

Hydrochemistry and source of high fluoride in groundwater of the Nairobi area, Kenya

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Abstract This study aims to identify the hydrogeochemical processes influencing the high fluoride concentrations in groundwater of the Nairobi area, Kenya. For this purpose 16 groundwater samples were collected and analysed. Fluoride concentrations above the WHO standard are found in the downstream areas. The high F^- concentrations are correlated with high sodium and pH and low Ca^{2+} concentrations. Weathering of sodium-rich alkaline igneous rocks causes a pH increase resulting in an increase in HCO_3^- and CO_3^{2-} by dissolution of CO_2 . Groundwater becomes oversaturated compared to calcite and calcite precipitation occurs, leading to a decrease in Ca^{2+} . This causes a sub-saturation with respect to fluorite and dissolution of fluorite increases the F^- concentration. These reactions were modelled using the PHREEQC model and the results showed a good agreement with the measured groundwater quality, indicating that the proposed reactions are plausible for explaining the observed concentrations in groundwater.

Key words hydrogeochemistry; fluoride; PHREEQC; Kenya

Hydrochimie et origine des fortes concentrations en fluorure dans l'eau souterraine de la région de Nairobi, au Kenya

Résumé L'objectif de cette étude est d'identifier les processus hydrogéochimiques qui influencent les fortes concentrations en fluorure dans l'eau souterraine de la région de Nairobi, au Kenya. Dans ce but, seize échantillons d'eau souterraine ont été collectés et analysés. Des concentrations en fluorure supérieures à la norme OMS ont été observées dans les zones aval. Les concentrations en F^- élevées sont corrélées avec de fortes concentrations en sodium, un pH élevé et de faibles concentrations en Ca^{2+} . La dissolution des roches ignées alcalines riches en sodium cause une augmentation du pH qui conduit à une augmentation des teneurs en HCO_3^- et en CO_3^{2-} par dissolution de CO_2 . Une sursaturation de l'eau souterraine en calcite conduit à sa précipitation et donc à une diminution de la teneur en Ca^{2+} . Cela cause une sous-saturation vis-à-vis de la fluorite et la dissolution de la fluorite augmente la concentration en F^- . Ces réactions ont été modélisées à l'aide du modèle PHREEQC et les résultats sont en bon accord avec les valeurs mesurées de la qualité de l'eau, ce qui indique que les réactions proposées sont plausibles pour expliquer les concentrations observées dans les eaux souterraines.

Mots clefs hydrogéochimie; fluorure; PHREEQC; Kenya

INTRODUCTION

The fast growth of Nairobi, Kenya, one of the fastest growing cities in Africa, has put enormous pressure on the existing water resources. The scarcity and unreliability of piped water and the heavily polluted surface water resources in the Nairobi area mean that groundwater is the only reliable alternative source of water in this area. Development of the groundwater supply in Nairobi and its environs has proceeded since the start of the 20th century, without adequate knowledge of the groundwater quality and quantity, and with the belief that groundwater is always potable and unlimited. Hydrochemical studies in the Nairobi area are very scarce. The few studies have been carried out elsewhere in areas adjacent to the study area (Maina & Gaciri, 1984), or are only mentioned as part of a larger study, such as the geology report (Saggerson, 1967, 1991) and the hydrogeology report of the area (Gevaerts, 1964).

High F^- concentrations in groundwater are found in many places of the world, but notably in Asia and Africa (Appelo & Postma, 2005). The East African Rift Valley is a known high fluoride region, e.g. in Tanzania (Nanyaro *et al.*, 1984) and in Ethiopia (Chernet *et al.*, 2001), and health problems associated with high fluoride ingested by humans are prevalent. Fluoride in drinking water constitutes a health hazard at concentrations higher than 3 mg L^{-1} , causing dental fluorosis and skeletal fluorosis (Appelo & Postma, 2005). Fluoride is basically brought into the groundwater

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by leaching from minerals in the rocks (Handa, 1975; Travi & Faye, 1991; Jacks *et al.*, 1993; Saxena & Ahmed, 2003). Clarke *et al.* (1990) found groundwater to contain up to $180 \text{ mg L}^{-1} \text{ F}^{-}$ at Lake Naivasha in Kenya and attributed these high concentrations to the leaching of the volcanic rocks in the East African Rift Valley. Saggerson (1991) reported fluoride concentrations up to 17 mg L^{-1} in the Nairobi area. Volcanic rocks may have high natural fluoride contents (Zack, 1980). In arid areas, evaporation may strongly increase the F^{-} concentration in water. Gupta *et al.* (2005) found high fluoride concentrations in India to be associated with evaporative enrichment, preferential dissolution of high sulphide-bearing minerals and thermal springs. Subba Rao (2003) found a difference in fluoride concentrations in pre- and post-monsoon water in India.

The aim of this study is to establish and understand the chemical processes determining the presence of fluoride in the groundwater of the Nairobi area, based on the study of the groundwater chemistry. Then, the assumed chemical processes are modelled with the PHREEQC code (Parkhurst & Appelo, 1999) in order to check the accuracy of the assumptions.

GEOLOGICAL AND HYDROGEOLOGICAL CONDITIONS

The city of Nairobi is situated about 50 km to the east of the East African Rift Valley. The Nairobi area is composed of a succession of lava and pyroclastics of Caenozoic age overlying a foundation of folded Precambrian schists and gneisses of the Mozambique Belt (Gaciri & Davies, 1993). The geological history of Nairobi is dominated by volcanic activity, whereby a thick succession of alkaline lavas and associated tuffs began accumulating in Mid-Miocene time and continued into the Upper Pleistocene. Almost the entire Nairobi area is covered by volcanic rocks derived from the Rift Valley region (Gaciri & Davies, 1993). The eruptive products of the volcanoes provide most of the topographic expression of Nairobi. The topography of the study area drops from 2000 m a.s.l. in the west to 1600 m a.s.l. in the east. The mass of the volcanic lava thins out appreciably in the easterly direction, with the eastern limits marked by erosional scarps forming the terminal walls of the more resistant lava sheets. Igneous material in the Nairobi area consists mainly of trachytes, phonolites and tuffs.

