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Evaluation of Trace Element Levels and their Ecotoxicological Relevance in Geothermal Wastewater of Olkaria East Field, Kenya

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ABSTRACT

Olkaria East geothermal field is one of the sectors of the Greater Olkaria geothermal area in the central sector of the Kenya Rift Valley. The field supports the 45 MWe power station. Monitoring of trace elements in the wastewater has been an ongoing process as one of the pollution control measures since 1993. Results indicate that concentration level of most trace elements in wastewater from most wells is low in relation to plant and animal water quality criteria except for As, Mo and B. With the reinjection of the wastewater, which has also been an ongoing reservoir management strategy, any potential ecotoxicological effects that might emanate from elevated levels would be avoided.

1. INTRODUCTION

Olkaria East field is one of the seven sectors of the Greater Olkaria geothermal area located in the central part of the Kenya Rift Valley to the south of Lake Naivasha, 120 km northwest of Nairobi. Other sectors are Northeast, Northwest, Southwest, Southeast, Central and Olkaria Domes fields for management purposes. Exploration for geothermal work started in the early 1950s when two wells were drilled at Olkaria. Olkaria East field supports a 45 MWe Olkaria I geothermal power plant fully commissioned in 1985. Thirty-three wells have been drilled, seven of which are make-up wells. The large volume of waste geothermal fluids generated during electricity production has been a major environmental concern especially with regard to Hells Gate National Park gazetted in 1984 An important aspect of the environmental management of geothermal development in this area has been the existence of Hells Gate National Park which supports wildlife species such as Buffalo (*Syncerus cafer*), Zebra (*Equus burchellis*), Grant's gazelle (*Gazelle grantii*), Thomson's gazelle (*Gazelle thomsonii*), Coke's hartebeest (*Alcephalus buselaphus*), Maasai giraffe (*Giraffa reticulata*) among others. It has been estimated that geothermal fluid is discharged from the 45 MW power station at flow rate of about 120 m^3/h (Merz and McLellan – Virkir, 1977). Each well under production is equipped with a wellhead separator and stabilizing pond systems for wastewater and solid residue settlement. Most of the separated water drains through open concrete channels into one main evaporation or infiltration lagoon for containment before reinjection. Such wastewater if not properly disposed off could be a potential ecotoxicological hazard to both fauna and flora due to the environmentally significant trace elements of they may contain.

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

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

2. METHODOLOGY

The sampling of wastewater for trace elements analysis in study was in two parts. First sampling took place on 19th August 2002 while the second one was on 21st August 2003. Geothermal wastewater from infiltration ponds of wells OW-2, OW-5, OW-7/8, OW-10, OW-16, OW-21, OW-22, OW-23, OW-24/28 and OW-32 in Olkaria East field were sampled (Figure 1). All sampling bottles and equipment were thoroughly acid washed before sampling. Bottles were filled with 10% HNO_3, left to stand overnight and then rinsed carefully with distilled water. In the two separate sampling periods, the samples were shipped to Iceland and then to *Analytica* Laboratory in Sweden for trace elements analysis. The samples were passed through a 0.45 µm Nuclepore cellulose fibre filter to remove particulates and preserved with concentrated Ultrex Supra pure nitric acid. The determination of unstable parameters such as pH was carried out in the Olkaria Geochemistry Laboratory. Based on the results of the past studies which did not take into account most of the elements, the concentration of the following trace and major elements were determined by ICP-SMS (Fe, Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Ti and Zn); ICP-AES (Ca, K, Mg, Na, S, Si, B and Sr) and AFS (Hg).

3. RESULTS

Geothermal wastewater from infiltration ponds of selected wells (OW-2, OW-5, OW-7/8, OW-10, OW-16, OW-21, OW-22, OW-23, OW-24/28 and OW-32) in Olkaria East field were analysed for the following trace elements: aluminium, arsenic, boron, barium, cadmium, cobalt, chromium, copper, mercury, manganese, molybdenum, nickel, lead and zinc in August 2002 and August 2003 (Table 1). Also presented is trace element analysis data from the ongoing KenGen environmental monitoring program of significant environmental chemical elements; and other published studies on Olkaria geothermal field (e.g. Simiyu, 1995, 2000; Simiyu and Tole, 2000). From the current study results Al, As, B, and Mo are the only trace constituents slightly elevated in wastewater of some wells.

