	24.5	0.141	1.63	114	0.216	0.221	<2.0	2.53
OW-29/30	1750	1170	1.83	<0.02	0.0059	0.227	0.643	46.3	0.111	3.71	209	0.131	0.257	2.22	3.20
OW-32	1890	1290	8.92	<0.05	0.0259	0.264	1.49	65.7	0.688	5.26	510	21.8	0.373	5.44	14.0
Olkaria I outfall	367	91.1	9.21	<0.009	0.206	29.8	9.4	684	0.741	24.3	23.9	3.38	2.38	4.04	41.6
IL-1	951	698	3.15	<0.09	0.0579	9.02	1.69	288	1.22	18.9	218	0.78	0.339	5.16	12.4
IL-2	1100	913	3.32	<0.08	0.0528	6.76	1.91	283	1.25	12.7	283	0.650	0.426	5.36	10.3
IL 1 and 2 outfall	1030	1270	3.88	<0.08	0.0451	4.84	1.81	0.231	0.744	14.9	396	0.859	0.432	9.76	10.2
Ol’Njorowa Gorge	1130	60	2.43	0.148	0.0651	0.724	1.55	2.07	1.02	11.2	214	0.323	0.629	4.24	13.7
Lake Naivasha	1850	1.71	9.22	0.0209	0.353	0.676	1.44	1520	0.973	90.2	3.65	1.14	0.636	1.44	10.3
LN No. 120 (2006) ^a	10	10	10	10	100	2000	50	10000	5	10000		300	50		1500
LN No. 120 (2006) ^b	20	10	10	10	100	2000	100	10000	5	10000		300	10		500
LN No. 120 (2006) ^c	5000	100	100	500	100	1500	50	1000					5000		2000
LN No. 120 (2006) ^d	50	10	100	10	100	100			1						
CCEM (1999) ^e	100	25 (IMAC)	1000	5	50	50			1				10		
CCME (1999) ^f	5000	25	1000	80	1000	50	500 - 1000		3		500	1000	100		50000
CCME (1999) ^g	5000	100	5	5	50	5 - 8	200 - 1000				10-50	200	200		1000-5000
EC (1990) ^h	200	5	5	5	100		100			50			50		
WHO (1990) ⁱ	200	5	1000	5	1000		1000		1	100	70	20	50		

Blanks: No set limit values; IMAC: Interim Maximum Acceptable Concentration.; ^aKenyan Guide Value (Maximum Allowable) for Sources of Domestic Water; ^bKenyan Maximum Allowable Limits for Effluents Discharge to the Environment; ^cKenyan Permissible Level for Irrigation Water; ^dKenyan Permissible Level for Recreational Water; ^eCanadian Maximum Acceptable Concentrations in Water for Community Use; ^fCanadian Maximum Acceptable Concentrations in Water for Livestock Watering; ^gCanadian Maximum Acceptable Concentrations in Water for Irrigation Purposes or Protection of Plants; ^hEuropean Community Maximum Allowable Concentrations for Drinking-Water Quality; ⁱWorld Health Organisation Maximum Allowable Concentrations for Drinking-Water Quality.

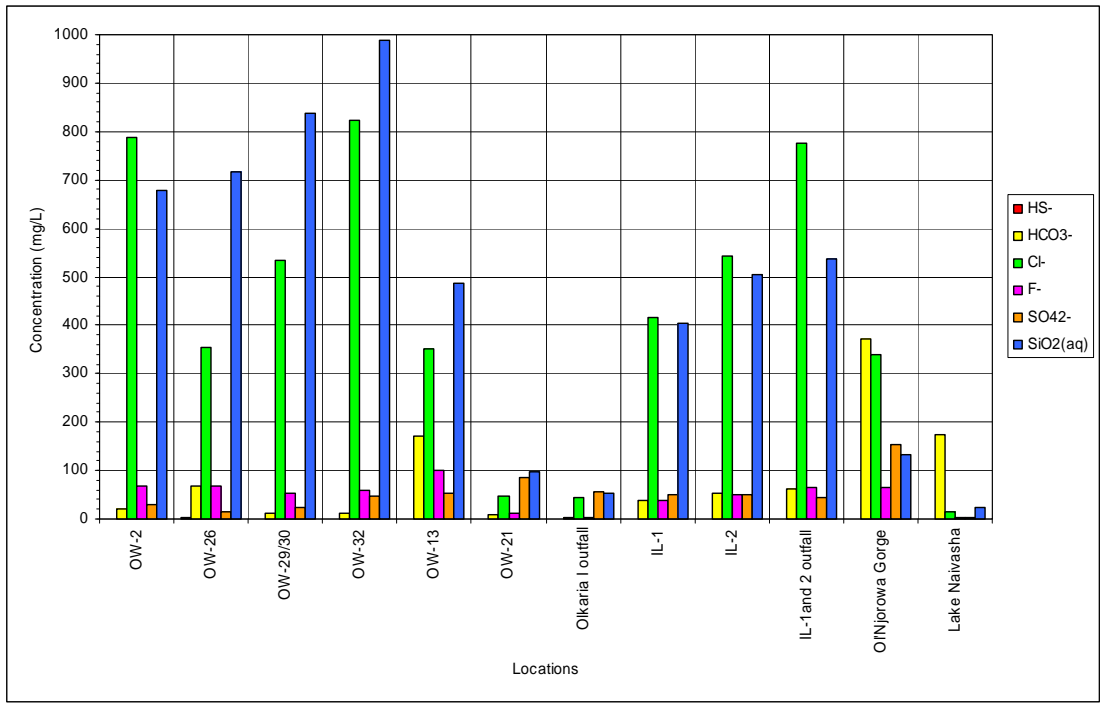
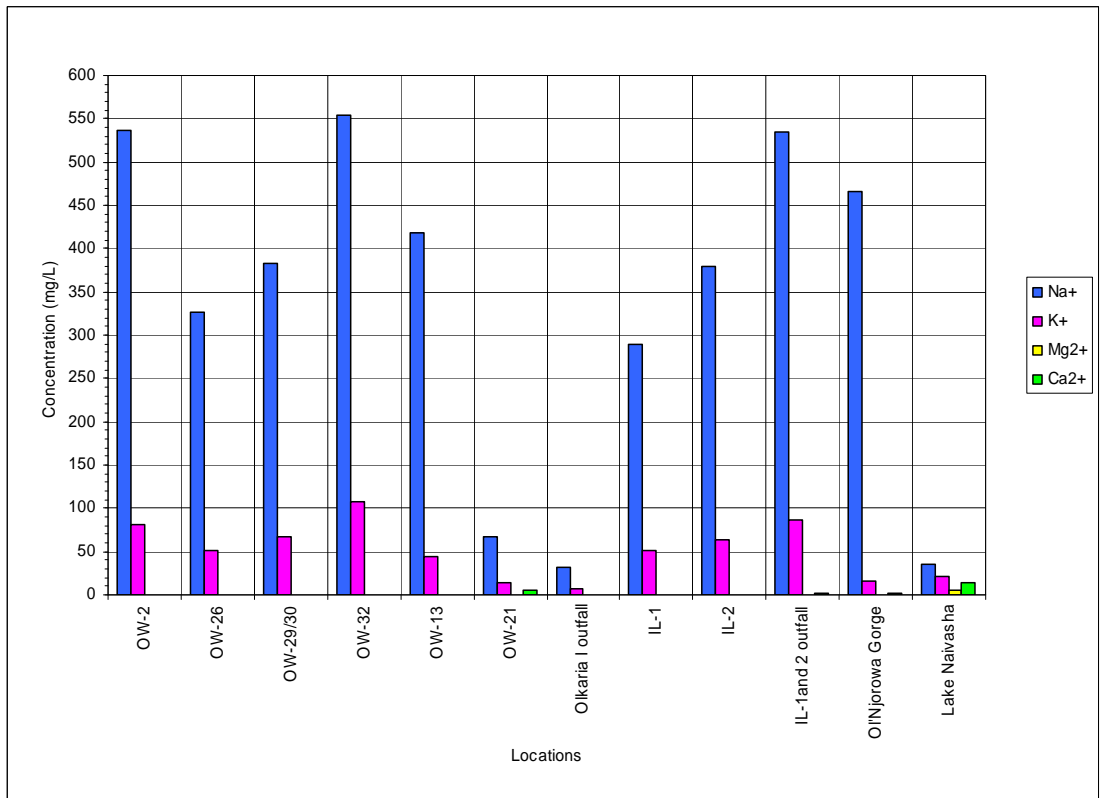


FIGURE 5: Selected major ion species concentrations in spent geothermal fluids from the Olkaria geothermal field, Ol'Njorowa Gorge thermal spring fluids, and Lake Naivasha water, Kenya (August, 2005)

The spent geothermal fluids had variable Na^+ concentrations, which ranged from 326 – 554 mg/L for discharging geothermal wells, 534 mg/L in Infiltration Lagoons 1 and 2 outfall, 67.3 – 419 mg/L in shut-in geothermal wells, and 289 – 379 mg/L in Infiltration Lagoons. The Na^+ concentration in Ol'Njorowa Gorge thermal spring fluids (466.0 mg/L) was within the range of concentrations of spent

geothermal fluids from discharging geothermal wells. All fluids sampled, except Olkaria I outfall fluids, had higher levels of Na^+ than Lake Naivasha water (35.2 mg/L).

Other cations in the spent geothermal fluids in order of relative abundance were K^+ , Ca^{2+} , and Mg^{2+} . The highest dissolved K^+ concentration was 107 mg/L in fluids from discharging geothermal well OW-32 and the lowest 6.44 mg/L in Olkaria I outfall fluids. The spent geothermal fluids were depleted in Ca^{2+} ions with the highest concentration 4.58 mg/L in fluids from shut-in well OW-21. Ca^{2+} concentration in Lake Naivasha water (15.0 mg/L) was higher than in all the hydrothermal fluids sampled. Mg^{2+} concentrations were below the detection limit (0.09 mg/L) in all the fluids with hydrothermal fluids component sampled. The Mg^{2+} concentration was, however, significantly elevated in Lake Naivasha water (5.93 mg/L).

Cl^- was the major dissolved anion in the spent geothermal fluids. Other anions were HCO_3^- , F^- , and SO_4^{2-} . The Cl^- concentrations ranged from 45.1 mg/L in Olkaria I outfall fluids to 822 mg/L in fluids from discharging geothermal well OW-32. The dissolved Cl^- concentrations were above 300 mg/L for all the fluids from discharging geothermal wells (350 – 822 mg/L), Infiltration Lagoons 1 and 2 outfall (776 mg/L), Infiltration Lagoons (417 – 543 mg/L), shut-in geothermal well OW-13 (350 mg/L). The Cl^- concentrations in spent geothermal fluids were comparatively close to those of the Ol’Njorowa Gorge thermal springs (338 mg/L) but higher than in Lake Naivasha water (15.5 mg/L).

The F^- concentrations of the spent geothermal fluids were higher than in Lake Naivasha water (1.71 mg/L) and ranged from 12.2 – 101.0 mg/L in fluids from shut-in geothermal wells, 52.6 – 69.0 mg/L in fluids from discharging geothermal wells, 64.2 mg/L in Infiltration Lagoon 1 and 2 outfall fluids, 38.0 - 50.0 mg/L in Infiltration Lagoons, and 3.99 mg/L in Olkaria I outfall fluid. The spent geothermal fluids from shut-in geothermal well OW-13 had the highest F^- concentration 101 mg/L. The F^- concentrations in the Infiltration Lagoons 1 and 2 outfall fluids were relatively close to those of the Ol’Njorowa Gorge thermal spring fluids (65.4 mg/L).

SO_4^{2-} concentrations were lower than 100 mg/L in all fluids sampled except those of Ol’Njorowa Gorge thermal springs. The highest SO_4^{2-} concentration was found in the fluids from shut-in geothermal well OW-21 (84.4 mg/L) and the lowest in the fluids from discharging geothermal well OW-26 (14.6 mg/L). The SO_4^{2-} concentrations in all the sampled fluids were lower than in Ol’Njorowa Gorge thermal springs (153 mg/L) and higher than the concentration in Lake Naivasha water (2.79 mg/L).

HCO_3^- concentrations in all the spent geothermal fluids were lower than in both Ol’Njorowa Gorge thermal spring fluids (371 mg/L) and Lake Naivasha water (174.4 mg/L). The highest aqueous HCO_3^- concentration was 171.3 mg/L in the fluids from shut-in well OW-13 and the lowest in Olkaria I outfall fluids (2.21 mg/L).

Aqueous silica concentrations were high in spent geothermal fluids. $\text{SiO}_2(\text{aq})$ concentrations in all sampled fluids were above 400 mg/L and higher than in both Ol’Njorowa Gorge thermal springs (133.9 mg/L) and Lake Naivasha water (23.6 mg/L). The highest value of $\text{SiO}_2(\text{aq})$ was recorded in fluids from discharging geothermal well OW-32 (987.9 mg/L) and the lowest in Olkaria I outfall (52.5 mg/L).

3.4 Dissolved trace element concentrations

The selected trace element concentrations in spent geothermal fluids are graphically presented in Figure 6.

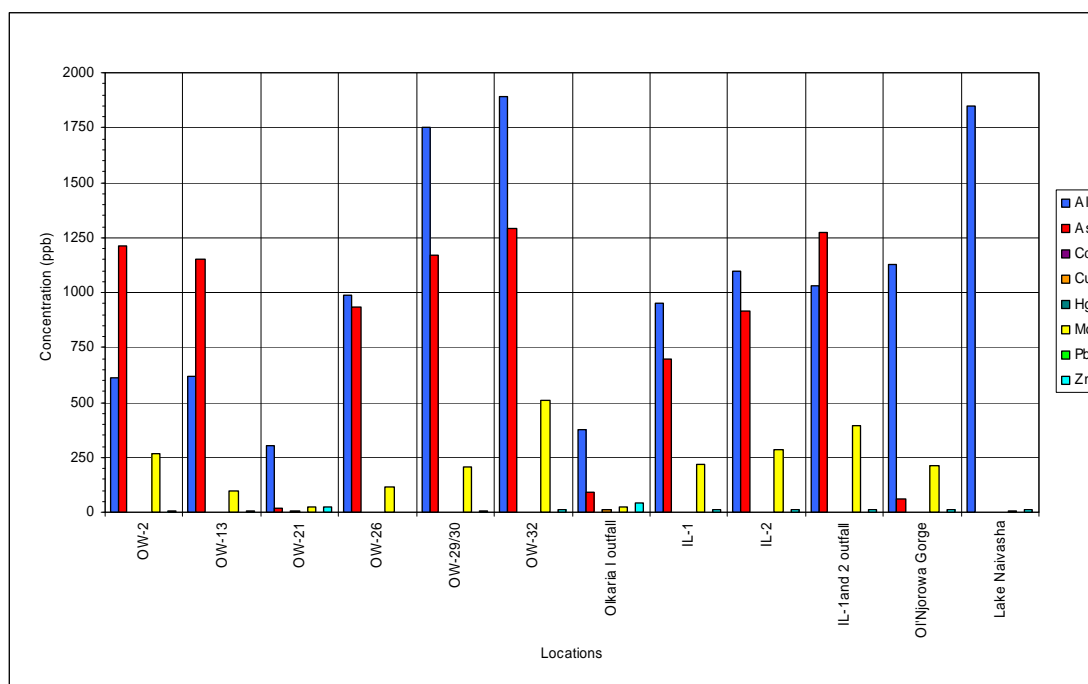


FIGURE 6: Selected trace element concentrations in spent geothermal fluids from the Olkaria geothermal field, Ol’Njorowa Gorge thermal springs, and Lake Naivasha water, Kenya (August, 2005)

The aluminium concentrations were high in all fluids sampled. The highest Al concentration was 1890 $\mu\text{g/L}$ in fluids from discharging geothermal well OW-32. The Al concentration in Lake Naivasha water (1850 $\mu\text{g/L}$) was higher than the average concentrations in fluids from discharging geothermal wells (1252 $\mu\text{g/L}$), Infiltration Lagoon 2 (1100 $\mu\text{g/L}$), Infiltration Lagoons 1 and 2 outfall (1030 $\mu\text{g/L}$), shut-in geothermal well OW-13 (618 $\mu\text{g/L}$), and Olkaria I outfall (367 $\mu\text{g/L}$). Aluminium concentration in Ol’Njorowa Gorge thermal springs (1130 $\mu\text{g/L}$) was within the range of the values for the Infiltration Lagoons.

The arsenic concentration in Lake Naivasha water (1.71 $\mu\text{g/L}$) was lower than in all the spent geothermal fluids with a hydrothermal component inclusive of Ol’Njorowa Gorge thermal spring fluids (60 $\mu\text{g/L}$). The aqueous As concentrations were elevated and were 1290 $\mu\text{g/L}$ in fluids from discharging geothermal well OW-32, 1270 $\mu\text{g/L}$ in the Infiltration Lagoons outfall fluids, an average of 1159 $\mu\text{g/L}$ in fluids from discharging geothermal wells, 1150 $\mu\text{g/L}$ in fluids from shut-in geothermal well OW-13, 913 $\mu\text{g/L}$ in Infiltration Lagoon 2 fluids, and 91.1 $\mu\text{g/L}$ in Olkaria I outfall fluids.

The cadmium concentrations were below the ICP-AES detection limits in all the spent geothermal fluids. The highest Cd concentration was in Ol’Njorowa Gorge thermal spring fluids (0.14 $\mu\text{g/L}$) followed by Lake Naivasha water (0.02 $\mu\text{g/L}$).

The copper concentration in Olkaria I outfall fluids (9.4 $\mu\text{g/L}$) was higher than in fluids from shut-in geothermal well OW-21 (3.1 $\mu\text{g/L}$), Infiltration Lagoon 1 (1.91 $\mu\text{g/L}$), Infiltration Lagoons outfall (1.8 $\mu\text{g/L}$), and discharging geothermal well OW-32 (1.49 $\mu\text{g/L}$). The average Cu concentration in the fluids of discharging geothermal wells was lower than in Ol’Njorowa Gorge thermal spring fluids (1.55 $\mu\text{g/L}$) and Lake Naivasha water (1.44 $\mu\text{g/L}$).

The lead concentration was highest in the fluids from shut-in geothermal well OW-21 (2.58 $\mu\text{g/L}$), followed by that from the Olkaria I outfall fluids (2.38 $\mu\text{g/L}$). The Pb concentrations in Ol’Njorowa Gorge thermal spring fluids (0.62 $\mu\text{g/L}$) and Lake Naivasha water (0.63 $\mu\text{g/L}$) were higher than in the

fluids from Infiltration Lagoon 1 and 2 outfall (0.43 µg/L), Infiltration Lagoon 2 (0.42 µg/L), and discharging geothermal well OW-32 (0.37 µg/L).

The mercury concentration was highest in the Infiltration Lagoon 1 fluids (1.25 µg/L). The Hg concentrations in Ol’Njorowa Gorge thermal spring fluids (1.02 µg/L) and Lake Naivasha water (0.97 µg/L) were higher than in fluids from Olkaria I and Infiltration Lagoons 1 and 2 outfall where Hg content was 0.74 µg/L, discharging geothermal well OW-32 (0.68 µg/L) and shut-in geothermal well OW-13 fluids (0.18 µg/L).

The molybdenum concentration in Lake Naivasha water (3.65 µg/L) was low in comparison to the levels of concentration in the rest of the fluids sampled with a hydrothermal component. The Mo concentration in Ol’Njorowa Gorge thermal spring fluids was 214 µg/L. The average Mo content in the fluids from the Infiltration Lagoons outfall fluids was 396 µg/L, fluids from discharging geothermal wells (274 µg/L), Infiltration Lagoons (250 µg/L), shut-in geothermal well OW-13 (96.2 µg/L), and Olkaria I outfall fluids (23.9 µg/L).

The zinc concentrations ranged from a high of 41.6 µg/L in Olkaria I outfall fluids, 22.3 µg/L in fluids from shut-in geothermal well OW-21, 14.0 µg/L in fluids from discharging geothermal well OW-32, 12.4 µg/L in Infiltration Lagoon 1, and 10.2 µg/L in Infiltration Lagoons 1 and 2 outfall fluids. Zn concentrations in Ol’Njorowa Gorge thermal spring fluids (13.7 µg/L) and Lake Naivasha water (10.3 µg/L) were comparable to concentrations in fluids from discharging geothermal well OW-32 and Infiltration Lagoons 1 and 2 outfall fluids, respectively.

3.5 The probable speciation of selected trace elements in spent geothermal fluids from the Olkaria geothermal field, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, Kenya using the EQ3/6 code

The probable distribution of Al, As, Cd, Cu, Pb, Hg, and Zn species was predicted using the EQ3/6 (Version 8) speciation-solubility code. The total dissolved major and trace inorganic component concentrations (Tables 1 and 2), were used as input data in the EQ3/6 NR input file for speciation calculations in the EQ 3/6 program. The organic species of the selected trace elements were not studied on the assumption that the organic-metal complexes were less likely to be formed in basic aqueous media with high alkalinity such as spent geothermal fluids (Korfali and Davies, 2004). The organic species are also extremely uncommon in geothermal fluids and are unlikely to form at temperatures of the geothermal systems but may form during biological activity in the outfalls. The EQ3/6 code performs computations and provides output files consisting of distribution of aqueous solute species in logs of activities and percentages of the species accounting for 99% or more of all aqueous major and trace inorganic species in the fluids contributing to aqueous mass balance equations at various pH values ranging from pH 2 - 10 with intervals of 0.2.

3.5.1 Aluminium

The probable distribution of aluminium species in spent geothermal fluids from discharging geothermal wells OW-2, OW-26, OW-29/30 and OW-32, shut-in geothermal wells OW-13 and OW-21, Olkaria I outfall and Infiltration Lagoons, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, is shown in Figures 7a, 7b, and 7c.

The percentages of species accounting for 99% or more of the total aqueous aluminium within the sampling locations at in-situ pH and temperatures are shown in Table 3.

The range of percentages of dominant aluminium species within the 7 categories of the sampling locations is presented in Table 4.

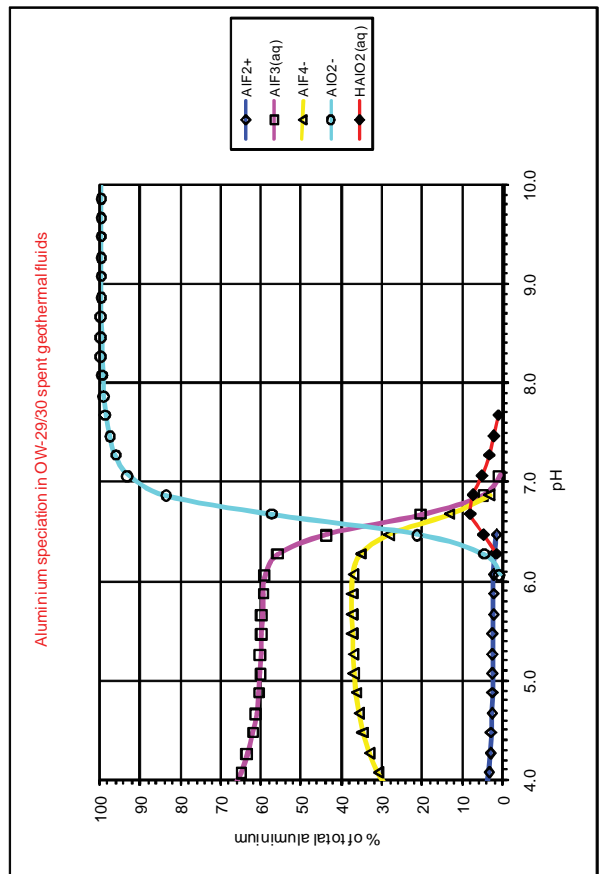
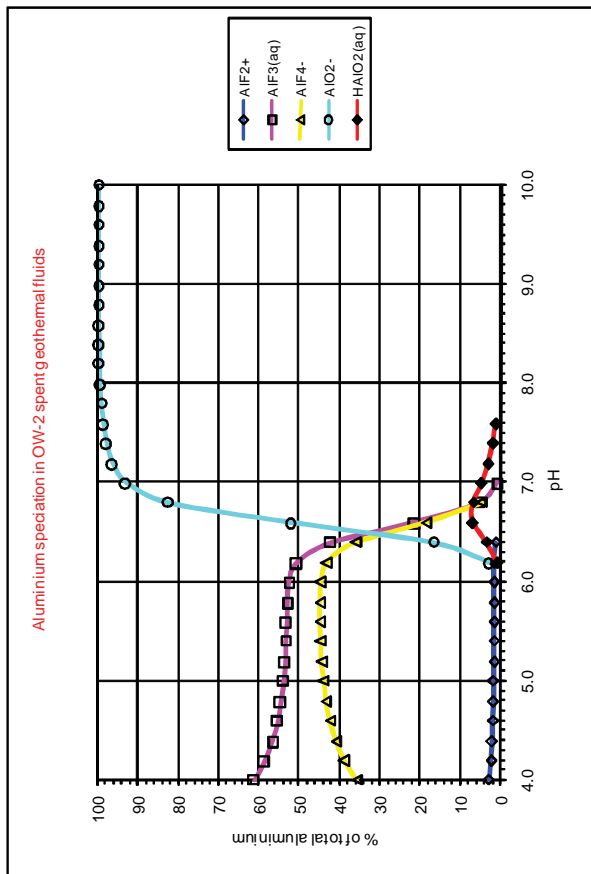
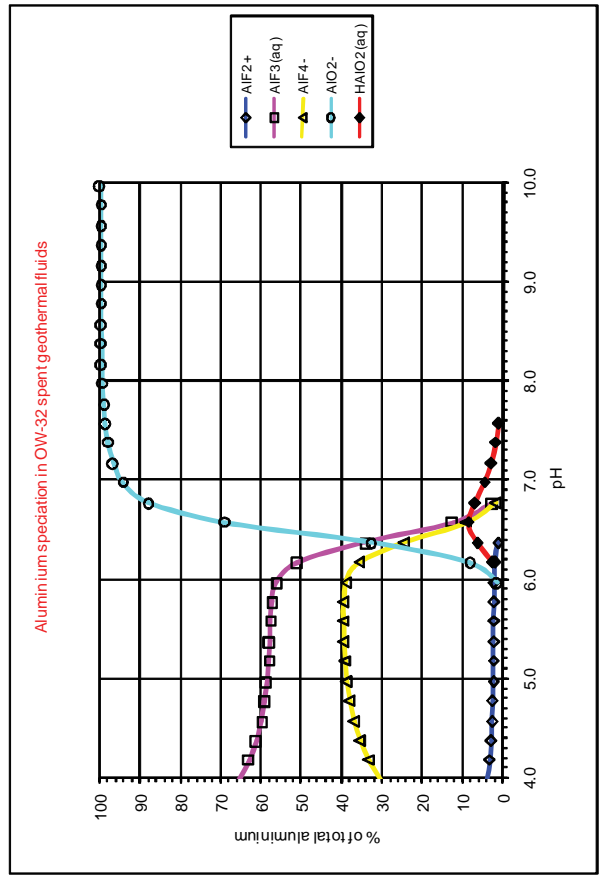
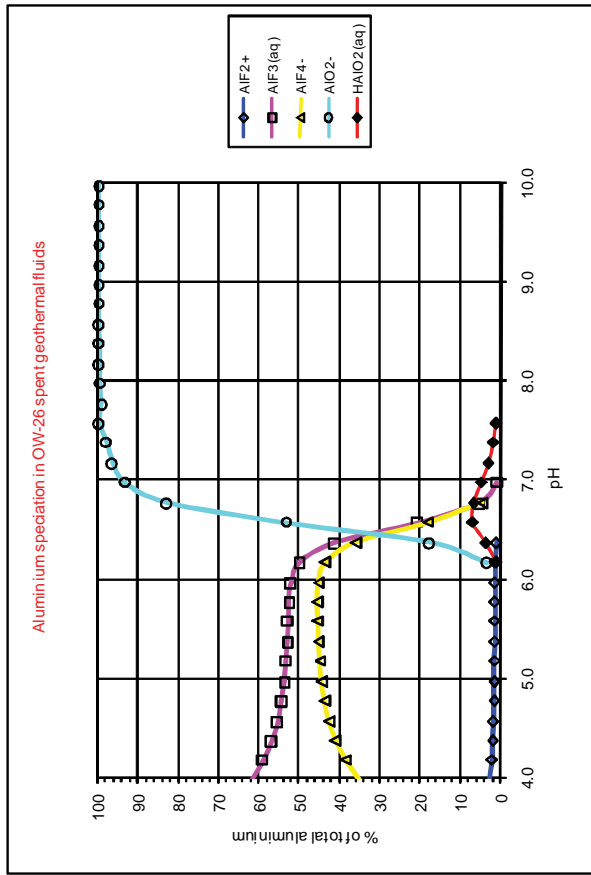


FIGURE 7a: Distribution curves for aluminum species in spent geothermal fluids from discharging geothermal wells

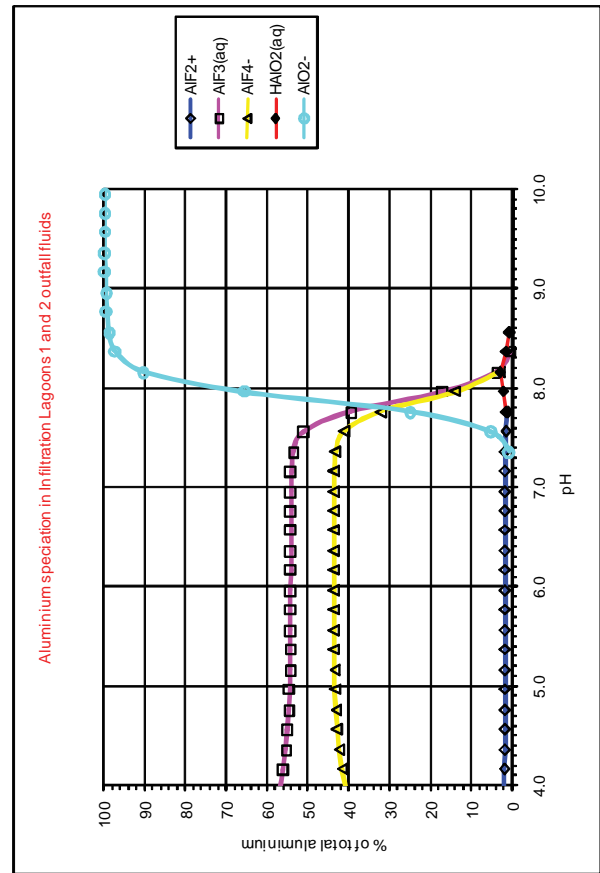
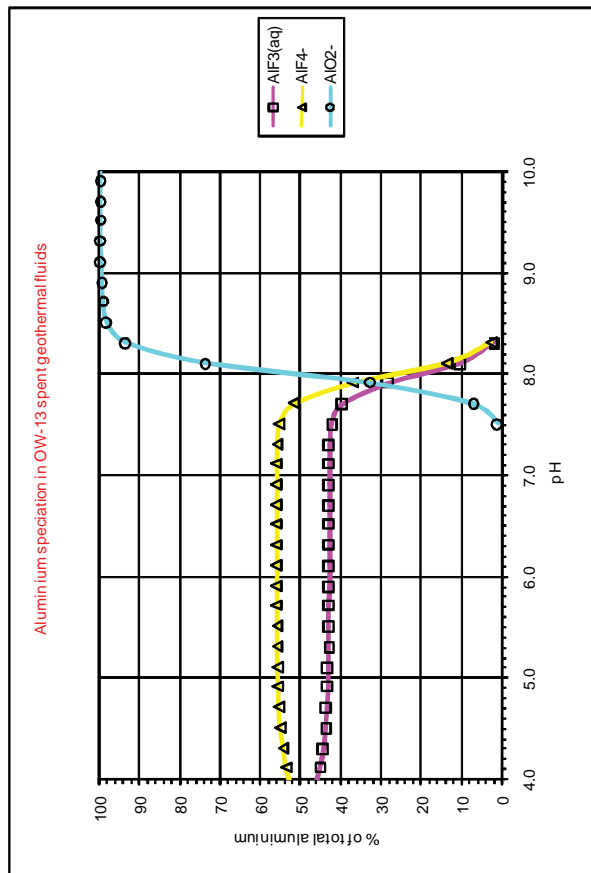
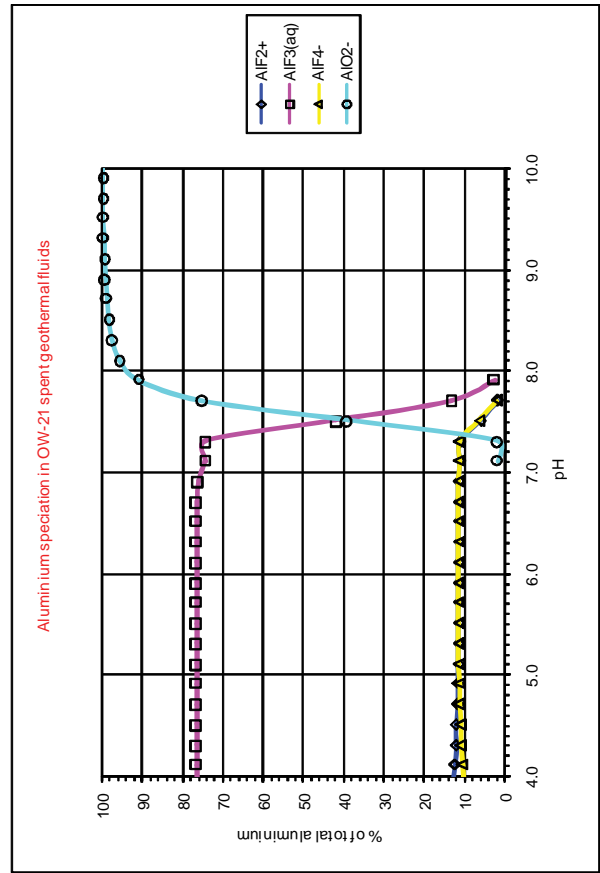
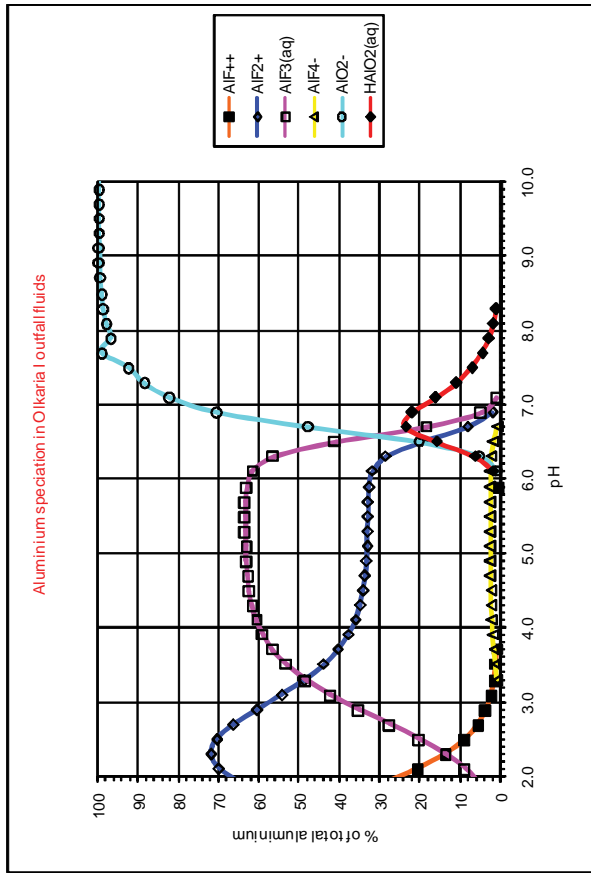