The main geological formations (Figs 1 and 2) in the Nairobi area are undifferentiated Ngong Basalt, Kandizi Phonolites, Nairobi Trachytes, Kerichwa Valley Tuffs, Nairobi Phonolites of Lower trachyte division, Athi Series and various forms of trachytes (Saggerson, 1991). Trachytes are fine-grained, extrusive igneous rocks with alkali feldspar and minor mafic minerals as the main components, and possibly a small amount of sodic plagioclase. Phonolites are grey to dark green extrusive rocks, usually with a porphyritic texture, and consist mainly of nepheline and alkali feldspar.

The porous and permeable Upper Athi Series forms the main aquifer in the region. This aquifer has a low storativity and a transmissivity, T of $5\text{--}50 \text{ m}^2/\text{d}$ (Foster & Tuinhof, 2005). Groundwater is recharged in the Rift Valley, which forms an elevated area with fractures in the west. Additional recharge occurs in the upstream parts of rivers related to fault lines and weathered zones (Foster & Tuinhof, 2005). Groundwater flow is mainly from the elevated areas in the west towards the lower areas in the east and follows the dip of the volcanic rocks in the area (Fig. 2). Infiltration of rainwater is greatly facilitated by the crumbly textured soils. Annual average rainfall amounts to 900 mm in the Nairobi area and 1200 mm in the Rift Valley to the west of the city. The area has medium groundwater recharge of between 15 and 150 mm/year (Struckmeier & Richts, 2006). Two rainy seasons occur, the first from mid-March to May, and the second from mid-October to mid-December.

The principal sources of fluoride are the volcanic deposits of the East African Rift System (Gaciri & Davies, 1993). These alkaline volcanic rocks of the Rift are rich in Na^{+} and F^{-} . Gaciri & Davies (1993) stated that the rocks of the East African Rift System are richer in F^{-} than other analogous rocks in the world. The volcanic rocks in the Rift are mainly composed of alkali basalts, basanites, thephrites, phonolites and trachytes (Williams, 1982). Gaciri & Davies (1993) found fluoride enrichment in groundwater along the flow direction and explained the variation in F^{-} by

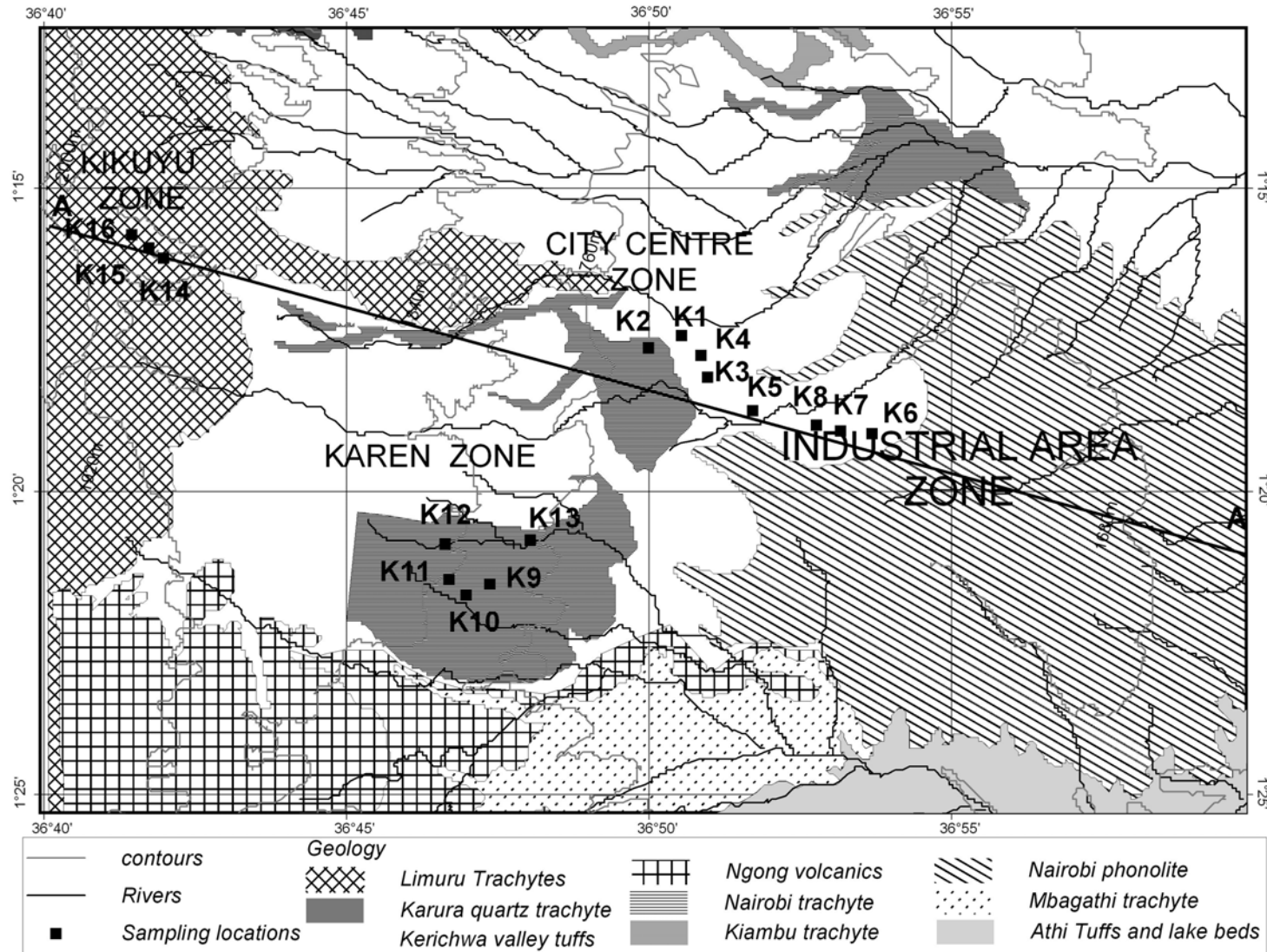


Fig. 1 Map of Nairobi area representing the geology, topography and hydrography.

