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# Drinking water quality in the Ethiopian section of the East African Rift Valley I—data and health aspects

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## Abstract

Drinking water samples were collected throughout the Ethiopian part of the Rift Valley, separated into water drawn from deep wells (deeper than 60 m), shallow wells (<60 m deep), hot springs ( $T > 36$  °C), springs ( $T < 32$  °C) and rivers. A total of 138 samples were analysed for 70 parameters (Ag, Al, As, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, NO<sub>2</sub>, NO<sub>3</sub>, Pb, Pr, Rb, Sb, Se, Si, Sm, Sn, SO<sub>4</sub>, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, temperature, pH, conductivity and alkalinity) with ion chromatography (anions), spectrometry (ICP-OES and ICP-MS, cations) and parameter-specific (e.g. titration) techniques. In terms of European water directives and WHO guidelines, 86% of all wells yield water that fails to pass the quality standards set for drinking water. The most problematic element is fluoride (F), for which 33% of all samples returned values above 1.5 mg/l and up to 11.6 mg/l. The incidence of dental and skeletal fluorosis is well documented in the Rift Valley. Another problematic element may be uranium (U)—47% of all wells yield water with concentrations above the newly suggested WHO maximum acceptable concentration (MAC) of 2 µg/l. Fortunately, only 7% of the collected samples are above the 10 µg/l EU-MAC for As in drinking water.

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## 1. Introduction

Increasing population density, and scarcity and pollution of surface waters pose a serious problem for drinking water supplies in Ethiopia. Furthermore, drinking water may not be available where the people live, and—according to tradition—

women often have to walk for hours to get the daily water ration for a family. Thus, the Ethiopian government and international donor agencies have often sponsored drilling of groundwater wells. The use of groundwater is thus increasing sharply in Ethiopia.

It is often assumed that natural, uncontaminated waters from deep (bedrock) wells are clean and healthy (Banks et al., 1998b). This is usually true with regards to bacteriological composition. The

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*inorganic chemical quality* of these waters is, however, rarely adequately tested before the wells are put into production. Due to variations in the regional geology and water/rock interactions, high concentrations of many chemical elements can occur in such waters. During the last 5–10 years several studies have shown that wells in areas with particular geological features yield water that does not meet established drinking water norms (e.g. Varsanyi et al., 1991; Bjorvatn et al., 1992, 1994; Edmunds and Trafford, 1993; Banks et al., 1995a,b, 1998a; Sæther et al., 1995; Reimann et al., 1996; Edmunds and Smedley, 1996; Smedley et al., 1996; Williams et al., 1996; Morland et al., 1997, 1998; Midtgård et al., 1998; Misund et al., 1999; Frengstad et al., 2000) without any influence from anthropogenic contamination. These studies also document that quite a number of elements for which no drinking water guideline values (GL) or maximum acceptable concentration limits (MAC) have been established can occur at unpleasantly high levels in natural well waters (e.g. Be, Th, Tl). In Norway, F and radon (Rn) are the most problematic elements (see Frengstad et al., 2000) in terms of possible health effects. In Hungary, Bangladesh and India, arsenic represents one of the most drastic examples of unwanted natural chemical ‘contamination’ of groundwater. Several 100 000 people in these regions suffer skin cancer due to high As concentrations in drinking water from drilled wells (Chatterjee et al., 1995; Das et al., 1995; Smith et al., 2000; Smedley and Kinniburgh, 2002).

After many years of use of drinking water from drilled wells in the Rift Valley, Ethiopia, dental and skeletal fluorosis has become a serious medical problem (Tekle-Haimanot et al., 1987; Tekle-Haimanot 1990; Kloos and Tekle-Haimanot, 1999). Fluorosis due to a high intake of fluoride from drinking waters has previously been reported from several parts of the world, e.g. Algeria and Kenya (Tjook, 1983), China (Zhaoli et al., 1989), India (Handa, 1975; Teotia et al., 1981), Sri Lanka (Dissanayake, 1991) and even Norway (Bjorvatn et al., 1992). High values of F in well water from the Rift Valley were reported as early as 1953 (Ockerse, 1953, Kenya).

A program to test drinking water from wells from all over Ethiopia for fluoride concentration is now under way. The Rift Valley is one of few active rifts on the Earth’s land area. Rocks in the Rift Valley are mostly young volcanic rocks. An abundance of thermal springs indicates the ongoing volcanic activity in the area. Volcanic emanations are often high in elements such as As, B, F and Li. Thus, it appeared advisable to have Rift Valley drinking water quality—in addition to F—characterised for as many chemical elements as possible. As part of an Ethiopian-wide sampling program, additional drinking water samples from the Rift Valley were collected for multi-element analysis. The first results are presented here.

Concerning the chemical quality of drinking water and health issues, most emphasis has been placed on *excessive amounts* of various elements. It should be noted, however, that water-related health problems can also occur due to element deficiencies. This problem is not covered by present-day water regulations. Such deficiencies occur most often in rural communities in developing countries, where mainly locally produced water and food are consumed. Deficiency-related health problems may result from low levels of elements such as F, I and Se in drinking water (F: Rajagopal and Tobin, 1991; I: Kelly and Sneddon, 1960; Se: Låg, 1984).

The present paper reports analytical results for 65 chemical elements and five additional parameters in 138 drinking water samples from various sources in the Rift Valley, Ethiopia. Although results for all elements are given, the discussion in this paper is focussed on a selection of elements that may have direct health relevance. This paper is the first publication in a series on various hydrogeochemical aspects of Rift Valley water sources. It is focused on the presentation of data and comparison of different drinking water sources (deep and shallow wells, springs, hot springs and river water) in relation to health aspects.