The lowest and highest arsenic concentrations were 11.4 ppb and 2020 ppb in wells OW-7/8 and OW-5 respectively (Figure 2). Arsenic concentrations in wells OW-10, OW-16 and OW-22 were 1690 ppb, 973 ppb, and 164 ppb respectively. These concentrations were however much lower than to the 1994 arsenic concentration of 5310, 4190 and 5110 ppb (Simiyu, 1995; Simiyu and Tole, 2000; Figure 3) observed in the respective well waters. There is no sufficient arsenic data from the ongoing monitoring program to establish the mean As levels over the years. These levels were however high compared to As levels in Lake Naivasha water (Sinclair Knight and Partners, 1994) and As levels in geothermal waters of Nesjavellir geothermal field, Iceland (Wetang'ula, 2004).

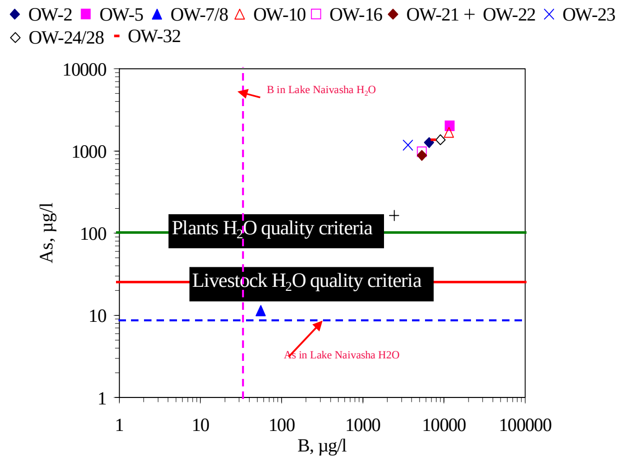

Figure 2. Relationship between As and B in wastewater of selected wells in Olkaria East field

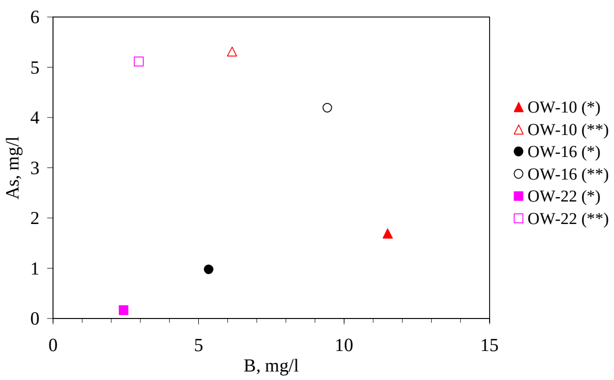

Figure 3. Arsenic and boron concentrations at wells OW-10, OW-16 and OW-22 based on different data sources. [(*) = current study, (**) = Simiyu, 1995].

For the period of August 2002/2003 Al was in the range of 577 to 8390 ppb in wells OW-22 and OW-7/8 respectively. The Al concentration of wastewater from wells OW-5, OW-10 and OW-32 were 1 ppm. Al concentration in the wastewater was higher compared to Lake Naivasha water. Al has not been among the key elements being monitored in the ongoing KenGen environmental monitoring program. The Al-B relationship (Figure 4) shows that Al is removed from the wastewater of most wells preferentially to B by $Al(OH)_3$ precipitation. The behaviour of Al could also be quantitatively interpreted by calculation of saturation of amorphous $Al(OH)_3$ which was not however done in this study.

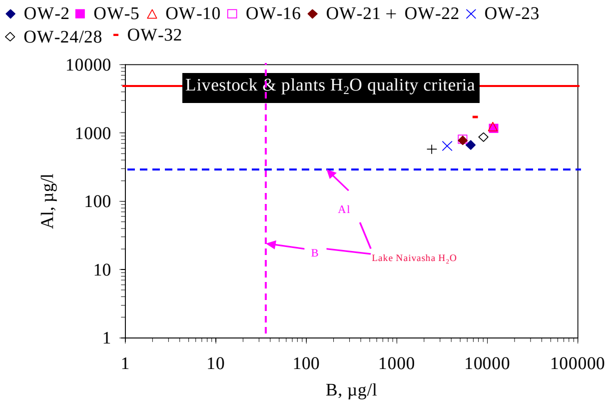

Figure 4. Relationship between Al and B in wastewater of selected well in Olkaria East field.