FIGURE 7b: Distribution curves for aluminium species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoon 1 and 2 outfall fluids

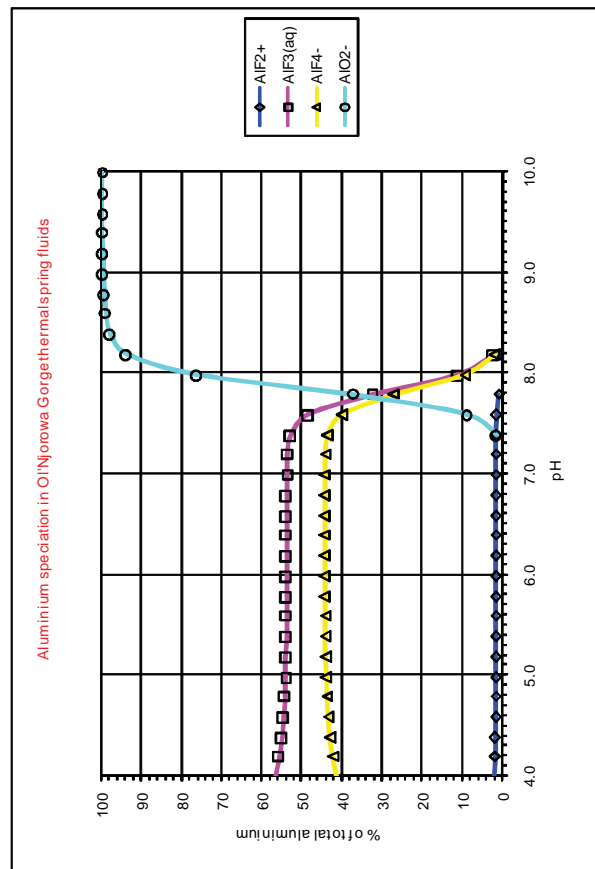
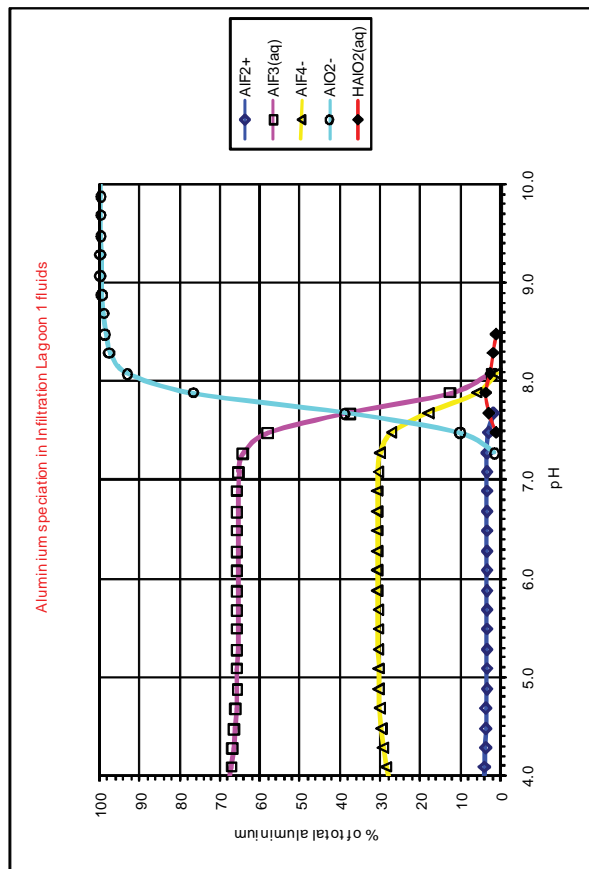
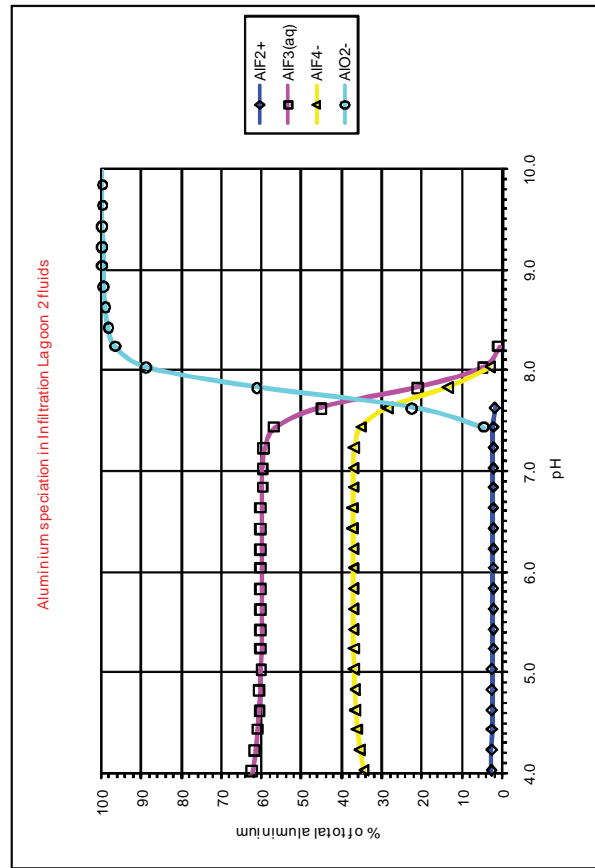
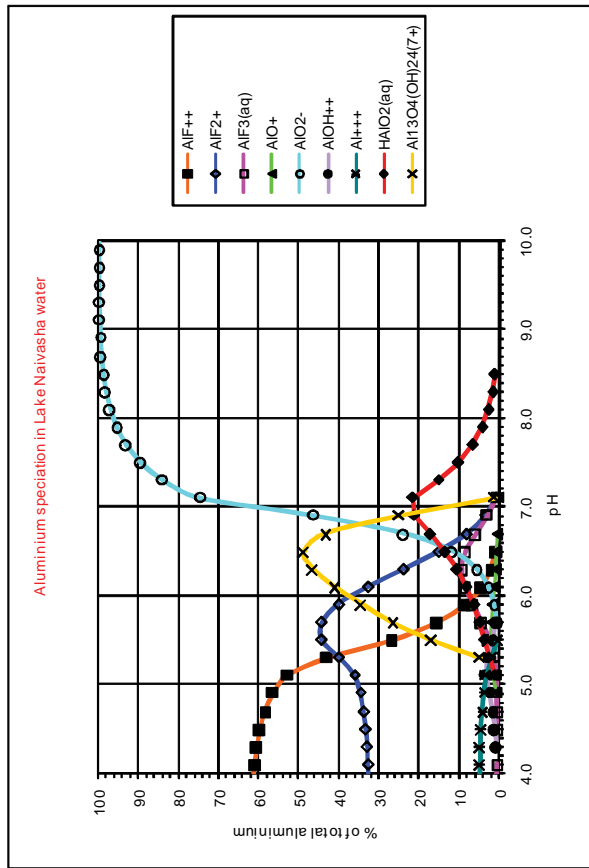


FIGURE 7c: Distribution curves for aluminium species in spent geothermal fluids from the Infiltration Lagoons 1 and 2, OI'Njorowa Gorge thermal spring fluids, and Lake Naivasha water

TABLE 3: Percentage composition of aluminium species at in-situ pH and temperatures within sampling locations

Location	In-situ pH	In-situ Temp (°C)	Total analytical concentration (µg/L)	Dominant species
OW-2	8.4	88.0	614	[AlO ₂] ⁻ (99.79%)
OW-13	8.7	27.1	618	[AlO ₂] ⁻ (99.25%)
OW-21	6.9	16.0	305	AlF ₃ (aq)(76.27%) [AlF ₂] ⁺ (11.55%) [AlF ₄] ⁻ (11.62%)
OW-26	8.9	91.0	988	[AlO ₂] ⁻ (99.95%)
OW-29/30	8.6	80.0	1750	[AlO ₂] ⁻ (99.86%)
OW-32	8.1	91.0	1890	[AlO ₂] ⁻ (99.68%)
Olkaria I outfall	2.7	38.0	367	[AlF ₂] ⁺ (66.35%) AlF ₃ (aq)(27.62%) [AlF ²⁺]
IL-1	8.4	23.1	951	[AlO ₂] ⁻ (98.69%) HAlO ₂ (aq)(1.2%)
IL-2	8.6	25.1	1100	[AlO ₂] ⁻ (99.17%)
IL-1 and 2 outfall	8.1	24.1	1030	[AlO ₂] ⁻ (90.59%) AlF ₃ (aq)(3.87%) [AlF ₄] ⁻ (3.24%) HAlO ₂ (aq)(2.17%)
Ol’Njorowa Gorge thermal springs	8.5	26.3	1130	[AlO ₂] ⁻ (99.04%)
Lake Naivasha	8.7	25.1	1850	[AlO ₂] ⁻ (99.28%)

TABLE 4: Percentage ranges for aluminium species in spent geothermal fluids from the Olkaria geothermal field, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, Kenya

Species	% range of aluminium species						
	Discharging wells (pH 8.1 – 8.9)	Shut-in wells (pH 6.9 – 8.7)	Olkaria I outfall (pH 2.7)	Lagoons (pH 8.1– 8.6)	Lagoons Outfall (pH 8.1)	Ol’Njorowa Gorge springs (pH 8.5)	Lake Naivasha (pH 8.7)
[AlO ₂] ⁻	99.68 – 99.95	99.25		98.69 – 99.17	90.59	99.04	99.28
AlF ₃ (aq)		76.27	27.62		3.87		
[AlF ₂] ⁺		11.55	66.35				
[AlF ₄] ⁻		11.62			3.24		
[AlF ²⁺]			5.75				
HAlO ₂ (aq)			1.2	1.2	2.17		

The Al-hydroxy complex [AlO₂]⁻ is the dominant species of dissolved Al in all the sampled fluids with in-situ pH > 7 (Table 4). The predominance of [AlO₂]⁻ was 99.68 - 99.95% in fluids from discharging geothermal wells, shut-in geothermal wells (99.25%), Lake Naivasha water (99.28%), Infiltration Lagoons (98.69 – 99.17%), Ol’Njorowa Gorge thermal spring fluids (99.04%), Infiltration Lagoons outfall (90.59%), but nil in the acidic fluids from Olkaria I outfall with in-situ pH of 2.7.

The dissolved Al also exists as Al-F complexes in fluids with in-situ pH < 8 such as in shut-in geothermal wells, Olkaria I outfall, and Infiltration Lagoons outfall. The dominant Al-F complexes are [AlF₂]⁺ (66.35%), AlF₃(aq) (27.62%), and [AlF²⁺] (5.75%) in Olkaria I outfall fluids; AlF₃(aq) (76.27%), [AlF₂]⁺ (11.55%), and [AlF₄]⁻ (11.62%), in fluids from shut-in geothermal wells; and minor percentages of AlF₃(aq) (3.87%), and [AlF₄]⁻ (3.24%) in fluids from the Infiltration Lagoons outfall. AlF₃(aq) is dominant in fluids with in-situ pH 6.9 such as in OW-21 (76.27%), and [AlF₂]⁺ in fluids from Olkaria I outfall (66.35%) with in-situ pH of 2.7.

The HAlO₂(aq) species occurs in minor amounts in fluids from the Infiltration Lagoons outfall (2.17%), 1.2% in Olkaria I outfall and Infiltration Lagoons, but nil in fluids from all the geothermal wells, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water.

3.5.2 Arsenic

The probable distribution of arsenic species in spent geothermal fluids from discharging geothermal wells OW-2, OW-26, OW-29/30 and OW-32, shut-in geothermal wells OW-13 and OW-21, Olkaria I

outfall and Infiltration Lagoons, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, is shown in Figures 8a, 8b, and 8c.

The percentages of species accounting for 99% or more of the total aqueous arsenic within the sampling locations at in-situ pH and temperatures are shown in Table 5.

The range of percentages of the dominant arsenic species within the 7 categories of the sampling locations is presented in Table 6.

The dominant dissolved As species in the fluids are inorganic arsenate-oxy-fluoride complexes $[\text{AsO}_3\text{F}]^{2-}$ and $[\text{HAsO}_3\text{F}]$. $[\text{AsO}_3\text{F}]^{2-}$ is dominant in all the sampled fluids within the in-situ pH range 6.9 – 8.9. The highest percentage of $[\text{AsO}_3\text{F}]^{2-}$ species was predicted in fluids from shut-in well OW-26 (99.95%) with a correspondingly high in-situ pH 8.9 and nil in Olkaria I outfall fluids with in-situ pH 2.7. Both species of arsenic are predominant in fluids of well OW-21 with pH 6.9. $[\text{HAsO}_3\text{F}]$ is the dominant As species in the acidic fluids of Olkaria I outfall (99.92%), 6.7% in shut-in geothermal well OW-21, but nil in fluids from discharging geothermal wells, Infiltration Lagoons and outfall, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water.

TABLE 5: Percentage composition of arsenic species at in-situ pH and temperatures within the sampling locations

Location	In-situ pH	In-situ Temp (°C)	Total analytical concentration (µg/L)	Dominant species
OW-2	8.4	88.0	1210	$[\text{AsO}_3\text{F}]^{2-}$ (99.83%)
OW-13	8.7	27.1	1150	$[\text{AsO}_3\text{F}]^{2-}$ (99.91%)
OW-21	6.9	16.0	20.3	$[\text{AsO}_3\text{F}]^{2-}$ (93.3%) $[\text{HAsO}_3\text{F}]$ (6.7%)
OW-26	8.9	91.0	934	$[\text{AsO}_3\text{F}]^{2-}$ (99.95%)
OW-29/30	8.6	80.0	1170	$[\text{AsO}_3\text{F}]^{2-}$ (99.9%)
OW-32	8.1	91.0	1290	$[\text{AsO}_3\text{F}]^{2-}$ (99.72%)
Olkaria I outfall	2.7	38.0	91.1	$[\text{HAsO}_3\text{F}]$ (99.92%)
IL-1	8.4	23.1	698	$[\text{AsO}_3\text{F}]^{2-}$ (99.83%)
IL-2	8.6	25.1	913	$[\text{AsO}_3\text{F}]^{2-}$ (99.89%)
IL-1 and 2 outfall	8.1	24.1	1270	$[\text{AsO}_3\text{F}]^{2-}$ (99.69%)
Ol’Njorowa Gorge thermal springs	8.5	26.3	60	$[\text{AsO}_3\text{F}]^{2-}$ (99.88%)
Lake Naivasha	8.7	25.1	1.71	$[\text{AsO}_3\text{F}]^{2-}$ (99.88%)

TABLE 6: Range of percentages for arsenic species in spent geothermal fluids from the Olkaria geothermal field, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, Kenya

Species	% range of arsenic species						
	Discharging geothermal wells (pH 8.1 – 8.9)	Shut-in geothermal wells (pH 6.9 – 8.7)	Olkaria I outfall (pH 2.7)	Infiltration lagoons (pH 8.1 – 8.6)	Infiltration lagoons outfall (pH 8.1)	Ol’Njorowa Gorge thermal springs (pH 8.5)	Lake Naivasha (pH 8.7)
$[\text{AsO}_3\text{F}]^{2-}$	99.72 – 99.95	93.3 – 99.91		99.83 – 99.89	99.69	99.88	99.88
$[\text{HAsO}_3\text{F}]$		6.7	99.92				

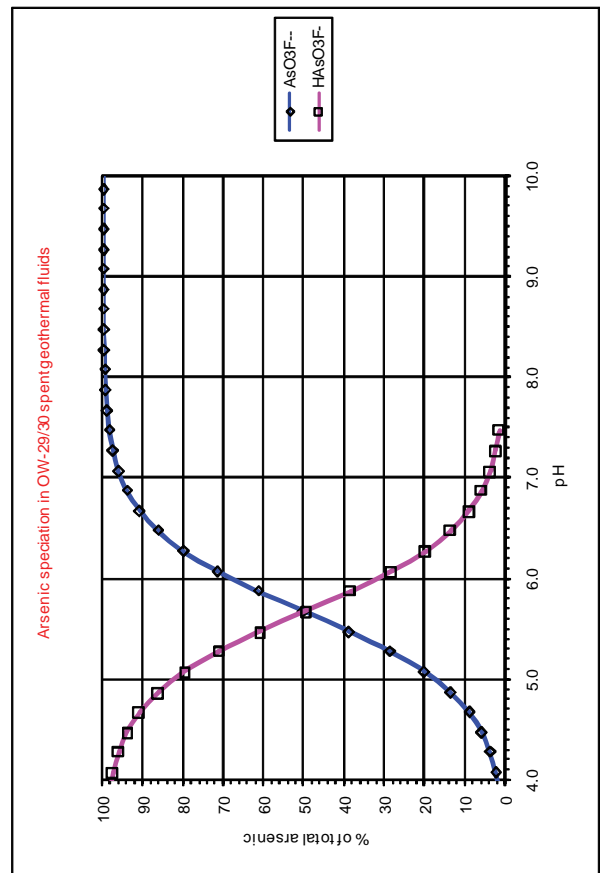
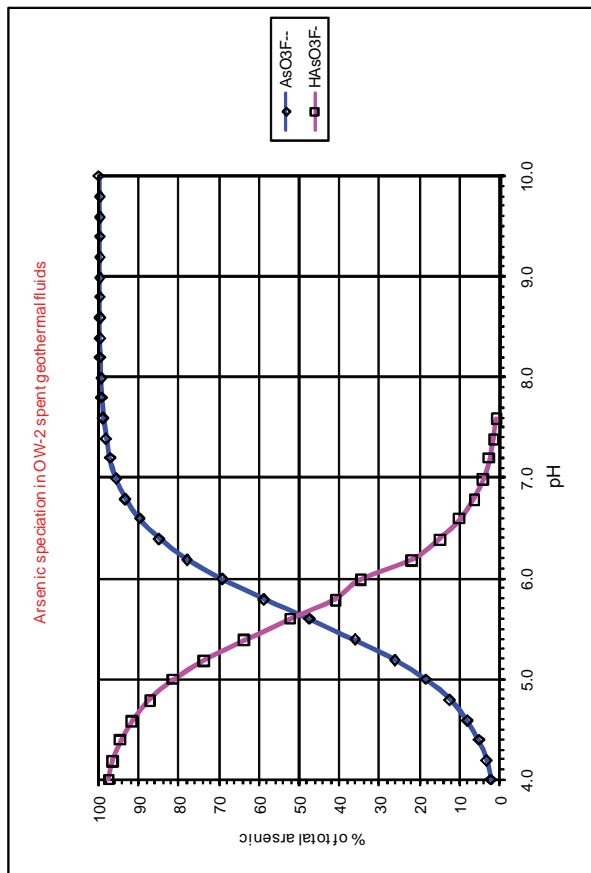
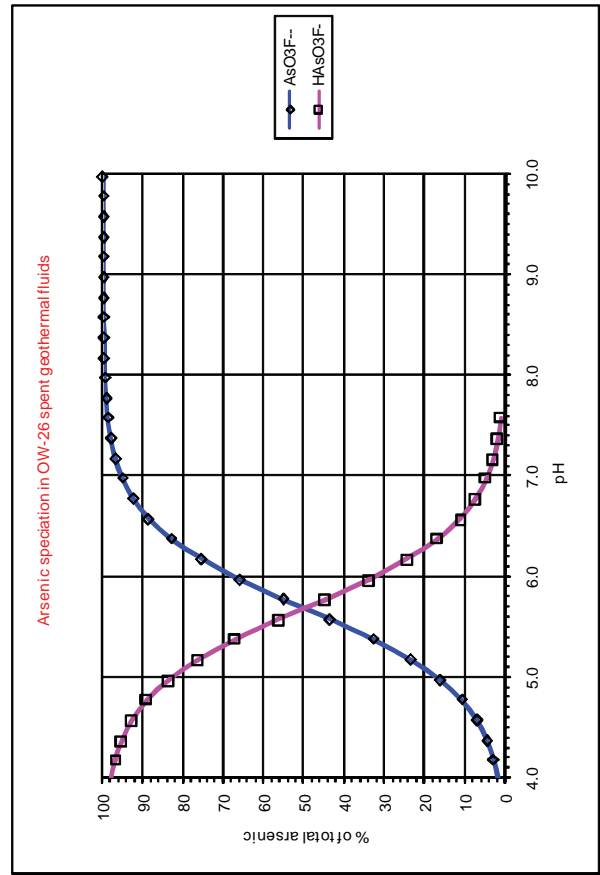
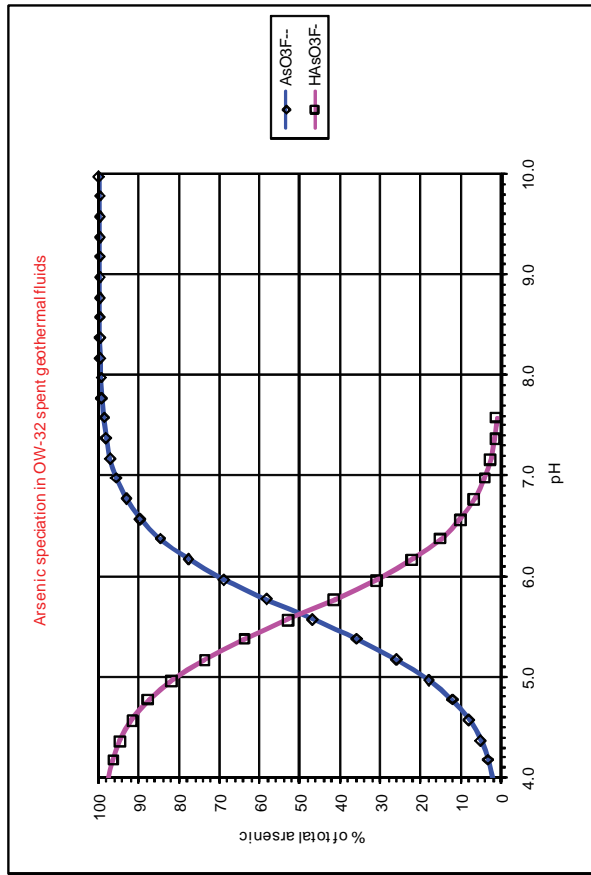


FIGURE 8a: Distribution curves for arsenic species in spent geothermal fluids from discharging geothermal wells

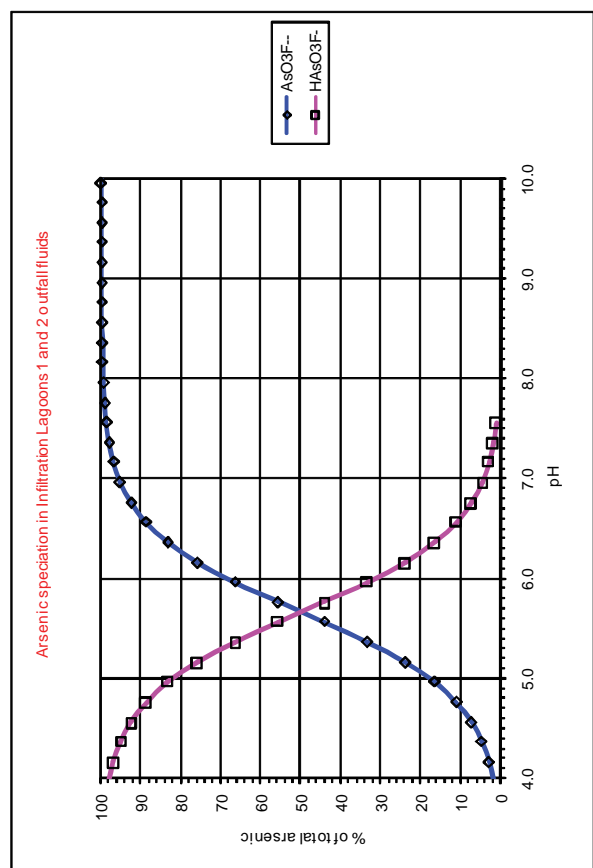
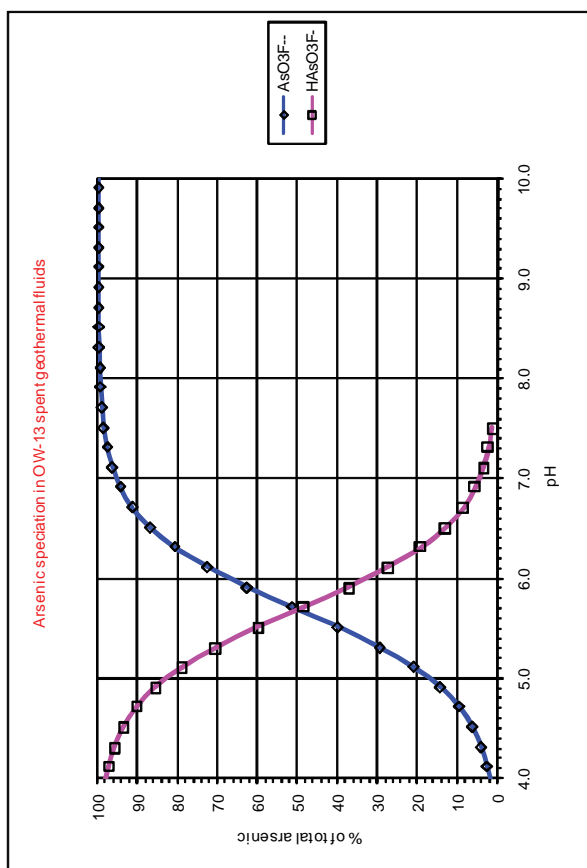
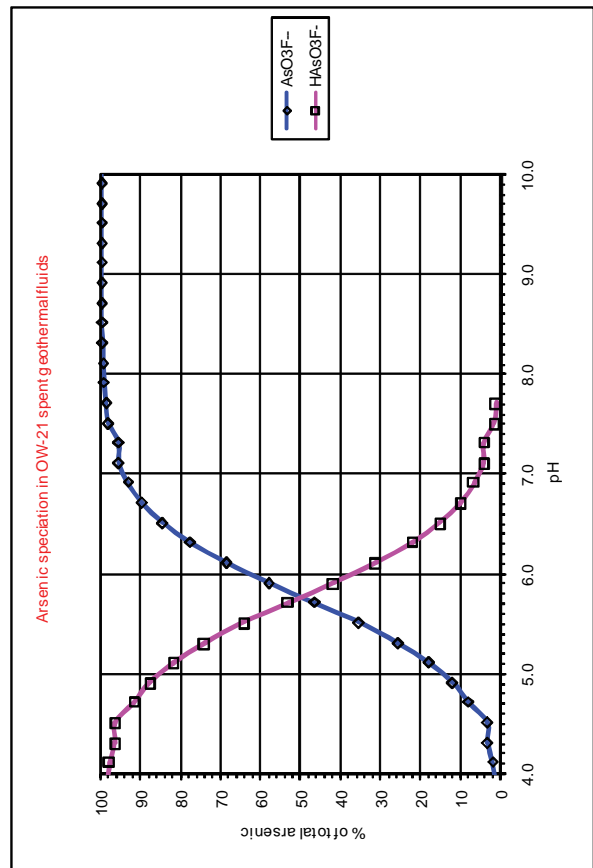
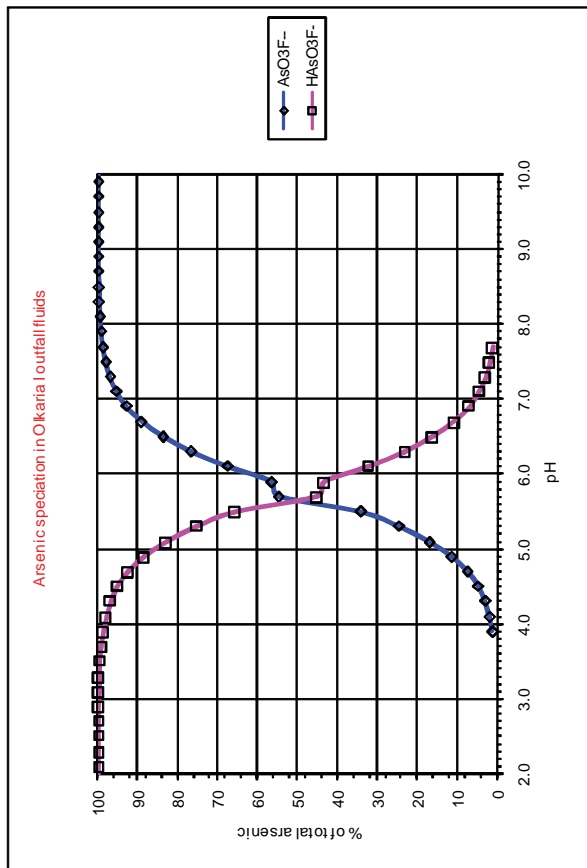


FIGURE 8b: Distribution curves for arsenic species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoons 1 and 2 outfalls

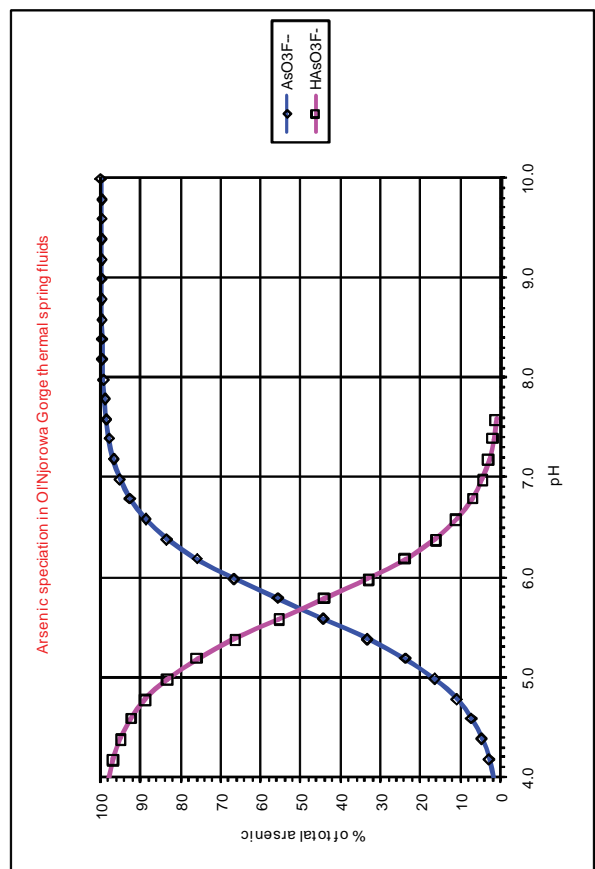
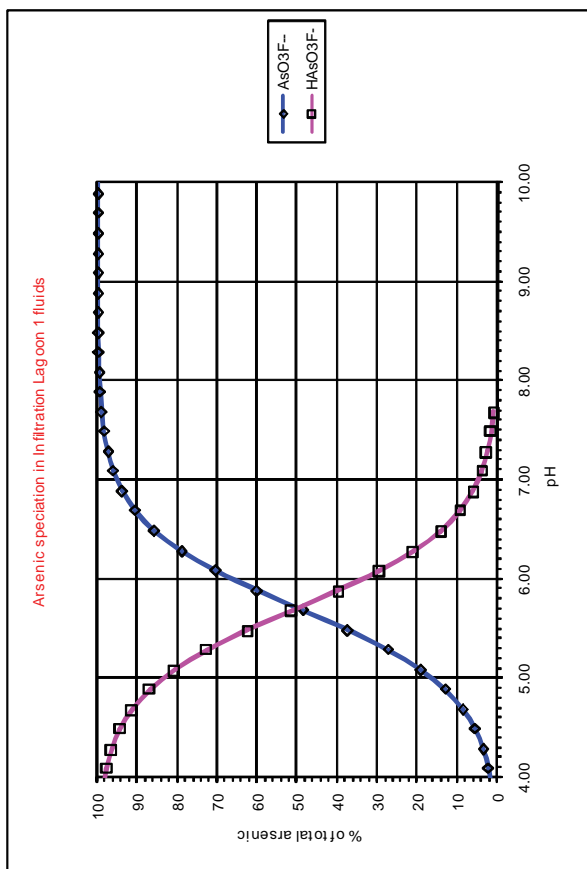
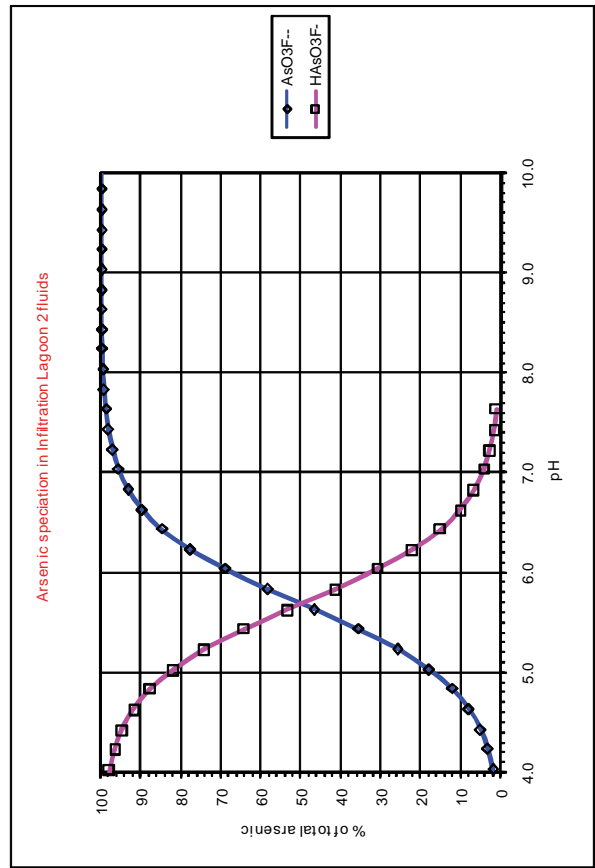
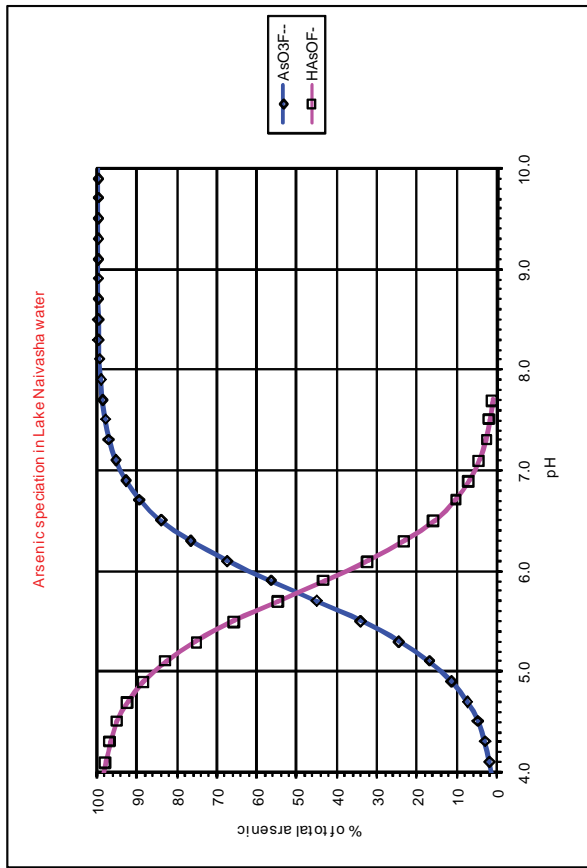


FIGURE 8c: Distribution curves for arsenic species in spent geothermal fluids from the Infiltration Lagoons 1 and 2, Ol'Njorowa Gorge thermal spring fluids, and Lake Naivasha water

3.5.3 Cadmium

The total dissolved cadmium concentrations are very low and in most sampled fluids below detection limit values. Cadmium speciation modelling was, therefore, based on concentrations at detection limit values and not the actual concentrations of the fluids. The assumption was that this would give a reasonable approximation to the probable species distribution of aqueous cadmium.