## 2. The survey area

Ethiopia is located in the north-eastern part of Africa, neighbouring Eritrea, Djibouti, Somalia, Kenya and the Sudan (Fig. 1). Ethiopia covers an

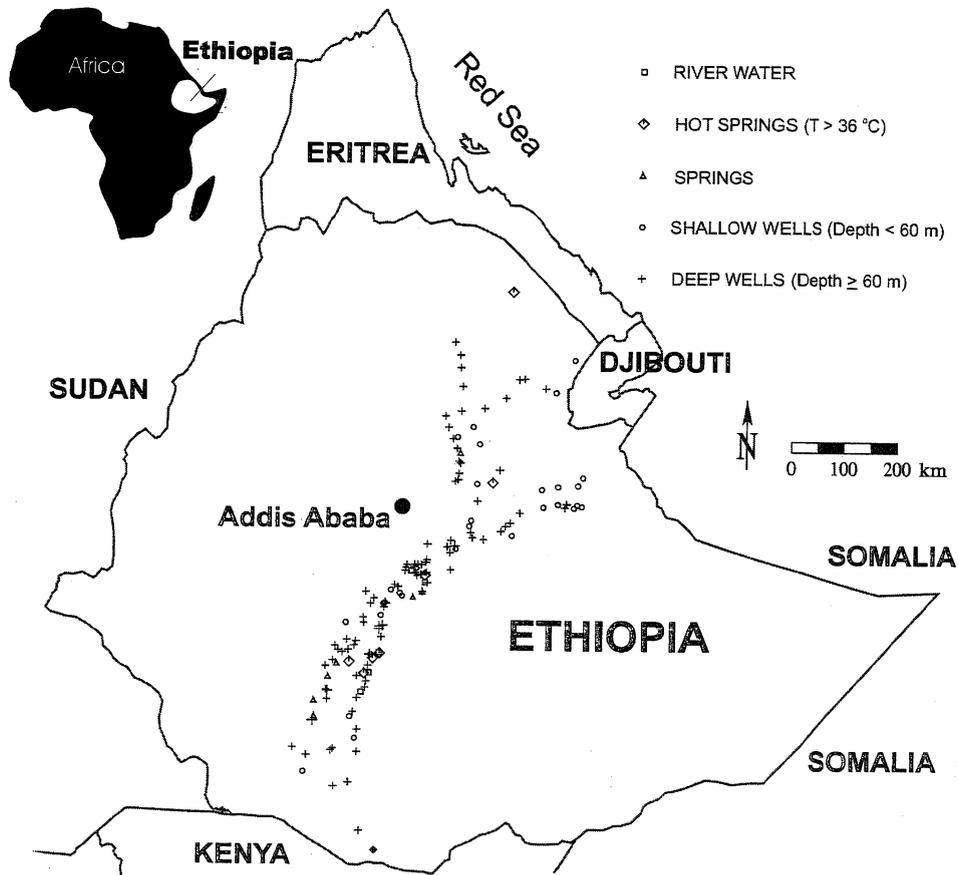


Fig. 1. Location of the sample sites in the Rift Valley, Ethiopia.

area of approximately 1 100 000 km<sup>2</sup>, of which the Ethiopian part of the Rift Valley constitutes nearly 30%. The population is approximately 60 000 000 people of which ~3 000 000 live in the capital, Addis Ababa.

The Rift Valley is the longest rift on the Earth's land surface. It starts in the Middle East, in Jordan and terminates after approximately 6400 km near Beira, on the coast of Mozambique (<http://www.yourdotcomforafrica.com>). The Rift Valley owes its existence to a deep-seated, linear strike-slip fault marking the boundary between the Arabian and African Plates. It is thus a linear zone of thinning and extension in the earth's crust, locally leading to development of new oceanic crust, e.g. in the Red Sea. The initial process leading to the development of the Rift Valley started approxi-

mately 50 000 000 years ago. The main tectonic activity responsible for today's appearance of the Rift Valley, with its associated volcanoes and tectonically defined lakes, happened, however, more recently, just 2–7 000 000 years ago (Merla et al., 1979). At the bottom of the Red Sea, the associated heat flow creates hot pools of brine that give rise to the formation of copper, zinc, manganese and iron deposits.

In Ethiopia the Rift Valley runs in a south-westerly direction through the whole country (Fig. 1). Active volcanoes are located on the Danakil Plain to the north. The main river in the area, the Awash, originates within the East African Rift Valley and flows into the Afar Triangle, but never reaches the Red Sea. Instead, the waters of the river spread out and evaporate in the Danakil

Depression. Eight lakes mark the central part of the Ethiopian Rift Valley. Due to the high evaporation rates, the waters of these lakes are alkaline and are not suited for human consumption. Some are rich in fish, and all are the sites of a rich animal life, especially birds. The main near-surface rock types in the Rift Valley are young volcanic rocks: ignimbrites, pumices, rhyolites, trachybasalts and fissural basalts, as well as Tertiary plateau basalts as the dominating rock unit. In addition, young Quaternary sediments, which can be alluvial, elluvial, colluvial or lacustrine, occur (Merla et al., 1979).

Elevation and geographic location produce three climatic zones. A cool zone occurs above 2400 m, where temperatures range from near 0 to 16 °C. A temperate zone occurs at elevations of 1500–2400 m, with temperatures from 16 to 30 °C. A hot zone follows below 1500 m, with both tropical and arid conditions, and daytime temperatures ranging from 27 to 50 °C. The main rainy season lasts from mid-June to mid-September (longer in the southern highlands). Intermittent showers from February to March usually precede it. The remainder of the year is generally dry. The mean annual rainfall in the Rift Valley is 725 mm.

### 3. Sampling

Most samples reported here were taken from drinking water wells in small villages and settlements scattered throughout the Ethiopian part of the Rift Valley. The wells were subdivided into 'deep wells' ( $N=88$ , depth  $\geq 60$  m or reportedly drilled in bedrock) and 'shallow wells' ( $N=32$ , depth  $< 60$  m or reportedly drilled or dug in sediments). The majority of deep wells thus draw water from bedrock, while the majority of shallow wells draw water from sediments. At present, no better subdivision of these wells was possible. To obtain a more complete picture of 'drinking water' quality in the Rift Valley, a few additional samples from springs ( $N=7$ ,  $T < 32$  °C), hot springs ( $N=7$ ,  $T > 36$  °C), and rivers ( $N=5$ ) were also collected and analysed (see Fig. 1).

A training program for sampling was carried out prior to regional sampling in the Rift Valley. It was decided to follow as closely as possible the

previously established standards in Norway (Reimann et al., 1996; Frengstad et al., 2000). A team of two samplers collected all samples during the year 2000. All necessary equipment was shipped from Norway or Germany to Ethiopia. Factory-new, unwashed 100-ml high-density polyethylene (HDPE) bottles were used for sampling. Different brands of plastic bottles had previously been thoroughly checked for possible contamination (Reimann et al., 1999a). No risk of contamination from such bottles was found for the parameters reported here, as long as the bottles are thoroughly rinsed with water prior to sampling.

In the field the bottles were rinsed three times with running water and then filled to the top. Sampling took place directly at the tap or the wellhead. In order to collect fresh well water, the water was left running for at least 5 min or until temperature and conductivity remained stable. In most cases, each of these wells supplies more than 100 people with their daily drinking water. The water, therefore, never accumulates over longer periods in the well. In contrast to Norway, temperature does not decrease while the water is running; on the contrary, the temperature may increase by 1–2 °C.