The boron concentrations varied from 55.3 ppb in the wastewater of well OW-7/8 to 11500 ppb and 11800 ppb in well OW-10 and OW-5 wastewater respectively. From As-Al-Mo-B relationships much of the B in wastewater from half of wells remains in solution compared to As, Al and Mo (Figures 2, 4 & 5). The boron concentration was however within the levels observed in the on going monitoring program and that documented in past studies (Simiyu, 1995; Simiyu and Tole, 2000; Figure 3).

Mercury concentration was in the range of 0.016 ppb to 9.31 ppb. Mercury concentration in the wastewater from wells OW-10, OW-16 and OW-22 was 0.13 ppb, 2.942 ppb and 0.0512 ppb respectively. This was however lower than the 940 ppb, 520 ppb and 5410 ppb (Simiyu, 1995; Simiyu and Tole, 2000) for same wells respectively during the 1994 analysis.

The lowest and highest molybdenum concentrations were 5.93 ppb and 700 ppb in wastewater from wells OW-7/8 and OW-5 respectively (Figure 5). Molybdenum concentrations in most well fluids were higher than levels reported in past studies. Cadmium, cobalt, copper, lead and zinc concentration levels in wastewater from most wells were low. The concentrations of Cd, Co and Pb were low compared to the 1994 levels (see Simiyu, 1995; Simiyu and Tole, 2000) while other trace elements were within the same concentration range in this study and previous studies (Table 1). Chromium and nickel concentration which have not been determined before were 518 ppb and 287 ppb respectively in wastewater from OW-7/8.

An evaluation of fluoride in the wastewater based on the KenGen trace element environmental monitoring program data (1997- 2003) show that fluoride concentration levels have been high all through compared to other elements. Its concentration has been variable over time with a mean fluoride concentration of around 70 ppm (Figure 6).

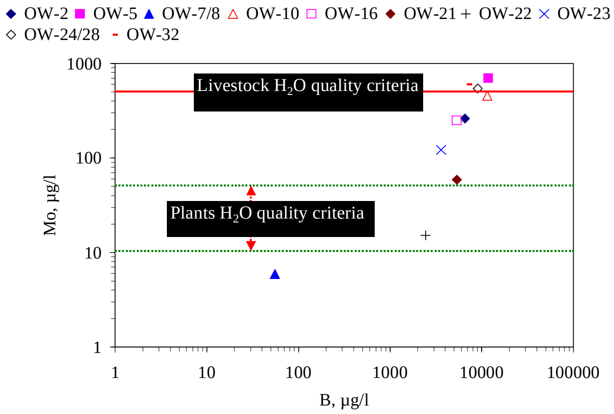

Figure 5. Relationship between Mo and B in wastewater of selected well in Olkaria East field.

4. DISCUSSION

Evaluation of trace elements concentrations (Al, As, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb and Zn) in the wastewater of 10 geothermal wells in the Olkaria East field in relation to plants and livestock/wildlife (mammals) water quality criteria (Table 2) show Al, As, B and Mo as the only trace elements that could pose a potential ecotoxicological hazard if the wastewater disposal option is not environmentally sound. The standards referred to are for protection of livestock thus once the water quality standards for livestock are attained, then all the wildlife in the Hells Gate National Park would have been protected. Moreover, the physiology of domestic and wildlife species especially ungulates is similar. Utilization of livestock water quality criteria is also of relevance bearing in mind that the area around the Park has also been frequently utilized by a nomadic pastoralist community (the Maasai) as grazing grounds for their livestock especially in dry season when grass is scarce elsewhere. An evaluation in relation to such standards will thus protect such livestock through containment of the wastewater.