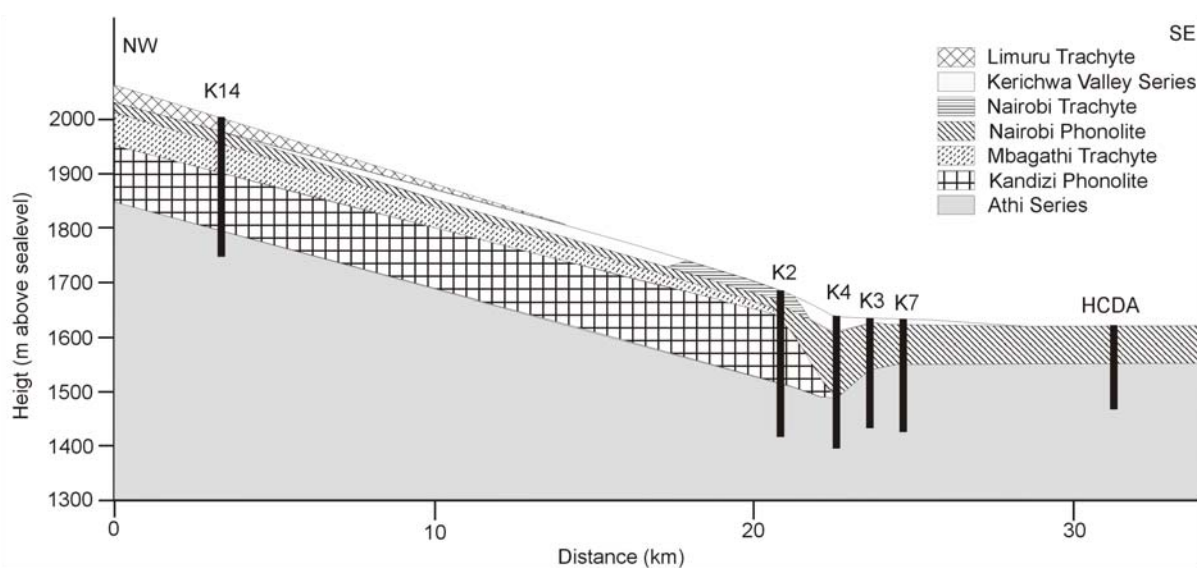


Fig. 2 Geological profile of the Nairobi area, section A–A'.

the difference in availability of F^- , which is linked to the volcanic activity and the composition of the volcanic rocks, and by the difference in residence times. According to Gaciri & Davies (1993), precipitation of $CaCO_3$ can remove fluoride from groundwater as F^- becomes incorporated in the $CaCO_3$ structure. Fluoride can also incorporate in Ca-phosphates.

According to Nanyaro *et al.* (1984), rock-forming minerals such as fluorite and topaz, and accessory minerals such as fluorapatite, fluormica and crydite, are sparingly soluble in water and do not play an important role. Villiaumite has a higher solubility product and can act as an important contributor of F^- in groundwater (Nanyaro *et al.*, 1984). Yet, Travi (1993) states that fluorapatite is the principal source for F^- in sedimentary basins, while in crystalline rocks, fluorite and adsorbed F (to phylitic minerals and microfissures) would be the main source. In this paper, hydrogeochemical modelling was used to demonstrate that the control of fluorite solubility is indeed a determinant of the high F^- concentrations in groundwater in the study area.

METHODS

The study area was divided into four zones, indicated in Fig. 1, based on water supply, land use, geological, and topographic considerations:

- The City Centre zone is a densely populated, built-up area, with few boreholes having an average depth of 220 m. It lies on the Kerichwa Valley Series and the Nairobi Trachyte with intercalated sediments and tuffs.
- The Industrial Area zone has many boreholes with high pumping rates, and an average borehole depth of 250 m. The Nairobi Phonolite and partly the Lower Kerichwa Valley Tuffs are the key geological formations.
- The Karen/Langata zone is characterized by extensive groundwater exploitation with boreholes of an average depth of 300 m. Geological formations are Nairobi Trachytes, Mbagathi Trachytes, Kandizi Phonolites and Athi Series.
- The Kikuyu zone is a recharge area with high rainfall and gentle slopes. Shallow wells and artesian springs are the main ways of groundwater exploitation. The geological formation underlying the Kikuyu zone is the Limuru Trachytes.

Sixteen boreholes for sampling were selected from the Drillers Register at the Ministry of Water Development, Nairobi, based on water supply, land use, geological and topographic considerations. In order to get a representative picture of the groundwater characteristics, at least

three boreholes were sampled from each zone. Water samples were analysed at the Central Water Laboratories, Ministry of Water Development, Nairobi, following protocols according to *Standard Methods for the Examination of Water and Wastewater* (Clesceri et al., 1997). Standard procedures were used for the physical-chemical determinations using volumetric (titrimetric), colorimetric and instrumental methods. Titrimetric methods were used for the parameters alkalinity, free CO₂, Cl⁻ and Ca²⁺. Photometric methods were used for NO₃⁻ and Fe²⁺. and Flame Atomic Absorption Spectrometry (FAAS) for Na⁺ and K⁺. The SO₄²⁻ concentration was measured turbidimetrically, the F⁻ content with a fluoridimeter and Mn²⁺ concentration with a persulphate method. The alkalinity was measured as CaCO₃ and converted to CO₃²⁻ and HCO₃⁻.