Because this study is supposed to reflect the quality of the water 'as drunk', the samples were not filtered. Reimann et al. (1999b) studied the influence of filtration on the chemistry of water samples from bedrock wells. The study showed that even unfiltered water samples satisfactorily reflect general water chemistry, as long as the medium collected is drinking water (i.e. by definition rather clean water, with low particulates) (Reimann et al., 1999b). This may not be true for river water and water from very shallow wells in sediments. However, it is rather easy to detect particulate contamination problems in the water chemistry, e.g. via high Al or rare-earth element concentrations.

Two 100-ml bottles were collected at each site. The first sample, which was intended for anion analyses, was left unfiltered and unacidified. The unfiltered water of the second sample was acidified with 2 ml of concentrated nitric acid (Merck, Ultrapure). This second sample was used later for cation analysis. The acid was tested for its trace

element content using the same analytical procedure as for the water samples. In the field, the samples were stored in a cool box and in the evening transferred to a refrigerator, where they were stored until shipment to the laboratory in Germany.

Several parameters, such as pH, electrical conductivity and temperature, were measured directly in the field. Alkalinity was determined at the sample site using a Hach titrator. To document the sampling conditions, the sampling site and the general landscape around the wells, a set of at least three photographs was taken at each sample site. A CD with these photos is available with the NGU Report (Reimann et al., 2002). If available, the well depth and the number of people receiving their drinking water from the various wells were recorded. Possible contamination sources within a radius of approximately 100 m around the well were noted.

#### 4. Analyses

All samples were shipped by courier to Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Hannover, Germany, after completion of the field sampling campaign. In the laboratory, pH, electrical conductivity and alkalinity were determined once more on the unacidified samples. These samples were used for anion analysis by ion chromatography (Br, Cl, F, NO<sub>2</sub>, NO<sub>3</sub> and SO<sub>4</sub>). Furthermore, the major elements Ca, K, Mg and Na were determined on these samples by inductively coupled plasma-optical emission spectrometry (ICP-OES) for quality control purposes. Note that only the values from the acidified samples were used later on.

The acidified samples were used for cation analysis by ICP-OES (Al, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Si, Sr, Ti, V and Zn) and inductively coupled plasma-mass spectrometry (ICP-MS) (Ag, Al, As, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn and Zr).

#### 4.1. Quality control

For quality control purposes, duplicate samples were taken in the field at a rate of 1 in 10. These were treated as completely separate samples, receiving their own sample number. The duplicates were thus not recognisable for the laboratory. Several blind samples were included to check for possible contamination sources. At the laboratory in Hannover, additional duplicates were prepared and analysed. The three international water standards NIST-1640, NIST-1643d and NIST-SLRS-4, as well as several in-house standards, were analysed on a routine basis over several months. Precision judged from the project duplicates is on average in the range of 10–14% for La, Fe, Ce, Cd and Sn. It is in the range of 5–10% for Pb, Se, Be, Ti, Y, Pr, Hf, Gd, Nd, Zr, Sb, Co, Cu and Ga. Precision is on average better than 5% for all other elements/parameters (Ag, Bi, electrical conductivity, Eu, Hg, Ho, In, Lu, NO<sub>2</sub>, Ta, Tb, Te, Tm, SO<sub>4</sub>, Cl, Ba, K, Si, W, Mg, Na, Ca, alkalinity, F, Dy, Sr, Cs, U, Li, Rb, Ge, B, V, Br, As, NO<sub>3</sub>, Er, Th, Mo, Yb, Ni, Tl, Cr, Sm, Al, I, Zn, Nb and Mn). Detailed results for the quality control can be found in Reimann et al. (2002). Results from quality control and direct comparison of results from the different techniques were used in the final selection of the data used for this publication (Table 1).

#### 5. Results

Table 1 summarises (median, minimum and maximum) the analytical results for the Rift Valley drinking water. It gives the analytical techniques used for the different elements/parameters and shows how many orders of magnitude the natural concentrations of the analysed elements cover in this data set. It provides additional information on water standards (European Union, 1998; WHO, 1993, 1998) and shows the percentage of samples above maximum acceptable concentration limits.

Observed natural concentration ranges cover between one and five orders of magnitude. For most elements the observed concentration range covers between three and four orders of magnitude.

Table 1

Technique used for analysis, analytical results [minimum (Min.), median (Med.) and maximum (Max.) values] for 'drinking water' collected from the Rift Valley, Ethiopia,  $N=138$

	Tech.	Unit	Min.	Med.	Max.	Ord.	EU Directive	WHO	>MAC (%)
Ag	MS	µg/l	<0.002	<0.002	0.021	1			
Al	MS	µg/l	39.7	85	3440	2	200 (MACi)		19
As	MS	µg/l	0.016	0.97	96	4	10 (MAC)	10 (P)	7
B	MS	µg/l	0.1	70	997	4	1000 (MACi)	500 (P)	10
Ba	MS	µg/l	0.23	16.3	305	3		700	
Be	MS	µg/l	<0.005	0.016	5.91	3		NAD	
Bi	MS	µg/l	<0.002	<0.002	0.03	1			
Br	MS	µg/l	3.64	175	6110	3			
Ca	OES	µg/l	2429	35665	196500	2			
Cd	MS	µg/l	<0.002	0.021	6.41	4	5 (MAC)	3	1
Ce	MS	µg/l	<0.002	0.06	24.6	4			
Cl	IC	µg/l	870	20250	1240000	3	250000 (MACi)		7
Co	MS	µg/l	<0.002	0.049	3.07	3			
Cr	MS	µg/l	<0.01	0.485	21.3	4	50 (MAC)	50 (P)	
Cs	MS	µg/l	<0.002	0.0305	12.1	4			
Cu	MS	µg/l	0.26	1.98	27	2	2000 (MAC weekly av.)	2000 (P)	
Dy	MS	µg/l	<0.002	0.008	2.06	3			
Er	MS	µg/l	<0.002	0.006	1.03	3			
Eu	MS	µg/l	<0.002	<0.002	0.42	3			
F	IC	µg/l	48	909	11600	2	1500 (MAC)	1500	33
Fe	OES	µg/l	1.5	48	18860	4	200 (MACi)		28
Ga	MS	µg/l	0.003	0.023	1.58	3			
Gd	MS	µg/l	<0.002	0.007	2.86	3			
Ge	MS	µg/l	0.014	0.295	11.6	3			
Hf	MS	µg/l	<0.002	0.004	0.4	3			
Hg	MS	µg/l	<0.01	<0.01	0.8	2	1 (MAC)	1	
Ho	MS	µg/l	<0.002	0.002	0.38	3			
I	MS	µg/l	0.31	11	961	3			
In	MS	µg/l	<0.002	<0.002	0.017	1			
K	OES	µg/l	598	7320	45800	2			
La	MS	µg/l	0.002	0.029	19.4	4			
Li	MS	µg/l	0.1	11	176	3			
Lu	MS	µg/l	<0.002	<0.002	0.13	2			
Mg	OES	µg/l	240	12045	116100	3			
Mn	MS	µg/l	<0.1	8.52	2440	4	50 (MACi)	50 (ATO)	21
Mo	MS	µg/l	<0.002	2.93	78.3	5		70	2
Na	OES	µg/l	3858	71750	595000	2	200000 (MAC)		17
Nb	MS	µg/l	<0.002	0.013	2.37	3			
Nd	MS	µg/l	0.002	0.0295	18.2	4			
Ni	MS	µg/l	0.086	0.74	11.2	2	20 (MAC)	20 (P)	
NO <sub>2</sub>	IC	µg/l	<5	<5	1120	3	500 (MAC)	200 (P) (chronic)	3
NO <sub>3</sub>	IC	µg/l	<50	3960	149000	4	50000 (MAC)	50000	7
Pb	MS	µg/l	0.023	0.45	46	3	10 (MAC weekly av.)	10	1
Pr	MS	µg/l	<0.002	0.007	4.97	4			
Rb	MS	µg/l	0.38	8.39	82	2			
Sb	MS	µg/l	<0.002	0.028	1.78	3	5 (MAC)	5 (P)	
Se	MS	µg/l	0.015	0.615	7.58	3	10 (MAC)	10	
Si	OES	µg/l	7427	35387	67881	1			
Sm	MS	µg/l	<0.002	0.007	3.47	4			
Sn	MS	µg/l	<0.002	0.018	7.48	4			
SO <sub>4</sub>	IC	µg/l	<50	14000	692000	4	250000 (MACi)		7
Sr	MS	µg/l	8.8	232	9850	3			