The probable distribution of cadmium species in spent geothermal fluids from discharging geothermal wells OW-2, OW-26, OW-29/30 and OW-32, shut-in geothermal wells OW-13 and OW-21, Olkaria I outfall and Infiltration Lagoons, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, are shown in Figures 9a, 9b, and 9c.

The percentage of species accounting for 99% or more of the total aqueous cadmium within the sampling location at in-situ pH and temperatures are shown in Table 7.

The range of percentages of the dominant cadmium species within the 7 categories of the sampling locations is presented in Table 8.

The speciation modelling predicted various soluble species of cadmium in all sampled fluids with minimal speciation in the acidic fluids from Olkaria I outfall (Table 8). It exists mainly as free Cd^{2+} ion, but also as $\text{CdO}(\text{aq})$, $[\text{CdCl}]^+$, $[\text{CdOH}]^+$, $\text{CdCO}_3(\text{aq})$, $\text{Cd}(\text{OH})\text{Cl}(\text{aq})$, $[\text{CdHCO}_3]^+$, $\text{CdCl}_2(\text{aq})$, $[\text{CdF}]^+$, and $[\text{Cd}(\text{CO}_3)_2]^{2-}$.

TABLE 7: Percentage composition of cadmium species at in-situ pH and temperatures within the sampling locations

Location	In-situ pH	In-situ temp (°C)	Total analytical concentration (µg/L)	Dominant species
OW-2	8.4	88.0	<0.05	CdCl^+ (35.05%) Cd^{2+} (31.52%) CdOH^+ (17.91%) $\text{CdO}(\text{aq})$ (9.44%) $\text{Cd}(\text{OH})\text{Cl}(\text{aq})$ (2.67%) $\text{CdCl}_2(\text{aq})$ (1.84%) CdF^+ (1.32%)
OW-13	8.7	27.1	<0.01	Cd^{2+} (55.61%) CdCl^+ (29.17%) $\text{Cd}(\text{OH})\text{Cl}(\text{aq})$ (5.31%) CdHCO_3^+ (2.71%) CdF^+ (2.07%) $\text{CdCO}_3(\text{aq})$ (1.89%) CdOH^+ (1.89%) $\text{CdCl}_2(\text{aq})$ (0.87%)
OW-21	6.9	16.0	<0.007	Cd^{2+} (90.16%) CdCl^+ (8.97%)
OW-26	8.9	91.0	<0.02	$\text{CdO}(\text{aq})$ (58.51%) CdOH^+ (24.57%) Cd^{2+} (9.12%) CdCl^+ (5.16%) $\text{Cd}(\text{OH})\text{Cl}(\text{aq})$ (1.51%) CdF^+ (0.45%)
OW-29/30	8.6	80.0	<0.02	Cd^{2+} (30.591%) CdCl^+ (23.82%) CdOH^+ (23.53%) $\text{CdO}(\text{aq})$ (16.3%) $\text{Cd}(\text{OH})\text{Cl}(\text{aq})$ (3.74%) CdF^+ (0.97%) $\text{CdCl}_2(\text{aq})$ (0.87%)
OW-32	8.1	91.0	<0.05	CdCl^+ (40.63%) Cd^{2+} (34.89%) CdOH^+ (13.85%) $\text{CdO}(\text{aq})$ (5.13%) $\text{CdCl}_2(\text{aq})$ (2.23%) $\text{Cd}(\text{OH})\text{Cl}(\text{aq})$ (1.84%) CdF^+ (1.3%)
Olkaria I outfall	2.7	38.0	<0.009	Cd^{2+} (90.09%) CdCl^+ (7.82%)
IL-1	8.4	23.1	<0.09	Cd^{2+} (54.57%) CdCl^+ (37.42%) $\text{Cd}(\text{OH})\text{Cl}(\text{aq})$ (3.95%) $\text{CdCl}_2(\text{aq})$ (1.46%) $\text{CdO}(\text{aq})$ (0.85%) CdF^+ (0.79%)
IL-2	8.6	25.1	<0.08	Cd^{2+} (48.47%) CdCl^+ (40.28%) $\text{Cd}(\text{OH})\text{Cl}(\text{aq})$ (6.02%) $\text{CdCl}_2(\text{aq})$ (1.93%) CdOH^+ (1.19%) CdF^+ (0.89%) CdHCO_3^+ (0.72%)
IL-1 and 2 outfall	8.1	24.1	<0.08	CdCl^+ (48.59%) Cd^{2+} (43.6%) $\text{CdCl}_2(\text{aq})$ (3.25%) $\text{Cd}(\text{OH})\text{Cl}(\text{aq})$ (2.39%) CdF^+ (0.95%) CdHCO_3^+ (0.71%)
Ol’Njorowa Gorge springs	8.5	26.3	0.14	Cd^{2+} (55.75%) CdCl^+ (27.41%) CdHCO_3^+ (5.69%) $\text{Cd}(\text{OH})\text{Cl}(\text{aq})$ (3.69%) $\text{CdCO}_3(\text{aq})$ (2.81%) CdOH^+ (1.3%) CdF^+ (1.3%) $\text{Cd}(\text{CO}_3)_2^{2-}$ (1.15%)
Lake Naivasha	8.7	25.1	0.02	Cd^{2+} (83.77%) CdCl^+ (27.41%) CdHCO_3^+ (5.42%) $\text{CdCO}_3(\text{aq})$ (3.84%) CdOH^+ (2.95%) CdCl^+ (2.6%) $\text{Cd}(\text{CO}_3)_2^{2-}$ (0.76%)

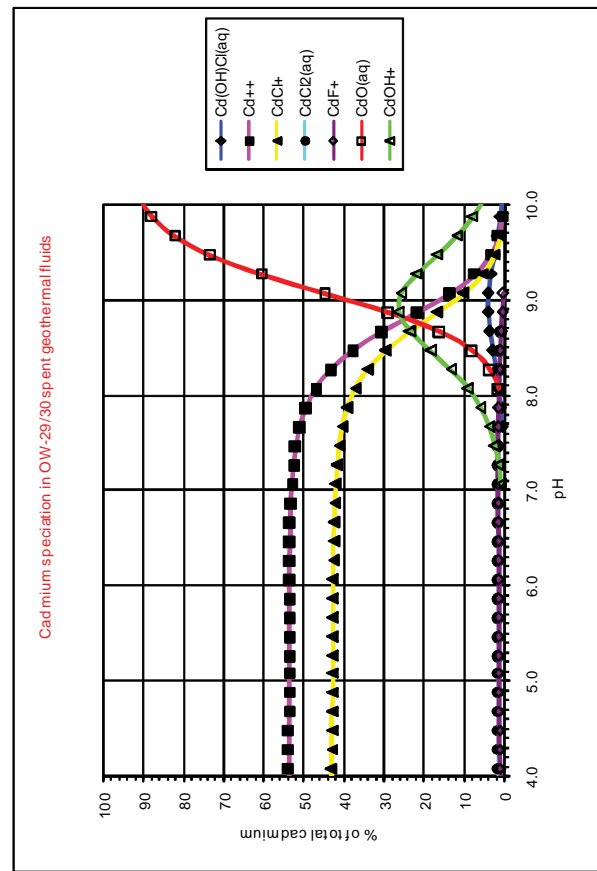
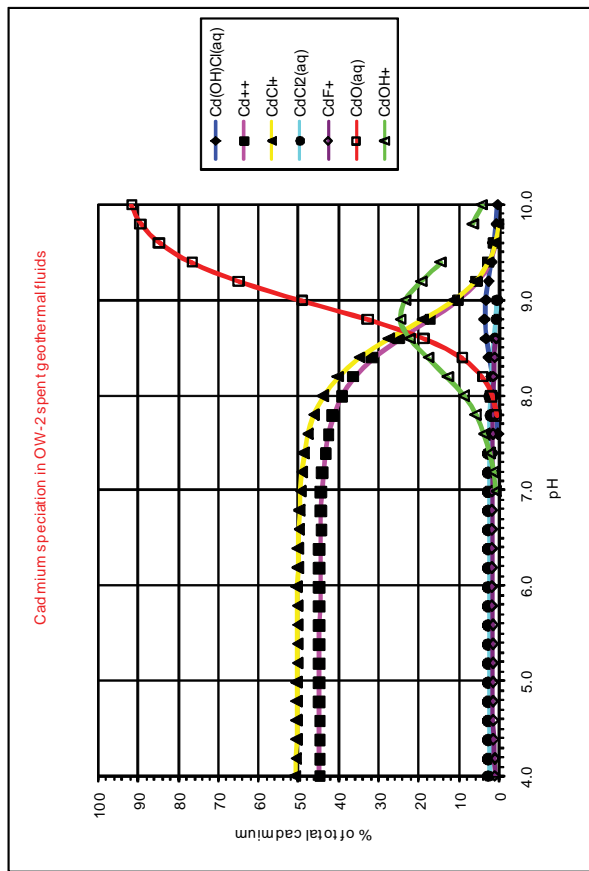
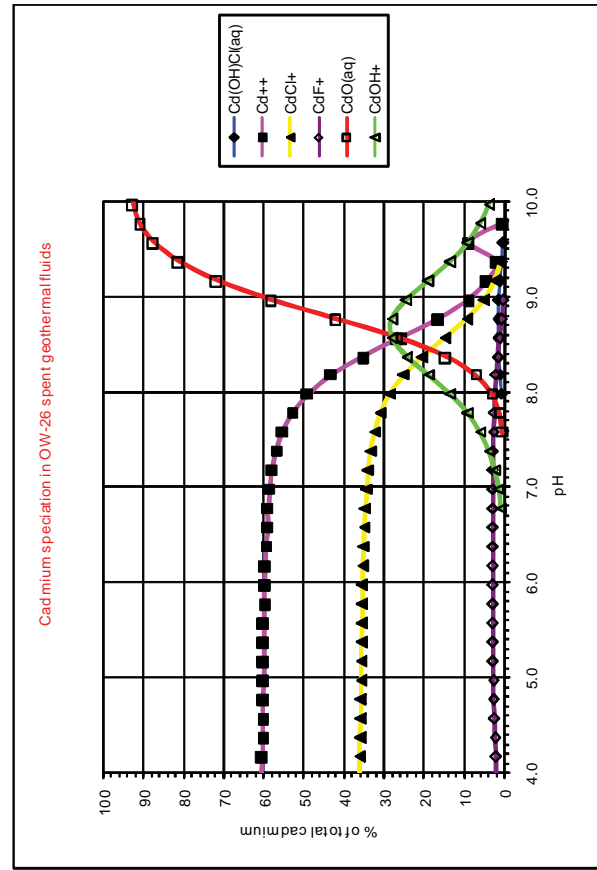
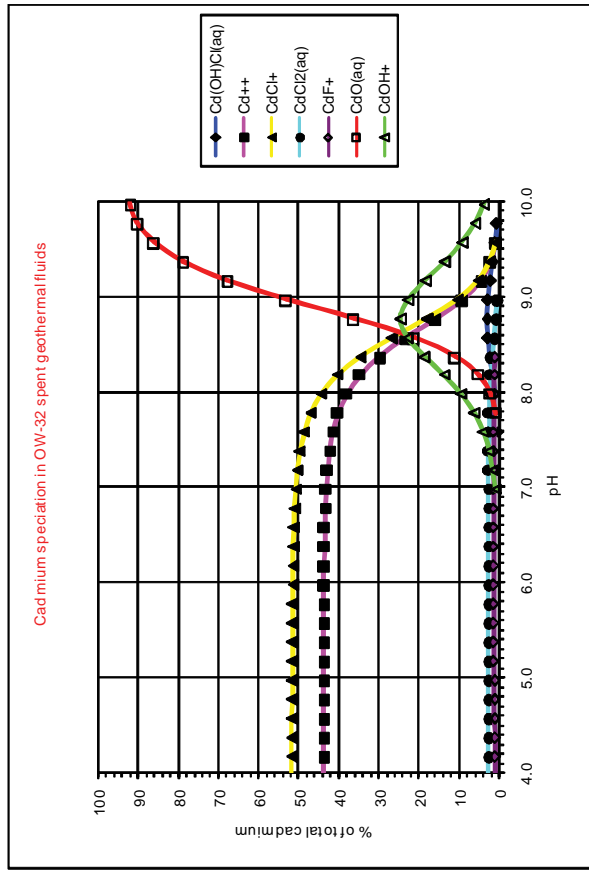


FIGURE 9a: Distribution curves for cadmium species in spent geothermal fluids from discharging geothermal wells

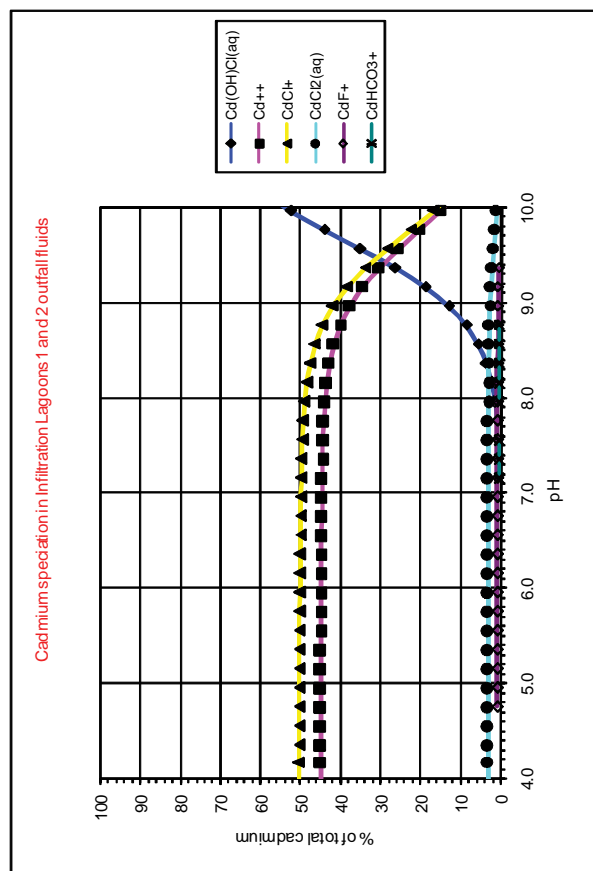
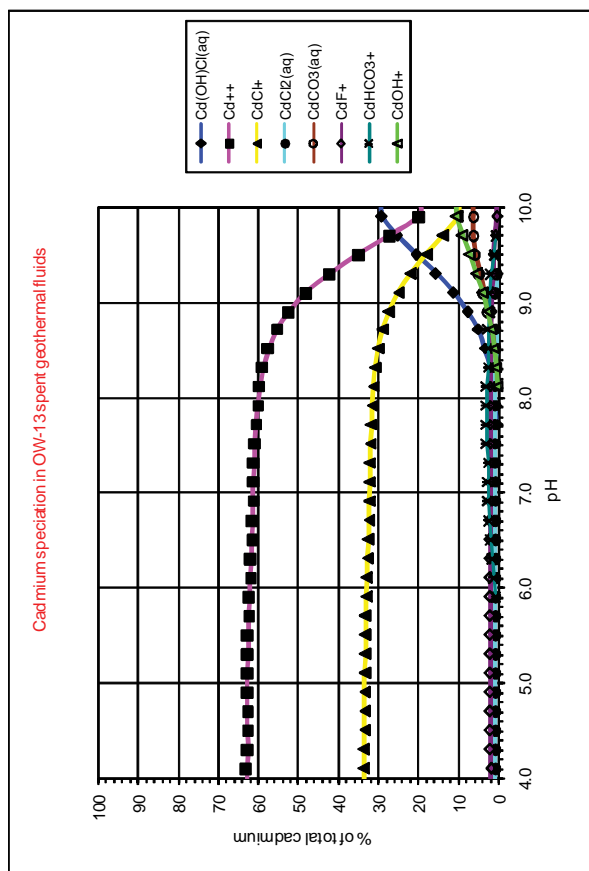
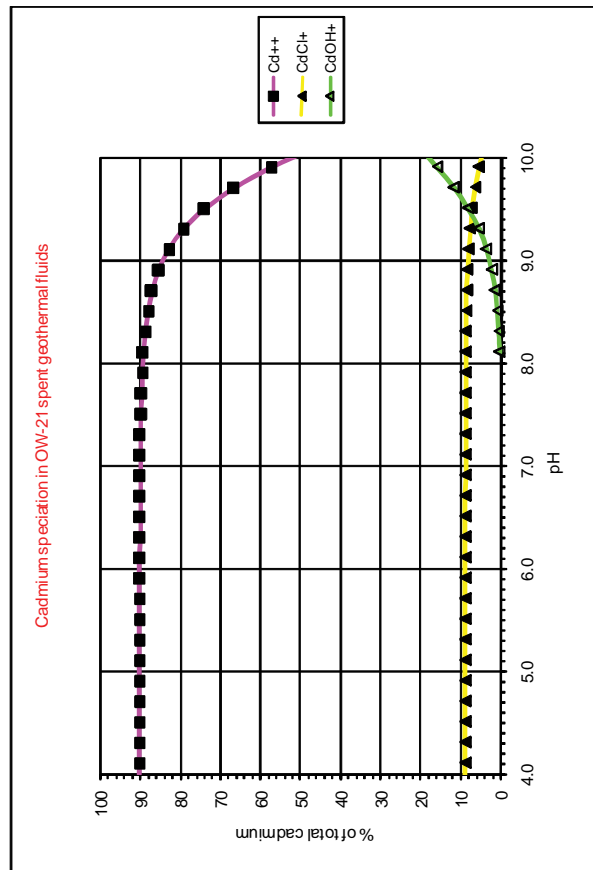
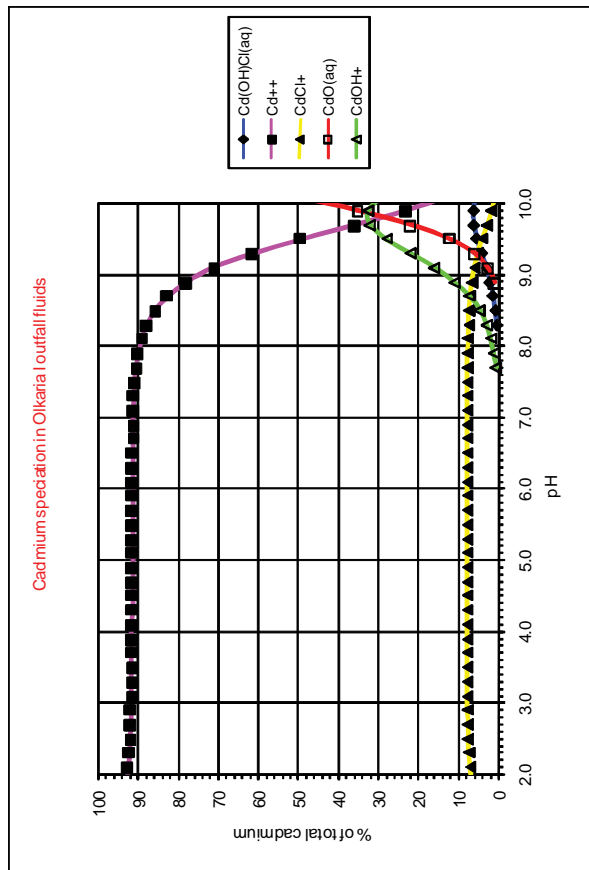


FIGURE 9b: Distribution curves for cadmium species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoons 1 and 2 outfalls.

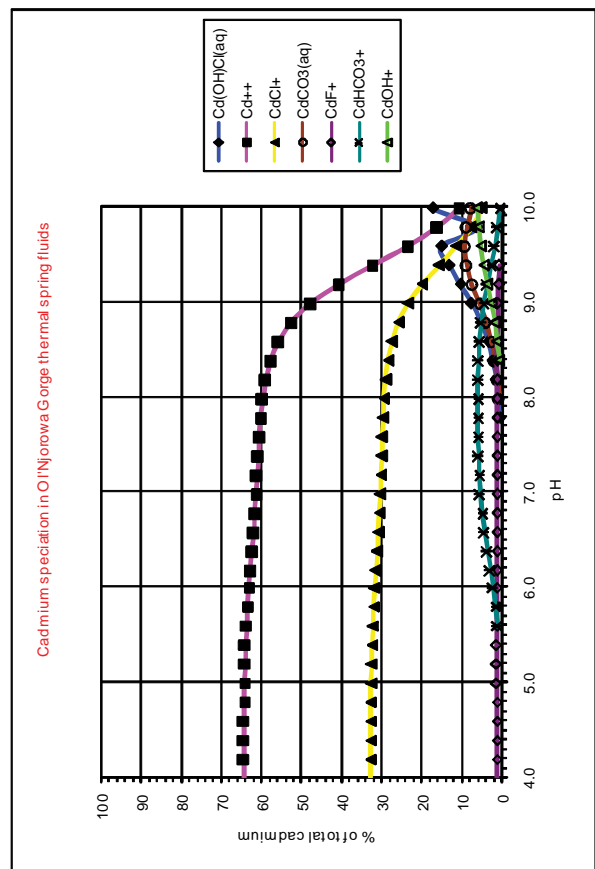
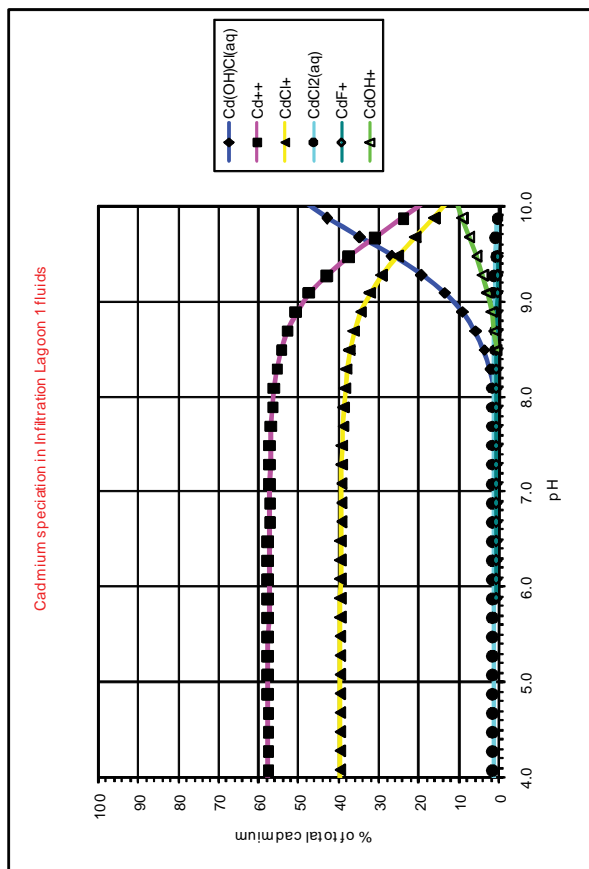
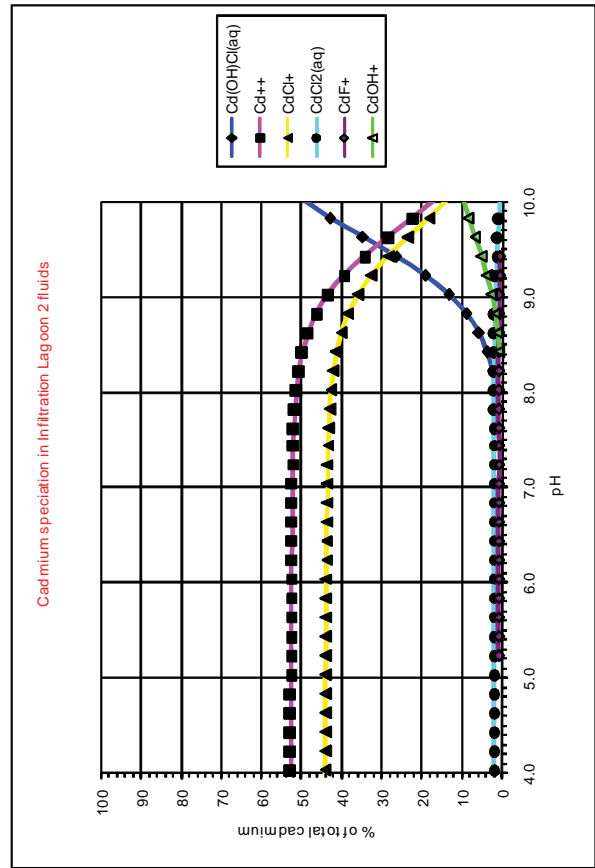
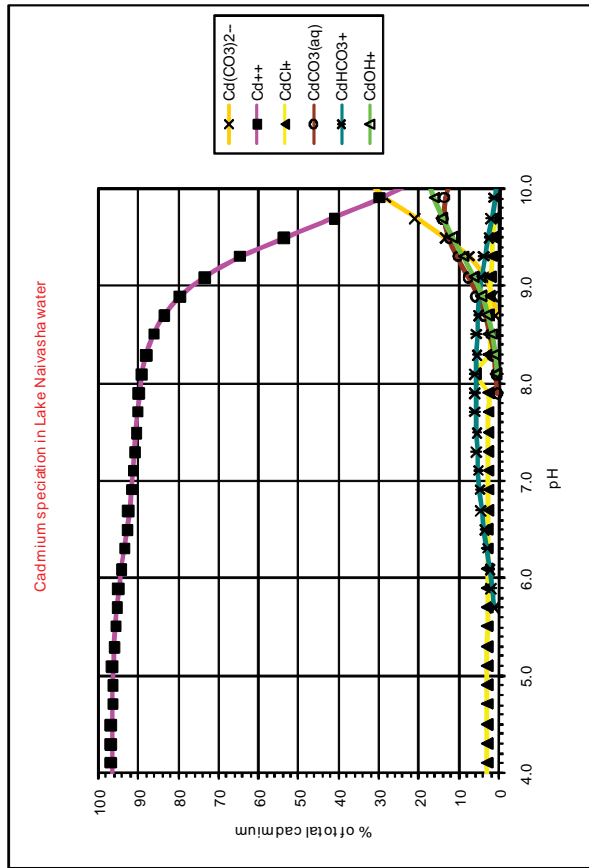


FIGURE 9c: Distribution curves for cadmium species in spent geothermal fluids from the Infiltration Lagoons 1 and 2, Ol'Njorowa Gorge thermal spring fluids, and Lake Naivasha water

TABLE 8: Range of percentages for cadmium species in spent geothermal fluids from the Olkaria geothermal field, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, Kenya

Species	% range of cadmium species						
	Discharging wells (pH 8.1–8.9)	Shut-in wells (pH 6.9–8.7)	Olkaria I outfall (pH 2.7)	Infiltration lagoons (pH 8.4 – 8.6)	Infiltration lagoons outfall (pH 8.1)	Ol’Njorowa Gorge thermal springs (pH 8.5)	Lake Naivasha (pH 8.7)
Cd ²⁺	9.12 – 34.89	55.61 – 90.16	90.09	48.47 – 54.57	43.6	55.75	83.77
CdO(aq)	5.13 – 58.51			0.85			
[CdCl] ⁺	5.16 – 40.63	8.97 – 29.17	7.82	37.42 – 40.28	48.59	27.41	2.61
[CdOH] ⁺	13.85 – 24.57	1.89		1.19			2.95
CdCO ₃ (aq)		1.89				2.81	3.84
Cd(OH)Cl(aq)	1.84 – 3.74	5.31		3.95 – 6.02	2.39	3.69	
[CdHCO ₃] ⁺		2.71		0.72	0.71	5.69	5.42
CdCl ₂ (aq)	0.87 – 2.23	0.87		1.46 – 1.93	3.25		
[CdF] ⁺	0.45 – 1.32	2.07		0.79	0.95	1.3	
[Cd(CO ₃) ₂] ²⁻						1.15	0.76

The free Cd²⁺ ion is the dominant dissolved Cd species with the highest percentage range of 55.61 – 90.16% in fluids from shut-in geothermal wells, Olkaria I outfall (90.09%), Lake Naivasha water (83.77%), Ol’Njorowa Gorge thermal springs (55.75%), Infiltration Lagoons (48.47 – 54.57%), and discharging geothermal wells (9.12 – 34.89%), in that order. The species CdO(aq) is predominant in fluids from discharging geothermal wells (5.13 – 58.51%), minor percentage in that of Infiltration Lagoons (0.85%), but nil in fluids from shut-in geothermal wells, Olkaria I outfall, Ol’Njorowa thermal springs, and Lake Naivasha water; cadmium chloride complex, [CdCl]⁺, in fluids from Infiltration Lagoons outfall (48.59%), Infiltration Lagoon fluids (37.42 – 40.28%), discharging geothermal wells (5.16 – 40.63%), shut-in geothermal wells (8.97 – 29.17%), Ol’Njorowa Gorge thermal spring fluids (27.41%), Olkaria I outfall (7.82%), and a minor percentage in Lake Naivasha water (2.61%); [CdOH]⁺ in fluids from discharging geothermal wells (13.85 – 24.57%), shut-in geothermal wells (1.89%), minor percentages in Lake Naivasha water (2.95%) and Infiltration Lagoons (1.19%), but nil in fluids from Olkaria I outfall, Infiltration Lagoons outfall, and Ol’Njorowa Gorge thermal springs; minor percentages of cadmium carbonate ion pair, CdCO₃(aq), in Lake Naivasha water (3.84%), Ol’Njorowa Gorge thermal spring fluids (2.81%), and fluids from shut-in geothermal wells (1.89%), but nil in fluids from discharging geothermal wells, Olkaria I outfall, and Infiltration Lagoons and outfall; Cd(OH)Cl(aq) in fluids from Infiltration Lagoons (3.95 – 6.02%), shut-in geothermal wells (5.31%), minor percentages in fluids from discharging geothermal wells (1.84 – 3.74%), Ol’Njorowa Gorge thermal springs (3.69%), and Infiltration Lagoons outfall (2.39%), but nil in Olkaria I outfall fluids and Lake Naivasha water; and cadmium bicarbonate complex, [CdHCO₃]⁺, in Ol’Njorowa Gorge thermal springs (5.69%), and Lake Naivasha water (5.42%), minor percentages in fluids from shut-in geothermal wells (2.71%), Infiltration Lagoons (0.72%), and Infiltration Lagoons outfall (0.71%), but nil in fluids from discharging geothermal wells and Olkaria I outfall.

The minor species of dissolved Cd are: CdCl₂(aq) in fluids from the Infiltration Lagoons outfall (3.25%), discharging geothermal wells (0.87 – 2.23%), Infiltration Lagoons (1.46 - 1.93%), and shut-in geothermal wells (0.87%); [CdF]⁺ in fluids from shut-in geothermal wells (2.07%), discharging geothermal wells (0.45 – 1.32%), Ol’Njorowa Gorge thermal springs (1.3%), and Infiltration Lagoons outfall (0.95%), and Infiltration Lagoons (0.79%); and cadmium dicarbonate complex, [Cd(CO₃)₂]²⁻ in fluids from Ol’Njorowa Gorge thermal springs (1.15%) and Lake Naivasha water (0.76%).