RESULTS AND DISCUSSION

The chemical results for the groundwater samples are given in Table 1. The error on the ionic balance was calculated in order to check the reliability of the analytical results. Four-fifths of the samples had an error smaller than 5%. The remaining samples had an error of less than 10%. The classification of Stuyfzand (1986) was applied to the groundwater samples and is represented in Table 2.

All of the sampling points belong to the fresh major type (Cl⁻ < 150 ppm), and are either very soft (code *: <1 meq/L hardness), or soft (code 0: 1–2 meq/L hardness). For all samples, except sample K15, Na⁺ is the strongest cation, while HCO₃⁻ is the strongest anion. The combination of the strongest members gives the NaHCO₃ subtype. For all these sampled points with a NaHCO₃ subtype, there is a surplus of {Na + K + Mg} corrected for seawater intrusion. This can be caused by dissolution of minerals containing Na⁺, K⁺, and/or Mg²⁺, such as feldspars (Stuyfzand, 1986), rather than freshening, since there is no evidence of marine transgressions in the area. Sample K15 has a CaCl subtype, and shows no {Na + K + Mg}-surplus. Figure 3 shows the location of the samples on a Piper diagram. Samples K15 and K16 lie in the centre of the diagram and show no clear bias towards any cation or anion. All the other samples are biased towards Na⁺ and HCO₃⁻. Samples K15 and K16 represent infiltration water, while the rest of the groundwater samples are influenced by different reactions leading to a predominance of Na⁺ and HCO₃⁻. The NaHCO₃ water type in this study evolves as a result of weathering of alkaline igneous deposits. The trachytes and tuffs in the Nairobi area are part of a wider East African alkaline suite where strongly alkaline series are recognized and characterized by a dominance of sodium over potassium (Saggerson, 1991).

Table 1 Analytical results.

| Sample | pH | EC | Na ⁺ | K ⁺ | Ca ²⁺ | Mg ²⁺ | Fe ²⁺ | Mn ²⁺ | Cl ⁻ | SO ₄ ²⁻ | HCO ₃ ⁻ | CO ₃ ²⁻ | NO ₃ ⁻ | F ⁻ | Free CO ₂ |
|--------|-----|-----|-----------------|----------------|------------------|------------------|------------------|------------------|-----------------|-------------------------------|-------------------------------|-------------------------------|------------------------------|----------------|----------------------|
| K1 | 8.6 | 265 | 77.5 | 5.4 | 1.6 | 1.5 | 0.20 | 0.04 | 8 | 3.7 | 131.1 | 2.3 | 1.20 | 9.60 | 0 |
| K2 | 8.4 | 290 | 80.0 | 6.3 | 2.4 | 1.9 | 0.37 | 0.02 | 12 | 10.0 | 133.9 | 1.5 | 1.50 | 9.60 | 4 |
| K3 | 8.6 | 350 | 80.0 | 6.4 | 1.5 | 1.5 | 0.21 | 0.00 | 31 | 17.0 | 135.9 | 2.4 | 1.90 | 9.30 | 0 |
| K4 | 8.7 | 298 | 75.0 | 5.7 | 1.6 | 1.9 | 0.16 | 0.00 | 11 | 9.0 | 140.1 | 3.2 | 1.40 | 10.50 | 0 |
| K5 | 9.0 | 357 | 88.0 | 7.5 | 3.2 | 1.4 | 0.22 | 0.02 | 15 | 15.4 | 170.0 | 7.6 | 1.60 | 10.30 | 0 |
| K6 | 8.5 | 662 | 175.0 | 10.0 | 5.6 | 3.9 | 0.21 | 0.04 | 26 | 33.0 | 344.0 | 4.9 | 4.40 | 10.20 | 0 |
| K7 | 8.8 | 467 | 122.5 | 6.8 | 2.4 | 2.4 | 0.12 | 0.01 | 26 | 27.7 | 229.3 | 6.5 | 2.00 | 10.00 | 0 |
| K8 | 9.1 | 444 | 112.5 | 7.8 | 2.4 | 1.0 | 0.10 | 0.00 | 21 | 13.4 | 209.6 | 11.9 | 2.30 | 10.30 | 0 |
| K9 | 9.1 | 319 | 61.0 | 10.0 | 10.4 | 4.4 | 0.09 | 0.01 | 13 | 0.6 | 172.8 | 9.8 | 2.30 | 1.60 | 18 |
| K10 | 8.5 | 340 | 73.0 | 8.1 | 9.6 | 0.5 | 0.15 | 0.01 | 13 | 1.4 | 174.4 | 2.5 | 1.60 | 4.10 | 20 |
| K11 | 8.2 | 324 | 64.0 | 9.4 | 8.0 | 4.4 | 0.22 | 0.01 | 13 | 0.6 | 174.4 | 1.2 | 1.60 | 1.70 | 6 |
| K12 | 8.4 | 412 | 90.0 | 8.8 | 3.2 | 2.9 | 0.20 | 0.01 | 33 | 10.9 | 188.9 | 2.1 | 1.20 | 2.80 | 10 |
| K13 | 9.5 | 439 | 100.0 | 5.8 | 3.2 | 5.3 | 0.14 | 0.01 | 26 | 4.3 | 185.4 | 26.4 | 1.80 | 1.00 | 0 |
| K14 | 8.2 | 319 | 47.5 | 9.8 | 19.2 | 3.4 | 1.41 | 0.60 | 14 | 0.3 | 179.2 | 1.3 | 1.10 | 0.33 | 18 |
| K15 | 7.3 | 254 | 25.0 | 7.0 | 14.4 | 6.8 | 0.44 | 1.20 | 44 | 0.3 | 70.3 | 0.1 | 1.30 | 0.29 | 152 |
| K16 | 8.0 | 286 | 35.0 | 7.4 | 15.2 | 5.3 | 2.94 | 0.20 | 42 | 3.1 | 88.0 | 0.4 | 3.10 | 0.29 | 108 |