Table 1 (Continued)

	Tech.	Unit	Min.	Med.	Max.	Ord.	EU Directive	WHO	>MAC (%)
Ta	MS	μg/l	<0.002	0.002	0.054	<b>2</b>			
Tb	MS	μg/l	<0.002	<0.002	0.41	<b>3</b>			
Te	MS	μg/l	<0.005	<0.005	0.019	<b>1</b>			
Th	MS	μg/l	<0.002	0.008	1.59	<b>3</b>			
Ti	MS	μg/l	0.3	4.74	264	3			
Tl	MS	μg/l	<0.002	0.005	0.15	<b>2</b>			
Tm	MS	μg/l	<0.002	<0.002	0.13	<b>2</b>			
U	MS	μg/l	0.005	1.84	48	4		2 (P)	(47)
V	MS	μg/l	0.093	13.35	235	3			
W	MS	μg/l	<0.002	0.011	3.81	<b>4</b>			
Y	MS	μg/l	0.003	0.068	10.3	4			
Yb	MS	μg/l	<0.002	0.005	0.77	<b>3</b>			
Zn	MS	μg/l	1.1	44	5140	4			
Zr	MS	μg/l	0.009	0.11	25	3			
T		°C	15.6	28.5	67.3				
pH			5.2	7.1	8.6		>6.5, <9.5		13
EC		μS/cm	52	719	3850		2500 (MACi)		1
Alkalinity		mg/l	15	341	1070				
ToHa	Calc.	°dH	0.4	7.6	51.6				
CaHa	Calc.	°dH	0.7	15.6	49.1				
Solids	Calc.	mg/l	34	598	2401				
IB	Calc.	±%	0	0.85	2.6				

Tech., technique used for analysis: MS, ICP-MS; OES, ICP-OES; IC, ion chromatography; Calc., calculated. Ord., orders of magnitude covered by the data [ $\log(\text{Max}/\text{Min})$ —a value of half of the detection limit is used for calculation of those elements for which the minimum concentration was below the detection limit (values in bold in the Ord. column). MAC: maximum acceptable concentration, European Union directive, chemical parameters. MACi: maximum acceptable concentration, European Union directive, indicator parameters. >MAC (%): percentage of samples exceeding the EU guidelines; where values are in brackets, there is no EU guideline, and the result represents the percentage of samples above the WHO guideline. *T*: temperature at time of sampling. EC: electrical conductivity. ToHa: total hardness (in degrees of German hardness). CaHa: carbonate hardness. Solids: sum of dissolved ions. IB: ion balance, as a measure of analytical quality. (P): provisional guideline value. (ATO): value is appearance-, taste- or odour-related. NAD: no adequate data available to permit recommendation.

European Union (EU) maximum acceptable concentration (MAC) levels are defined for only 18 (19 if NO<sub>2</sub>/NO<sub>3</sub> are counted separately) out of the 65 analysed elements (and pH and electrical conductivity). Of these 18 elements, the following six did not show any values exceeding the MAC (Table 1): Cr, Cu, Hg, Ni, Sb and Se (EU standard). For some elements only one of the two cited authorities suggest an action level (Al, Ba, Br, Cl, Fe, Mo, Na, SO<sub>4</sub>, U). One of the largest differences in opinion between the authorities exists for U, for which the EU has not defined any MAC, the US EPA (2001) has recently set a MAC of 30 μg/l and WHO (1998) suggests a provisional value of 2 μg/l, based on toxicological considerations. In general, it is an interesting exercise to compare different versions of documents

defining MAC values, e.g. the old EU regulation, (European Union, 1980) with the recent regulations (European Union, 1998).

If the compliance failures were added up, a staggering 78% of all drinking water samples from the Rift Valley would fail to pass the current EU drinking water directives. Fluorine is the element with the highest single percentage of failure: 33% of all samples are above 1.5 mg/l F. The maximum concentration reported in this study is 11.6 mg/l F.

The EU has not set any MAC for uranium. Only 2% of the drinking waters fall above the US EPA MAC uranium concentrations. If, however, the WHO-suggested value of 2 μg/l U is taken, 47% of all samples would fail and U would pose an even bigger problem than F.

Adverse health effects of too high arsenic values in drinking water have recently received much attention (e.g. Smith et al., 2000). Fortunately, only nine samples (6.5%) fall above the MAC of 10  $\mu\text{g/l}$  As. Arsenic is thus not a major problem in Rift Valley drinking water.

