

2016-01-25

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Elisante, Eliapenda

Springer

DOI 10.1007/s12665-015-5015-1

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Assessment of sources and transformation of nitrate in groundwater on the slopes of Mount Meru, Tanzania

Eliapenda Elisante^{1,2} · Alfred N. N. Muzuka¹ 

Received: 7 August 2015 / Accepted: 21 September 2015
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Abstract The stable isotope compositions of nitrogen-nitrate ($^{15}\text{N-NO}_3^-$) and oxygen-nitrate ($^{18}\text{O-NO}_3^-$), and concentration of nutrients (NO_3^- , NH_4^+ , NO_2^- , PO_4^{3-}) for water samples collected from springs, shallow wells and boreholes during dry and wet seasons were used to investigate sources and biogeochemical transformation of NO_3^- in groundwater along the slopes of Mount Meru. About 80 % of all water sources had nitrate concentration higher than background concentration of 10 mg/l during both seasons, while NH_4^+ and NO_2^- concentrations were very low probably due to nitrification. Concentrations of NO_3^- above 50 mg/l were observed in some water sources. Concentrations of PO_4^{3-} in all groundwater sources were very low during the two seasons owing to dilution and adsorption. The $\delta^{15}\text{N-NO}_3^-$ for boreholes waters averaged $+11.6 \pm 2.1$ and $+10.7 \pm 2.1$ ‰ during dry and wet seasons, respectively. Similarly, the $\delta^{18}\text{O-NO}_3^-$ of borehole waters for the wet and dry seasons averaged $+5.2 \pm 1.3$ and $+4.6 \pm 1.9$ ‰, respectively. With regard to dug wells, the $\delta^{15}\text{N-NO}_3^-$ of well water averaged $+13.3 \pm 2.5$ and $+12.5 \pm 2.3$ ‰ during dry and wet seasons, respectively, while the $\delta^{18}\text{O-NO}_3^-$ for the wet and dry seasons averaged $+7 \pm 2.3$ and $+6.4 \pm 2.1$ ‰, respectively. The $\delta^{15}\text{N-NO}_3^-$, for springs averaged

$+11.2 \pm 2.2$ ‰ during dry season and $+11.7 \pm 3.5$ ‰ during wet season whereas the $\delta^{18}\text{O-NO}_3^-$ for the wet and dry seasons averaged $+7.3 \pm 3.6$ and $+5.9 \pm 2.6$ ‰, respectively. The isotopic data suggested that the source of NO_3^- in the water sources are dominated by sewage and/or animal manure and to less extent, soil organic N. Few samples collected in close proximity of manure heaps and sanitary facilities had $\delta^{15}\text{N}$ values between 16 and 20 ‰ suggesting occurrence of denitrification.

Keywords Groundwater · Nutrients sources · Biogeochemical transformations · Stable isotopes · Meru Tanzania

Introduction

There is an increasing demand for groundwater in Tanzania owing to rapid population growth, deterioration in quality and quantity of surface water, insufficient water supplies by water authorities, and effects of climate change (Mato 2002; Mjemah 2007; Rwebugisa 2008; Kashaigili 2012; Mtoni et al. 2013; Elisante and Muzuka 2015). Because of this, groundwater is the main source of water to about 70 % of inhabitants in Meru District Council, located on the slopes of mount Meru, Northern Tanzania (Meru District Council 2013). Although groundwater is considered to be available close to the point of use and always clean and safe, its quality is uncertain due to the natural processes and significant land use changes that do not take into account impacts in the underlying aquifers. This calls for determination of groundwater quality and identification of the contamination sources so as to understand the actual cause of water quality deterioration and coming up with water quality remediation and control mechanisms.

✉ Alfred N. N. Muzuka
alfred.muzuka@nm-aist.ac.tz

¹ Department of Water and Environmental Sciences and Engineering, School of Materials, Energy Water and Environmental Sciences (MEWES), Nelson Mandela African Institution of Science and Technology (NM-AIST), P. O. Box 447, Arusha, Tanzania

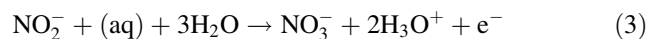
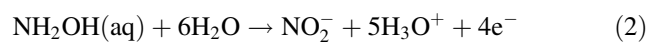
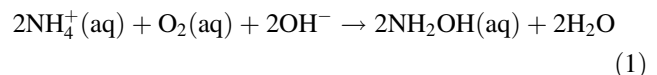
² Department of Physical Sciences, Faculty of Science, Sokoine University of Agriculture (SUA), P.O Box 3038, Morogoro, Tanzania