Aluminium concentration levels in the wastewater were generally low at all wells evaluated with exception at well OW-7/8 where the level was higher than the Al water quality criteria for protection of plants and livestock. The arsenic concentration level in the wastewater was above the 25µg/L and 100 µg/L (CCME, 1999) water quality criteria levels for livestock and plants respectively. Concentrations in most well wastewater was higher than 164 ppb with the highest being 2020 ppb. Though the levels are above the plant and livestock water quality criteria levels, studies elsewhere have shown that toxicity of arsenic to plants or animals is dependent on the arsenic species present. Thus the potential toxicity of arsenic to plants around the geothermal wastewaters will be governed by its speciation and not the total arsenic concentration. It has been shown that some forms of arsenic such as sodium arsenate and arsenic trioxide are extremely toxic to plants. For example arsenic concentration in water as low as 1-15.2 µg/L of As(V) have been reported to inhibit growth in certain aquatic plants resulting in noticeable changes in plant community (Sanders and Cibik, 1985). For animals that might be exposed arsenic, there is little evidence that arsenic is carcinogenic to mammals. However, it does cause teratogenic effects in many species (Eisler, 1988). Animals, both domestic and wildlife especially mammals in the study area may be exposed to arsenic mainly by ingestion of contaminated water or vegetation. With regard to mammals acute or sub-acute arsenic poisoning is much more common than chronic poisoning. The probability of chronic exposure of animals in the Olkaria area to arsenic is postulated to be rare because arsenic detoxification and excretion is very rapid in most mammalian species (Woolson, 1975). For example exposure of domestic sheep to a 58 mg/kg dietary concentration of arsenic showed no outward visible effects. The tissue arsenic increased after a 3-week exposure but then declined rapidly after return to low arsenic diet. It is however, worth to observe that beneficial effects of arsenic have also been reported in silkworms, rats, goats, and pigs at low dietary concentrations and low doses have been known to stimulate growth in plants and animals (Eisler, 1988, 1994).

The boron concentration was high in geothermal wastewater from most wells evaluated. Thus it also becomes of concern, as its environmental effects are most noticeable in plants. The concentration at wells OW-2, OW-5, OW-10, OW-24/28 and OW-32 was beyond the 500-6000 µg/L boron plant tolerance ranges in water. Though boron is an essential trace element for the growth and development of higher plants, the range between insufficiency and excess is usually narrow. Gupta et al. (1985) for instance found that some plants show signs of deficiency when boron concentrations in the soil solution are <2 mg/L and show toxic effects at concentrations >5 mg/L. In another ecological risk assessment for a natural community of aquatic plants it was concluded that, with median concentrations of 3.6-5.9 mg/L, patterns of leaf tissue discoloration (yellowing) may indicate adverse ecological impacts of boron on vegetation (Powell et al., 1997).

Animals may also be exposed to high boron concentration in geothermal wastewater especially in dry season when surface drinking water in the areas becomes scarce. Boron concentration at some wells was above the 5000 µg/L (CCME, 1999) boron water criteria level for animals with the highest boron concentration being 11800 µg/L at well OW-5. This was still below the boron concentration levels that have been shown to cause deleterious growth effects in animals. For example, 150 mg/L of boron in drinking water has been reported to cause growth retardation in cattle (Eisler, 1990). For animals exposed to high boron concentration, potential ecotoxicological effects from the consumption of boron contaminated water are unlikely to be observed as several studies elsewhere have shown that animals to avoid boron contaminated drinking water. For example, rats and cattle rejected boron contaminated drinking water containing as little as 1 mg/L B (Dixon et al. 1976) and >29 mg/L B (Green and Weeth, 1977) respectively.

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

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

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

High fluoride wastewaters may contaminate vegetation and if fed on by animals will cause a condition known as fluorosis, which affects the bones and teeth of the animals. Plants can also be affected by fluoride toxicity and a synergistic effect of combined SO_2 and fluoride is recognized in plants in areas affected by atmospheric pollution (Alloway and Ayres, 1997). This high fluoride level in the geothermal wastewater is typical for most waters in the Kenyan rift, thus a proper disposal mechanism to preclude vegetation contamination is required to protect the animals.

5. CONCLUSIONS

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

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REFERENCES

Alloway, B.J and Ayres, D.C.: Chemical principles of environmental pollution. Blackie Academic & Professional. London (1997).

CCME (Canadian Council of Ministers of the Environment).: Canadian environmental quality guidelines, Winnipeg (1999). Updated 2002.

Dixon, R.L., Lee, I.P., and Sherins, R.J.: Methods to assess reproductive effects of environmental chemicals: studies of cadmium and boron administered orally, submitted to *Environ. Health perspect*. (1976) 13:59-67.

Eisler, R.: *Arsenic hazards to fish, wildlife and invertebrates: A synoptic review*. U.S. Fish and Wildlife Service Biological Report 85(1.12), 92p (1988).

Eiser, R.: *Molybdenum hazards to fish, wildlife and invertebrates*: *A synoptic review*. U.S. Fish and Wildlife Service, Biological Report 85(1.19). 61p (1989).

Eisler, R.: Boron hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish and Wildlife Service Biological Report 85(1.20). 32p (1990).