High  $\text{NO}_2/\text{NO}_3$  concentrations in drinking waters point often towards contamination. Wells with high  $\text{NO}_2/\text{NO}_3$  values should be checked for bacterial contamination. Nine samples (6.5%) fall above the MAC for  $\text{NO}_3$ . Nitrogen species should be measured in an as short a time span after sampling as possible. This was not viable in this project and the values reported must be treated as preliminary.

Given the quite different origin of the drinking water samples, it was decided to divide these samples further into several data subsets (deep wells, shallow wells, hot springs, springs and river water) for plotting of results. Selected elements are presented in cumulative distribution function (CDF) diagrams (Fig. 2). The different subsets are shown with different symbols in these diagrams and MAC values are noted where applicable. For some elements, regional distribution maps were drawn (Fig. 3). Mapping techniques used follow the suggestions of Kürzl (1988).

## 6. Discussion

High concentrations of As, F, Na,  $\text{NO}_2/\text{NO}_3$  and U in drinking water may have direct health implications. Compliance failures of many of the other elements (e.g. Al, Cl, Fe, Mn,  $\text{SO}_4$ ) are of a more aesthetic nature (staining of laundry, odour, taste, 'feel' of the water) or limit the use of the water for practical purposes.

No drinking water standards are defined by EU, WHO or US EPA (note that drinking water standards exist in Russia for several of these elements; Kirjuhin et al., 1993) for Ag, Be, Bi, Br, Ca, Ce, Co, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, I, In, K, La, Li, Lu, Mg, Nb, Pr, Rb, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Tl, Tm, V, W, Y, Yb, Zn or Zr. Several of these elements have documented health effects. For others, for example the rare earth elements, our knowledge about health effects is rather limited (Hirano and Suzuki, 1996).

When comparing the Rift Valley data to other published data sets covering the same suite of elements in drinking water from European countries (e.g. Reimann et al., 1996; Misund et al., 1999; Frengstad et al., 2000) it is clear that the Ethiopian waters show rather high median values (often an order of magnitude higher than the Norwegian groundwater data given in Frengstad et al., 2000) for the elements Al, As, Br, Cd, F, Fe, Ga, Ge, I, K, Mo, Na,  $\text{NO}_3$ , Pb, Rb, Se, Si, Ti, V, Zn and Zr.

The examples shown in the CDF diagrams (Fig. 2a–l) demonstrate that there are clear compositional differences between the water types. Deep and shallow groundwaters usually show quite comparable concentrations and element variation. Exceptions are the elements B, Br, Ca, Cl, I, Na, Ni,  $\text{NO}_3$ ,  $\text{SO}_4$ , Sr and Ti. These are all higher in the shallow wells (for examples see Fig. 2c,f,i,k). Potassium (K), Rb, Si and Zr are higher in the deep wells. Some elements show clearly higher values in river and spring waters: Al, Ba (river only), Be, Ce, Co (river), Cu, Dy, Er, Eu, Fe, Ga, Gd, In, La, Lu, Mn, Nb, Nd, Ni, Pb, Pr, Sm, Tb, Te, Th, Tm, Ti, Y, Yb and Zr (for examples see Fig. 2a,d). The combination of Al with the rare earth elements is a clear indication of particulate 'contamination' playing a role in explaining many of these high values. Surface waters should clearly be field-filtered prior to analysis. Elements that are relatively enriched in the hot springs include As, B, Bi, Cl, Cs, F, Ge, K, Li, Mo, Na, Rb, Sb, Se,  $\text{SO}_4$ , Tl, and W (for examples see Fig. 2b,c,e,g). This is a typical hydrothermal geochemical signal. Another suite of elements shows especially low values in the surface (river) or near-surface waters (springs): As, B, Br, Ca, Cd, Cl, F, Ge, I, Li, Mg, Mo, Se, Si,  $\text{SO}_4$ , Sr, W and Zn (for examples see Fig. 2b,c,e,f,g,j,k,l). This demonstrates the influence of the input of precipitation to these waters. The similar behaviour of river and spring water indicates that the springs are shallow-seated and thus vulnerable to contamination (as also shown by high  $\text{NO}_2/\text{NO}_3$  in the springs).

The maps (Fig. 3; maps for all elements are given in Reimann et al., 2002) show that there are clusters of high values of certain elements in certain geographical areas within the Rift Valley.