EC in $\mu\text{S}/\text{cm}$ and all concentrations in mg L^{-1}

Table 2 Stuyfzand classification and saturation index for calcite and fluorite.

| Sample | Stuyfzand ⁽¹⁾ | SI calcite ⁽²⁾ | SI fluorite ⁽²⁾ |
|--------|--------------------------|---------------------------|----------------------------|
| K1 | F*NaHCO ₃ + | -0.5 | -0.59 |
| K2 | F*NaHCO ₃ + | -0.51 | -0.42 |
| K3 | F*NaHCO ₃ + | -0.54 | -0.68 |
| K4 | F*NaHCO ₃ + | -0.39 | -0.53 |
| K5 | F*NaHCO ₃ + | 0.23 | -0.3 |
| K6 | F*NaHCO ₃ + | 0.26 | -0.12 |
| K7 | F*NaHCO ₃ + | 0.03 | -0.47 |
| K8 | F*NaHCO ₃ + | 0.25 | -0.46 |
| K9 | F*NaHCO ₃ + | 0.83 | -1.4 |
| K10 | F*NaHCO ₃ + | 0.3 | -0.57 |
| K11 | F*NaHCO ₃ + | -0.06 | -1.41 |
| K12 | F*NaHCO ₃ + | -0.26 | -1.39 |
| K13 | F*NaHCO ₃ + | 0.61 | -2.42 |
| K14 | F0NaHCO ₃ + | 0.32 | -2.45 |
| K15 | F0CaCl0 | -1.03 | -2.66 |
| K16 | F0NaHCO ₃ + | -0.26 | -2.64 |

⁽¹⁾ Stuyfzand (1986),

⁽²⁾ calculated with PHREEQC2 (Parkhurst & Appelo, 1999)

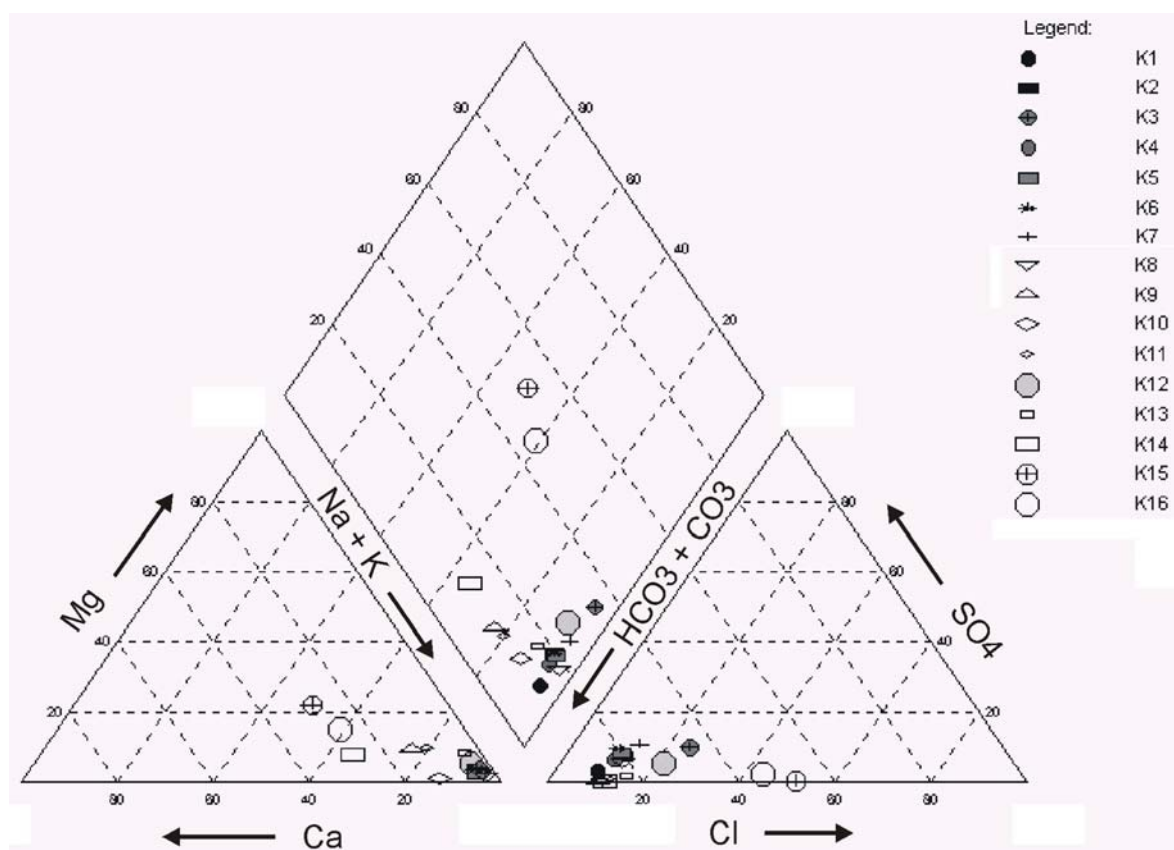


Fig. 3 Piper diagram with indication of the groundwater samples.