Eisler, R.: A review of arsenic hazards to plants and animals with emphasis on fisheries and wildlife resources. In: *Arsenic in the environment, part II: Human health and ecosystem effects*. J.O. Nriagu, ed. John Wiley & Sons, New York. p. 185-259 (1994).

Green, G.H., and Weeth, H.J.: Responses of heifers ingesting boron in water, submitted to *J. Anim. Sci*. 46, 812-818 (1977).

Gupta, U.C., Jame, Y.W., Campbell, C.A., Leyshon, A.J., and Nicholaichuk, W.: Boron toxicity and deficiency: a review, submitted to *Can. J. Soil Sci*. 65, 381-409 (1985).

Merz & McLellan – Virkir.: Report on geothermal development at Olkaria. Report prepared for the Kenya Power Company Ltd (1977).

Osweiler, G.D., Carson, T.L., and Bucks, W.B, (eds). : *Clinical and diagnostic veterinary toxicology*, 3rd ed. Kendall/Hunt Publishing Co., Dubuque, Iowa. (1985).

Powell, R.L., Kimerle, R.A., Coyle, G.T., and Best, G.R.: Ecological risk assessment of a wetland exposed to boron, submitted to *Environmental Toxico. Chem.* 16, 2409-2414 (1997).

Sanders, J.G., and Cibik, S.J.: Adaptive behaviours of euryhaline phytoplankton communities to arsenic stress, submitted to *Marine Ecol. Prog. Ser*. 22:199-205 (1985).

Simiyu, G.M.: Levels of selected trace elements in Olkaria geothermal fluids and their implications to the environment. Master of Philosophy thesis, Moi University, 115p (1995).

Simiyu, G.M.: Levels of selected trace elements in Olkaria geothermal field and their health implications for grazing wild animals (Zebra *Equus burchelli* and Buffalo *Syncerus caffer*) in Hell's Gate National Park, Kenya. Doctor of Philosophy thesis, Moi University, 131p (2000).

Simiyu, G. and Tole, M.: Concentrations of trace elements in waters, soils and plants of Olkaria geothermal field, Kenya. *Proceedings,* World Geothermal Congress, Kyushu-Tohoku, Japan (2000).

Sinclair Knight and Partners.: Environmental assessment report for Northeast Olkaria Power Station Development Project (1994).

US Dept of the Interior (USDI).: Guidelines for interpretation of the biological effects of selected constituents in biota, water and sediment (1998).

Wetang'ula, G.N.: Assessment of Geothermal Wastewater Disposal Effects, Case Studies: Nesjavellir (Iceland) and Olkaria (Kenya) Field. M.Sc Thesis, Department of Biology, University of Iceland 175p (2004)

Were, J.O.: Aspects of waste management and pollution control in Olkaria geothermal field, Kenya.UNU-Geothermal Training Programme, Reykjavik, Iceland. Report 16. p423-460 (1998).

Woolson, E.A. (ed.).: Arsenical pesticides. Am. Chem. Soc. Symp. Ser. 7. 176p (1975).