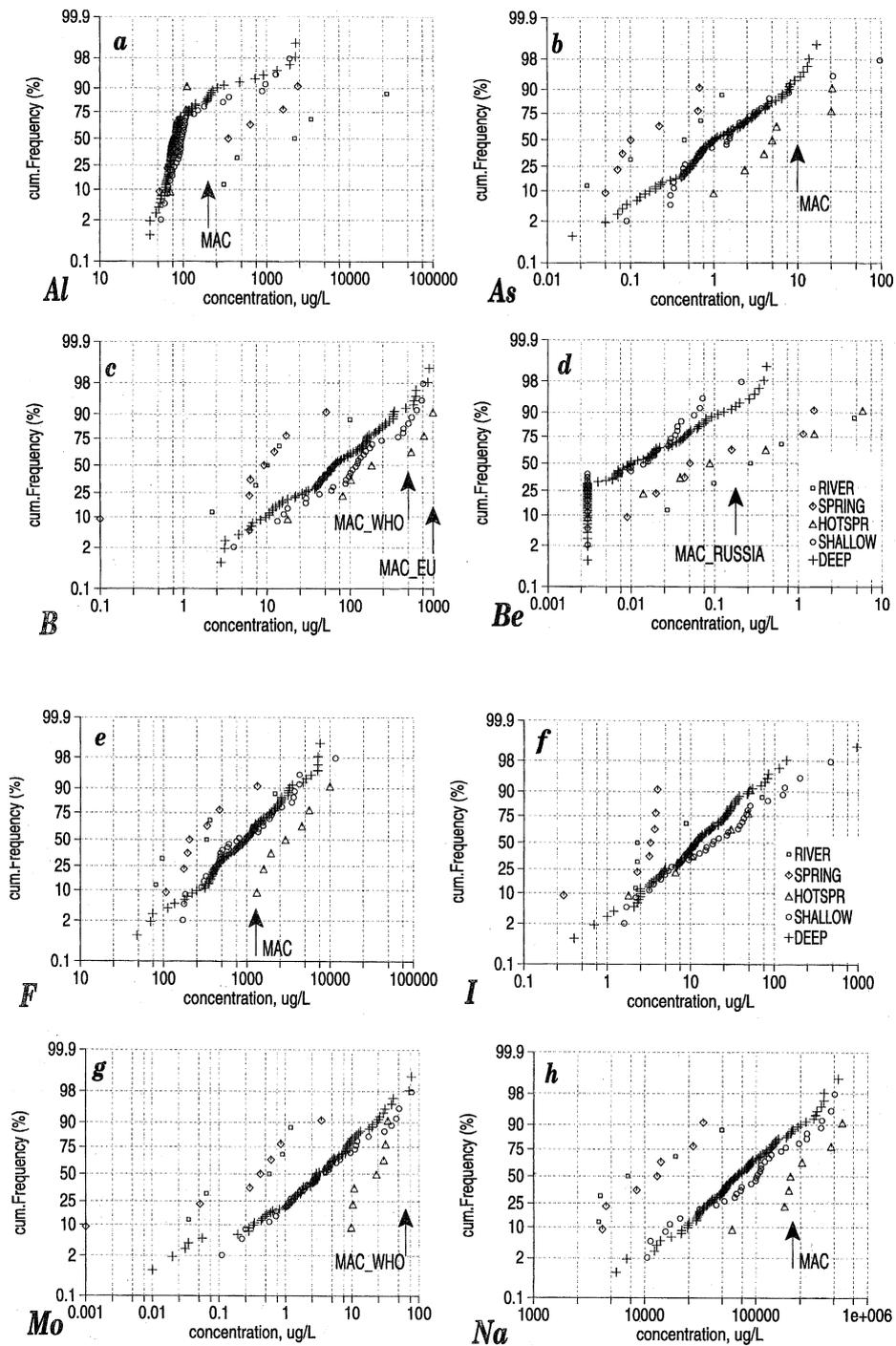


Fig. 2. CDF diagrams for selected elements. Different water types marked by different symbols; MAC values indicated where applicable.

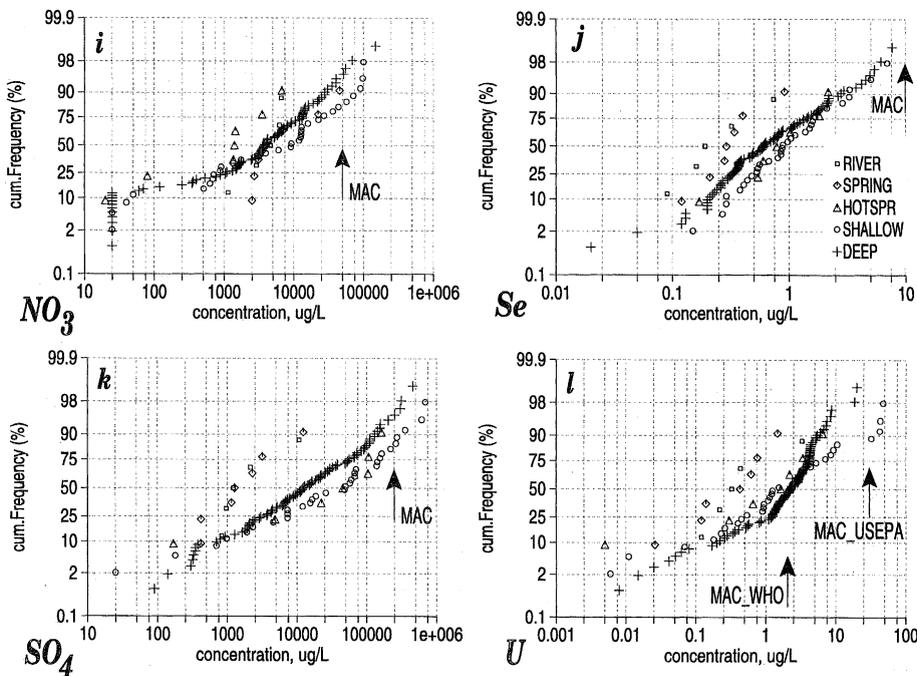


Fig. 2 (Continued).

The elements As, B, F, Ge, I, Li, Mo, Na, Rb, Sb, Ta, U and W show a cluster of high values in the centre of the Rift Valley, where the deepest wells are drilled. This indicates that a hydrothermal component contributes to the high concentrations of these elements in the well waters. Other elements show a cluster of high values towards the northern part of the survey area: B, Br, Ca, Cl, Mg, NO<sub>3</sub> and SO<sub>4</sub> and we can speculate on high evaporation rates playing a decisive role in the composition of these waters.

The medical observations of the incidence of dental fluorosis and crippling fluorosis in the Rift Valley were the starting point for this study (Tekle-Haimanot et al., 1987; Tekle-Haimanot, 1990; Kloos and Tekle-Haimanot, 1999). One-third (33%) of all drinking water samples collected returned values exceeding the EU and WHO MAC of 1.5 mg/l F (Table 1 and Fig. 2e). For warm waters (above 25 °C) or in tropical countries with a high daily intake of drinking water, an action level of 0.7 mg/l F has been suggested (Galagan and Lamson, 1953; Galagan and Vermillion, 1957;

Richards et al., 1967; Evans and Stamm, 1991). Even levels below 0.7 mg/l in drinking water may result in minute changes in the dental enamel. Of greater significance to human health is skeletal fluorosis, which may develop after long-term intake of drinking water with a fluoride concentration above 4 mg/l. Crippling fluorosis is observed at values above 10 mg/l F (Dissanayake, 1991). A total of 58% of all samples surpass the level of 0.7 mg/l F (Fig. 2e) and action is clearly required. There are a number of rather simple and cheap techniques for removing excess F from water. Experiments have shown that fluoride can be efficiently removed from water by the use of the following methods:

- Reaction of the water with crushed pottery and/or tropical soil. Tropical soil (Hauge et al. 1994; Zevenbergen et al., 1996) and pottery made of tropical soil (Padmasiri et al., 1995) often contain calcium and aluminium oxide. These are probably the active ingredients. Substantial amounts of F can be removed from the water