3.5.4 Copper

The probable distribution of copper species in spent geothermal fluids from discharging geothermal wells OW-2, OW-26, OW-29/30 and OW-32, shut-in geothermal wells OW-13 and OW-21, Olkaria I outfall and Infiltration Lagoons, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, is shown in Figures 10a, 10b, and 10c.

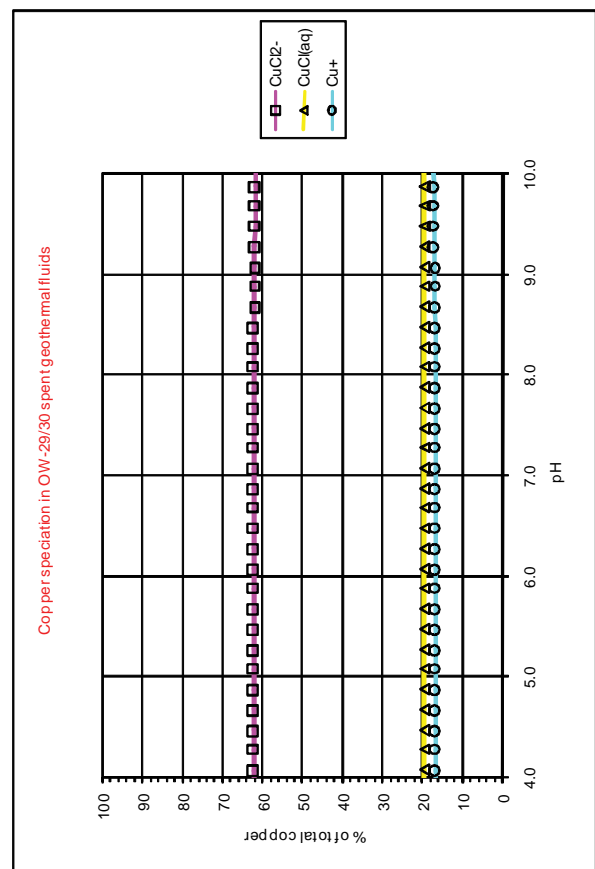
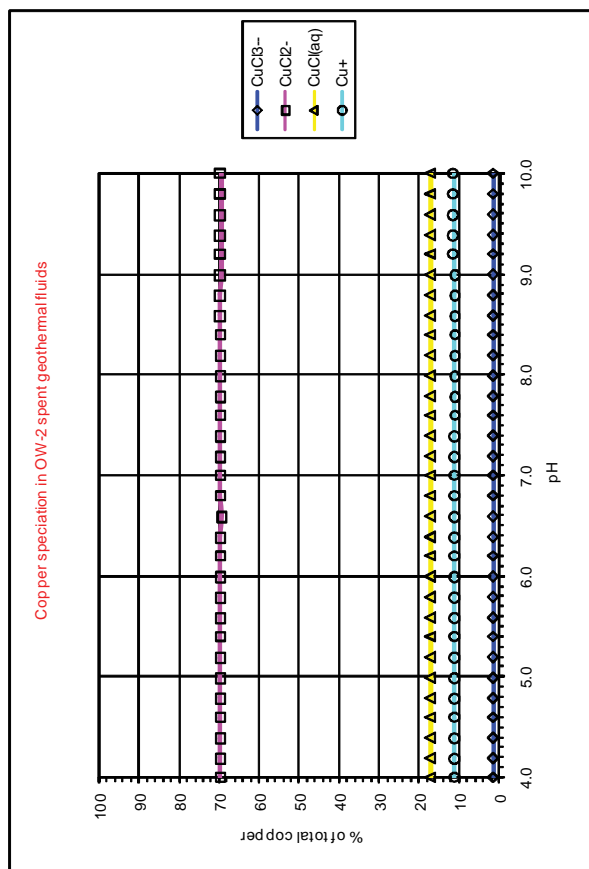
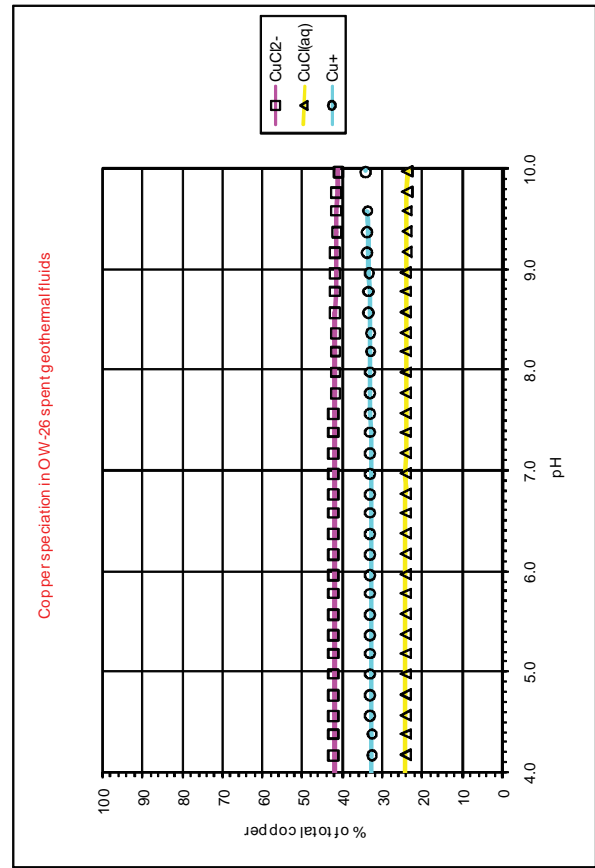
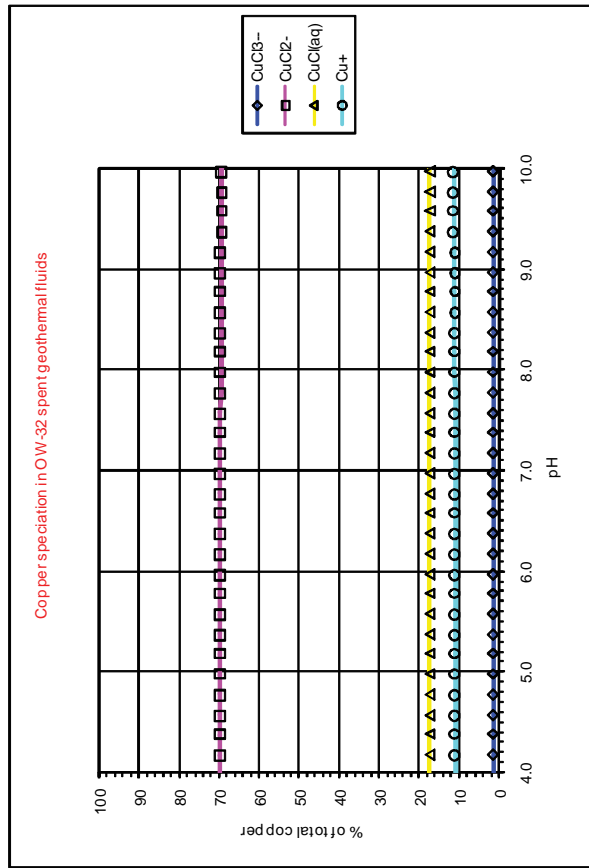


FIGURE 10a: Distribution curves for copper species in spent geothermal fluids from discharging geothermal wells

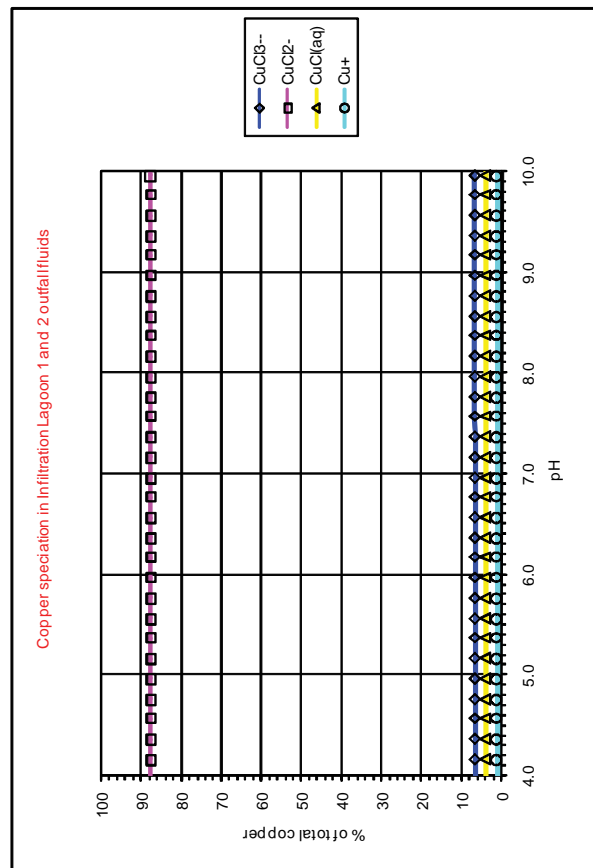
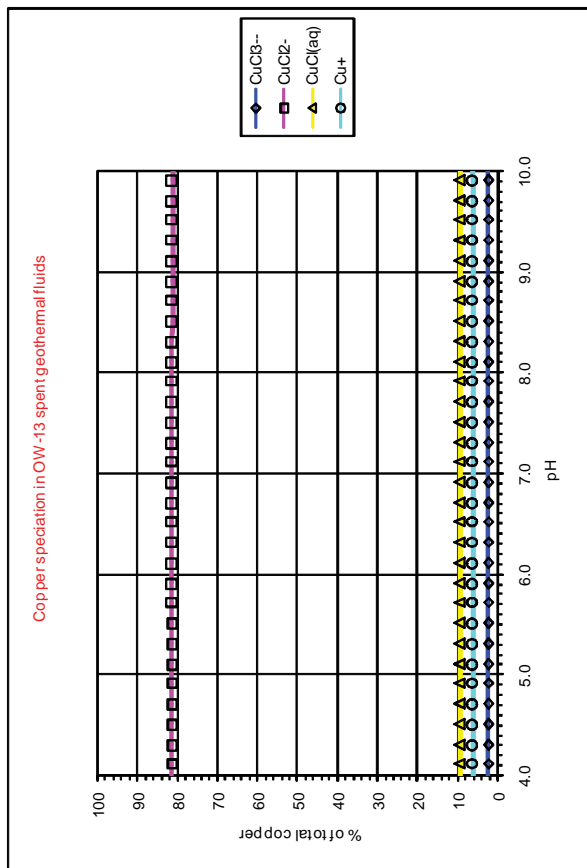
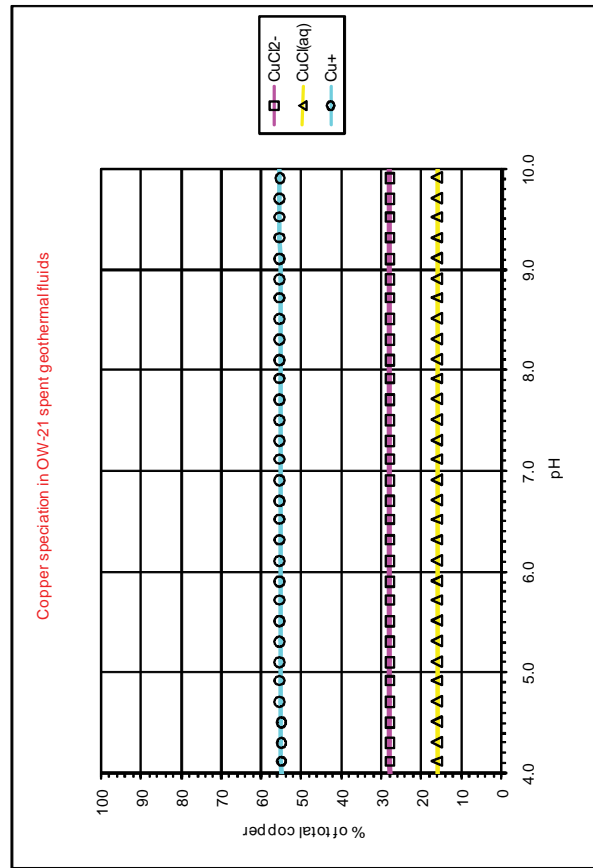
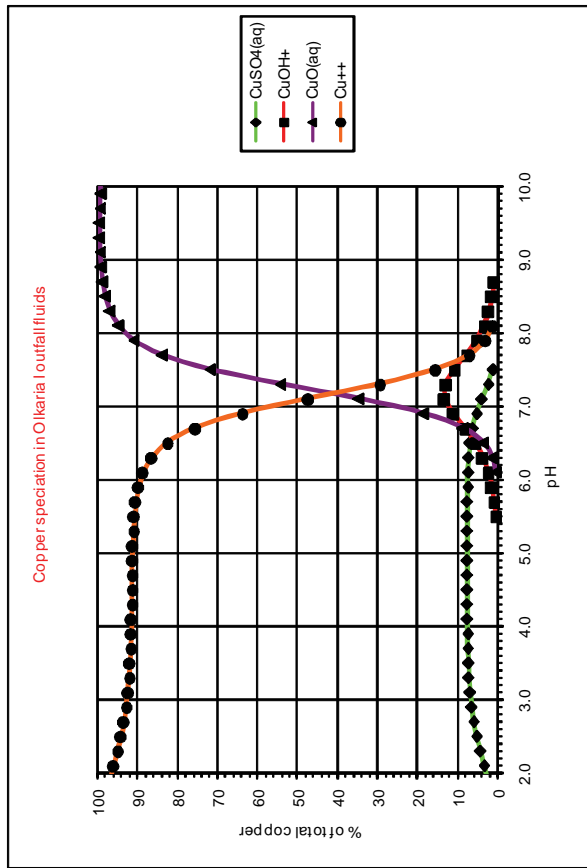


FIGURE 10b: Distribution curves for copper species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoons 1 and 2 outfalls

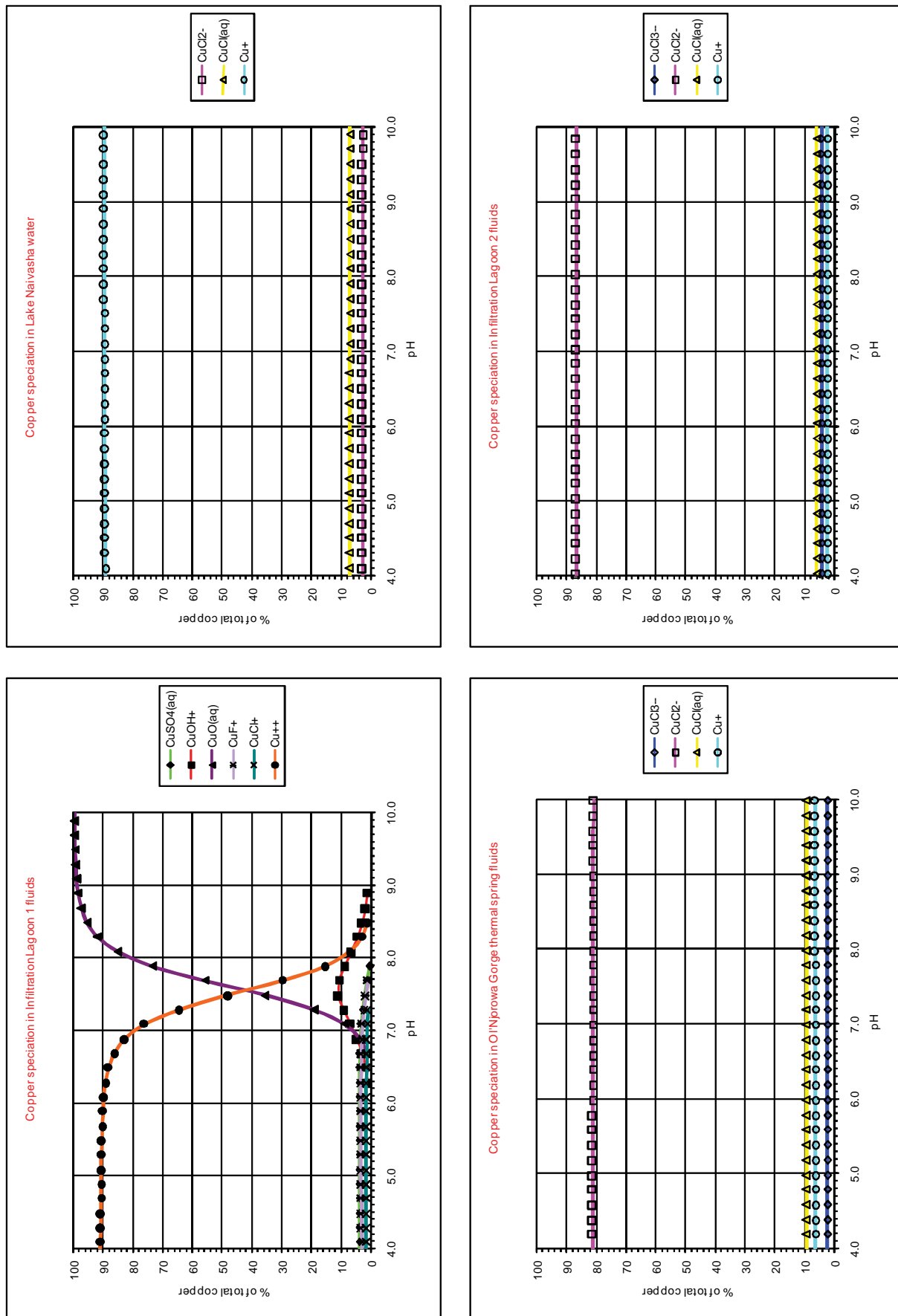


FIGURE 10c: Distribution curves for copper species in spent geothermal fluids from the Olkaria I outfall, Infiltration Lagoons, Ol'Njorowa Gorge thermal spring fluids, and Lake Naivasha water

The percentages of species accounting for 99% or more of the total aqueous copper within the sampling locations at in-situ pH and temperatures are shown in Table 9.

The range of percentages of the dominant copper species within the 7 categories of the sampling locations is presented in Table 10.

The speciation modelling predicted various copper species in all sampled fluids with minimal speciation in the acidic fluids from Olkaria I outfall with in-situ pH 2.7 and the highest dissolved Cu concentration (9.4 µg/L) and maximum speciation in fluids from Infiltration Lagoons 1 and 2 with in situ pH range 8.1 – 8.6 and Cu concentration range 1.69 -1.91 µg/L (Table 10). The dominant dissolved copper species are chloro complexes, $[\text{CuCl}_2]^-$, and $[\text{CuCl}_3]^{2-}$, and copper chloride ion pair, $\text{CuCl}(\text{aq})$, in all the sampled fluids with in-situ pH > 7, except that from Olkaria I outfall. Other dissolved copper species are $\text{CuO}(\text{aq})$, $\text{CuSO}_4(\text{aq})$, $[\text{CuOH}]^+$, Cu^{2+} , and Cu^+ .

TABLE 9: Percentage composition of copper species at in-situ pH and temperatures within the sampling locations

Location	In-situ pH	In-situ Temp (°C)	Total analytical concentration (µg/L)	Dominant species
OW-2	8.4	88.0	0.54	$[\text{CuCl}_2]^-$ (69.85%) $\text{CuCl}(\text{aq})$ (17.36%) $[\text{CuCl}_3]^{2-}$ (1.52%)
OW-13	8.7	27.1	1.66	$[\text{CuCl}_2]^-$ (81.5%) $\text{CuCl}(\text{aq})$ (9.66%) Cu^+ (6.35%) $[\text{CuCl}_3]^{2-}$ (2.49%)
OW-21	6.9	16.0	3.1	Cu^+ (55.44%) $[\text{CuCl}_2]^-$ (28.19%) $\text{CuCl}(\text{aq})$ (16.22%)
OW-26	8.9	91.0	0.48	$[\text{CuCl}_2]^-$ (41.83%) Cu^+ (33.6%) $\text{CuCl}(\text{aq})$ (24.19%)
OW-29/30	8.6	80.0	0.64	$[\text{CuCl}_2]^-$ (62.25%) $\text{CuCl}(\text{aq})$ (19.7%) Cu^+ (17.07%)
OW-32	8.1	91.0	1.49	$[\text{CuCl}_2]^-$ (69.76%) $\text{CuCl}(\text{aq})$ (17.5%) Cu^+ (11.2%) $[\text{CuCl}_3]^{2-}$ (1.54%)
Olkaria I outfall	2.7	38.0	9.4	Cu^{2+} (93.51%) $\text{CuSO}_4(\text{aq})$ (6.16%)
IL-1	8.4	23.1	1.69	$\text{CuO}(\text{aq})$ (95.6%) $[\text{CuOH}]^+$ (2.97%) Cu^{2+} (1.29%)
IL-2	8.6	25.1	1.91	$[\text{CuCl}_2]^-$ (86.95%) $\text{CuCl}(\text{aq})$ (6.16%) $[\text{CuCl}_3]^{2-}$ (4.38%) Cu^+ (2.5%)
IL-1 and 2 outfall	8.1	24.1	1.81	$[\text{CuCl}_2]^-$ (87.81%) $[\text{CuCl}_3]^{2-}$ (6.78%) $\text{CuCl}(\text{aq})$ (4.2%) Cu^+ (1.22%)
Ol’Njorowa Gorge thermal springs	8.5	26.3	1.55	$[\text{CuCl}_2]^-$ (81.21%) $\text{CuCl}(\text{aq})$ (9.69%) Cu^+ (6.6%) $[\text{CuCl}_3]^{2-}$ (2.5%)
Lake Naivasha	8.7	25.1	1.44	Cu^+ (89.76%) $\text{CuCl}(\text{aq})$ (7.29%) $[\text{CuCl}_2]^-$ (2.95%)

TABLE 10: Range of percentages for copper species in spent geothermal fluids from the Olkaria geothermal field, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, Kenya

Species	% range of copper species						
	Discharging geothermal wells (pH 8.1 – 8.9)	Shut-in geothermal wells (pH 6.9 – 8.7)	Olkaria I outfall (pH 2.7)	Infiltration lagoons (pH 8.1 – 8.6)	Infiltration lagoons outfall (pH 8.1)	Ol’Njorowa Gorge thermal springs (pH 8.5)	Lake Naivasha (pH 8.7)
$[\text{CuCl}_2]^-$	41.83 – 69.85	28.19 – 81.5		86.95	87.81	81.21	2.95
$\text{CuCl}(\text{aq})$	19.7 – 24.19	9.66 – 16.22		6.16	4.2	9.69	7.29
Cu^+	11.2 – 33.6	6.35 – 55.44		2.5	1.22	6.6	89.76
$[\text{CuCl}_3]^{2-}$	1.52 – 1.54	2.49		4.38	6.78	2.5	
Cu^{2+}			93.51	1.29			
$\text{CuSO}_4(\text{aq})$			6.16				
$\text{CuO}(\text{aq})$				95.6			
$[\text{CuOH}]^+$				2.97			

The relative abundance of $[\text{CuCl}_2]^-$ species is 87.81% in fluids from the Infiltration Lagoons outfall, 86.95% in fluids from the Infiltration Lagoons, 81.21% in Ol’Njorowa Gorge thermal spring fluids, 28.19 – 81.5% in fluids from shut-in geothermal wells, 41.83 – 69.85% in fluids from discharging

geothermal wells, a minor percentage of 2.95% in Lake Naivasha water, and nil in Olkaria I outfall fluids. The species $\text{CuCl}(\text{aq})$ occurs in fluids from discharging geothermal wells (19.7 – 24.19%), shut-in geothermal wells (9.66 – 16.22%), Ol’Njorowa Gorge thermal spring fluids (9.69%), Lake Naivasha water (7.29%), Infiltration Lagoons (6.16%), minor percentage in Infiltration Lagoons outfall (4.2%), but nil in Olkaria I outfall fluids. The species $[\text{CuCl}_3]^{2-}$ is observed in fluids from the Infiltration Lagoons outfall (6.78%), minor percentages in those from the Infiltration Lagoons (4.38%), Ol’Njorowa Gorge thermal spring fluids (2.5%), shut-in geothermal well fluids (2.49%), but nil in Lake Naivasha water, and Olkaria I outfall fluids.

The species $\text{CuO}(\text{aq})$ is dominant in fluids from Infiltration Lagoon 1 (95.6%) with an in-situ pH of 8.4 but nil in all other fluids. The free divalent Cu^{2+} ion is predominant in fluids from Olkaria I outfall (93.51%) with an in-situ pH 2.7, minor percentage of 1.29% in fluids from the Infiltration Lagoon 1 whose DOC concentration (0.058 mg/L) is the highest, but nil in fluid samples from all the geothermal wells, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water with the highest DOC of 1.254 mg/L. The free monovalent Cu^+ ion is predominant in fluids from Lake Naivasha water (89.76%) with an in-situ pH 8.7, fluids from shut-in geothermal wells (6.35 – 55.44%), discharging geothermal wells (11.2 – 33.6), Ol’Njorowa Gorge thermal spring fluids (6.6%), minor percentage in fluids from the Infiltration Lagoons (2.5%) and Infiltration lagoons outfall (1.22%), but nil in fluid samples from Olkaria I outfall. The copper sulphate ion pair, $\text{CuSO}_4(\text{aq})$, species is observed in fluids from Olkaria I outfall (6.16%) and copper hydroxyl complex, $[\text{CuOH}]^+$ in minor percentage (2.97%) in fluids from Infiltration Lagoons, but nil in other fluids for both species.

3.5.5 Lead

The probable distribution of lead species in spent geothermal fluids from discharging geothermal wells OW-2, OW-26, OW-29/30 and OW-32, shut-in geothermal wells OW-13 and OW-21, Olkaria I outfall and Infiltration Lagoons, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, is shown in Figures 11a, 11b, and 11c.

The percentages of species accounting for 99% or more of the total aqueous lead within the sampling locations at in-situ pH and temperatures are shown in Table 11.

The range of percentages of the dominant lead species within the 7 categories of the sampling locations is presented in Table 12.

The speciation modelling predictions display minimal Pb speciation of inorganic complexes in all fluid samples. The dominant Pb species in all the fluids, except from Olkaria I outfall, is $\text{Pb}(\text{HS})_2(\text{aq})$. Other aqueous Pb species are $\text{PbO}(\text{aq})$, $[\text{PbOH}]^+$, Pb^{2+} , $[\text{PbCl}]^+$, and $[\text{HPbO}_2]^-$.

The relative abundance of $\text{Pb}(\text{HS})_2(\text{aq})$ range from 34.32 – 99.75% with the highest percentage range 94.24 - 99.75% in fluids from shut-in geothermal wells. Pb also occurs in the form of $\text{PbO}(\text{aq})$ in discharging geothermal wells (4.85 – 51.79%) but nil in all other fluid samples. The species $[\text{PbOH}]^+$ occurs in fluids from the Infiltration Lagoons 1 and 2 (12.87 – 98.29%) with an in-situ pH range 8.4 - 8.6, discharging geothermal wells (1.21 – 13.2%), Infiltration Lagoons outfall (12.87%), shut-in geothermal wells (5.61%), minor percentages in Lake Naivasha water (2.44%) and Ol’Njorowa Gorge thermal spring fluids (1.64%), but nil in Olkaria I outfall fluids. The free Pb^{2+} ion, is dominant in fluids from Olkaria I outfall (96.81%) with and in-situ pH 2.7, a minor percentage in Infiltration Lagoon 1 (0.71%), but nil in the fluids from all the geothermal wells, Infiltration Lagoons outfall, Ol’Njorowa Gorge thermal springs, and Lake Naivasha water.

Other minor lead species observed are chloro complex, $[\text{PbCl}]^+$, in fluids from Olkaria I outfall (2.84%) and complex species $[\text{HPbO}_2]^-$, in fluids from discharging geothermal wells (0.77 - 1.92%), but nil in the rest of the fluids.

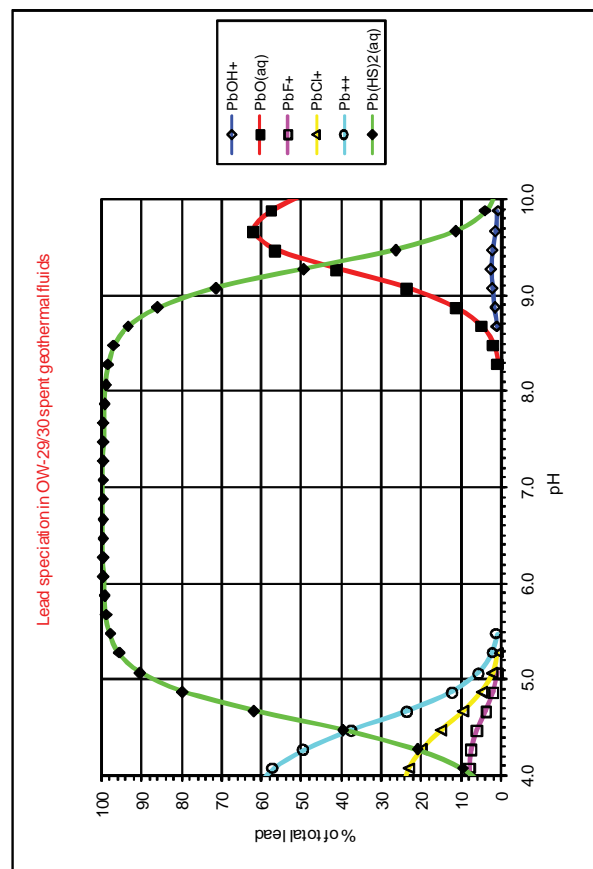
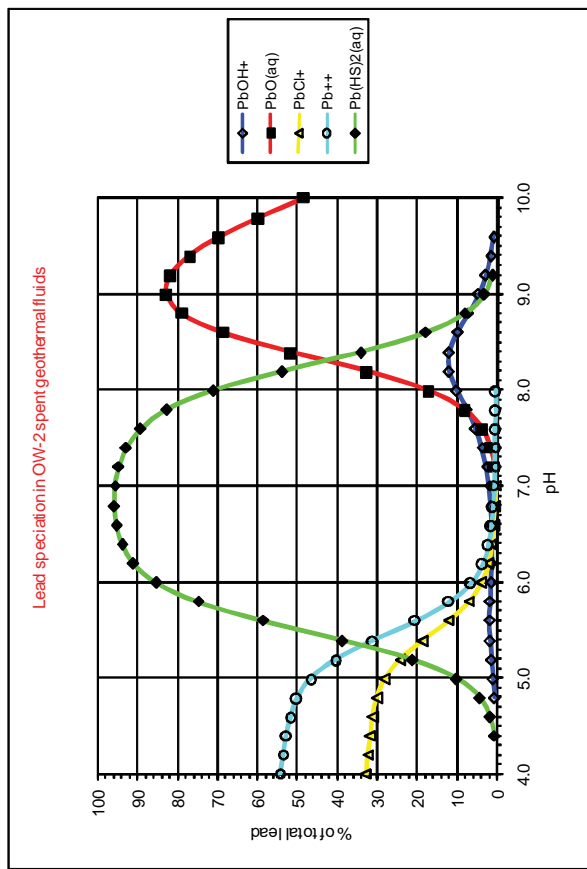
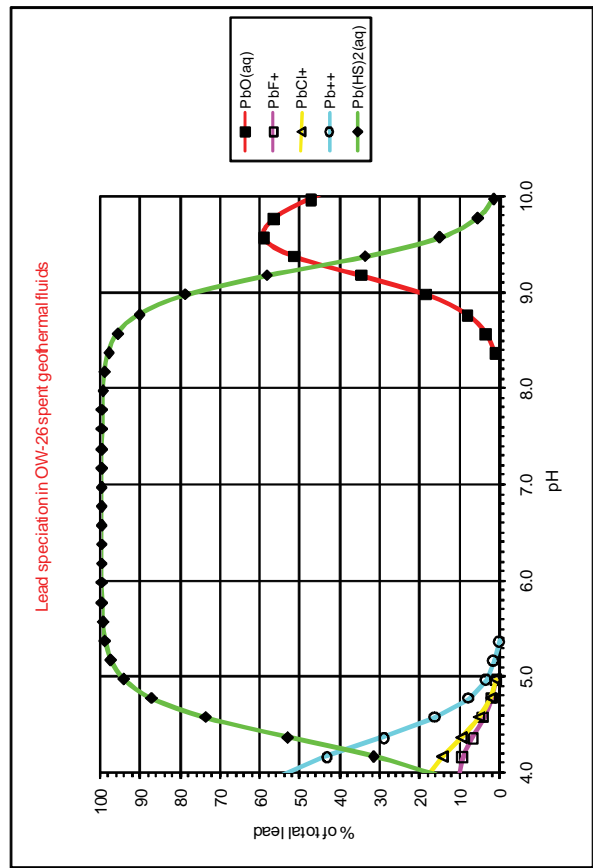
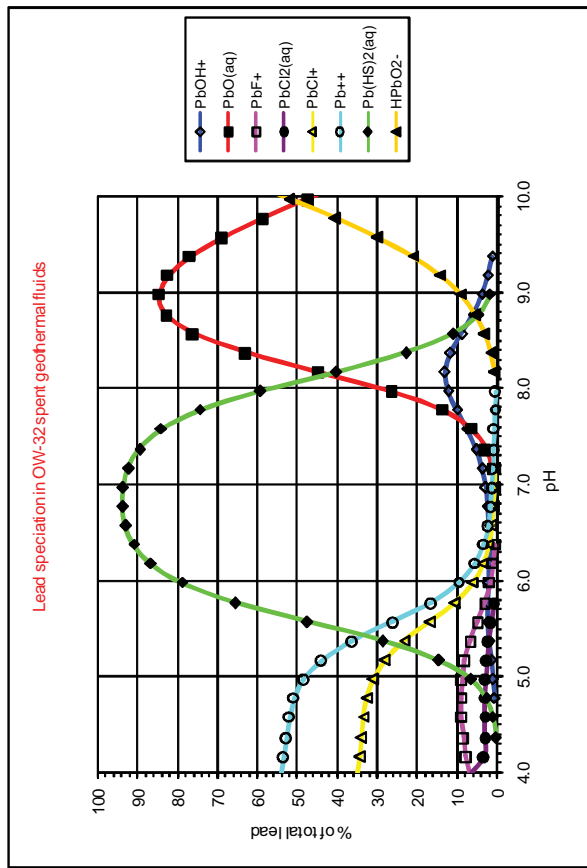