Nitrogen, phosphorus and potassium are essential to crop growth and can be provided through soil and/or added fertilizers. However, when available in excess to plant requirements, such nutrients may be leached to groundwater (Jalali 2005). Furthermore, wastewater may contain high values of such nutrients leading to groundwater contamination when discharged to the ground (Jalali 2005; Kiptum and Ndambuki 2012). Nitrogen occurs in the soil in the form of NO_3^- , NO_2^- , NH_4^+ , and organic nitrogen where the most readily available forms for plants are NO_3^- and NH_4^+ . Unless added, NO_2^- and NH_4^+ are always present in the groundwater at very low concentrations because they are immediately converted to NO_3^- or evaporated as NH_3 . In general, NO_3^- occurs in pristine groundwater at very low concentration ranging from below detection point to about 10 mg/l, the maximum background concentration (ECETOC 1988; Nishikawa et al. 2003; Wendland et al. 2005). Elevated concentration of NO_3^- in groundwater ranging from background concentration values to above 50 mg/l indicates contamination due to human activities (Wendland et al. 2005). Higher concentration of NO_3^- in water exceeding 50 mg/l leads to human health problems like gastric problems, decreased functioning of the thyroid gland, haemoglobinopathy and cancer due to formation of nitrosamines (WHO 2008; Gatseva and Argirova 2008).

Isotopic compositions of nitrogen-nitrate ($\delta^{15}\text{N}-\text{NO}_3^-$) and oxygen-nitrate ($\delta^{18}\text{O}-\text{NO}_3^-$) for nitrate from different sources often are distinct, and therefore offer a direct means of source and sink identification of nitrate in groundwater aquifers (Aravena et al. 1993; Aravena and Mayer 2010). Additionally, $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ can be used to retrieve NO_3^- transformation processes (Kendall 1998). For instance, the $\delta^{15}\text{N}-\text{NO}_3^-$ differs significantly between one generated biologically in soils and/or aquatic system and one formed chemically in the atmosphere. According to Kendall (1998) $\delta^{15}\text{N}$ of fertilizers ranges from -4 to $+4$ ‰ and averages $+2.75 \pm 0.76$ ‰, while that of atmospheric nitrate ranges from -15 to $+1$ ‰ and averages $+2.3 \pm 2.4$ ‰. Highly enriched $\delta^{15}\text{N}-\text{NO}_3^-$ values can be observed for manure and sewage, where the $\delta^{15}\text{N}-\text{NO}_3^-$ of manure ranges from $+10$ to $+22$ ‰ with mean value of $+14.4$ ‰, while that of sewage ranges from $+6.7$ to $+18.2$ ‰ with an average of $+11.1$ ‰ (Kreitler 1979). Other sources of nitrate in groundwater may include soil organic matter, with isotopic values ranging from 0 to $+8$ ‰ with average of $+4.9$ ‰ (Kreitler 1979; Aravena et al. 1993; Aravena and Mayer 2010) and $+3$ to $+9$ ‰ averaging 5.7 ‰ (Fogg et al. 1998).

Since the $\delta^{15}\text{N}-\text{NO}_3^-$ from different sources overlap, the use of $\delta^{18}\text{O}$ can disentangle sources of NO_3^- (Kendall et al. 2007). The $\delta^{18}\text{O}-\text{NO}_3^-$ fluctuates depending on

whether the source of oxygen is absolutely atmospheric, or a combination of groundwater oxygen and atmospheric oxygen. Atmospherically derived nitrate has relatively high $\delta^{18}\text{O}-\text{NO}_3^-$ usually ranging between $+20$ and $+70$ ‰ (Kendall 1998; Kendall et al. 2007). Synthetic nitrate fertilizers have $\delta^{18}\text{O}-\text{NO}_3^-$ ranging between $+18$ and $+26$ ‰ owing to fractionation during the manufacturing process (Silva et al. 2002). Theoretically, according to Casciotti et al. (2010) nitrification is a multistep reaction which consumes dissolved oxygen (DO) during the formation of hydroxyl amine, an intermediate product (Eq. 1). Water is the source of other two (2) oxygen atoms used during the formation of NO_2^- and NO_3^- (Eqs. 2, 3).