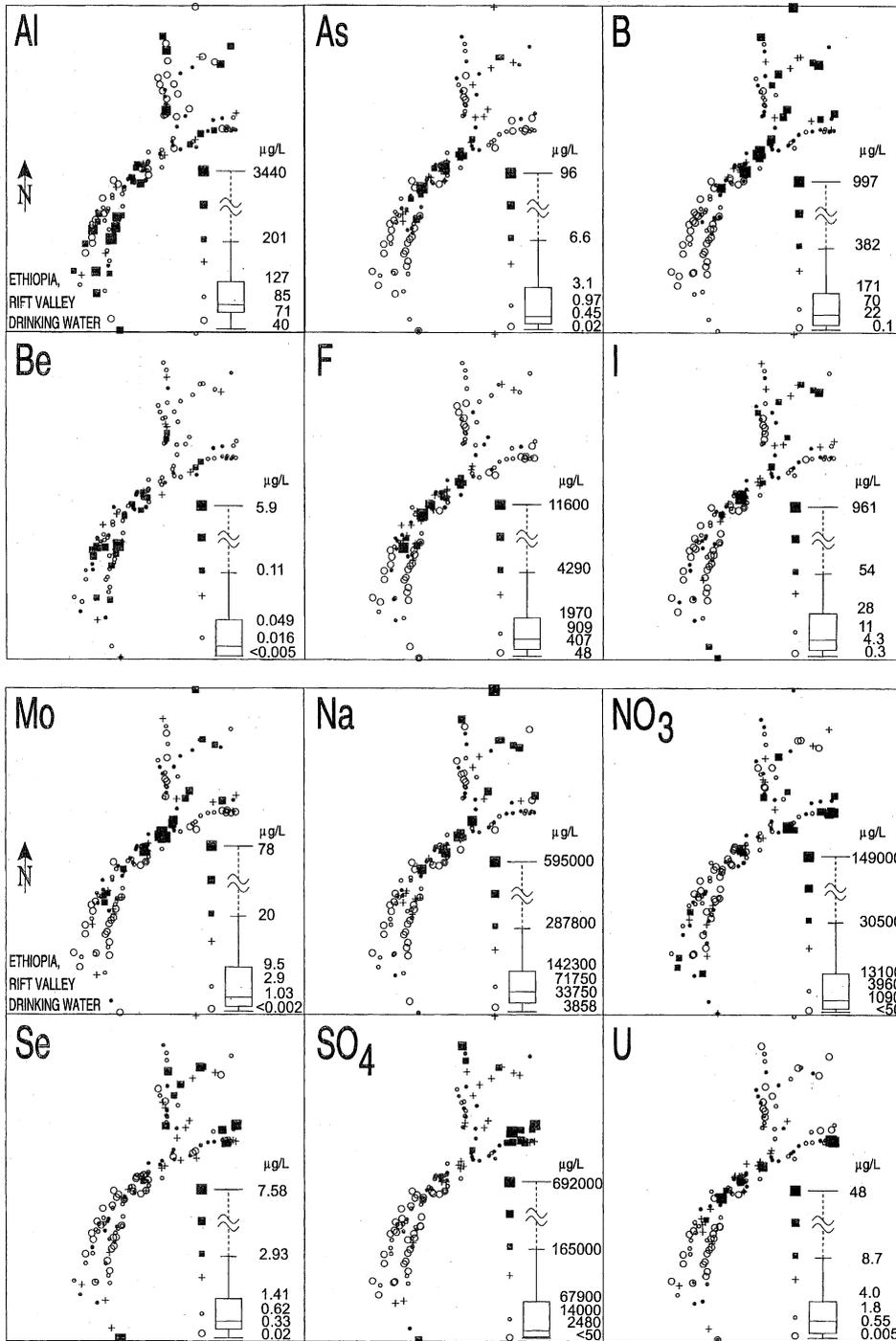


Fig. 3. Regional distribution maps for selected elements in Ethiopian Rift Valley drinking water.

after a retention time of some hours. To re-teach the population to use pottery instead of plastic for storing their drinking water might thus be advantageous.

- Burned (fish) bones (Dunckley and Malthus, 1961; Bhargava and Killedar, 1992; Killedar and Barghava, 1993), in which apatite is probably the active ingredient.
- Treatment with mineral apatite, calcium phosphate or aluminium phosphate (Qianjie and Hanwen, 1992; Dieye et al., 1994).
- Water treatment with other aluminosilicate minerals that adsorb fluoride or admit ion exchange reactions of fluoride against hydroxide. Kaolinite clays and crushed serpentinite are efficient (Jinadasa et al., 1991) and fly ash may also be efficient (Jinadasa et al., 1988; Chaturvedi et al., 1990).

As mentioned above, the geographical distribution of the samples, with a cluster of all the high values in the centre of the Ethiopian part of the Rift valley, suggests a hydrothermal origin for these high F concentrations. It also suggests that nearby water resources with more acceptable fluoride concentrations may often exist. Fluoride is quite mobile under most geochemical conditions. In water, the stability field of fluorite ( $\text{CaF}_2$ ) limits the possible F concentrations; high F concentrations will thus mostly occur in low-Ca waters. Fluorine is one of the elements with a very narrow range of 'healthy' concentrations in drinking water. However, because F is ubiquitous in nature, health effects due to actual fluoride deficiencies are hard to prove. As demonstrated by Dean et al. (1939), low-fluoride drinking water is—in caries-prone populations—associated with elevated incidence of dental caries.

At present we do not have sufficient data on the occurrence of endemic diseases in the Rift Valley to link these directly with the element concentrations observed in the drinking waters. Fortunately, no element other than F appears to occur at such high concentrations that the health of the general population is directly threatened. Uranium, however, poses an even greater problem than F if the WHO proposed MAC for U in drinking water is taken seriously (Fig. 21). Reimann et al. (1996)

reported natural U concentrations spanning six orders of magnitude in Norwegian bedrock groundwater (maximum concentration 2 mg/l). Uranium in drinking water from bedrock wells is thus an element that should certainly receive more attention from health authorities. Removal of U from drinking water may require relatively expensive techniques, such as reverse osmosis or distillation.

Chatterjee et al. (1995) and Das et al. (1995) have reported dramatic effects (skin cancer) due to very high As concentrations in drinking water in West Bengal. High As concentrations are often observed in hydrothermal systems. This was one of the reasons for initiating this project. Fortunately only nine samples exceed the new MAC of 10  $\mu\text{g/l}$  As. The CDF diagram (Fig. 2b) suggests that hot springs are especially prone to high As concentrations. Human consumption from these waters should probably be banned. Boron, Be, F, Ge, K, Li, Mo and Na were all high in the hot spring waters, while iodine was at unusually low concentrations. More than 25% of all samples would fall above the MAC of 2  $\mu\text{g/l}$  that was also discussed when the MAC was recently lowered from 50 to 10  $\mu\text{g/l}$  (Fig. 2b). Usually As levels in drinking water are much lower ( $< 1 \mu\text{g/l}$ ; Reimann and de Caritat, 1998). Most cases of high values of As in water are related to the occurrence of sulfide minerals such as arsenopyrite and pyrite. In aqueous systems, As is highly soluble over a wide pH/Eh range. Fe and Eh both have an influence on the concentration of As observed in groundwater (Matisoff et al., 1989; Varsanyi et al., 1991). In the Rift Valley the high As values in the hot springs and the cluster of high values in the centre of the Rift Valley both point to a hydrothermal origin.