FIGURE 11a: Distribution curves for lead species in spent geothermal fluids from discharging geothermal wells

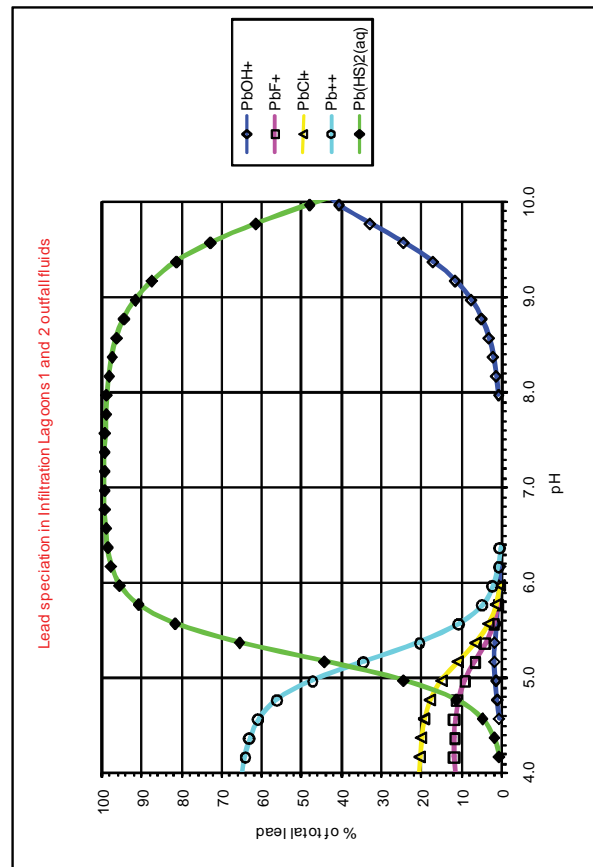
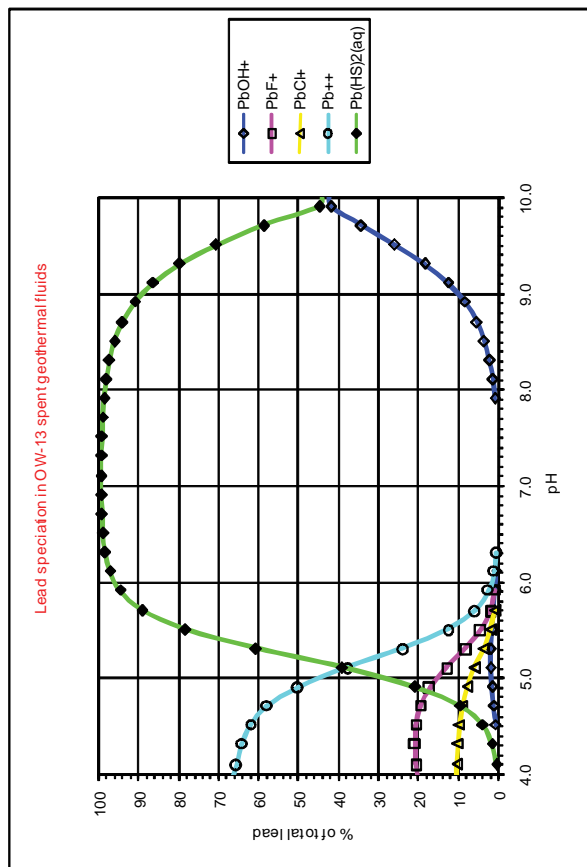
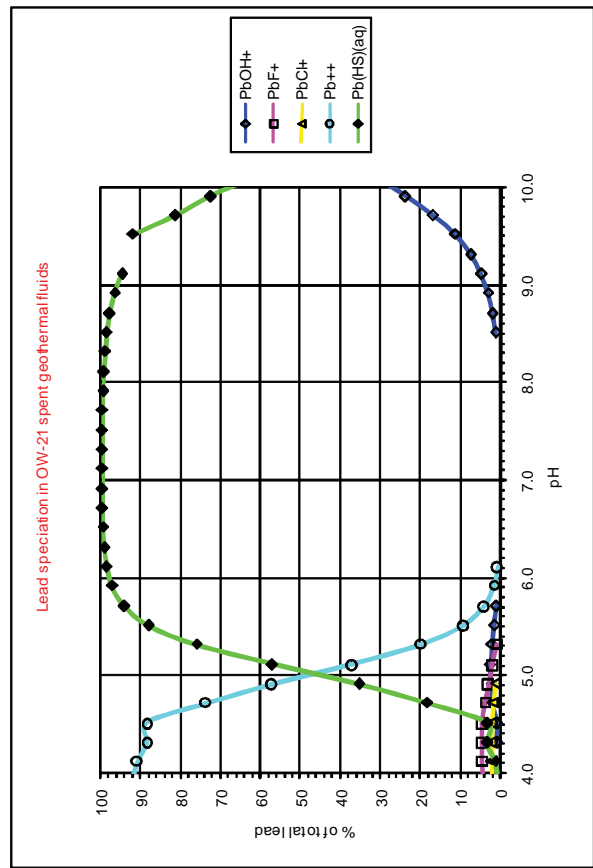
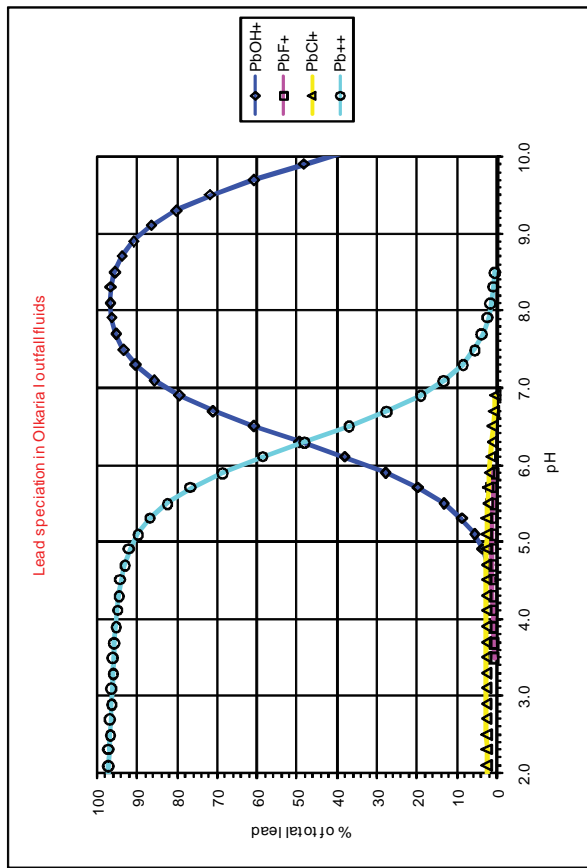


FIGURE 11b: Distribution curves for lead species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoons 1 and 2 outfalls

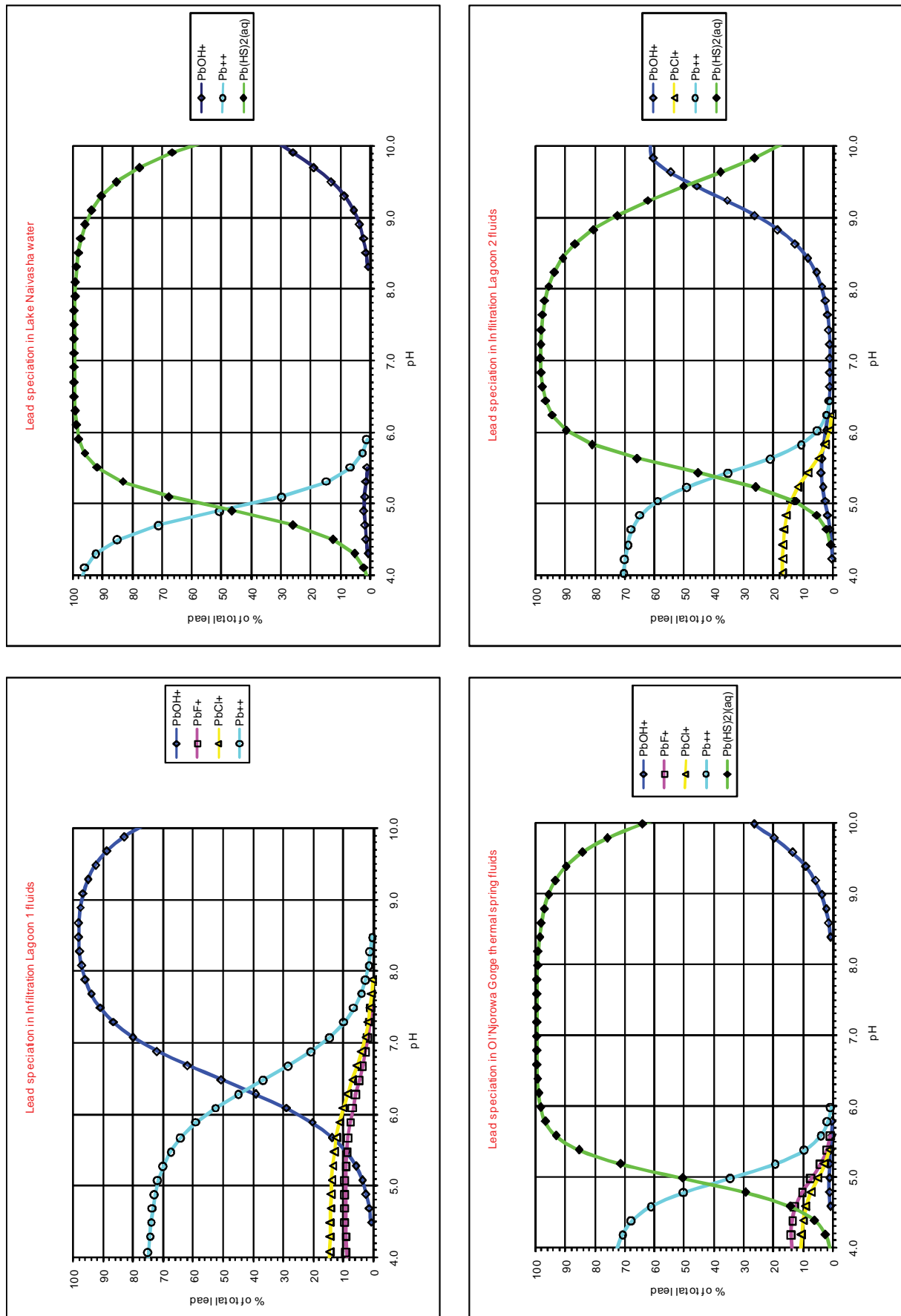


FIGURE 11c: Distribution curves for lead species in spent geothermal fluids from the Infiltration Lagoons 1 and 2, Ol'Njorowa Gorge thermal spring fluids, and Lake Naivasha water

TABLE 11: Percentage composition of lead species at in-situ pH and temperatures within the sampling locations

Location	In-situ pH	In-situ Temp (°C)	Total analytical concentration (µg/L)	Dominant species
OW-2	8.4	88.0	0.24	PbO(aq)(51.79%) Pb(HS) ₂ (aq)(34.32%) [PbOH] ⁺ (12.11%)
OW-13	8.7	27.1	0.79	Pb(HS) ₂ (aq)(94.24%) [PbOH] ⁺ (5.61%)
OW-21	6.9	16.0	2.58	Pb(HS) ₂ (aq)(99.75%)
OW-26	8.9	91.0	0.22	Pb(HS) ₂ (aq)(78.77%) PbO(aq)(18.37%) [HPbO ₂] ⁻ (1.92%)
OW-29/30	8.6	80.0	0.25	Pb(HS) ₂ (aq)(93.67%) PbO(aq)(4.85%) [PbOH] ⁺ (1.21%)
OW-32	8.1	91.0	0.37	PbO(aq)(44.76%) Pb(HS) ₂ (aq)(40.53%) [PbOH] ⁺ (13.2%) [HPbO ₂] ⁻ (0.77%)
Olkaria I outfall	2.7	38.0	2.38	Pb ²⁺ (96.81%) [PbCl] ⁺ (2.84%)
IL-1	8.4	23.1	0.33	[PbOH] ⁺ (98.29%) Pb ²⁺ (0.71%)
IL-2	8.6	25.1	0.42	Pb(HS) ₂ (aq)(86.87%) [PbOH] ⁺ (12.87%)
IL-1 and 2 outfall	8.1	24.1	0.43	Pb(HS) ₂ (aq)(98.48%) [PbOH] ⁺ (12.87%)
Ol’Njorowa Gorge thermal springs	8.5	26.3	0.62	Pb(HS) ₂ (aq)(98.31%) [PbOH] ⁺ (1.64%)
Lake Naivasha	8.7	25.1	0.63	Pb(HS) ₂ (aq)(97.5%) [PbOH] ⁺ (2.44%)

TABLE 12: Range of percentages for lead species in spent geothermal fluids from the Olkaria geothermal field, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, Kenya

Species	% range of lead species						
	Discharging geothermal wells (pH 8.1 – 8.9)	Shut-in geothermal wells (pH 6.9 – 9.8)	Olkaria I outfall (pH 2.7)	Infiltration lagoons (pH 8.4 – 8.6)	Infiltration lagoons outfall (pH 8.1)	Ol’Njorowa Gorge thermal springs (pH 8.5)	Lake Naivasha (pH 8.7)
Pb(HS) ₂ (aq)	34.32 – 93.67	94.24 – 99.75		86.87	98.48	98.31	97.5
PbO(aq)	4.85 – 51.79						
[PbOH] ⁺	1.21 – 13.2	5.61		12.87 – 98.29	12.87	1.64	2.44
[HPbO ₂] ⁻	0.77 – 1.92						
Pb ²⁺			96.81	0.71			
[PbCl] ⁺			2.84				

3.5.6 Mercury

Mercury is extremely volatile in its elemental form (Hg⁰). The Hg₂²⁺ ion species, which is the dominant Hg species in spent geothermal fluids, is easily reduced to the elemental mercury, Hg⁰. Therefore, some Hg tends to be lost from solution through reduction and volatilization between sampling and sample analysis unless precautions are taken through addition of strong oxidation agents. Therefore, speciation modelling for aqueous Hg is for lower Hg concentrations than the actual original concentrations since no oxidation agents were added during sampling. However, this is unlikely to affect the results of speciation modelling. The Hg₂²⁺ ion species is expected to predominate to quite high Hg concentrations and in-situ pH in most of the sampled fluids.

The probable distribution of mercury species in spent geothermal fluids from discharging geothermal wells OW-2, OW-26, OW-29/30 and OW-32, shut-in geothermal wells OW-13 and OW-21, Olkaria I outfall and Infiltration Lagoons, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, is shown in Figures 12a, 12b, and 12c.

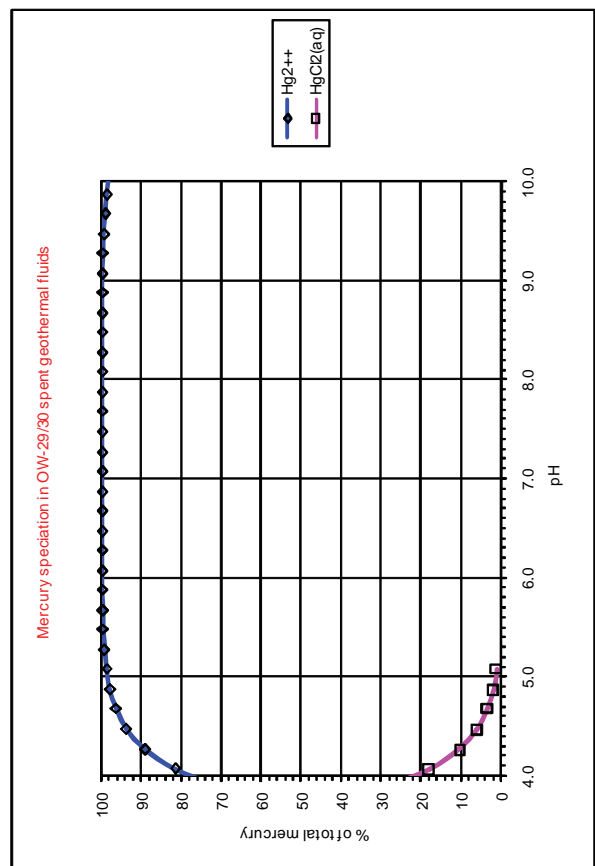
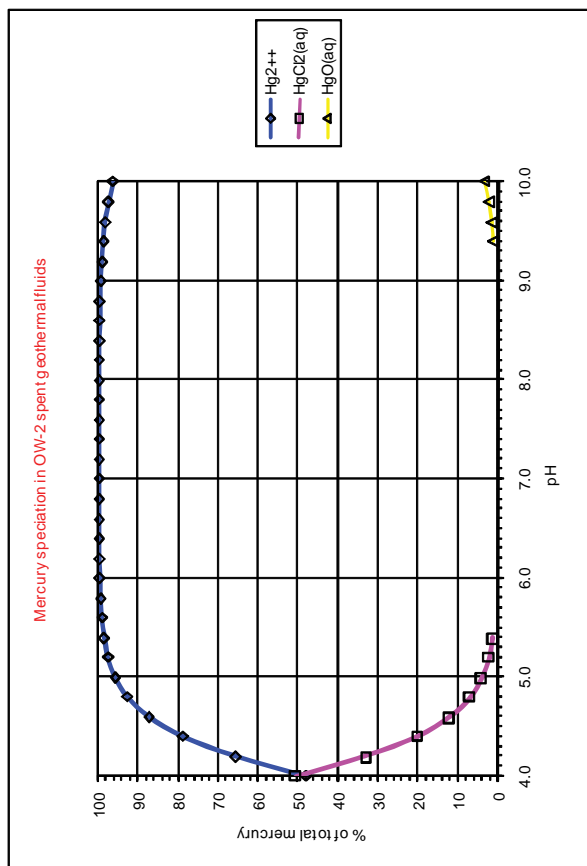
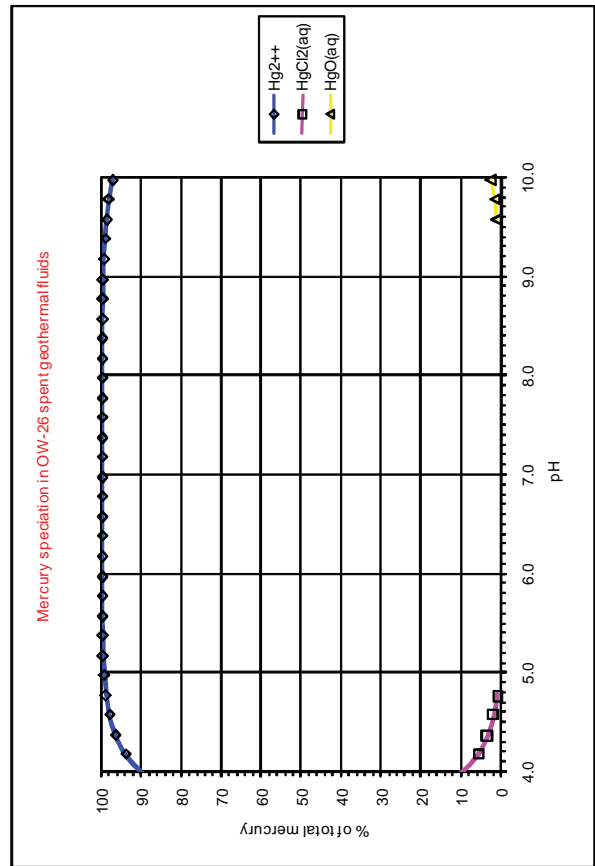
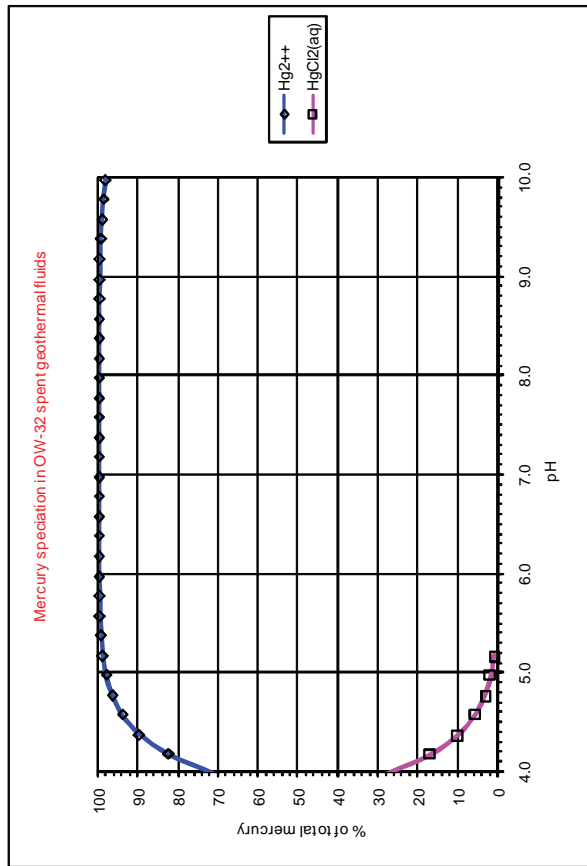


FIGURE 12a: Distribution curves for mercury species in spent geothermal fluids from discharging geothermal wells

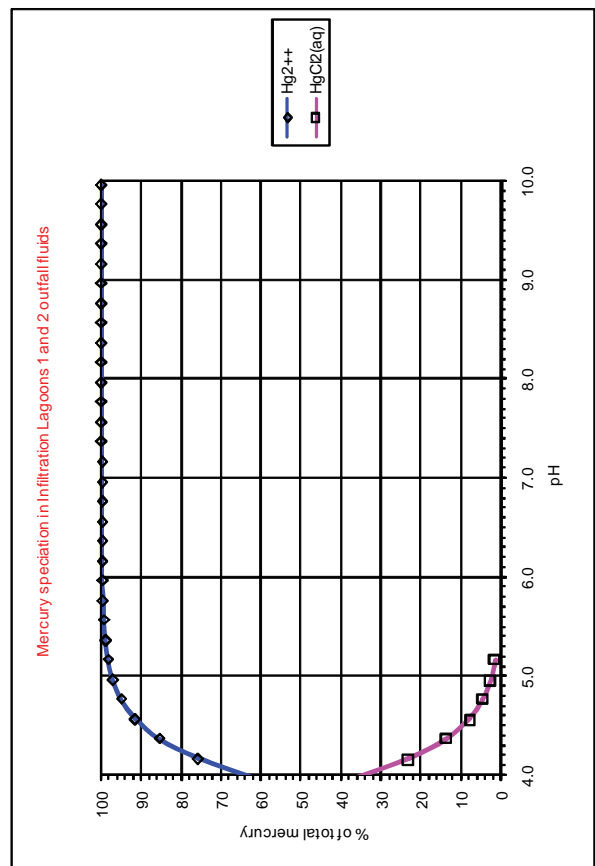
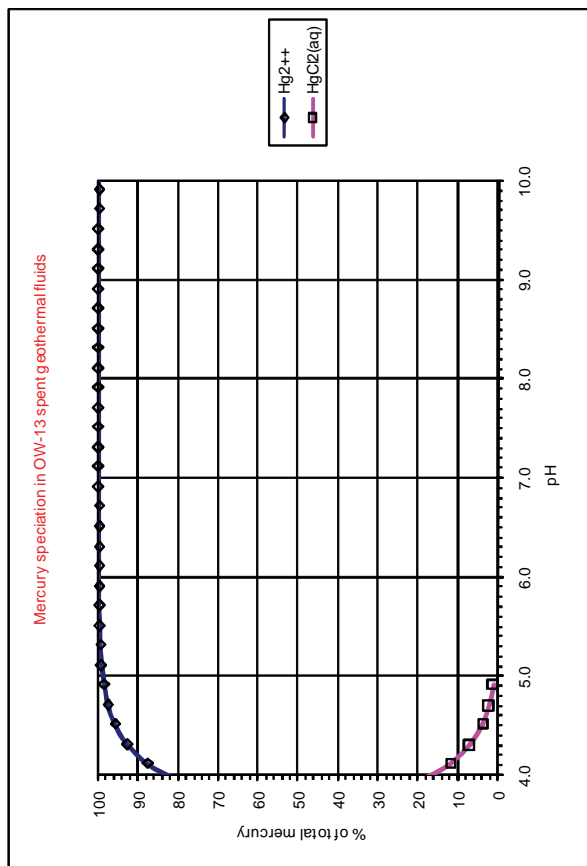
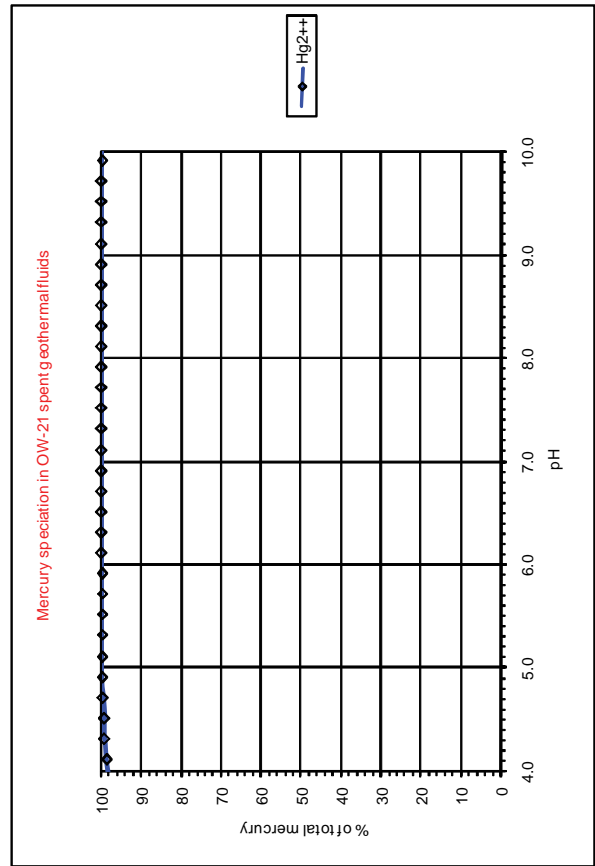
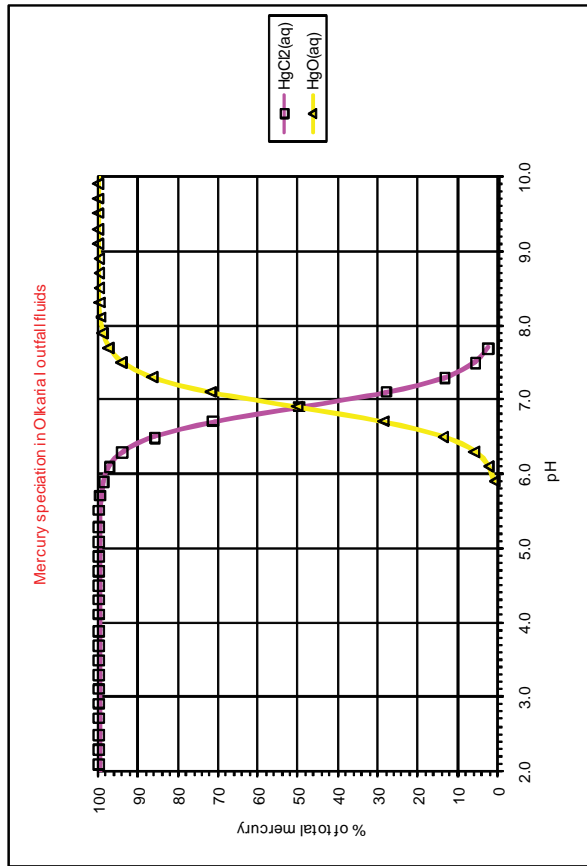


FIGURE 12b: Distribution curves for mercury species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoons 1 and 2 outfalls

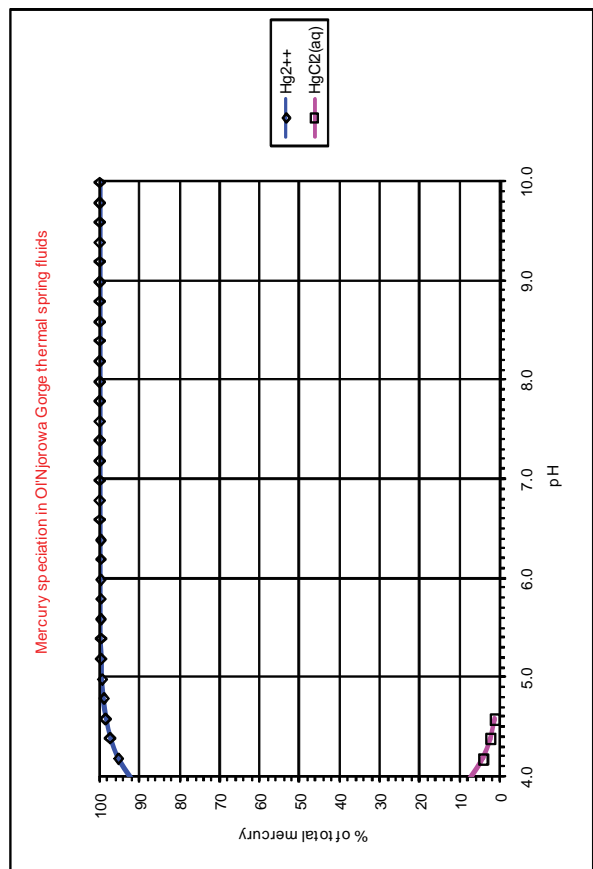
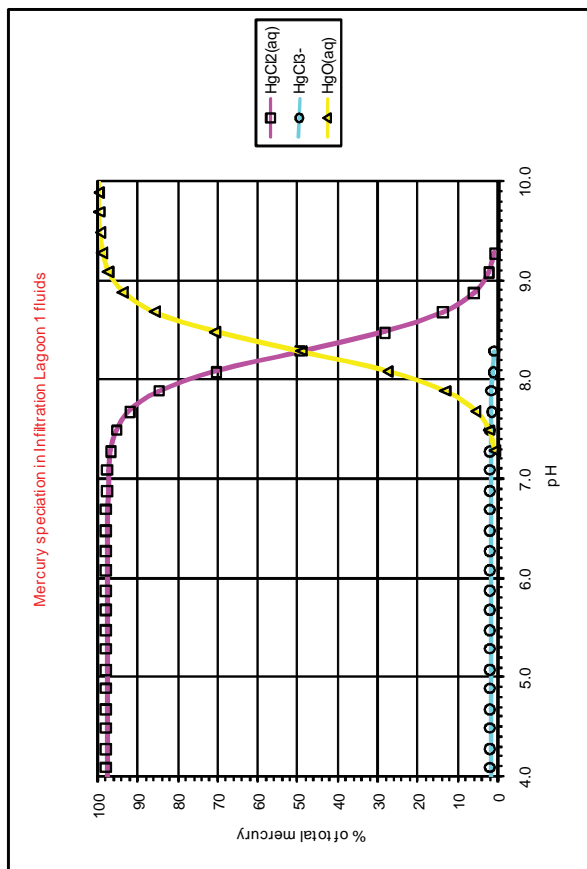
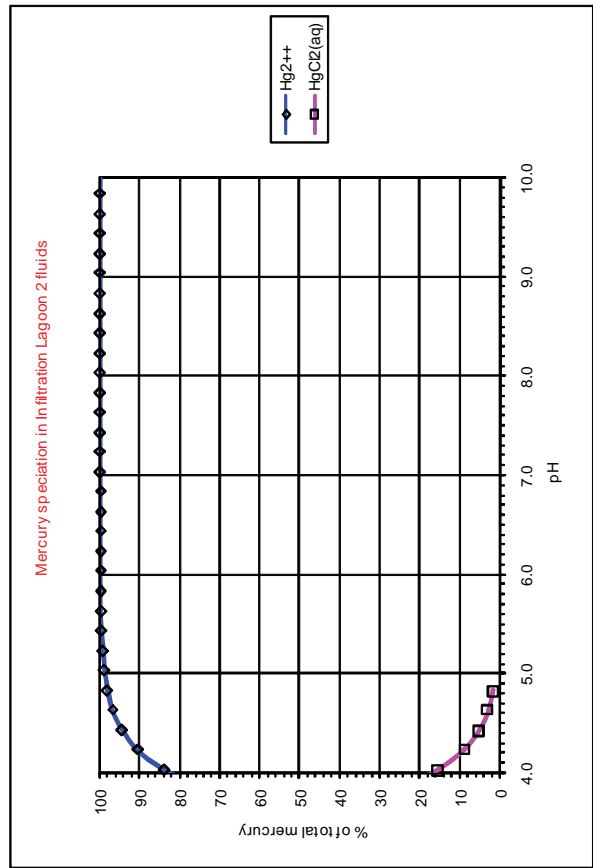
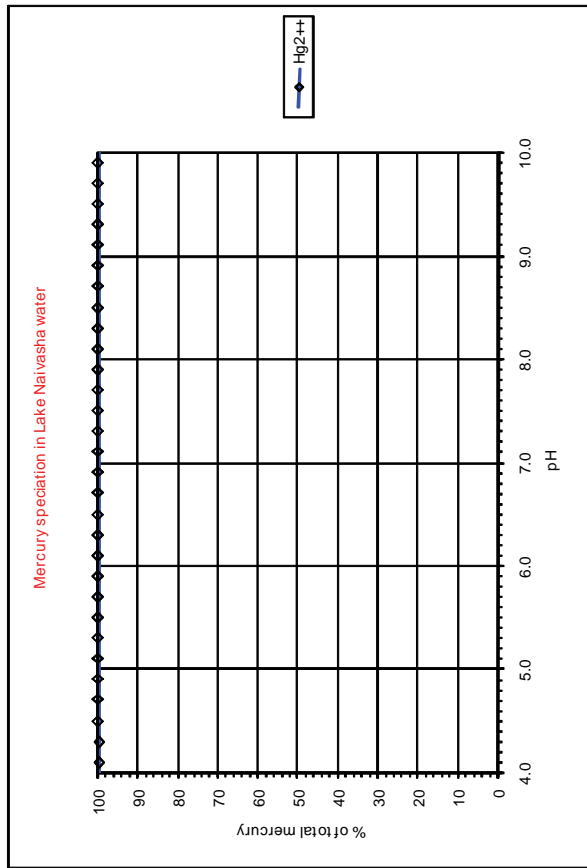


FIGURE 12c: Distribution curves for mercury species in spent geothermal fluids from the Infiltration Lagoons 1 and 2, Ol'Njorowa Gorge thermal spring fluids, and Lake Naivasha water

The percentages of species accounting for 99% or more of the total aqueous mercury within the sampling locations at in-situ pH and temperatures are shown in Table 13.