The $\delta^{18}\text{O}-\text{NO}_3^-$ produced by nitrification can be calculated using Eq. 4 (Aravena and Mayer 2010)

$$\delta^{18}\text{O} - \text{NO}_3^- = 2/3\delta^{18}\text{O} - \text{H}_2\text{O} + 1/3\delta^{18}\text{O} - \text{O}_2 \quad (4)$$

The $\delta^{18}\text{O}$ values of atmospheric O_2 is approximately $+23.88$ ‰ (Kroopnick and Craig 1972; Barkan and Luz 2003) while $\delta^{18}\text{O}-\text{H}_2\text{O}$ for the groundwater usually is negative and depends on elevation above sea level and geographic location (Casciotti et al. 2010). The $\delta^{18}\text{O}-\text{H}_2\text{O}$ value for Tanzania varies widely from place to place depending on elevation, distance from the ocean, etc. (Nkotagu and Mbwambo 2000; Mckenzie et al. 2010; Pittalis 2010). For example Nkotagu and Mbwambo (2000) reported the $\delta^{18}\text{O}-\text{H}_2\text{O}$ values ranging from -14.1 to $+3$ ‰ with an average of -2.9 ‰ around lake Tanganyika. Narrower range values (from -6.39 to -2.79 ‰) of $\delta^{18}\text{O}-\text{H}_2\text{O}$ were reported by Mckenzie et al. (2010) in Kilimanjaro close to mount Meru and Pittalis (2010) around mount Meru. Groundwater samples tend to have $\delta^{18}\text{O}-\text{NO}_3^-$ values between calculated minimum and maximum values (Aravena and Mayer 2010). In addition, a slight $\delta^{18}\text{O}-\text{NO}_3^-$ enrichment likely resulting from evaporation, respiration and transpiration may occur depending on the field conditions (Kendall 1998; Aravena and Mayer 2010).

Apart from source identification, $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ can be used as tools to trace biogeochemical transformations processes influencing concentration of nitrate in the groundwater (Silva et al. 2002; Kendall et al. 2007). While nitrification increases the concentration of nitrate in the groundwater, denitrification is the main process attenuating nitrate in contaminated waters (Aravena and Mayer 2010). Denitrification in the groundwater may be indicated

by an increase of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ by a ratio of about 2:1 (Panno et al. 2001; Pastén-Zapata et al. 2014). In addition, in the presence of reducing substances like organic carbon, the groundwater oxidised substances are reduced according to the following sequence; O_2 , NO_3^- , Mn(IV) , Fe(III) , SO_4^{2-} then HCO_3^- (Hiscock 2005). While nitrification process may continue until DO is very low (ca 0.3 mg/l), denitrification process occurs when levels of DO are less than 1 mg/l (Aravena and Mayer 2010; Pastén-Zapata et al. 2014).

In this study, nutrients contamination of the groundwater aquifers beneath areas with various human activities was investigated using different approaches. The present study utilised $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate dissolved in groundwater in combination with some chemical data like DO and concentrations of NO_3^- , NH_4^+ , NO_2^- , PO_4^{3-} to ascertain the sources and processes affecting nitrate concentration in the aquifers along the slopes of Mount Meru. The main objective of the study was to assess the nutrients contamination in groundwater and to ascertain sources, extent of pollution and biogeochemical transformation of nitrate to inform future management decisions for protecting groundwater quality.

Methodology

Description of the study area

The study was conducted along the slopes of Mount Meru in two administrative wards of Akeri and Kikwe, and Usariver Township (Fig. 1). These wards are located within the Meru district council, Arusha, Tanzania (Fig. 1). The population of the study area is unevenly distributed with high population density found on the highlands (Akeri and Usariver; Fig. 1). According to the Population and Housing Census of 2012, Akeri ward has a population of 13,699, Kikwe 10,795 and Usa River township, 23,437 (NBS and Office of Chief Statistician Zanzibar 2013). On average Meru District Council has a population growth rate of 3.1 % and a population density of 228 inhabitants per square kilometres (inh./Km^2) (Meru District Council 2013), which is four times higher than the national population density of 51 inh./Km^2 (NBS and Office of Chief Statistician Zanzibar 2013). Such population density is expected to increase pressure over water resources.