Excessive levels of nitrate in drinking water have caused serious illness and sometimes death. Nitrates and nitrites have the potential to cause the following effects from a lifetime exposure at levels above the MAC: diuresis, increased starchy deposits and haemorrhaging of the spleen (US EPA fact sheet on nitrate). Excessive nitrate concentrations in water are mainly related to pollution (with agriculture as the main source). It is thus no surprise that higher values are observed in springs and shallow wells (Fig. 2i). High values of  $\text{NO}_3$

in some of the Rift Valley wells demonstrate that more care is needed in well construction and safeguarding of wellheads against contamination. This is much easier than treating contaminated waters. Wells returning high  $\text{NO}_3$  should be analysed for bacterial contamination and field-checked by a hydrogeologist for construction and protection against pollution.

Selenium, at trace levels, is essential in the human and animal diet and its deficiency has received much attention. It causes symptoms such as muscular degeneration, impeded growth, fertility disorders, anaemia and liver disease (Låg, 1984). Keshan and Kaschin–Beck diseases, reported on a regional scale from China, are caused by Se deficiency. At ingested concentrations of 10 mg/day and higher, gastro-intestinal ailments, skin-discoloration and tooth decay may occur (Tebbutt, 1983).

The EU (and WHO) MAC for Se in drinking water is 10  $\mu\text{g}/\text{l}$ . None of our samples exceeded this value (Fig. 2j). Selenium is again one of those elements for which a minimum guideline level would probably be of more importance than an upper MAC. Selenium behaves geochemically quite similarly to S. Its mobility is high under acid and oxidising conditions, very high under neutral–alkaline conditions and very low under reducing conditions. Naturally, Se occurs in trace amounts in many sulfidic ores. In elemental form Se is insoluble and thus is non-toxic. It has a strong affinity to organic matter. Concentrations observed in Rift Valley drinking water ranged from 0.015 to 7.6  $\mu\text{g}/\text{l}$  (Table 1, Fig. 2j). Median Se values were lower in spring and river water than in the wells (Fig. 2j). Compared to Norwegian bedrock groundwater (Frengstad et al., 2000), Se concentrations in the Ethiopian drinking water are rather high (median Norway: 0.20  $\mu\text{g}/\text{l}$ , median Rift Valley: 0.62  $\mu\text{g}/\text{l}$ ).

There is no EU MAC for Mo; WHO, however, has suggested a MAC value of 70  $\mu\text{g}/\text{l}$ . Three samples exceed the WHO MAC, although the maximum concentration observed is still very close to the MAC: 78.3  $\mu\text{g}/\text{l}$  (Fig. 2g). Mo is an essential trace element. Its toxicity is species-dependent; it is, for example, more toxic to cows and sheep (depending on the Cu/Mo ratio) than

to humans. High Mo values in forage can prevent the uptake of Cu and are known to cause severe problems in animal husbandry (e.g. Webb, 1971). The mobility of Mo is very low under reducing conditions; under oxidising and acid conditions it is high and under neutral–alkaline conditions it is very high. The fact that the hot springs show, on average, higher Mo values than springs, rivers and wells points towards a hydrothermal origin.

Several of the elements that are not covered by MAC values are deemed to have health effects. It has, for example, long been suspected that there is a causal link between water hardness (dissolved Ca and Mg) and cardiovascular disease (e.g. Gardner, 1976). It appears that there is a weak inverse relationship between drinking water hardness and cardiovascular disease mortality (COMA, 1994). This might actually warrant setting a lower Ca limit (minimum acceptable concentration; MIC) for drinking water. For iodine (Fig. 2f), serious health effects of suboptimal (deficiency) as well as of excess concentrations are well documented. Fuge and Johnson (1986) reviewed the geochemistry of I. The main problem is probably I deficiency causing goitre and cretinism (Kelly and Sneddon, 1960). This is an element for which a lower as well as an upper concentration limit should be defined. People with high blood pressure should not consume water with a Na concentration above 1000 mg/l as their daily drinking water (compare Fig. 2h).

Furthermore, there are a number of elements that are rather toxic and/or carcinogenic for which no MAC has been defined, probably often under the assumption that “natural concentrations in water must be very low” (WHO, 1993; statement with regard to Be). Table 1 shows that the natural concentrations of all elements analysed cover between one and five orders of magnitude, and some surprisingly high concentrations for ‘rarities’ can be found in natural drinking water. For many of these elements, little is known about health effects at drinking water concentrations. Be (Fig. 2d), Br, Th and Tl are probably four elements that have received far too little attention and need more discussion from a health perspective. From a Norwegian perspective, Rn (not reported here) is a further element that can show dangerously high

concentrations in waters from bedrock wells (Banks et al., 1995b; Reimann et al., 1996; Morland et al., 1998).

The chemical composition of some of the water samples (e.g. high B; Fig. 2c) makes them unsuitable for irrigation. This fact should also be considered in the context of sustainable development of the natural resources in the Rift Valley.

## 7. Conclusions

In total, a staggering 78% of all samples from the Ethiopian Rift Valley would fail to pass the current EU drinking water regulations. This number increases to 86% if the WHO-proposed value for U is also used. At present the high F concentrations pose the most serious health problem in these drinking waters. Uranium might be considered an even bigger problem at the WHO proposed MAC. Fortunately, As and many other harmful elements show mostly acceptable concentrations.

Although a high proportion of all wells do not fulfil European drinking water guidelines, it should be kept in mind that in most cases the well water is preferable to polluted surface water. The point is that the chemical composition of the water must be analysed so as to flag actions required for unwanted constituents. In many cases it is rather easy and cheap to treat the water for inorganic chemical constituents once a problem is recognised.

It should be noted that the natural concentrations of most of the elements analysed cover between three and four orders of magnitude. Surprisingly high natural concentrations are observed for a number of elements for which no MAC values have been proposed (e.g. Be, Br, Co, Li, Nb, Si, Sr, Te, Th, Tl and V). These elements may warrant a toxicological assessment. Be, Br, Th and Tl are probably the four elements needing most urgent attention from a health perspective. It must also be noted that for a number of elements, deficiency may be the more important health problem. Public authorities might be well advised to establish MIC values for such elements (e.g. Ca, I, Se).

This study demonstrates the necessity of documenting natural element concentrations and variation in drinking water resources on a regional

scale. This must be carried out for as many elements as can be analysed with today's techniques in different geological settings, to provide fingerprints of the different types of water.

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