The range of percentages of the dominant mercury species within the 7 categories of the sampling locations is presented in Table 14.

The dominant dissolved mercury species in the sampled fluids are the inorganic mercurous ion $[\text{Hg}_2]^{2+}$, mercuric chloride, $\text{HgCl}_2(\text{aq})$, and mercuric oxide, $\text{HgO}(\text{aq})$. The free mercurous ion, $[\text{Hg}_2]^{2+}$, species accounted for > 99% in all the fluids except those from the acidic Olkaria I outfall with in-situ pH of 2.7 and Infiltration Lagoon 1. $\text{HgCl}_2(\text{aq})$ is observed in fluids from Olkaria I outfall (99.8%), Infiltration Lagoon 1 (28.55%), but nil in fluids from geothermal wells, Infiltration Lagoons outfall, Ol’Njorowa Gorge thermal springs, and Lake Naivasha water. $\text{HgO}(\text{aq})$ species occurs in fluids from Infiltration Lagoon 1 (70.83%) but nil in all the other sampled fluids.

TABLE 13: Percentage composition of mercury species at in-situ pH and temperatures within the sampling locations

Location	In-situ pH	In-situ Temp (°C)	Total analytical concentration (µg/L)	Dominant species
OW-2	8.4	88.0	0.09	$[\text{Hg}_2]^{2+}$ (99.85%)
OW-13	8.7	27.1	0.18	$[\text{Hg}_2]^{2+}$ (100%)
OW-21	6.9	16.0	0.03	$[\text{Hg}_2]^{2+}$ (100%)
OW-26	8.9	91.0	0.14	$[\text{Hg}_2]^{2+}$ (99.64%)
OW-29/30	8.6	80.0	0.11	$[\text{Hg}_2]^{2+}$ (99.89%)
OW-32	8.1	91.0	0.68	$[\text{Hg}_2]^{2+}$ (99.95%)
Olkaria I outfall	2.7	38.0	0.74	$\text{HgCl}_2(\text{aq})$ (99.8%)
IL-1	8.4	23.1	1.22	$\text{HgO}(\text{aq})$ (70.83%) $\text{HgCl}_2(\text{aq})$ (28.55%)
IL-2	8.6	25.1	1.25	$[\text{Hg}_2]^{2+}$ (100%)
IL-1 and 2 outfall	8.1	24.1	0.74	$[\text{Hg}_2]^{2+}$ (100%)
Ol’Njorowa Gorge thermal springs	8.5	26.3	1.02	$[\text{Hg}_2]^{2+}$ (100%)
Lake Naivasha	8.7	25.1	0.97	$[\text{Hg}_2]^{2+}$ (100%)

TABLE 14: Range of percentages for mercury species in spent geothermal fluids from the Olkaria geothermal field, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, Kenya

Species	% range of mercury species						
	Discharging geothermal wells (pH 8.1 – 8.9)	Shut-in geothermal wells (pH 6.9 – 9.8)	Olkaria I outfall (pH 2.7)	Infiltration lagoons (pH 8.4 – 8.6)	Infiltration lagoons outfall (pH 8.1)	Ol’Njorowa Gorge thermal springs (pH 8.5)	Lake Naivasha (pH 8.7)
$[\text{Hg}_2]^{2+}$	99.64 – 99.95	100		100	100	100	100
$\text{HgCl}_2(\text{aq})$			99.8	28.55			
$\text{HgO}(\text{aq})$				70.83			

3.5.7 Zinc

The probable distribution of zinc species in spent geothermal fluids from discharging geothermal wells OW-2, OW-26, OW-29/30 and OW-32, shut-in geothermal wells OW-13 and OW-21, Olkaria I outfall and Infiltration Lagoons, Ol’Njorowa Gorge thermal spring fluids, and Lake Naivasha water, are shown in Figures 13a, 13b, and 13c.

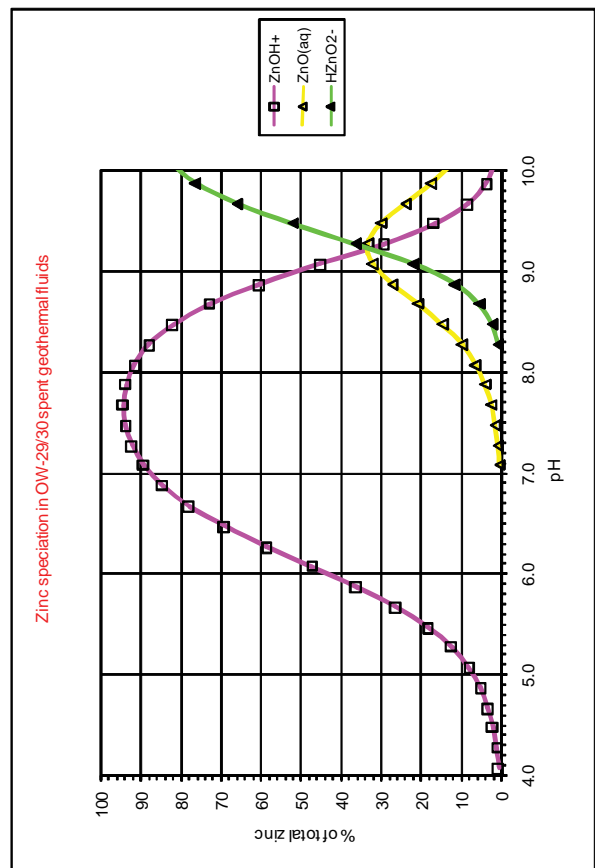
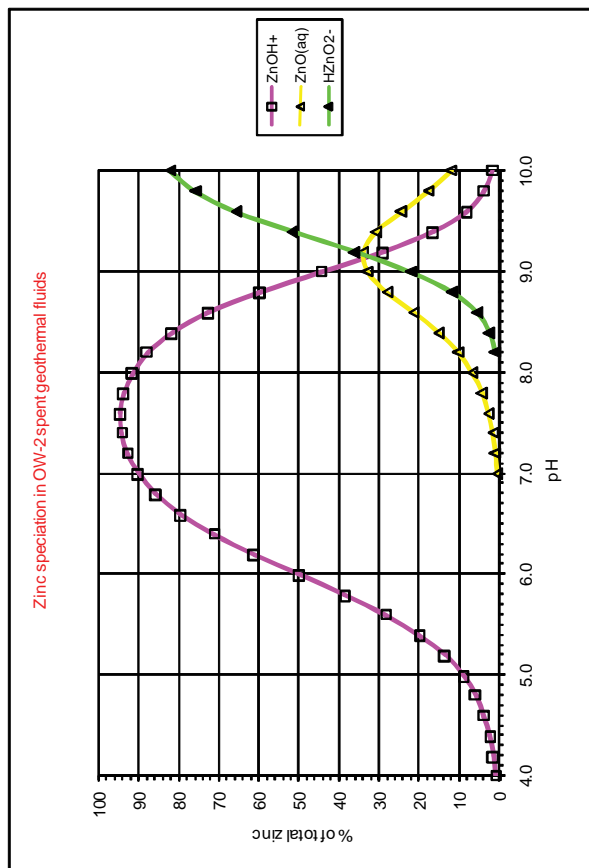
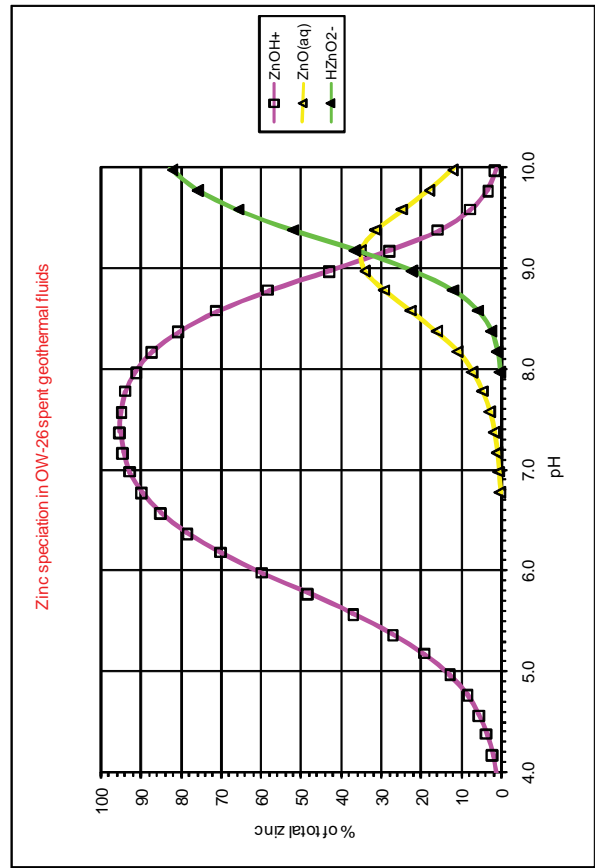
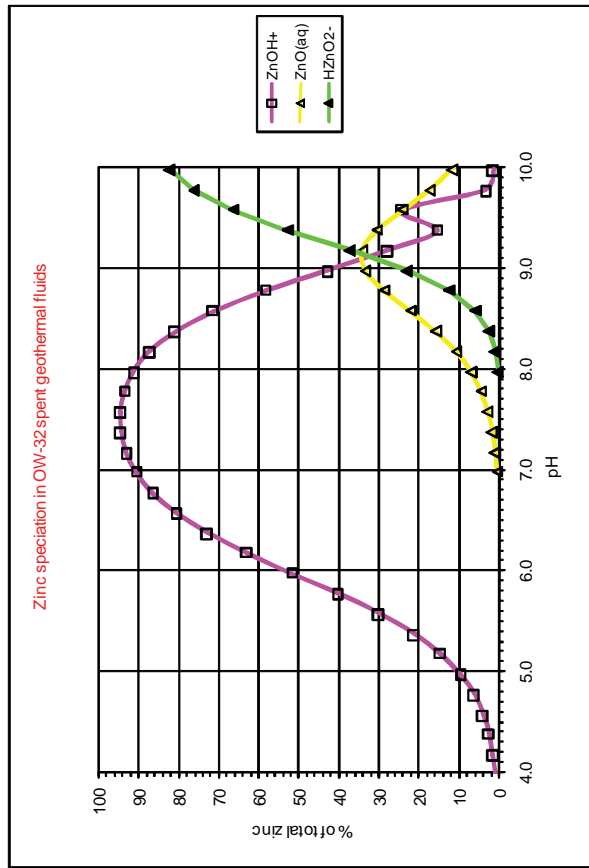


FIGURE 13a: Distribution curves for zinc species in spent geothermal fluids from discharging geothermal wells

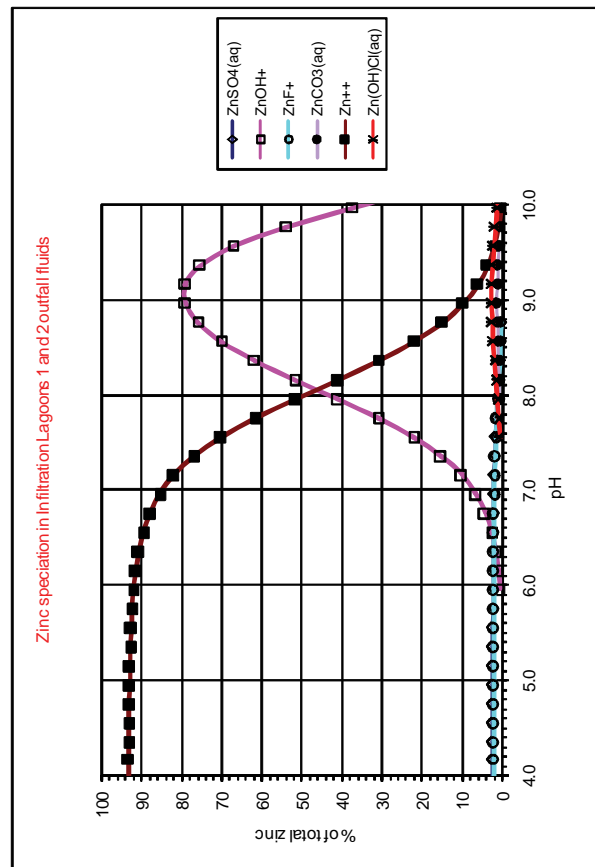
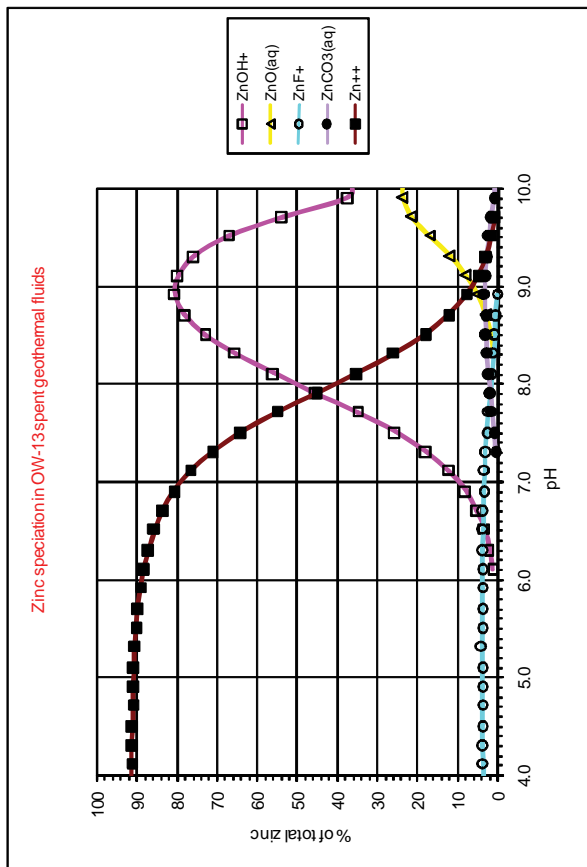
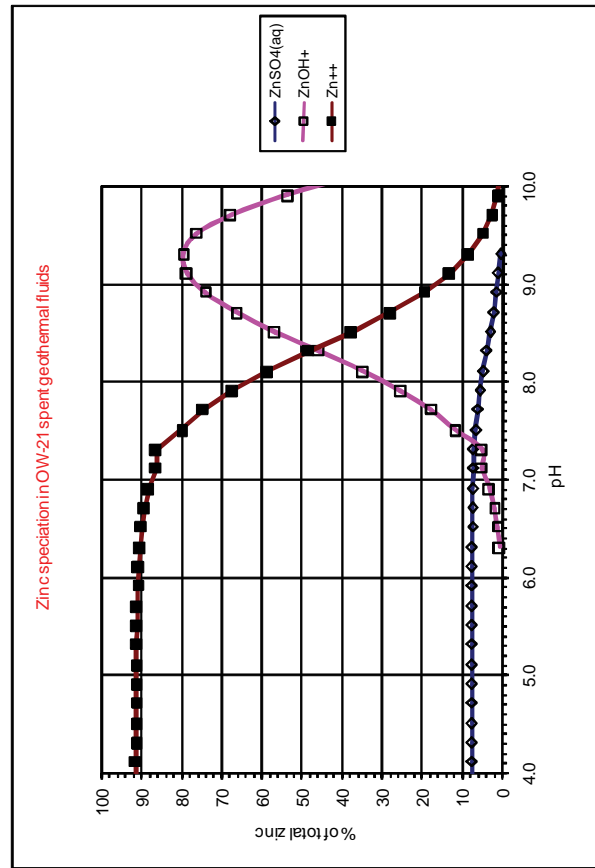
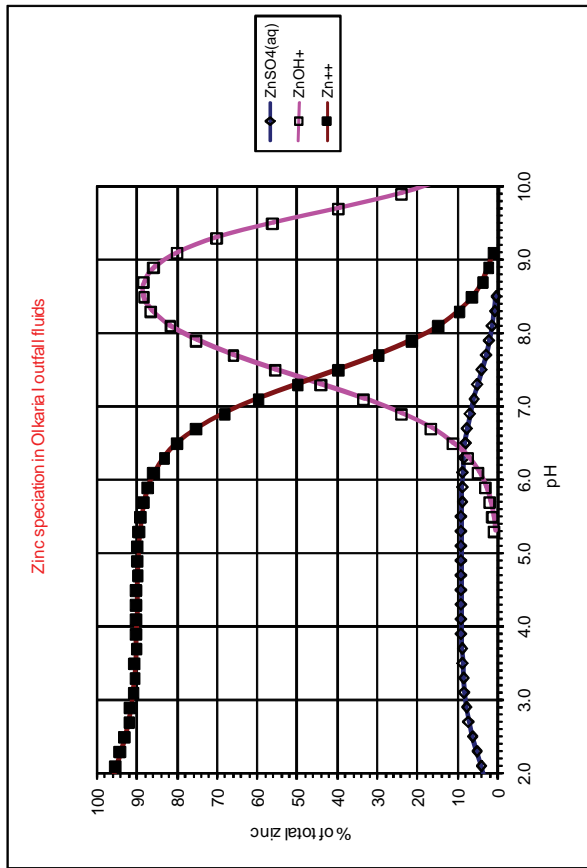


FIGURE 13b: Distribution curves for zinc species in spent geothermal fluids from shut-in geothermal wells and the Olkaria I and Infiltration Lagoons 1 and 2 outfalls

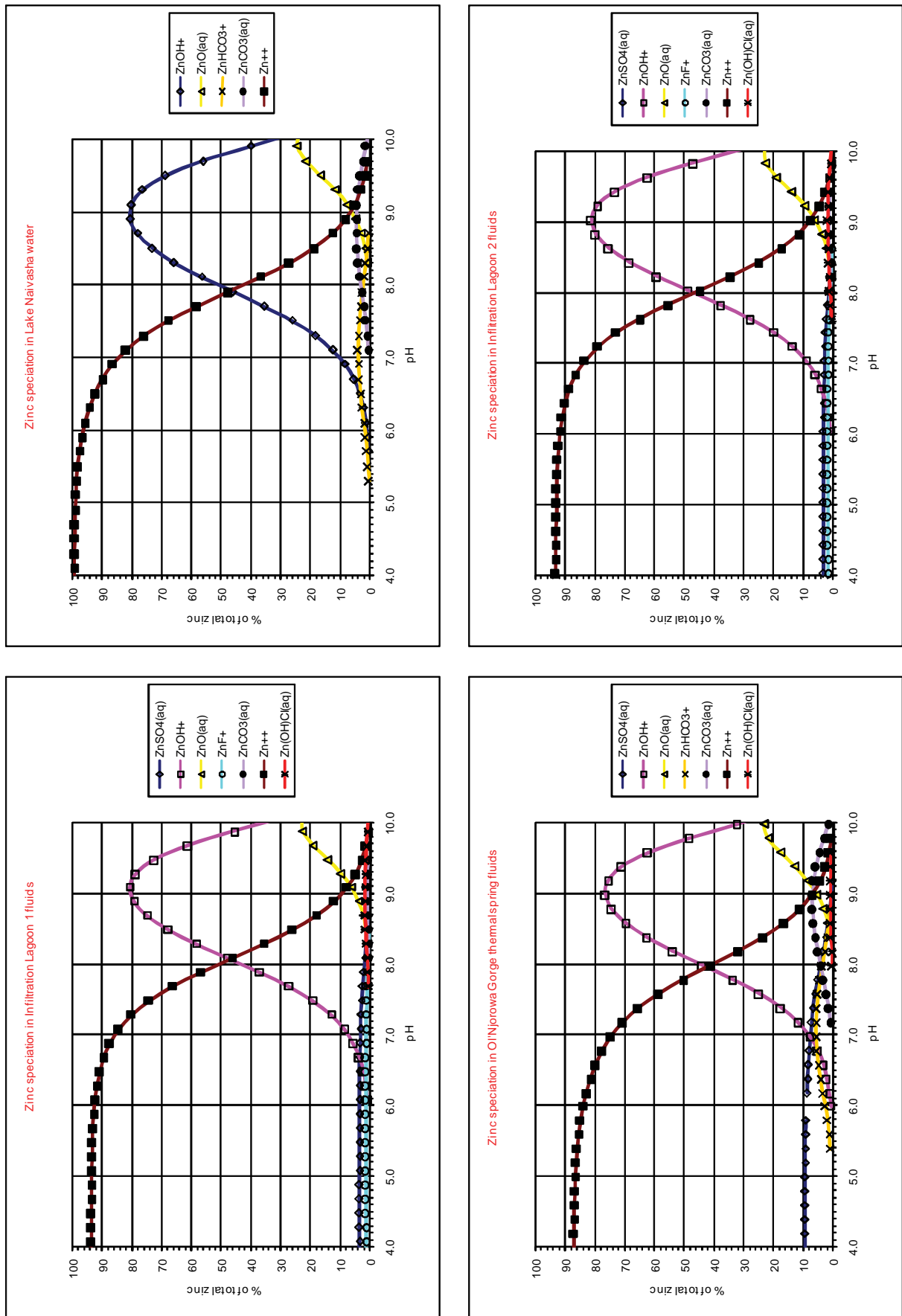


FIGURE 13c: Distribution curves for zinc species in spent geothermal fluids from the Infiltration Lagoons 1 and 2, Ol'Njorowa Gorge thermal springs, and Lake Naivasha water

The percentages of species accounting for 99% or more of the total aqueous zinc within the sampling locations at in-situ pH and temperatures are shown in Table 15.

The range of percentages of the dominant zinc species within the 7 categories of the sampling locations is presented in Table 16.

TABLE 15: Percentage composition of zinc species at in-situ pH and temperatures within the sampling locations

Location	In-situ pH	In-situ Temp (°C)	Total analytical concentration (µg/L)	Dominant species
OW-2	8.4	88.0	4.15	[ZnOH] ⁺ (81.78%) [HZnO ₂] ⁻ (2.57%)
OW-13	8.7	27.1	7.46	[ZnOH] ⁺ (78.26%) Zn ²⁺ (12.35%) ZnCO ₃ (aq)(3.28%) ZnO(aq)(3.17%) Zn(OH)Cl(aq)(0.93%) [ZnF] ⁺ (0.55%) ZnHCO ₃ ⁺ (0.52%)
OW-21	6.9	16.0	22.3	Zn ²⁺ (88.28%) ZnSO ₄ (aq)(7.52%) [ZnOH] ⁺ (3.33%)
OW-26	8.9	91.0	2.53	[ZnOH] ⁺ (42.96%) ZnO(aq)(34.37%) [HZnO ₂] ⁻ (22.54%)
OW-29/30	8.6	80.0	3.2	[ZnOH] ⁺ (73.16%) ZnO(aq)(20.92%) [HZnO ₂] ⁻ (5.69%)
OW-32	8.1	91.0	14	[ZnOH] ⁺ (87.42%) ZnO(aq)(10.88%) [HZnO ₂] ⁻ (1.18%)
Olkaria I outfall	2.7	38.0	41.6	Zn ²⁺ (92.28%) ZnSO ₄ (aq)(7.37%)
IL-1	8.4	23.1	12.4	[ZnOH] ⁺ (67.83%) Zn ²⁺ (26.23%) Zn(OH)Cl(aq)(1.5%) ZnO(aq)(1.35%) ZnSO ₄ (aq)(1.02%) ZnCO ₃ (aq)(1.01%) [ZnF] ⁺ (0.45%)
IL-2	8.6	25.1	10.3	[ZnOH] ⁺ (75.61%) Zn ²⁺ (17.5%) ZnO(aq)(2.31%) Zn(OH)Cl(aq)(1.72%) ZnCO ₃ (aq)(1.19%) ZnSO ₄ (aq)(0.62%) [ZnF] ⁺ (0.38%)
IL-1 and 2 outfall	8.1	24.1	10.2	[ZnOH] ⁺ (51.91%) Zn ²⁺ (41.19%) Zn(OH)Cl(aq)(1.8%) ZnSO ₄ (aq)(1.13%) [ZnF] ⁺ (1.08%) ZnCO ₃ (aq)(1.02%) [ZnCl] ⁺ (0.75%) [ZnHCO ₃] ⁺ (0.56%)
Ol’Njorowa Gorge thermal springs	8.5	26.3	13.7	ZnOH] ⁺ (69.94%) Zn ²⁺ (16.49%) ZnCO ₃ (aq)(6.76%) ZnO(aq)(2%) ZnSO ₄ (aq)(1.71%) [ZnHCO ₃] ⁺ (1.45%) Zn(OH)Cl(aq)(0.86%)
Lake Naivasha	8.7	25.1	10.3	ZnOH] ⁺ (78.38%) Zn ²⁺ (12.81%) ZnCO ₃ (aq)(4.69%) ZnO(aq)(3.04%) [ZnHCO ₃] ⁺ (0.69%)

TABLE 16: Range of percentages for zinc species in spent geothermal fluids from the Olkaria geothermal field, Ol’Njorowa Gorge thermal springs, and Lake Naivasha water, Kenya

Species	% range of zinc species						
	Discharging geothermal wells (pH 8.1 – 8.9)	Shut-in geothermal wells (pH 6.9 – 9.8)	Olkaria I outfall (pH 2.7)	Infiltration lagoons (pH 8.4 – 8.6)	Infiltration Lagoons outfall (pH 8.1)	Ol’Njorowa Gorge thermal springs (pH 8.5)	Lake Naivasha (pH 8.7)
[ZnOH] ⁺	42.96 – 87.42	3.33 – 78.26		67.83 – 75.61	51.91	69.94	78.38
Zn ²⁺		12.35 – 88.28	92.28	17.5 – 26.23	41.19	16.49	12.81
ZnO(aq)	10.88 – 34.37	3.17		1.35 – 2.31		2	3.04
[HZnO ₂] ⁻	1.18 – 22.54						
ZnSO ₄ (aq)		7.52	7.37	0.62 – 1.02	1.13	1.71	
ZnCO ₃ (aq)		3.28		1.01 – 1.19	1.02	6.76	4.69
Zn(OH)Cl(aq)		0.93		1.5 – 1.72	1.8	0.86	
[ZnF] ⁺		0.55		0.38 – 0.45	1.08		
[ZnHCO ₃] ⁺		0.52			0.56	1.45	0.69

The speciation modelling for aqueous zinc predicts various soluble species in the sampled fluids with minimal speciation in acidic fluids from Olkaria I outfall with the highest Zn content (41.6 µg/L) and fluids from discharging geothermal wells as shown in Table 16. The dominant Zn species are the hydroxyl complex, [ZnOH]⁺, in all the fluids except those from Olkaria I outfall and the free Zn²⁺ ion,

in all the fluids except those from discharging geothermal wells. Other Zn species are ZnO(aq), [HZnO₂]⁻, ZnSO₄(aq), ZnCO₃(aq), Zn(OH)Cl(aq), [ZnF]⁺, and [ZnHCO₃]⁺.

The highest percentage range of the species [ZnOH]⁺ is in the fluids from discharging geothermal wells (42 - 87.42 %), Lake Naivasha water (78.38%), fluids from shut-in geothermal wells (3.33 – 78.26%), Infiltration Lagoons (67.83 – 75.61), Ol’Njorowa Gorge thermal spring fluids (69.94%, and Infiltration Lagoons outfall fluids (51.91%). The free Zn²⁺ ion is dominant in fluids from Olkaria I outfall (92.28%), shut-in geothermal wells (12.35 – 88.28%), Infiltration Lagoons outfall (41.19%), Infiltration Lagoons (17.5 – 26.23%), Ol’Njorowa Gorge thermal spring fluids (16.49%), and Lake Naivasha water (12.81%), but nil in fluids from discharging geothermal wells.

Other species of dissolved zinc include ZnO(aq) in spent geothermal fluids from discharging geothermal wells (10.88 – 34.37%), minor percentages in fluids from shut-in geothermal wells (3.17%), Lake Naivasha water (3.04%), Infiltration Lagoons (1.35 – 2.31%), and Ol’Njorowa Gorge thermal spring fluids (2%), but nil in fluids from Olkaria I outfall and Infiltration Lagoons outfall; [HZnO₂]⁻ complex in spent geothermal fluids from discharging geothermal wells (1.18 – 22.54%) but nil in all other fluids; Zinc Sulphate ion pair, ZnSO₄(aq), in fluids from shut-in geothermal wells (7.52%) and Olkaria I outfall (7.37%), minor percentages in fluids from Ol’Njorowa Gorge thermal spring fluids (1.71%), fluids from the Infiltration Lagoons outfall (1.13%), and Infiltration Lagoons (0.62 - 1.02%), but nil in fluids from discharging geothermal wells and Lake Naivasha water; and Zinc Carbonate ion pair, ZnCO₃(aq), in Ol’Njorowa Gorge thermal spring fluids (6.76%), minor percentages in Lake Naivasha water (4.69%), fluids from shut-in geothermal wells (3.28%), Infiltration Lagoons (1.01 – 1.19%), and Infiltration Lagoons outfall (1.02%), and nil in fluids from discharging geothermal wells, Olkaria I outfall, and Ol’Njorowa Gorge thermal springs.

Other minor species of zinc are Zn(OH)Cl(aq) in fluids from Infiltration Lagoons 1 and 2, Infiltration Lagoons outfall, shut-in geothermal wells, and Ol’Njorowa Gorge thermal spring fluids; [ZnF]⁺ in fluids from Infiltration Lagoons outfall, Infiltration Lagoons 1 and 2, and shut-in geothermal wells; and [ZnHCO₃]⁺ in fluids from Ol’Njorowa Gorge thermal springs, Lake Naivasha water, and fluids from Infiltration Lagoons outfall and shut-in geothermal wells.

4. DISCUSSION

4.1 Omissions, errors and uncertainties

The total dissolved concentrations of B, Li, H₂S, NH₃, SiO₂(aq), and inorganic ligands (HCO₃⁻, NO₂⁻, and NO₃⁻), which are indicative chemical components of geothermal fluids, and organic ligand species, were not analysed. B and Li in particular, are toxic to flora and fauna. B as well as Cl, are soluble conservative constituents, which do not take part in water-rock interactions after dissolution from the rocks. They are highly mobile elements and therefore one of the useful chemical tracers and geoindicators of relative mobility of trace elements in hydrothermal brine and mixing of the same with surface derived or meteoric waters. The environmental and health risk assessments of surface discharge of spent geothermal fluids need to include B and Li. The HCO₃⁻, HS⁻, H₂AsO₄⁻, CrO₄⁻, SiO₂(aq), MoO₄²⁻, and HPO₄²⁻ concentrations used in the speciation model calculations in the EQ3/6 code were estimated from the total dissolved CO₂, S and SO₄²⁻, As, Cr, Si, Mo, and P concentrations, respectively. The analytical results for Ba, Co, Cr, Fe, Mn, Ni, and Sr were omitted in the interpretations. Co, Cr, Fe, Mn, and Ni, according to Arnórsson (2006) are trace elements in steel products and the high total dissolved concentrations in the sampled fluids may be due to contamination rather than from spent geothermal fluids. Ba and Sr are of less environmental and health significance. Aqueous Mo speciation was also omitted due to lack of relevant information on ecotoxicity of the various Mo species.

Errors of 2% in analyses performed using IC and Selective Ion Electrode and 1% (for values > 1.0 mg/L) and 5% (for values < 1.0 mg/L) in analyses performed using ICP-AES, ICP-SFMS, and AFS have been established based on both the reproducibility of in-house analytical laboratory standards and internationally accepted methods (EURACHEM/CITAC, 2000).

The uncertainties of ICP-AES, ICP-SFMS, and AFS analyses for the major and trace elements were calculated with a coverage factor of 2, which gives a confidence limit level of approximately 95% according to the definitions of the Organization of International Standards, Geneva-Switzerland (ISO, 1993). The uncertainties of the elemental analyses ranged from 12% for Ca, Mg, S, and Sr to 59% for As. The calculated uncertainty of the dissolved Cd concentrations was 21% and could be due to Mo interference (Omberg, 2006).