Agriculture and livestock keeping are the primary livelihood activities in the study area. Small holder agriculture includes maize, sweet potatoes and beans, while coffee farming is practiced in small scale and large scale. Commercial flower farming is also extensively undertaken in the area. In addition to small-scale agriculture, zero grazing animal (cattle, goats, sheep) husbandries are

practiced particularly on the highlands, where their manure is applied in the farms. These activities make use of the groundwater and river systems for irrigation purposes, both at small and large scale (Meru District Council 2013).

The study area suffers from poor water and sanitation services. Only 30 % of population receives safe and clean water while the remaining uses water of unknown quality (Meru District Council 2013). Pit latrines are the most used sanitation facilities. About 50,692 (88 %) out of 57,605 households in the District Council use pit latrines of varying depth while others use indiscriminate way of sanitation including open defecation (Meru District Council 2013). High density of pit latrines probably poses a risk to groundwater quality.

The lithology of Meru district is predominantly volcanic with patches of alluvial deposits (Wilkinson et al. 1983; Dawson 1992; Ghiglieri et al. 2010). The soils are well drained, dark sandy loams and relatively fertile with high moisture holding capacity (Meru District Council 2013).

Reconnaissance survey

Groundwater sources [boreholes (BH), shallow wells (W) and springs (S); Fig. 1] in the study area were identified and their precise locations were determined using hand-held Garmin global positioning system (GPS) and plotted on a map of Tanzania with ArcGIS version 10.1 software (ESRI, Redlands, Calif.). Together with location of the well, the information on the water sources such as elevation above the sea level, depth and hydraulic head was recorded.

Sample collection and pre-treatment

A total of 67 (14 boreholes, 31 shallow wells, and 22 springs) water samples were collected for analysis of nutrients and isotopic composition of NO_3^- ($\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$) during dry (August–October 2013) and wet (March–April 2014) seasons. Water samples from boreholes and wells having installed water pumps were collected after pumping for a sufficient time to ensure that the stagnant water in the borehole was replaced by fresh water from the aquifer. Sampling of water was carried out using a bailer in shallow wells without an installed pump. Groundwater samples for NO_3^- , NH_4^+ and NO_2^- , determination were collected using a 500-ml prewashed, high-density polyethylene (HDPE) bottles while those for PO_4^{3-} determination were collected using 500-ml amber glass bottles. Samples for $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ determination were collected in 100-ml high-density polyethylene (HDPE) bottles. The samples were transported while in ice-cold containers to the Ngurdoto Defluoridation Water Research laboratory (NDWRL), Arusha for preparation