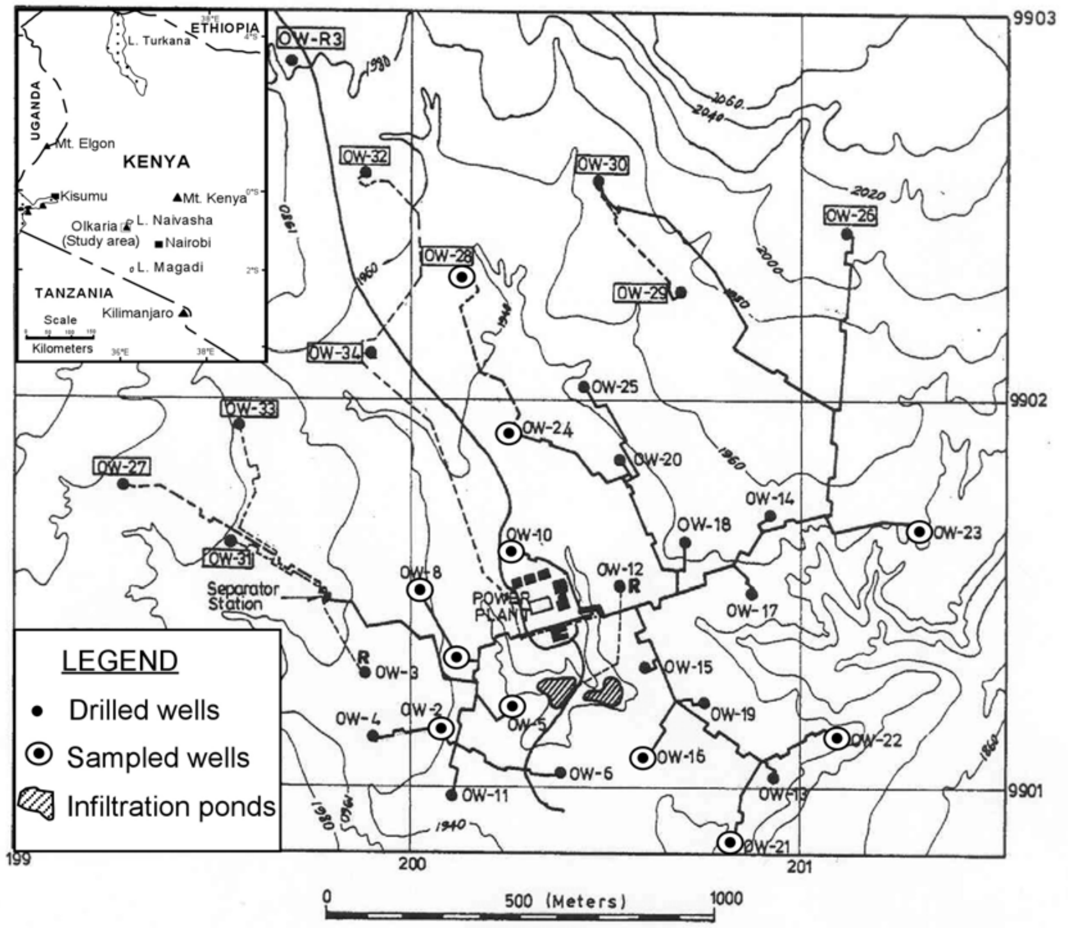

Figure 1 Location of Olkaria field and sampling points of the wastewater in the East field during the 2002/2003 study