4.2 Comparison with reported data from previous studies in Olkaria

Comparison of trace element data from the present (August 2005) and previous (October 1997, March 1998, August 2000, and 2003) studies of fluids from geothermal wells OW-2, OW-21, and OW-32 in the Olkaria East geothermal field, indicate that the data reported by Wetang'ula (2004) for Al, As, Mo, and Pb concentrations, are comparable for spent geothermal fluids from well OW-2, Al, As and Mo concentrations comparable for spent geothermal fluids from discharging geothermal wells OW-32, Cu, Hg and Zn concentrations lower in fluids from shut-in geothermal well OW-2, and Cu, Pb, Hg, and Zn concentrations lower in fluids from well OW-32. Aqueous Cd concentrations are higher in fluids from both well OW-2 and OW-32. The trace element concentrations for fluids from well OW-21 were highly variable. The aqueous Cu and Zn concentrations were comparable, Al, As, and Mo concentrations lower, and Pb and Hg concentrations higher. The 2000 data for aqueous Cd concentration was higher than 2005 data, both 1997 and 1998 Cu and Pb concentrations higher than both 2003 and 2005 data, and 1997, 1998 and 2000 aqueous Zn concentrations higher than both 2003 and 2005 data. The results of this study are, however, consistent with the previous data reported by Wetang'ula (2004), for Al, As, and Mo, and not for Cd, Cu, Pb, and Hg though both were based on the total dissolved concentrations of the trace elements in spent geothermal fluids. In contrast, Simiyu (1998) reported 6400 µg/L for Zn, 100 µg/L for Pb, and 20 µg/L for Cu in fluids of OW-21, which were far higher by factors of up to 286 for Zn, 38 for Pb, and 6 for Cu. Likewise, in the Olkaria environmental monitoring programme (March 1998) 600 and 100 µg/L for Pb, 130 and 150 µg/L for Cu, and 2990 and 100 µg/L for Zn were reported, which were far higher by factors of up to 232 and

404 for Pb, 41 and 276 for Cu, and 134 and 24 for Zn in fluids of OW-21 and OW-2, respectively, and in August 2000, 37 µg/L for Zn in fluids of OW-2, which was higher by a factor of up to 8, and 39 µg/L for Cd and 20000 µg/L of Zn in fluids of OW-21, were reported, which were higher by factors of up to 5571 for Cd and 896 for Zn. The earlier 1997 – 2000 studies were based on analysis of the total recoverable concentrations of the trace elements. These analyses include undissolved species of trace elements adsorbed on particulate matter in the fluid samples, which are not critical in terms of elemental mobility, bioavailability, and toxicity to humans, animals, and plants.

The aqueous Cu and Zn concentrations were lower in the Infiltration Lagoons 1 and 2 outfall fluids than in the Infiltration Lagoon 1 and Olkaria I outfall fluids. Aqueous Cd and Hg concentrations were both lower in the Infiltration Lagoons 1 and 2 outfall fluids but higher for Cd and the same for Hg in Olkaria I outfall fluids. In contrast, Al, As, Pb, and Mo concentrations were higher in Infiltration Lagoons 1 and 2 outfall fluids than in Infiltration Lagoon 2 and Olkaria I outfall fluids. These observations may be an indication of some degree of either both precipitation and adsorption onto sediments or filtration of Cd, Cu, Hg, and Zn, and enrichment of Al, As, Pb, and Mo, in fluids from the Infiltration Lagoons. The rate of uptake by the aquatic plants flourishing in the Infiltration Lagoons may be higher for aqueous Cd, Cu, Hg, and Zn and lower for aqueous Al, As, Pb, and Mo. These observations confirm the results of previous studies of Simiyu (1994), who reported trace element enrichment in soils in contact with waters in Olkaria area by factors of up to 6000 for Zn; 500 for Cu, 240 for Pb; and 125 for Cd. In plants, these elements are concentrated by factors of up to 7800 for Zn; 2250 for Cu; 625 for Pb; and 259 for Cd, in the case of green algae in direct contact with geothermal fluids in the infiltration lagoons. An investigation of the potential use of the Infiltration Lagoons as “wetlands” for purification of spent geothermal fluids of the trace elements load is essential.

4.3 Comparison with reported data from other geothermal fields

The chemical composition of geothermal fluids is extremely variable as indicated in Table 17 for some selected geothermal fields.

The chemistry of the spent geothermal fluids is largely dependent on the geochemistry of the reservoir and the operating conditions of the power plant, which vary from one field to another (Webster, 1998). Most geothermal fluids from high temperature fields may contain high concentrations of at least one of the following chemical contaminants Al, As, B, Hg, and in some cases F, as shown in Table 17. The concentrations of these constituents are largely controlled by their influx into the deep circulating geothermal fluids, which extract them from either enclosing rocks or degassing magma. High concentrations of trace metals and metalloids are associated with high temperature brines as in Salton Sea, California, USA. For example, arsenic concentrations ranging from < 10 – 50,000 µg/L in geothermal water has been reported in several parts of the world, including hot springs from parts of USA, Japan, New Zealand, Chile, Iceland, Kamchatka, France and Dominica (White et al., 1963; Ellis and Mahon, 1977; Welch, et al., 1988, 2000; Wilkie and Herring, 1988, 1998; Criaud and Fouillac, 1989; Yokoyama et al., 1993; Robinson et al., 1995; Thompson et al, 1995; Smedley and Kinniburgh, 2002).

4.4 Evaluation of compliance with the Kenyan standards and some relevant international environmental guidelines

4.4.1 Physical parameters

The in-situ temperatures of all the fluids of discharging geothermal wells OW-2, OW-26, OW-29/30, and OW-32, were above the Kenyan maximum permissible level for recreational waters, which specify a maximum permissible level of 30 °C (Legal Notice No. 120, 2006).

TABLE 17: Concentrations of chemical constituents of spent geothermal fluids from some selected geothermal fields

Location	SiO ₂ (aq) mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	F mg/L	Cl mg/L	B mg/L	Cu (µg/L)	Zn (µg/L)	Al (µg/L)	Pb (µg/L)	Cd (µg/L)	As (µg/L)	Hg (µg/L)	Source
Olkaria OW-2, Kenya	679.3	536	81.2	0.585	<0.09	66.9	788		0.543	4.15	614	0.247	<0.05	1210	0.093	1
Olkaria OW-32, Kenya	987.9	554	107	0.396	<0.09	57.9	822		1.49	14.0	1890	0.373	<0.05	1290	0.688	1
Krafla, separator water, Iceland	631	253	32.6	3.75	<0.09				0.197	5.2	1.46	7.5	<0.002	59.5	0.0039	2
Reykjanes, RN-09, Iceland	738	8160	1720	1850	1.01			9.89	1.84	0.0112	86.8	0.369	0.171	138	0	3
Salton Sea 1 California, USA	400	50400	17500	28000	54	15.0	155000	390						12000	6.0	4
Wairakei 24, New Zealand	557	1256	200	26.7	0.02	6.9	2183	26.2						4700	0.2	4
Cerro Prieto 5, Mexico	790	6950	1670	395	0.45	1.9	12900	19.0						2300	0.05	5

1: Current Study, 2005; 2: Armannsson and Olafsson, 2002; 3: The Icelandic National Energy Authority data; 4: Ellis and Mahon, 1977; and 5: Truessedell et al., 1981.

The pH of spent geothermal fluids from discharging geothermal wells OW-2 and OW-32, shut-in geothermal well OW-21, fluids of Infiltration Lagoon 1, Infiltration Lagoons 1 and 2 outfall, and Ol’Njorowa Gorge thermal spring fluids, were in compliance with the pH range 6.5 – 8.5 recommended by the European Community (EC) and World Health Organization (WHO) (Meybeck et al., 1990) guidelines for drinking-water quality, and the Kenyan guide value (maximum permissible) for sources of domestic water, maximum allowable limits for effluent discharge to the environment, and the permissible level for irrigation water. The pH values for all the fluids, except those from Olkaria I outfall, were in compliance with the Kenyan permissible levels (pH 6.0 – 9.0) for recreational water. The pH 2.7 for Olkaria I outfall fluids, however, places the fluids below the Kenyan pH limit for sources of domestic water, effluent discharge to the environment, and permissible level for irrigation water and both the EC and WHO guidelines for drinking-water quality. The pH values of 8.6 for OW-29/30 and Infiltration Lagoon 2, 8.7 for OW-13 and Lake Naivasha water, and 8.9 for OW-26, is slightly above both the EC and WHO maximum permissible pH limits for human consumption, and the Kenyan maximum permissible limit for sources of domestic water, effluent discharge to the environment, and permissible level for irrigation water.

The TDS values for fluids from discharging geothermal wells, shut-in geothermal well OW-13, and Infiltration Lagoons outfall, were above the Kenyan maximum permissible value of 1200 mg/L for sources of domestic water, effluent discharge to the environment, and the permissible level for irrigation water.

4.4.2 Major ion species

The total dissolved Na⁺ concentrations in spent geothermal fluids, except for those from shut-in well OW-21, Olkaria I outfall, and Lake Naivasha water, were above the WHO (200 mg/L) and EC (150 - 175 mg/L) maximum permissible concentrations for human consumption.

The dissolved Cl⁻ concentrations in all fluid samples, except for those from shut-in geothermal well OW-21, Olkaria I outfall, and Lake Naivasha water, were above the WHO guideline for drinking-water quality and the Kenyan standard for effluent discharge to the environment, both of which specify a maximum permissible limit of 250 mg/L of Cl⁻. The aqueous Cl⁻ concentrations in all fluids were also above the Kenyan permissible level of 0.01 mg/L Cl⁻ for irrigation water and the EC guideline for drinking-water quality (25 mg/L).

The total dissolved F⁻ concentrations of in all fluid samples were above the Kenyan permissible level for irrigation

water (1.0 mg/L), guide values for sources of domestic water, maximum permissible limit for effluent discharge to the environment, the Canadian maximum acceptable concentrations for community use, and the WHO maximum permissible concentrations for drinking-water quality. The Kenyan standards, Canadian, and WHO guidelines specify 1.5 mg/L of F⁻ for sources of domestic water, effluent discharge into the environment, water for community use and human consumption. The F⁻ concentration in Lake Naivasha water, was in compliance with both the Canadian maximum acceptable concentration for livestock watering (1 - 2 mg/L) and the stringent EC maximum permissible concentration for human consumption (1.5 – 1.7 mg/L). All other fluids had F⁻ concentrations above the Canadian and EC guidelines for drinking-water quality.

The total dissolved SO₄²⁻ concentrations of in all d fluid samples, except from wells OW-26 (14.6 mg/L) and OW-29/30 (24.6 mg/L), and Lake Naivasha water, were above the stringent European Community (25 mg/L) recommended maximum permissible concentration for human consumption. The SO₄²⁻ concentrations, however, were in compliance with the WHO guideline value of 400 mg/L for drinking-water quality.

4.4.3 Trace element species

The total dissolved Cd, Cu, Pb, Hg, and Zn concentrations in all sampled fluids were within the Kenyan maximum permissible limits for effluent discharge to the environment (Legal Notice No. 120, 2006). Arsenic levels in all sampled fluids, except for Lake Naivasha water, were above the Kenyan limit (20.0 µg/L As) for effluent discharge to the environment. The dissolved Al, Cd, Cu, Pb, and Zn concentrations were in compliance with the Kenyan guide values for sources of domestic water, and permissible levels for irrigation and recreational waters for all sampled fluids. Arsenic concentrations in all sampled fluids, except for those from shut-in geothermal well OW-21 and the Olkaria I outfall, Ol’Njorowa Gorge thermal springs, and Lake Naivasha water, were above those of the Kenyan water quality standard for sources of domestic water (10 µg/L), and permissible levels for both irrigation (100 µg/L) and recreational (50 µg/L) waters

Aqueous Hg concentrations in all sampled fluids, except for those from Infiltration Lagoon 1 and 2, and Ol’Njorowa Gorge thermal springs, were in compliance with the Kenyan permissible level for recreational water (1.0 µg/L).

The Al concentrations in all sampled fluids, As in all fluids, except those from geothermal well OW-21 and Lake Naivasha water, and Hg in all the fluids, except those from Infiltration Lagoons 1 and 2, and Ol’Njorowa Gorge thermal springs, were above the Canadian maximum acceptable concentrations for community use (CCME, 1999), which recommends 100 µg/L of Al, 25 µg/L of As, and 1.0 µg/L of Hg. Aqueous Ba, Cd, and Pb concentrations were in compliance with the Canadian water quality guidelines for domestic use. The dissolved Al, Cd, Cu, Pb, Hg, Mo, and Zn concentrations in all fluids were within the Canadian maximum acceptable concentrations for livestock watering (CCME, 1999). Arsenic concentrations in spent geothermal fluids from wells OW-2 (1210 µg/L), OW-13 (1150 µg/L), OW-26 (934 µg/L), OW-29/30 (1170 µg/L), OW-32 (1290 µg/L), Olkaria I outfall (91.1 µg/L), Infiltration Lagoon 1 (698 µg/L), Infiltration Lagoon 2 (913 µg/L), Infiltration Lagoons 1 and 2 outfall (1270 µg/L), and Ol’Njorowa Gorge thermal springs (60 µg/L), were above the Canadian maximum acceptable concentration of 25 µg/L As for livestock watering. Similarly, aqueous Al, Cd, Cu, Pb, and Zn concentrations were in compliance with the Canadian water quality criteria for irrigation purposes or protection of plants (CCME, 1999). Aqueous As concentrations in fluids from wells OW-2, OW-13, OW-26, OW-29/30, OW-32, Infiltration Lagoon 1, Infiltration Lagoon 2, and Infiltration Lagoons 1 and 2 outfall and Mo in all fluid samples, except from well OW-21 (22.4 µg/L) and Lake Naivasha water (3.65 µg/L), were above the Canadian maximum acceptable concentration of 100 µg/L for As and 10 – 50 µg/L for Mo for irrigation purposes or protection of plants.

Aqueous Pb and Zn concentrations in all fluid samples were in compliance with the Canadian water quality guidelines for protection of aquatic life in fresh water ecosystems (CCME, 1999). Cd concentrations in all fluid samples, except for those from Ol’Njorowa Gorge thermal springs (0.14

$\mu\text{g/L}$) and Cu concentrations in all fluid samples, except for those from Olkaria I outfall ($9.4 \mu\text{g/L}$), were within the Canadian water quality guideline values of $0.017 \mu\text{g/L}$ for Cd and $2 - 4 \mu\text{g/L}$ for Cu, recommended for protection of aquatic life in freshwater. The dissolved As concentrations in all the fluids, except for those from Lake Naivasha water, Hg concentrations in spent geothermal fluids from well OW-32, Olkaria I outfall, Infiltration Lagoon 1, Infiltration Lagoon 2, Infiltration Lagoons outfall, and Ol'Njorowa Gorge thermal springs, and Lake Naivasha water, and Mo in all fluid samples, except for those from Olkaria I outfall ($23.9 \mu\text{g/L}$), were above the Canadian water quality guidelines of $5.0 \mu\text{g/L}$ for As, $1 - 7 \mu\text{g/L}$ for Hg, and $73 \mu\text{g/L}$ for Mo, recommended for protection of aquatic life in freshwater ecosystems.

Aqueous Al concentrations in all fluid samples were above the WHO and the stringent EC guidelines for drinking-water quality, both of which specify $200 \mu\text{g/L}$ of Al (Figure 28). Aqueous Cd, Cu and Pb concentrations in all the fluids; Hg in all the fluids, except those from Infiltration Lagoon 1, Infiltration Lagoon 2, and Ol'Njorowa Gorge thermal springs; and Mo in fluids from well OW-21 ($22.4 \mu\text{g/L}$) and Lake Naivasha water ($3.65 \mu\text{g/L}$) were in compliance with the WHO guideline for drinking-water quality, which specify $1.0 \mu\text{g/L}$ for Hg and $70 \mu\text{g/L}$ for Mo (Figure 28). Aqueous Al and Cd concentrations in all fluid samples were above the WHO guidelines for drinking-water quality.

4.5 Variations in pH, temperature, DOC, TDS, and conductivity values

The pH values for the spent geothermal fluids were within the pH range of most natural waters, which varies from pH 5.0 – 9.0 (Andrews et al., 2004) except for Olkaria I outfall fluids, which had the lowest pH 2.7. A pH of 2.7 is very acidic and the effluents are corrosive. Lower pH values can occur in dilute waters with high organic content and higher values in eutrophic water, groundwater, brines, and salt lakes (Onindo, 1995). However, absorption of acid non-condensable gases (CO_2 , H_2S , and NH_3) or retention of strong acidic anions (SO_4^{2-} and Cl^-) in excess condensates and blow-downs from Olkaria I power station could be responsible for the highly acidic character of the effluents from Olkaria I power station and may not be an indication of high concentrations of DOC. The ranges of pH for fluids from shut-in geothermal wells showed wide variations. This may be attributed to the differences in the duration of exposure to atmospheric conditions. The elevated pH of Lake Naivasha water (pH 8.7), however, may be an indication of eutrophic conditions in Lake Naivasha. The spent geothermal fluids were saline with high pH values. The high alkaline nature of the spent geothermal fluids may be the reason for the low DOC values recorded. According to Onindo (1995), high in-situ temperatures during fluid discharge may also facilitate rapid decomposition of dissolved organic matter. However, there is no evidence of correlation between DOC concentrations and both temperature and pH for all fluid samples as expected. There is a good positive correlation between the TDS concentrations and conductivity values determined for the fluids.

The range of TDS values indicates the sampled fluids as chemically benign and thus less corrosive and toxic. The conductivity values, however, are high, and this may be attributed to a high degree of mineralization of the spent geothermal fluids arising from hydrothermal water-rock interactions and subsequent dissolution of minerals from the sub-surface rocks. The conductivity of most freshwater lakes ranges from $10 - 1000 \mu\text{Scm}^{-1}$ but may exceed $1000 \mu\text{Scm}^{-1}$ in polluted freshwaters (Onindo, 1995). The conductivity value recorded for Lake Naivasha water ($325 \mu\text{Scm}^{-1}$) may be an indication of the fact that Lake Naivasha is not yet in the category of a highly polluted freshwater ecosystem.

4.6 Correlations between the major ion species

The spent geothermal fluids have a higher relative abundance of $\text{SiO}_2(\text{aq})$, Cl^- , F^- , SO_4^{2-} , Na^+ , and K^+ than Lake Naivasha water. Compared to Lake Naivasha water, Ol'Njorowa Gorge thermal springs, have higher concentrations of $\text{SiO}_2(\text{aq})$, Cl^- , HCO_3^- , F^- , SO_4^{2-} , and Na^+ , but lower concentrations of all other elements such as Ca^{2+} , K^+ , and Mg^{2+} .

The fluids of the Olkaria East geothermal field are enriched in Na^+ and Cl^- ions, have relatively low HCO_3^- concentrations and may therefore be classified as Na - Cl water-type. There is an overall good positive correlation between Na^+ , K^+ , and Cl^- species.

These results are consistent with previous data reported by Omenda (2000). In contrast, Ol’Njorowa Gorge thermal springs, are enriched in Na^+ and HCO_3^- and Cl^- and are classified as Na - HCO_3^- - Cl water-type. Compared to Lake Naivasha water and Ol’Njorowa Gorge thermal spring fluids, the spent geothermal fluids of the Olkaria East geothermal field are heavily depleted in Ca^{2+} and Mg^{2+} . The Ol’Njorowa Gorge thermal spring fluids and the spent geothermal fluids from the Olkaria East geothermal field are distinctively different in chemical composition though their origins may be the same. Therefore, the spent geothermal fluids discharged into the conditioning ponds and infiltration lagoons cannot be the source of the thermal springs in Ol’Njorowa Gorge.

The F^- concentrations were high in all fluid samples. The results confirm exceptionally high F^- concentrations in Kenyan rift waters including Lake Naivasha water. Therefore, natural and not anthropogenic sources of surface discharge of geothermal fluids may constitute a source of F^- contamination to natural water bodies around Olkaria geothermal field. The high F^- levels may cause bone problems in children and livestock. Nevertheless, low and stable levels of F^- are required to maintain dental health, prevent teeth mottling in children, and prevent fluorosis in livestock.

The relative abundance of SO_4^{2-} and HS^- in all sampled fluids was significantly low. The low SO_4^{2-} and HS^- concentrations could be due to loss through reduction to sulphide and precipitation of elemental sulphur, respectively.

4.7 Spatial variations in the concentrations of selected trace elements and correlations with the major ion species

The spent geothermal fluids from the Olkaria East geothermal field have significant aqueous Al, As, and Mo concentrations and trace amounts of Cd, Cu, Pb, Hg, and Zn. The highest dissolved Al (1890 $\mu\text{g/L}$), As (1290 $\mu\text{g/L}$), and Mo (510 $\mu\text{g/L}$) concentrations were in spent geothermal fluids from discharging geothermal well OW-32; Cd (< 0.09 $\mu\text{g/L}$) in Infiltration Lagoon 1 fluid; Cu (9.4 $\mu\text{g/L}$) and Zn (41.6 $\mu\text{g/L}$) in Olkaria I outfall fluid; Pb (2.58 $\mu\text{g/L}$) in spent geothermal fluids from shut-in geothermal well OW-21; and Hg (1.25 $\mu\text{g/L}$) in the Infiltration Lagoons. Aqueous Cd concentrations in spent geothermal fluids from Olkaria were lower than in both Ol’Njorowa Gorge thermal spring fluids (0.14 $\mu\text{g/L}$) and Lake Naivasha water (0.02 (0.14 $\mu\text{g/L}$)). The aqueous Al concentrations were high in all sampled fluids including Lake Naivasha water. This is probably due to the ubiquity of Al-F bearing minerals in the geological environment of the Kenyan rift. Aqueous As and Mo concentrations in spent geothermal fluids and Ol’Njorowa Gorge thermal spring fluids were higher than in Lake Naivasha water. This is due to the high mobility of As and Mo species in hydrothermal fluids.

Aqueous Al concentrations were > 400 $\mu\text{g/L}$ in all the spent geothermal fluids with $\text{pH} > 7$, $\text{F}^- > 50$ mg/L , $\text{SiO}_2(\text{aq}) > 120$ mg/L , and $\text{Na}^+ > 280$ mg/L . The correlations of Al with pH , F^- , $\text{SiO}_2(\text{aq})$, and Na^+ species are presented in Figure 14. F^- , $\text{SiO}_2(\text{aq})$, and Na^+ , which occur in abundance in spent geothermal fluids and most water bodies in the Kenyan rift, may be indicative of the significant role these species, besides OH^- ions, play in aqueous mobility of Al in geothermal fluids assuming that Al a “hard” metal would prefer the hardest donor atoms (Stefansson and Arnórsson, 2000).

Aqueous As concentrations were > 600 $\mu\text{g/L}$ in spent geothermal fluids with $\text{pH} < 7$, $\text{Cl}^- > 300$ mg/L , and $\text{SiO}_2(\text{aq}) > 400$ mg/L . Although there were no significant positive correlations of As with $\text{SiO}_2(\text{aq})$ and Cl^- as indicated in Figure 15, these species with high relative abundance in spent geothermal fluids of Olkaria, may be of significance in transport of and high As concentrations in the hydrothermal fluids.

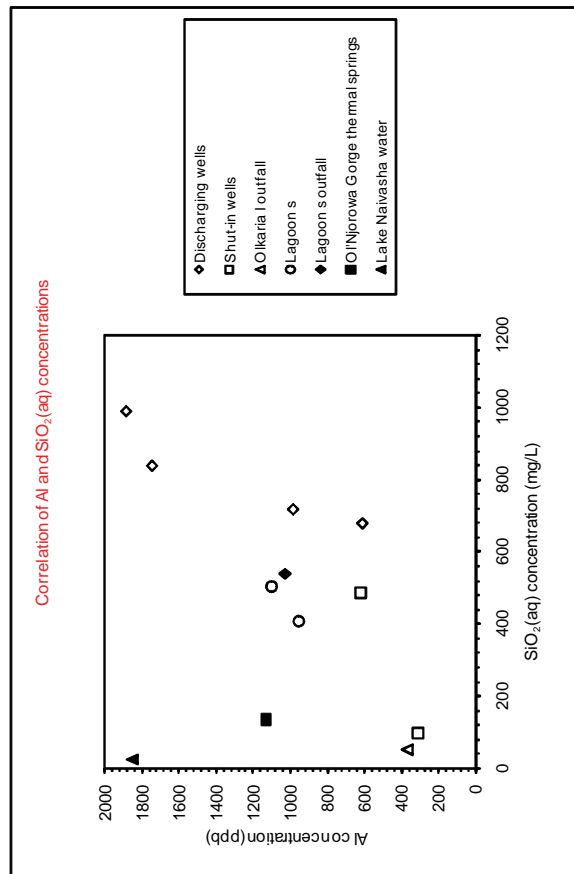
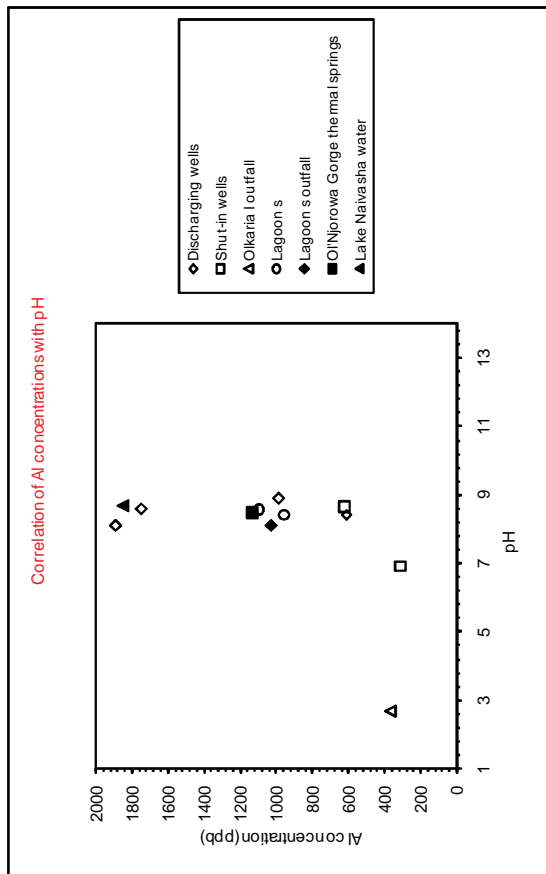
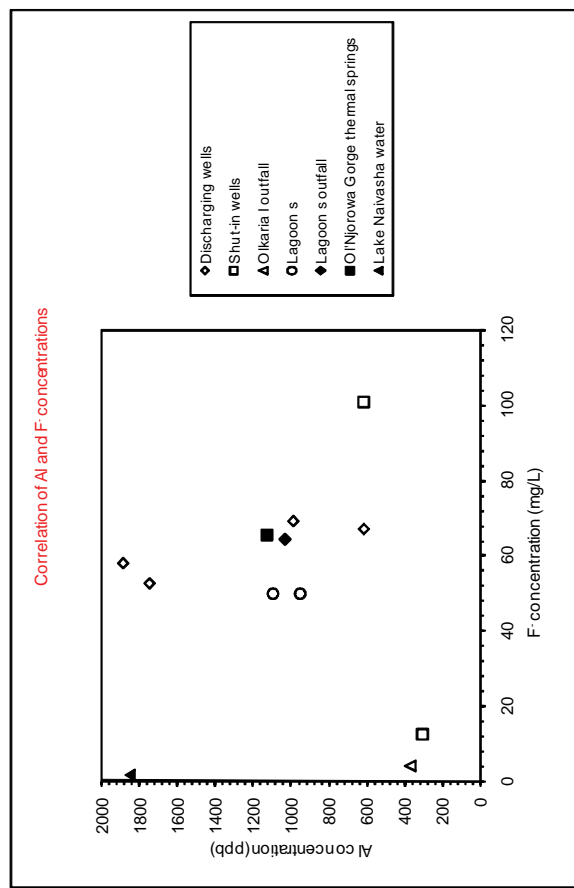
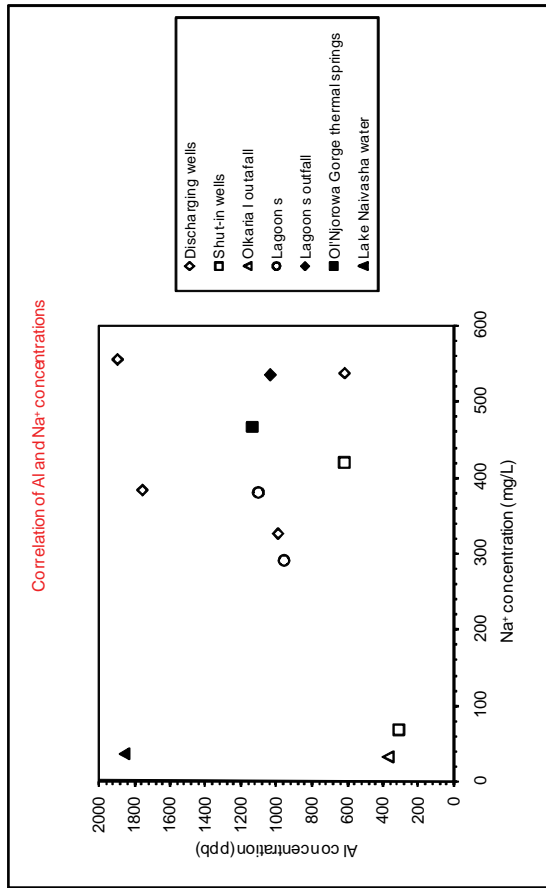


FIGURE 14: The correlations of aqueous Al with pH, F⁻, SiO₂(aq), and Na⁺

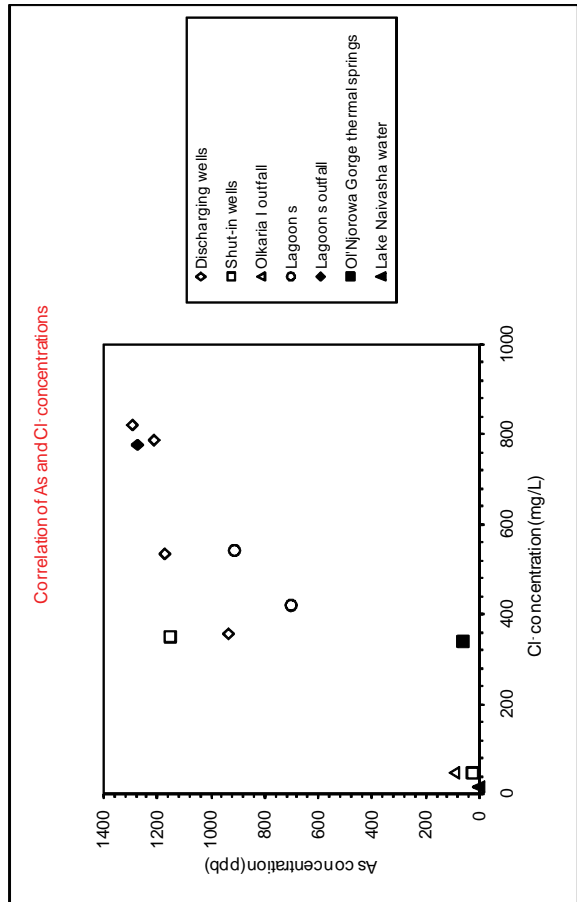
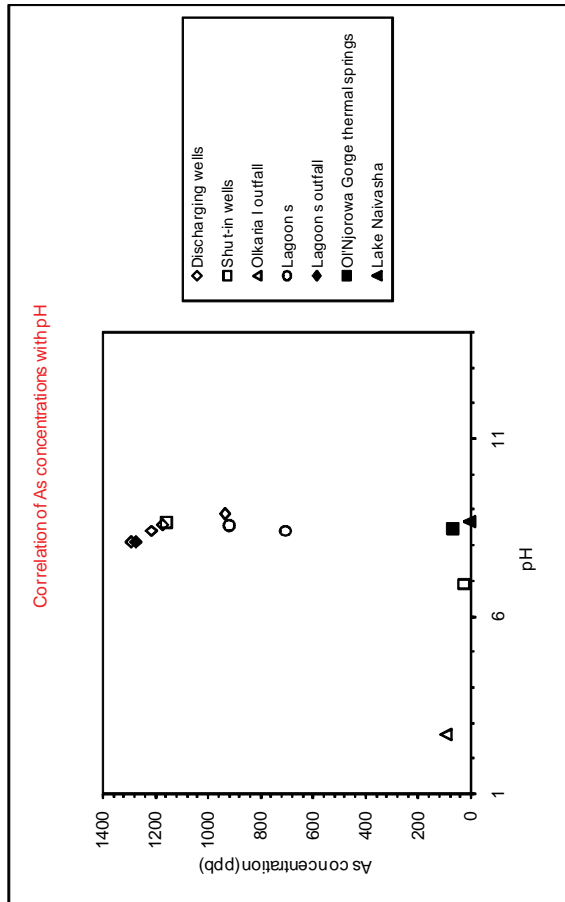
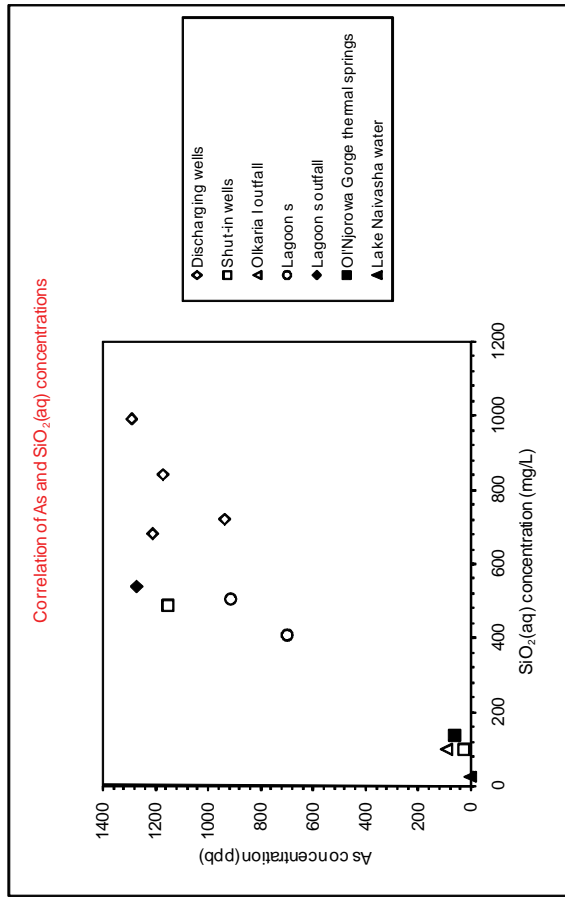


FIGURE 15: The correlations of aqueous As with pH, Cl⁻, and SiO₂(aq)

Waters of geothermal systems hosted by volcanic trachytes are high in As and other trace elements but relatively low in both H₂S and Al as in the case of Olkaria East field, Kenya. Welch et al., (2000) noted a general relationship between As and salinity in geothermal waters from USA. Despite lack of significant positive correlation between As and Cl, geothermal waters with As concentrations > 1000 µg/L mostly had Cl concentrations of 800 mg/L or more. Wilkie and Herring (1998) noted the high alkalinity and pH values (average pH 8.3) as well as high Cl concentrations of As rich geothermal waters in Long Valley. As concentrations in the range 500 - 4600 µg/L were reported for 26 geothermal water samples analysed from 5 geothermal fields in Kyushu, Japan, (Yokoyama et al., 1993). The waters are typically of Na-Cl type.