Figure 4 shows the evolution of different parameters along the direction of groundwater flow. The pH and TDS increase from the Kikuyu to the Industrial Area zone from 7.3 to 9.1 and from 166 to 458 mg L⁻¹, respectively (Fig. 4). The F⁻ concentration is very low in the Kikuyu zone and

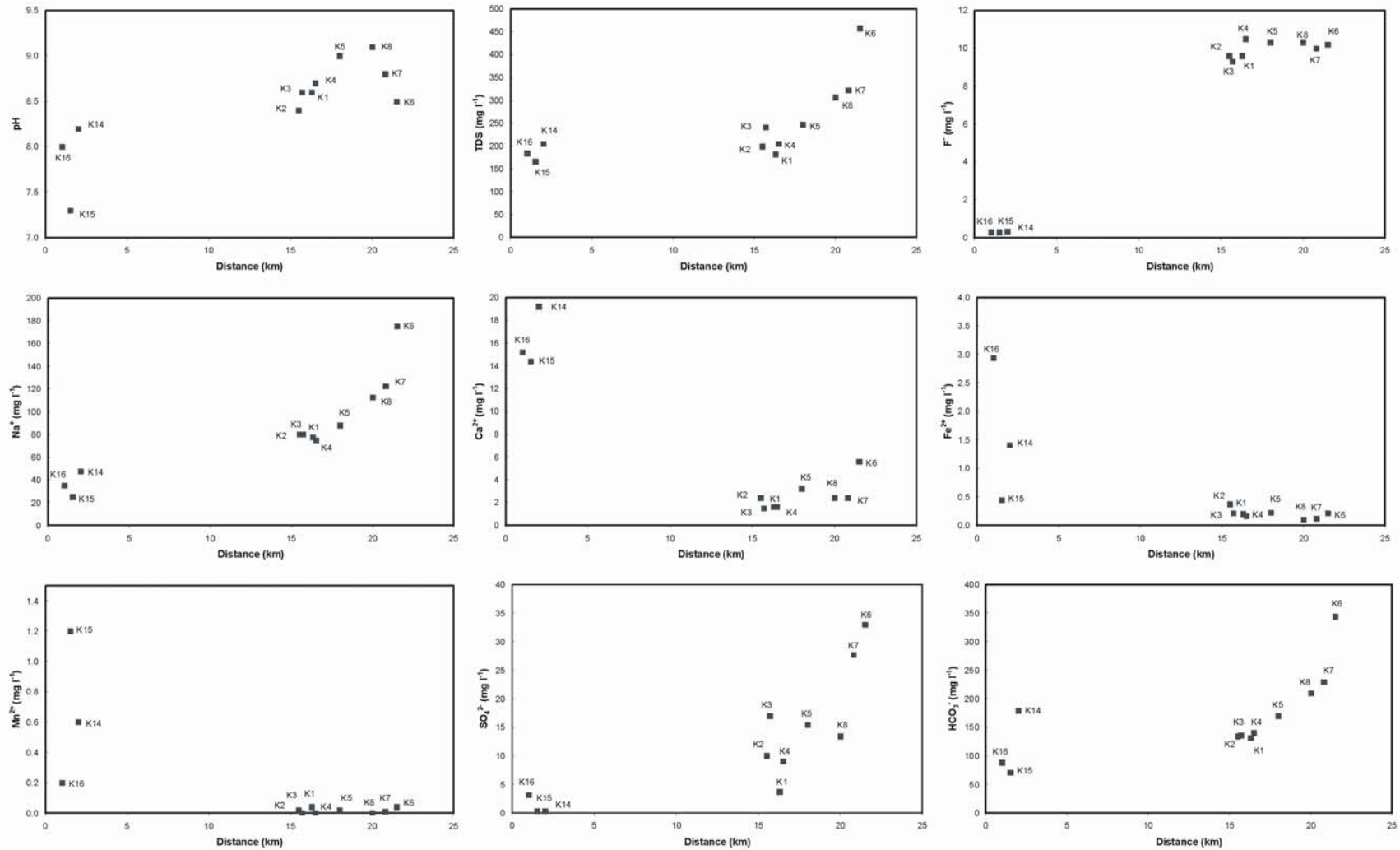


Fig. 4 Evolution of different parameters along the direction of groundwater flow (for location of the flow line see profile in Figs 1 and 2).

increases strongly, to more than 10 mg L⁻¹, in the City Centre and Industrial Area (Fig. 4). Sodium increases from 20 mg L⁻¹ in the Kikuyu zone to 175 mg L⁻¹ in the Industrial Area zone. Calcium, in contrast, decreases from 19.2 mg L⁻¹ in Kikuyu zone to 1.5 mg L⁻¹ in the Industrial Area zone. Iron and manganese both diminish along the direction of groundwater flow. A rise in sulphate and bicarbonate is observed along the flow line (Fig. 4).

If equilibrium with fluorite imposes a constraint on the groundwater composition, then water with a high natural Ca²⁺ concentration will generally contain a low F⁻ concentration, while groundwater with a low Ca²⁺ concentration will be rich in F⁻ (Appelo & Postma, 2005). Figure 5 shows cross-plots for Ca²⁺ vs F⁻, Na⁺ vs F⁻ and Ca²⁺ vs Na⁺. Three groups of samples can be observed on these cross-plots. The first group contains the samples K14, K15 and K16 with low F⁻ and Na⁺ concentrations and high Ca²⁺ concentrations. These samples were taken in the Kikuyu zone in the west of the study area and closest to the East African Rift Valley System. These samples correspond best to infiltration water. The Na⁺ and F⁻ contents are low, since groundwater has just infiltrated and not enough time has passed for the influence of mineral weathering of the volcanic rocks to be observed. The second group contains the samples K9–K13 from the Karen zone. These samples have intermediate Ca²⁺, Na⁺ and F⁻ concentrations. The third group of samples contains K1–K8 and is situated in the City Centre zone and the western Industrial Area zone. This third group is characterized by high F⁻ and Na⁺ and low Ca²⁺ concentrations. A clear evolution can be observed from the Kikuyu zone, closest to the recharge area, to the Karen zone and City Centre and Industrial Area zone. The F⁻ and Na⁺ concentrations in groundwater increase, while the Ca²⁺ concentration decreases.