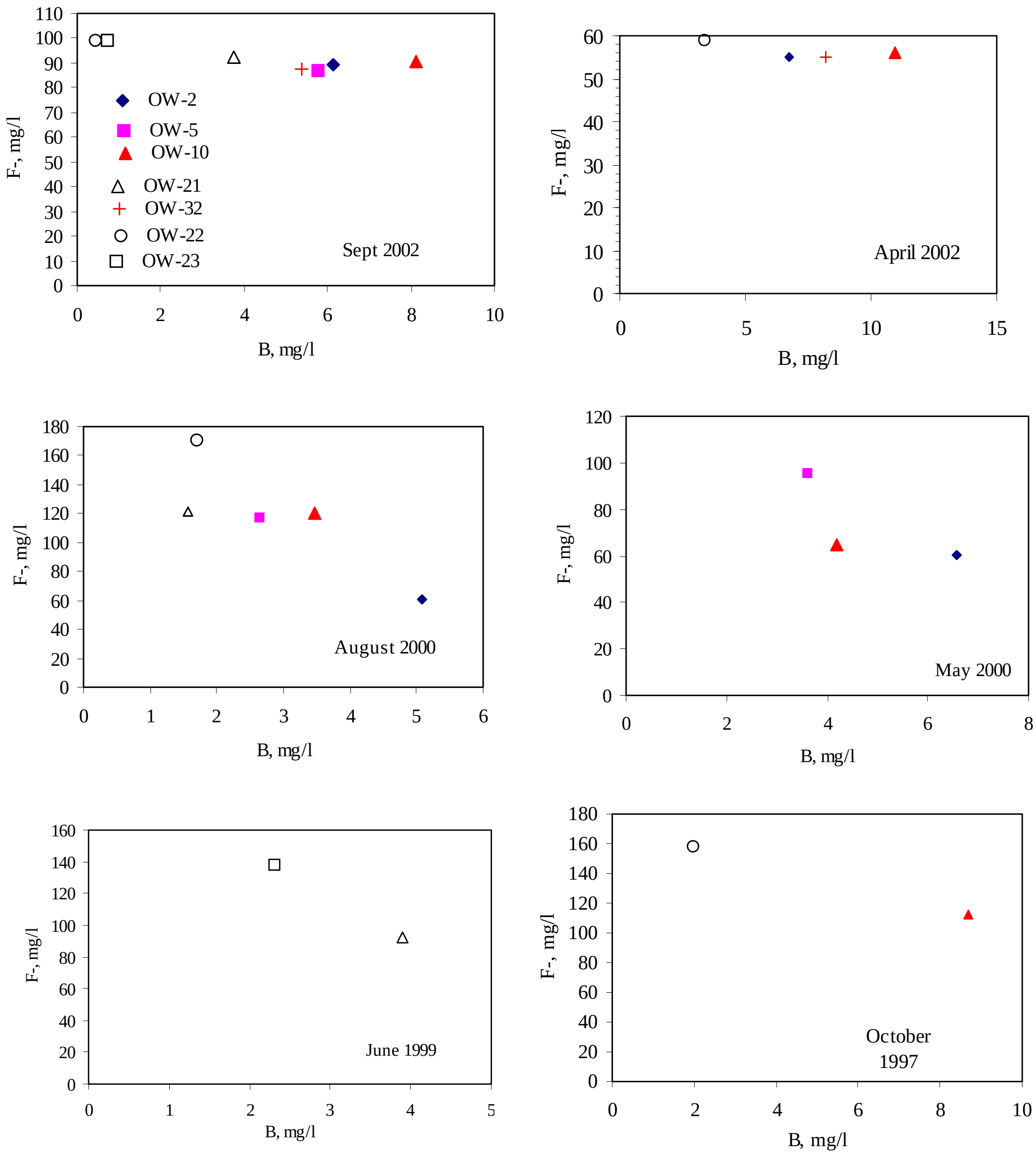

Figure 6 Concentration of boron and fluoride in selected wells of Olkaria East field (1997-2003).

Table 1. Trace elements levels in wastewater of selected Olkaria East field wells for different periods

	Al	As	B	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb
August 2002 and 2003 (Wetang'ula, 2004)											
OW-2	665	1265	6555	0.02	0.05	0.35	2.02	0.454	262	0.5	0.204
OW-5	1160	2020	11800	0.06	<0.05	0.656	3.5	0.285	700	<0.5	1.86
OW-7/8	8390	11.4	55.3	0.0966	5.04	518	4.86	1.76	5.93	287	1.45
OW-10	1240	1690	11500	<0.03	0.08	7.56	1.76	0.13	454	3.08	0.362
OW-16	807	973	5350	0.035	0.05	0.614	7.17	2.942	250	1.13	1.32
OW-21	778	885	5350	<0.002	0.02	0.563	1.92	0.016	58.9	0.297	0.563
OW-22	577	164	2435	0.0095	0.0165	0.288	1.59	0.0512	15.2	0.612	0.19
OW-23	646	1180	3600	<0.02	<0.05	0.524	7.5	2.87	122	<0.5	0.29
OW-24/28	869	1370	9060	<0.04	<0.05	0.658	3.0	9.31	544	<0.5	0.126
OW-32	1705	1365	6960	0.05	0.05	0.539	14.2	6.8	601	5.12	0.687
August 2000 (Environmental monitoring program-Olkaria)											
OW-2			5090	BDL							BDL
OW-5			2650	11							BDL
OW-7/8			2410	BDL							BDL
OW-10			3480	30							BDL
OW-21			1570	39							BDL
OW-22			1700	BDL							BDL
OW-24/28			1910	BDL							BDL
March 1998 (Environmental monitoring program-Olkaria)											
OW-2							150				100
OW-10							20				100
OW-21							130				600
OW-22											100
September 1993-February 1994 (Simiyu, 1995; Simiyu & Tole, 2000)											
OW-10		5310	6150	5.0			7.0	940			33
OW-16		4190	9430	8.0			7.0	520			37
OW-22		5110	2950	4.0			19	5410			39
October 1997-January 1999 (Simiyu, 2000)											
OW-15				3.0	5.0		7.0		39		30
OW-25				1.0	2.0		5.0		11		7
Units: µg/l (ppb); BDL = below detection limit; Blank cell = Not determined											

Table 2. Permissible limits of various trace elements for Livestock and plants water quality (CCME, 1999)

	Livestock Water Quality Criteria (µg/l)	Plant Water Quality Criteria (µg/l)
Al	5000	5000
As	25	100
B	5000	500-6000
Cd	80	5.1
Co	1000	50
Cr	50	4.9-8
Cu	500-1000	200-1000
Hg	3.0	
Mo	500	10-50
Ni	1000	200
Pb	100	200
Zn	50,000	1000-5000