The correlations of Cd, Cu, Pb, and Zn with pH are presented in Figure 16. No significant positive correlations were observed with the major anions, SiO₂(aq), Cl⁻, and F⁻ but minor correlations with pH, HCO₃⁻, HS⁻, and SO₄²⁻. The Cl⁻ ion with a high relative abundance and chloro-complexes (Liu et al., 2001), and HCO₃⁻, HS⁻, and SO₄²⁻ ligands which occur in minor quantities, may be of significance in the transport and loss through precipitation of insoluble salts, respectively of Cd, Cu, Pb, and Zn in spent geothermal fluids. Aqueous Cu concentrations were < 2.0 µg/L, Pb and Zn concentrations < 1.0 µg/L for all fluids with pH > 7 (Figure 16).

Hg showed no evidence of correlation with pH and nearly all the major anion species HCO₃⁻, Cl⁻, HS⁻, F⁻, SiO₂(aq), and SO₄²⁻.

4.8 Assessment of the potential environmental and health risks of the predicted species of selected trace elements

The results of speciation modelling for aqueous Al are consistent with other reported data for geothermal brine. Tagirov and Schott (2001) reported that in acidic to neutral hydrothermal fluids and F concentrations > 1 mg/L, the fluoride complexes AlF_n³⁻ⁿ dominate Al speciation at temperatures < 100 °C. At moderately acidic to alkaline pH, Al(OH)₄⁻ is the dominant aqueous Al species. No toxic monomeric aqueous Al species were predicted for all the sampled fluids at in-situ pH and temperatures. Aqueous Al has been found to be more toxic in the pH range 4.8 - 5.4, which is related to its aqueous speciation in aquatic systems. The acute toxicity of Al is attributed to inorganic monomeric Al species consisting of free hexahydrate [Al(H₂O)₆]³⁺ at pH 4 and hydrolysis products [Al(OH)(H₂O)₅]²⁺ and [Al(OH)₂(H₂O)₄]⁺ with pH increase from pH 4 – 6 (Kloppel et al., 1997; Andrews et al., 2004). Hydrolysed Al and Al-F species predicted for the spent geothermal fluids and other aqueous systems around Olkaria geothermal field are less toxic and therefore pose no environmental and health risks.

The speciation modelling for aqueous As predicted no aqueous inorganic trivalent arsenite species, which are considered to be more toxic and mobile than inorganic pentavalent arsenate species (Webster, 1998). These results are consistent with reported data for a geothermal fluid sample from Kyusu, Japan, where As was present as As(V) (Yokoyama et al., 1993). In well-oxygenated fluids, As occurs in the pentavalent arsenate state, As(V), which is thermodynamically stable. Arsenic in the predicted forms poses no environmental and health risks to the aquatic and terrestrial ecosystems around the Olkaria geothermal field.

Although the total dissolved Cd concentrations were below detection limits in all sampled fluids, except those from Ol'Njorowa Gorge thermal springs and Lake Naivasha water, speciation modelling predictions may have implications for Cd mobility, bioavailability, and toxicity in aquatic and terrestrial ecosystems around Olkaria. The free divalent ion Cd²⁺, which is considered to be labile and toxic, is the dominant aqueous Cd species in all the sampled fluids, except those from discharging geothermal wells OW-2, OW-26, and OW-32, and Infiltration Lagoons outfall. There was a decline in the relative abundance of Cd²⁺ species in all the sampled fluids with in-situ pH > 8. The highest percentages of Cd²⁺ species were predicted for fluids from Olkaria I outfall and shut-in well OW-21 with in-situ pH < 7. This shows that Cd forms weaker aqueous and surface complexes than do other

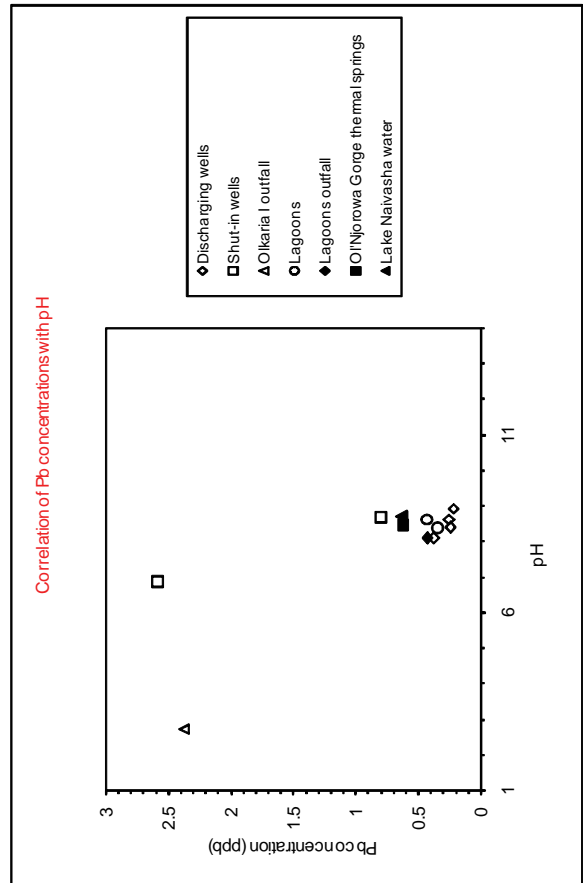
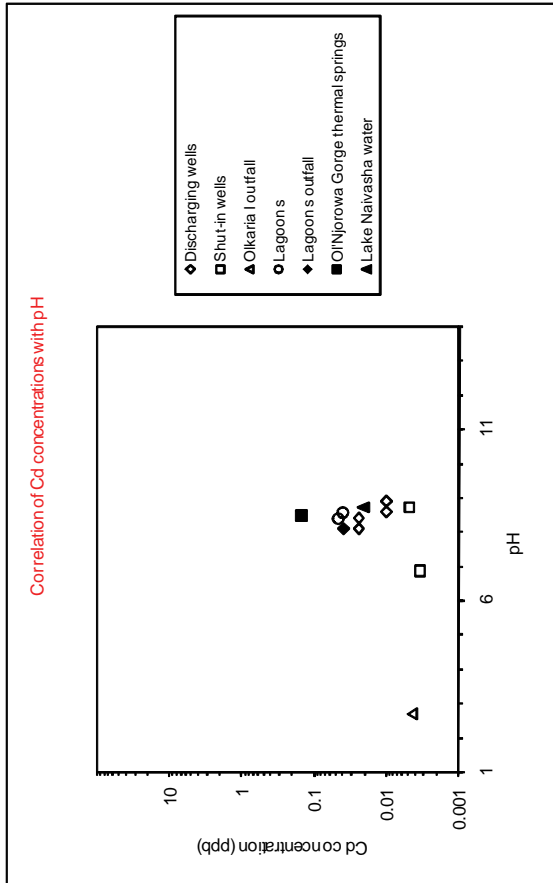
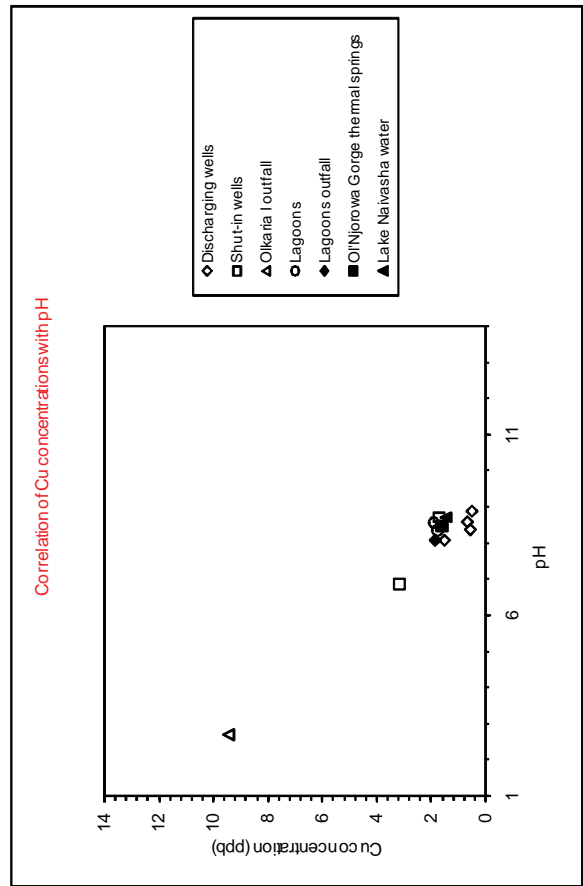
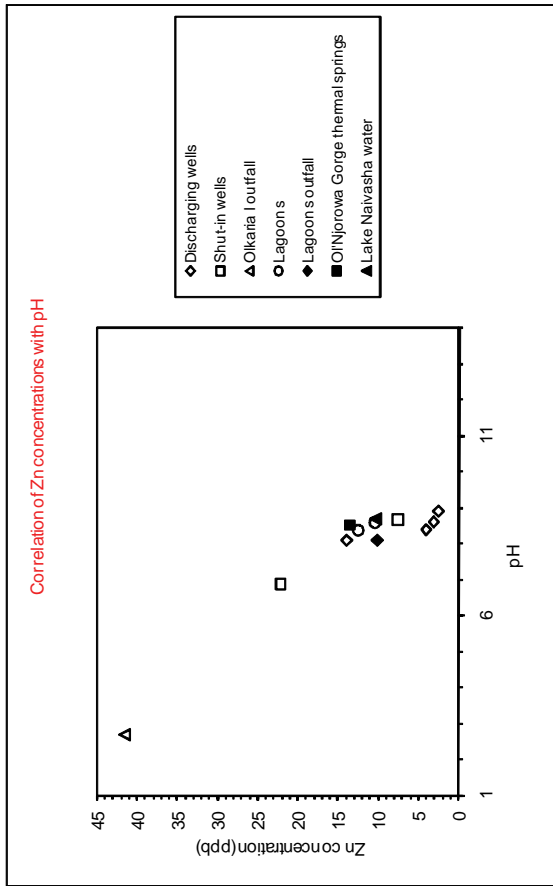


FIGURE 16: The correlations of aqueous Cd, Cu, Pb and Zn with pH

heavy metals, and exhibit a higher mobility under slightly acidic conditions (Onindo, 1995; Boily and Fein, 1996). In air-saturated natural water systems such as Lake Naivasha water, fluids from Ol'Njorowa thermal springs, and shut-in geothermal wells, Cd may be precipitated as carbonate or adsorbed onto particulate matter. The aqueous Cd concentrations in all fluids with pH < 7 such as Olkaria I outfall fluids and shut-in geothermal wells OW-13 and 21 fluids was below the detection levels and in all probability low and for that reason pose no environmental and health risks to the aquatic and terrestrial ecosystems around Olkaria geothermal field.

The aqueous Cu bioavailability and potential toxicity in aquatic and terrestrial ecosystems is related to both the oxidation state and copper speciation. Increasing evidence indicates that the free divalent Cu^{2+} ion concentration and the kinetics of dissociation of metal complexes control the bioavailability of copper (Sloof et al., 1989; Xue and Sunda, 1997; Murray-Gulde et al., 2005). Among the complexed copper, hydroxyl species, $[\text{Cu}(\text{OH})]^+$ and $\text{Cu}(\text{OH})_2(\text{aq})$ at higher pH values, display some toxicity (De Schampelaere and Janssen, 2002) while copper-inorganic carbon species (e.g. CuHCO_3^+ , CuCO_3 , and $\text{Cu}(\text{CO}_3)^{2-}$), chloro $[\text{CuCl}_n]^{-(n-2)}$ and sulphate species, are much less toxic or not toxic at all (Devez et al., 2005). Based on the speciation modelling predictions, which are consistent with the findings of previous research on hydrothermal fluids (Liu et al., 2001; Sherman, 2006) and toxicity of aqueous Cu species in contaminated aquatic systems, dissolved Cu in all the fluids around Olkaria geothermal field poses no environmental and health risks except in the acidic fluids of Olkaria I outfall due to the presence of the free divalent Cu^{2+} ion, and fluids from Infiltration Lagoon 1 due to the presence of the species Cu^{2+} , $[\text{Cu}(\text{OH})]^+$ complex, and $\text{CuO}(\text{aq})$.

The results of speciation modelling predicted in fluids from Olkaria I outfall and Infiltration Lagoon 1 the occurrence of the free hydrated Pb^{2+} ion, which is the assumed labile and toxic species (Korfali and Davies, 2004). The dissolved Pb in sampled fluids from Olkaria I outfall and the Infiltration Lagoon 1, may pose environmental and health risks. However, many inorganic Pb inorganic salts, such as sulphides, hydroxides, and chlorides are sparingly soluble in spent geothermal brine, making them biologically less available and thus less harmful.

The speciation modelling predictions for Hg are consistent with other reported data for geothermal brine under oxidizing conditions, as well as freshwaters. Webster (1998) reported the occurrence of Hg as dissolved elemental $\text{Hg}^0(\text{aq})$ species in geothermal fluids under strongly reducing conditions, and as elemental $\text{Hg}^0(\text{aq})$, mercurous Hg_2^{2+} and mercuric Hg^{2+} ions, and HgCl_2 in freshwaters. The organic complexes of mercury e.g. methyl-mercury, aryl-mercury, and alkoxyalkyl-mercury formed as a result of the catalytic action of numerous micro-organisms, contribute to acute toxicity of Hg in aquatic systems but the dissolved elemental and inorganic species of Hg are non-toxic (Webster, 1998). Based on the results of speciation modelling for Hg with inorganic complexes, which indicate that Hg_2^{2+} dominate Hg speciation in all the sampled fluids, except those from Olkaria I outfall where $\text{HgCl}_2(\text{aq})$ predominates, Hg in all the sampled fluids around Olkaria geothermal field poses no environmental and health risks.

The free hydrated ion Zn^{2+} , which is assumed to be more labile and bioavailable in aquatic systems, was reported in all the fluids except those from discharging geothermal wells. The highest percentage of Zn^{2+} was (92.8%) in Olkaria I outfall fluids with the lowest in-situ pH 2.7 and the highest Zn concentration (41.6 mg/L). Therefore, dissolved Zn in spent geothermal fluids from shut-in wells, Olkaria I outfall, Infiltration Lagoons, and other aquatic systems around Olkaria geothermal field may pose environmental and health risks.

The results of speciation modelling with inorganic ligands predict occurrence of toxic Cd species in all the sampled fluids, Cu and Pb species in fluids from Olkaria I outfall and Infiltration Lagoon 1, and Zn species in fluids from Olkaria I outfall and shut-in geothermal wells and non-toxic Al, As, and Hg species in all the sampled fluids around Olkaria. These observations confirm that neither total recoverable nor dissolved elemental concentrations are reliable predictors of toxicity of trace elements in aqueous systems. Some methyl arsenic compounds e.g. trimethylarsines and methyl arsenic acids, occur naturally in aquatic systems as a consequence of progressive addition of CH_3^+ groups to

inorganic As by algae or bacteria. Organic arsenicals also exert their toxic effects *in vivo* in animals by first metabolizing to the trivalent arsenoxide form. Cd salts e.g. sulphides, carbonates, or oxides, are practically insoluble in water. However, these can be converted to water-soluble salts in natural waters under the influence of oxygen and organic acids. In the presence of naturally occurring ligands, hydrated Cu^{2+} can be kept in solution up to pH 8 and above and replaced by a variety of ligands to form different complexes. Pb also forms relatively strong complexes with organic ligands containing the donor atoms S, N, and O. Generally, strong organic complexes are neither labile nor bioavailable to organisms (Allen and Hansen, 1996). Dissolved Hg can bind to carbon, forming HgCH_3^+ and $\text{Hg}(\text{CH}_3)_2$. Bacterial methylation of inorganic mercury is also possible in aquatic systems. These reactions lead to Hg bioaccumulation up the food chains. Therefore, further work on speciation of the trace elements with natural organic ligands e.g. citrate, carboxylic acid anions etc., is recommended for accurate predictions of elemental mobility, bioavailability, and toxicity to humans, animals, and plants.

4.9 Alternative environmental pollution control options

Based on the research findings, the following environmental pollution control options are recommended for detoxification of the toxic trace element species in spent geothermal fluids from the Olkaria geothermal field: (1) adjustment of pH of spent geothermal fluids with $\text{pH} < 7$ on discharge to the surface environment; (2) introduction of appropriate inorganic or organic ligands and chelating chemicals; and (3) modifications and use of the Infiltration Lagoons at Olkaria East geothermal field as constructed wetlands.

4.9.1 Detoxification through pH adjustment

The correlations of aqueous Cd, Cu, Pb, and Zn with pH and HCO_3^- concentrations indicate low concentrations of the trace elements with increasing pH and bicarbonate concentrations. Routh and Ikramuddin (1996) also reported that dissolution of $\text{CaCO}_3(\text{aq})$, increases fluid pH and thereby immobilizes the trace elements through either precipitation or adsorption onto sediments. The addition of aqueous calcium carbonate to spent geothermal fluids with $\text{pH} < 7$, is recommended. However, continued trace element enrichment in sediments of Infiltration Lagoons may prove hazardous to filter feeding and aquatic organisms.

4.9.2 Detoxification with inorganic or organic ligands and chelating chemicals

The model predicted toxic trace elements Cu, Pb, and Zn in some spent geothermal fluids from the Olkaria East geothermal field, may be purified through the use of inorganic carbonate ligands, which increase metal-carbonate complexes in solution. These restrict the presence of free aqueous metal ion species to low concentrations (Ruth and Ikramuddin, 1996). Among the potential organic ligands and chelating chemicals recommended for use in the detoxification process are citrate and carboxylic acid anions and N-(2-acetomido)iminodiacetic acid (ADA) for Pb extraction, pyridine-2, 6-dicarboxylic acid (PDA) for Zn extraction, and S-carboxymethyl-L-cysteine (SCMC) for Cu extraction. Hong et al. (2001) have investigated the potential of chelating agents (ADA, PDA, and SCMC) in removing and recovery of heavy metals from contaminated media e.g. soils and mine tailings ponds. Acetic acid is considered to be the abundant organic acid in many geothermal systems and reports of numerous experimental studies of metal-acetate complexes have demonstrated their potential in transport of significant amounts of metals e.g. Al, Zn, Fe, Mg, Ca, Pb, and rare earth elements (Benezeth and Palmer, 1998). Under acidic conditions, as in Olkaria I outfall fluids, common metal oxides e.g. Al-hydroxide, aluminosilicate, and Fe-hydroxide surface sites are positively charged and adsorption of cations does not generally occur. However, multifunctional organic ligands e.g. citrate, that adsorb onto oxide surface sites in acidic to neutral conditions can change the surface charge from positive or neutral to negative, thereby creating adsorption sites for the toxic metal cations. Boily and Fein (1996) reported that in the presence of citrate, Cd adsorption on common mineral surfaces is enhanced between pH 3.5 and 7.22, and reduces it above pH 7.2. The aqueous complexation of carboxylic acid

anions with the aqueous metal ions of Cu, Pb, and Zn, may further enhance their thermal stability and significantly lower their potential mobility, bioavailability, and toxicity to humans, animals, and plants.

4.9.3 Reconstruction and use of the Infiltration Lagoons as “wetlands”

A simple scheme consisting of a series of 3 interconnected Infiltration Lagoons is recommended. This could involve modifications of the existing Lagoons to allow for controlled and quantifiable flow of spent geothermal fluids. Effectiveness of the scheme could be investigated through periodical analysis of the chemical composition of the inlet, residual, and outfall fluids, sediments, and samples of biota e.g. *green algae* and *typha latifolia spp*, inhabiting the Infiltration Lagoons.

4.10 Critical environmental data gaps, future monitoring, and research needs

The main environmental data gaps for the Olkaria geothermal field are lack of scientifically proven data on: (1) the model predicted free ions or labile complex species of the toxic trace elements Cd, Cu, Pb, and Zn and their effective complexation capacities; (2) the dispersion, ecotoxicological relevance, and specific biomarkers of the model predicted toxic trace element species; and (3) the general trends in environmental contamination, attributed to geothermal energy development.

To confirm the occurrence of the model predicted labile or free metal ions and complex species and the effective complexation capacities of the toxic trace elements, use of voltammetric analytical techniques such as Anodic Stripping Voltammetry (ASV), Cathodic Stripping Voltammetry (CSV), Differential Pulse Polarography (DPP), and Differential Pulse Anodic Stripping Voltammetry (DPASV), which is a combination of the DPP and ASV techniques, is recommended. ASV, CSV, and DPP analyses are very sensitive and have been applied to measurements of reducible metal ions in solution and soil at environmentally significant concentrations. Onindo (1995) analyzed natural waters for labile As, Cu, Cd, and Pb using ASV and labile Al and Zn using CSV, while Reddy et al. (1982) used DPP at the hanging mercury drop electrode (HMDE) for simultaneous determination of Cd, Cu, Pb, and Zn in soil. Further speciation modelling study on the effect of trace element dispersion due to dissolution-precipitation reactions and adsorption on soil and sediment sorption sites consisting of common minerals e.g. Fe-hydroxide, is recommended. Direct monitoring of toxicity of the spent geothermal fluids is also essential. This may be achieved through the use of bioassays and biosensors, which assess bioavailability of contaminants directly by measuring the biological response of a selected plant e.g. *algae spp.* or animal species. The techniques are sensitive, inexpensive, rapid, and simple compared to chemical analysis. An investigation of the potential use of specific biomarkers, which provide observable biological responses to trace element pollution at individual plant or animal level or below demonstrating a departure from the normal status (Walker et al., 2001), is also recommended. Examples of metal-specific biomarkers, which are detoxification mechanisms developed by organisms, include the inhibition of an enzyme of the haem pathway aminolaevulinic (ALAD) for Pb and the induction of metallothioneins (MTs) for Cd in animals and phytochelatin (PCs) for detoxification of As, Cd, Cu, Pb, and Zn in plants.

5. SUMMARY

The speciation study confirms the 2003 data for trace element concentrations in the spent geothermal fluids from the Olkaria East geothermal field. There are, however, notable inconsistencies compared to the 1997 – 2000 monitoring data for Olkaria, for which were reported higher trace element concentrations. This is mainly due to the analytical procedure adopted, which was for total recoverable elemental concentrations. The range of TDS concentrations (< 4000 mg/L) and speciation modelling predictions indicate that the spent geothermal fluids from discharging wells in Olkaria East field are chemically benign, are thus less corrosive and toxic with the exception of fluids from the Olkaria I outfall, Infiltration Lagoons, and shut-in geothermal wells. The spent geothermal fluids have a higher relative abundance of $\text{SiO}_2(\text{aq})$, Cl^- , F^- , SO_4^{2-} , Na^+ , and K^+ ion species than Lake Naivasha water. In comparison to both Lake Naivasha water and Ol’Njorowa Gorge thermal springs, the fluids are heavily depleted in Ca^{2+} and Mg^{2+} species, enriched in Na^+ and Cl^- ions, and have relatively low concentrations of HCO_3^- . The fluids of Olkaria East geothermal field may, therefore, be classified as Na - Cl water-type.

The spent geothermal fluids from Olkaria East field have high aqueous Al, As, and Mo concentrations, low Cu, Pb, Hg, and Zn concentrations, and Cd concentrations below detection limits. The highest dissolved concentrations of Al (1890 $\mu\text{g/L}$), As (1290 $\mu\text{g/L}$), and Mo (510 $\mu\text{g/L}$) were in spent geothermal fluids from discharging geothermal well OW-32; Cd (< 0.09 $\mu\text{g/L}$) in Infiltration Lagoon 1; Cu (9.4 $\mu\text{g/L}$) and Zn (41.6 $\mu\text{g/L}$) in Olkaria I outfall; Pb (2.58 $\mu\text{g/L}$) in spent geothermal fluids from shut-in geothermal well OW-21; and Hg (1.25 $\mu\text{g/L}$) in the Infiltration Lagoons. Aqueous Cd concentrations in spent geothermal fluids were lower than in both Ol’Njorowa Gorge thermal spring fluids (0.14 $\mu\text{g/L}$) and Lake Naivasha water (0.02 $\mu\text{g/L}$). The aqueous Al concentrations were high in all sampled fluids including Lake Naivasha water. This is probably due to the ubiquity of Al-F bearing minerals in the geological environment of the Kenyan rift. Aqueous As and Mo concentrations in the spent geothermal and Ol’Njorowa Gorge thermal spring fluids were higher than in Lake Naivasha water. This may be due to the high mobility of As and Mo in hydrothermal fluids. There were positive correlations of aqueous Al concentrations with $\text{SiO}_2(\text{aq})$, F^- , and Na^+ , which may be an indication of the significant roles these species play, besides OH^- , in mobility of aqueous Al. Likewise, correlations of As with $\text{SiO}_2(\text{aq})$ and Cl^- , though not so good, may also be an indication of the species significance in As transport and high concentrations. The correlations of Cd, Cu, Pb, and Zn with Cl^- , chloro-complexes, and HCO_3^- , HS^- , and SO_4^{2-} ligands, which occur in minor quantities in spent geothermal fluid, though not so good, may be of significance in the transport and elemental loss through precipitation of their insoluble salts. This may be the reason for low Cu, Pb, and Zn concentrations and Cd concentrations below detection limit. Low aqueous Hg concentrations may be attributed to loss as aerosols due to the high volatile nature of Hg in its elemental form.

The F^- concentrations in all fluids were above the Kenyan water quality standard for effluent discharge to the terrestrial environment, irrigation water, and sources of domestic water; the Canadian water quality guidelines for community use and livestock watering; and EC and WHO guidelines for drinking-water quality. The As concentrations in all fluids were above the Kenyan water quality standard for effluent discharge to the terrestrial environment, recreational water, sources of domestic water, and irrigation water. The Hg concentrations in spent geothermal fluids, except from the Infiltration Lagoons, were in compliance with the Kenyan water quality standard for recreational water. The dissolved Al, Cd, Cu, Pb, Hg, Mo, and Zn concentrations in all fluids were in compliance with the Canadian water quality guideline for livestock watering, except for As. Aqueous Al, Cd, Cu, Pb, and Zn concentrations were in compliance with the Canadian water quality guidelines for protection of plants, except for As and Mo.

The speciation modelling at in-situ pH and temperatures predicted that Al, As, Cd, Cu, Pb, Hg, and Zn speciation is dominated by:

- 1) Al-F complexes in acidic to neutral fluids and Al-hydroxyl complexes in moderately acidic to alkaline fluids;
- 2) Pentavalent arsenate-oxy-fluoro species;

- 3) Free Cd^{2+} ion with increasing predominance in fluids with $\text{pH} < 8$;
- 4) Complexed copper-inorganic chloro $[\text{CuCl}_n]^{-(n-2)}$ and SO_4^{2-} species in moderately acidic to alkaline fluids and free Cu^{2+} ion, $\text{CuO}(\text{aq})$, and $[\text{Cu}(\text{OH})]^+$ complex in acidic to neutral fluids;
- 5) Free Pb^{2+} ion in Olkaria I outfall with in-situ $\text{pH} 2.7$ and Infiltration Lagoon 1 and hydroxyl complex $[\text{PbOH}]^+$ species in all fluids;
- 6) Mercurous Hg_2^{2+} and mercuric Hg^{+2} ions in all fluids; and
- 7) Free Zn^{2+} ion in all fluids except those from discharging geothermal wells.

While, the model predicted that aqueous Al, As, and Hg species pose no environmental and health risks, the free hydrated ions Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} , and $\text{CuO}(\text{aq})$ and $[\text{Cu}(\text{OH})]^+$ complex species are more labile, bioavailable, and toxic to humans, animals, and plants. The aqueous Cd concentrations in all fluids were below the detection levels and in all probability low. Therefore, the model predicted toxic Cd species is of less environmental health concern. However, further work on the toxic trace element speciation with organic complexes and dissolution-precipitation and adsorption on soil and sediments, measurement of labile species and fluid complexation capacities, and use of bioassays and biomarkers, are recommended for accurate predictions of their mobility, bioavailability, and toxicity to humans, animals, and plants around the Olkaria geothermal field.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In conclusion, the total recoverable or dissolved trace element concentrations adopted in the national standards and international criteria or guidelines for environmental health quality are not reliable predictors of trace element toxicity. The spent geothermal fluids from the discharging wells in the Olkaria East geothermal field are chemically benign. With increased hot fluid re-injection and incorporation of detoxification and recovery procedures (pH adjustment, use of appropriate organic complexes or chelating chemicals) and constructed wetlands for acidic to neutral fluids from Olkaria I outfall, shut-in geothermal wells, and the Infiltration Lagoons, the environmental health risks of the model predicted toxic Cu, Pb, and Zn species and other elements As, Hg, and Mo are made negligible.

6.2 Recommendations

To supplement the hot fluid re-injection system, the following alternative environmental pollution control options are recommended for detoxification and recovery of model predicted toxic species of Cu, Pb, and Zn in spent geothermal fluids from Olkaria East geothermal field: (1) using $\text{CaCO}_3^{2-}(\text{aq})$ for adjustment of pH of spent geothermal fluids with $\text{pH} < 7$ on discharge to the surface environment; (2) introduction of inorganic (CO_3^{2-}) or organic (citrate and carboxylic acids) ligands and chelating chemicals (ADA for Pb extraction, PDA for Zn extraction, and SCMC for Cu extraction); and (3) modifications of the Infiltration Lagoons into a series of 3 interconnected lagoons with controlled fluid flows as in “constructed wetlands”. The identified environmental research and monitoring data gaps in Olkaria geothermal field can be bridged through: (1) voltammetric (ASV, CSV, and DPP) measurements of the labile free ions and complex species and complexation capacities of Al, As, Cd, Cu, Pb, Hg, and Zn in spent geothermal fluids, soil, and sediments; (2) speciation modelling with organic ligands and for dissolution-precipitation reactions and adsorption on soil and sediment samples to investigate dispersion of the trace elements; (3) use of bioassays or biosensors to directly measure the toxicological effects of spent geothermal fluids; (4) biochemical measurements of metal-specific biomarkers e.g. inhibition of ALAD for Pb detoxification, induction of MTs for Cd detoxification in animals and PCs for As, Cd, Cu, Pb, and Zn detoxification in plants for environmental risk assessment of the chemical contaminants; and (5) use of same analytical procedures to generate data for environmental contamination or pollution trend analysis, attributed to geothermal energy development.

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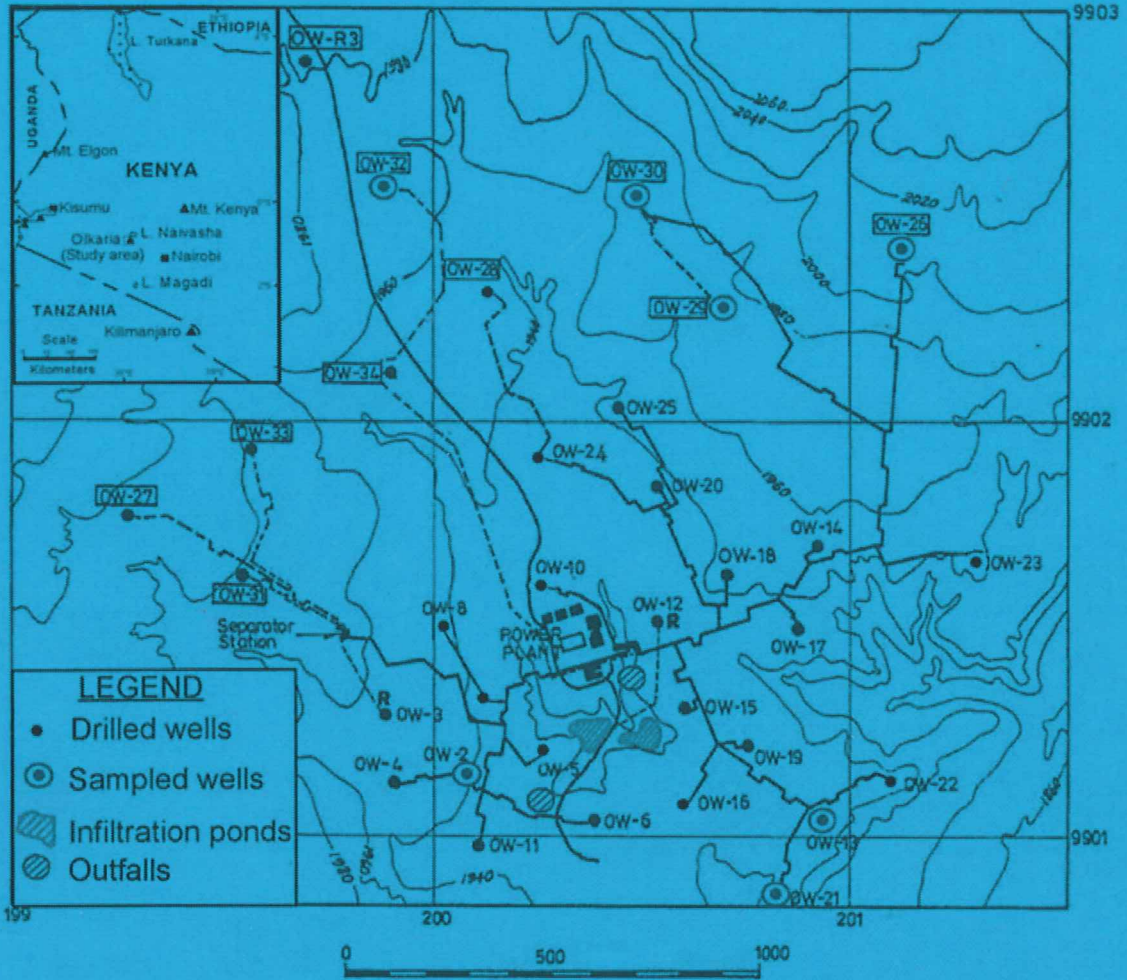
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