The saturation state of minerals affecting the hydrochemistry of the study area is determined by use of the PHREEQC code. PHREEQC is a computer program for calculating the speciation and simulating chemical reactions and transport processes in natural or polluted water (Parkhurst & Appelo, 1999). The results of the saturation index (SI) calculations for calcite and fluorite are given in Table 2. Most groundwaters are close to saturation with respect to calcite and sub-saturated with respect to fluorite. The samples K14, K15 and K16 from the Kikuyu zone show a strong sub-saturation for fluorite with SI between -2 and -3. Samples from the City Centre and Industrial Area zone have a less negative saturation index, ranging between -1 and 0. Groundwater samples from the Karen zone have intermediary saturation indices for fluorite.

The cross-plots for Ca–F, Na–F and Ca–Na, combined with the calculated saturation indices for calcite and fluorite, suggest that the major source for F⁻ in groundwater in the Nairobi area originates from the dissolution of fluorite (CaF₂). Groundwater with low Ca²⁺ content is sub-saturated with respect to fluorite, and fluorite will have a tendency to dissolve. The cross-plots in Fig. 5 show that the low Ca²⁺ concentrations are coupled to high Na⁺ contents. Therefore, it seems reasonable to assume that the weathering of Na-feldspars is responsible for the decrease in Ca²⁺.

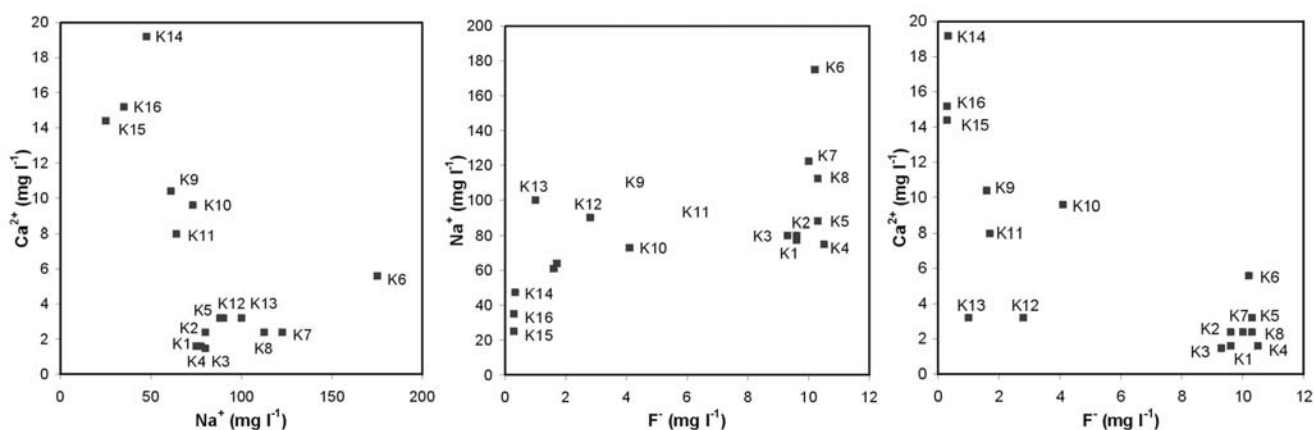


Fig. 5 Cross-plots for Ca²⁺, Na⁺ and F⁻.

Weathering of feldspars consumes protons and causes a rise in pH. Due to this pH increase, the equilibrium with CO_2 will no longer be attained, and more HCO_3^- and CO_3^{2-} will be produced while more CO_2 will dissolve. The increase in CO_3^{2-} results in calcite precipitation, as the solution becomes supersaturated compared to calcite. The precipitation of calcite causes a drop in Ca^{2+} , which makes the solution sub-saturated compared to fluorite. Fluorite will dissolve leading to elevated fluoride concentrations in groundwater. The increase in pH is also responsible for the decrease in iron and manganese (Fig. 4). At higher pH, $\text{Fe}^{2+/3+}$ and Mn^{2+} are no longer stable and will precipitate as oxides and hydroxides or as siderite (FeCO_3) and rhodochrosite (MnCO_3).

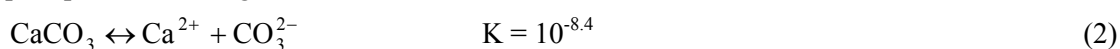
HYDROCHEMICAL MODEL

The hypothesis that fluoride comes into solution by means of weathering of Na-feldspars was modelled with PHREEQC in order to check the correctness of this assumption. The PHREEQC model is based on the equilibrium chemistry of aqueous solutions that react with minerals, gases, solid solutions, ionic exchangers and sorption surfaces; but it also offers the possibility to simulate kinetic reactions. The program produces speciation and saturation calculations, and one-dimensional transport calculations with reversible reactions, surface complexation, ionic exchange, irreversible reactions, kinetic controlled reactions, mixing of solutions and temperature exchange (Parkhurst & Appelo, 1999).

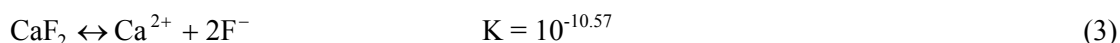
In the model, the reactions of Na-feldspar dissolution, CO_2 dissolution, calcite precipitation and fluorite dissolution are modelled in order to see the influence on the dissolved F^- concentrations in solution. The starting solution has a pH of 7 in which 1.0 mmol Ca^{2+} is dissolved until equilibrium with calcite is reached and 0.5 mmol C^{4+} until a pCO_2 of 10^{-2} is reached. Groundwater is brought to equilibrium with calcite and fluorite. A solution of 2.5 mmol Na-feldspar is weathered in 50 steps and, therefore, 2.5 mmol of H^+ is added in the model, as during the weathering of albite (e.g. to kaolinite) hydrogen is consumed during the reaction:



The Ca^{2+} concentration in groundwater is regulated by the calcite equilibrium. Because of the increase in pH and alkalinity, the equilibrium with calcite will no longer be attained and calcite will precipitate according to:



Thus, Ca^{2+} will be removed from the system. Due to the decrease in Ca^{2+} content, the equilibrium with fluorite will no longer be attained and fluorite will dissolve:



The dissolution of fluorite will lead to higher fluoride concentrations in the groundwater. In Fig. 6 the results of this model are shown. On the x -axis the Ca^{2+} concentration is plotted vs the F^- concentration and pH on the y -axis. Lines indicate the concentrations calculated with PHREEQC, the measured concentrations of the samples are indicated by dots. The calculated pH vs Ca^{2+} is indicated with a solid black line and shows good similarity with the measured values. The calculated Ca^{2+} vs F^- is plotted as the remaining lines on Fig. 6. The calculation was repeated for different saturation states of fluorite. The different lines show the calculations for a saturation index of 0, -0.25, -0.50, -0.75, -1.00 and -2.00. The dots represent the measured F^- vs Ca^{2+} . For each sample the saturation index vs fluorite obtained during the speciation calculations with PHREEQC is indicated. When the saturation index of the individual samples is compared to the model results, a good match is observed. The saturation state towards fluorite increases along the direction of groundwater flow. The samples of the Kikuyu zone have low saturation state compared to fluorite and this SI increases in the samples of the Karen zone and the Industrial Area and City Centre zone. This slow increase in saturation state shows that only small amounts of fluorite are available for dissolution as groundwater flows through the volcanic deposits.

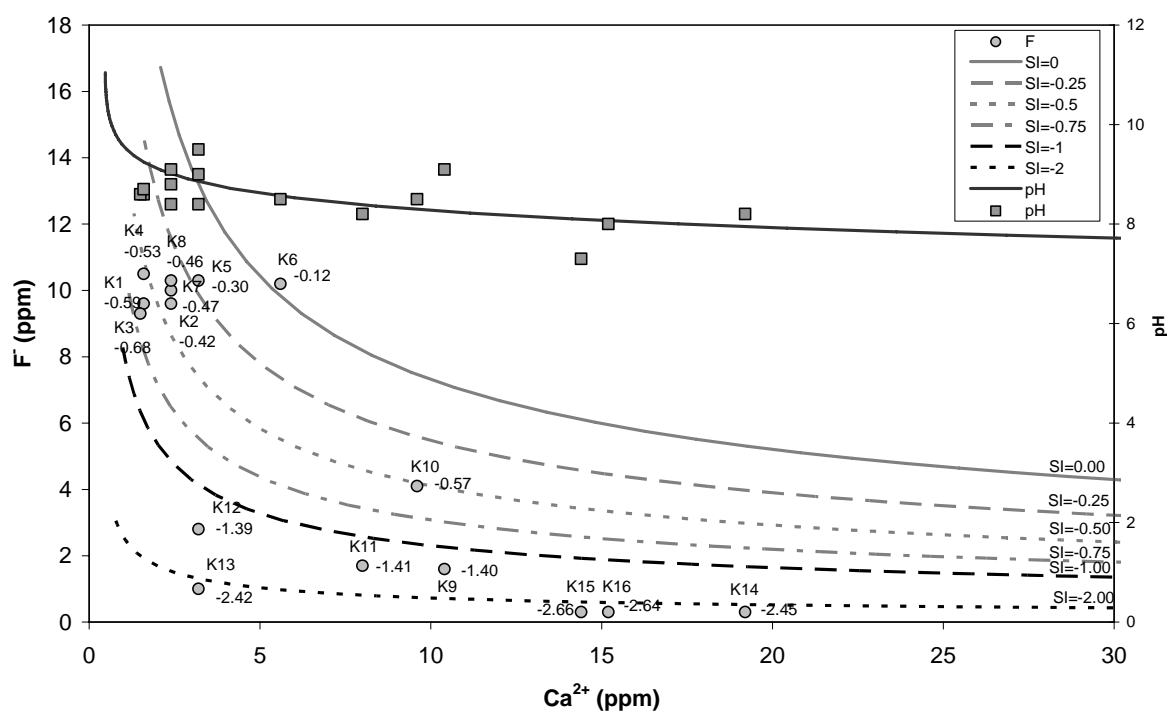


Fig. 6 Results of the PHREEQC modelling (lines) compared with the measured values.

CONCLUSIONS

Fluoride in the Nairobi area reaches concentrations far above the WHO guideline value of 1.5 mg L^{-1} (WHO, 1984). Areas with high fluoride have been identified and possible causes of excessive fluoride have been investigated. The F^- concentration increases along the direction of groundwater flow from the Kikuyu zone to the Industrial Area zone. High fluoride concentrations are linked to high sodium contents and pH, and low Ca^{2+} concentrations. The weathering of Na-rich volcanic rocks increases pH which in turn triggers the dissolution of CO_2 . The consequent increase in HCO_3^- and CO_3^{2-} causes oversaturation in the groundwater compared to calcite, leading to the precipitation of this mineral. This precipitation lowers the Ca^{2+} concentration in solution and leads to a sub-saturation for fluorite in the system. As a result, fluorite will dissolve and an increase in F^- concentration is observed. A hydrogeochemical model was constructed with the reactions aiming to verify the potential of the proposed reactions to account for the observed concentrations in groundwater of the Nairobi area. The results of this model showed good similarity with the observed concentrations in groundwater.

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