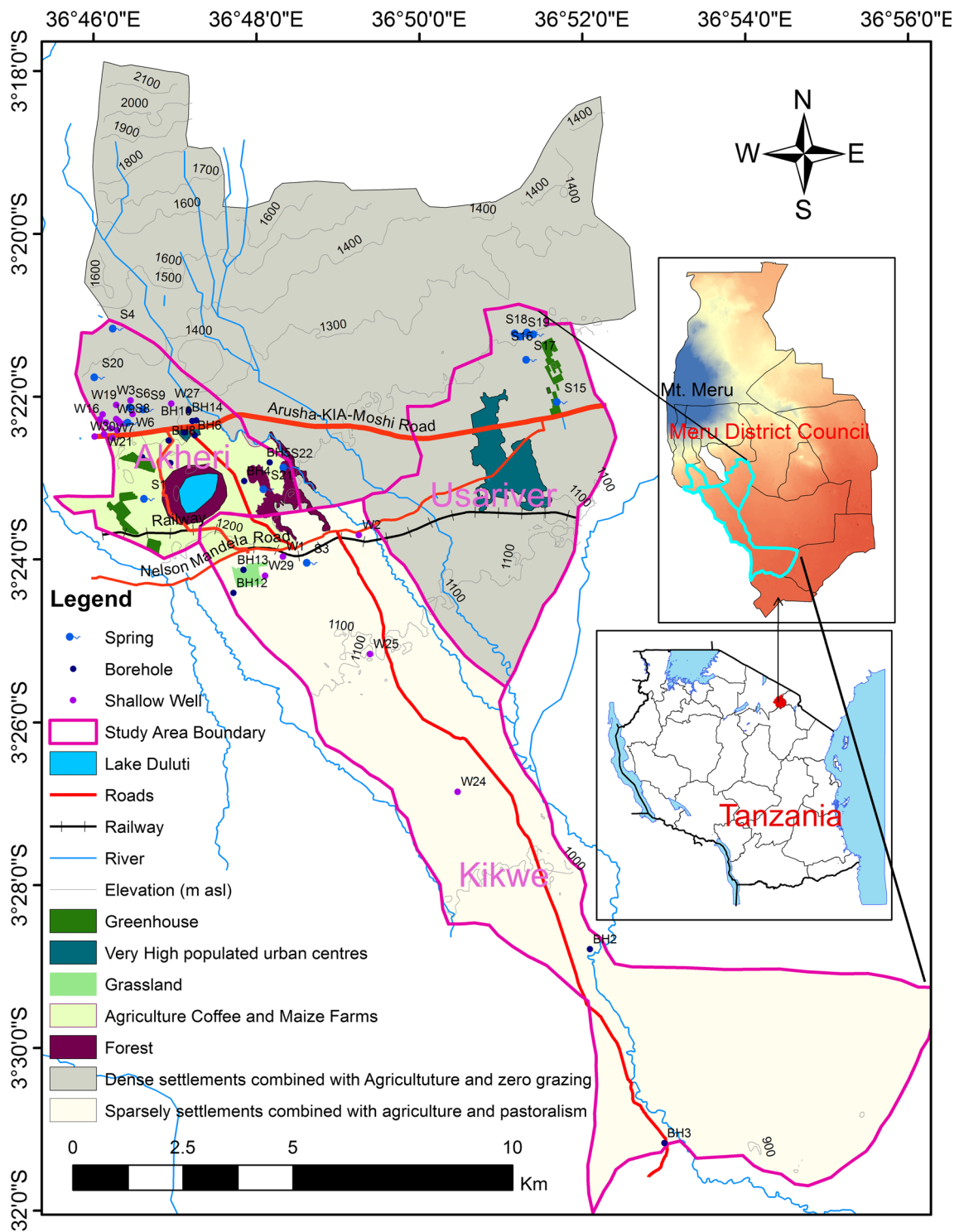


Fig. 1 Map of the study area

and analysis within 6 h of collection. Onsite measurement of pH, temperature, conductivity (EC), dissolved oxygen (DO) and total dissolved solids (TDS) was carried out during sampling campaign using Eijkelpamp 18.52.SA Model pH/mV/EC/T/Sal/TDS/DO multimeter.

Pre-treatment and analysis of water samples

Determination of concentration of NH_4^+ , NO_3^- , NO_2^- and PO_4^{3-} , utilised HACH spectrophotometer (Model DR/2400, USA) at the NDWRL. For each season, 30 samples

from different water sources (10 boreholes, 11 shallow wells and 9 springs) with detectable NO_3^- concentration were randomly selected for $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ determination. Nitrate was removed using sulphamic acid according to Granger and Sigman (2009) then filtered, frozen in 30-ml HDPE bottles before shipping to US for analysis. The $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ were determined by gas chromatography/isotope ratio mass spectrometry (GC/IRMS) with online cryo-trapping at the Stable Isotope Facility at the University of California Davis, California, USA. Isotopic analysis was done after the quantitative conversion of NO_3^- into N_2O using denitrifying bacteria that lacked an active N_2O reductase (Granger and Sigman 2009).

Data analysis

The sources and transformation processes of nitrate in the groundwater were inferred using isotopic values of nitrogen-nitrate and oxygen-nitrate. Theoretical $\delta^{18}\text{O}-\text{NO}_3^-$ of groundwater in the study area was estimated using Eq. 4 as per Aravena and Mayer (2010). Estimation of $\delta^{18}\text{O}-\text{H}_2\text{O}$ in the groundwater was done using a minimum of -6.39‰ and maximum of -2.79‰ values (Pittalis 2010; McKenzie et al. 2010). To ascertain the sources and transformation

processes of nitrate in the groundwater, the isotopic values were compared with some reported chemical data from the same water sources.

Statistical analysis

STATISTICA™ StatSoft8.0 software was used to perform all statistical analyses. Means, standard deviation and standard error were calculated for different parameters, and where appropriate, significant relationships between different parameters were studied using multiple correlations. Significant differences between means were determined using multivariate analysis of variance.

Results

Concentration of nutrients in the groundwater

Groundwater quality varied from place to place, type of water source (boreholes, shallow wells or springs) and depth. Ammonium (NH_4^+) concentration in shallow wells, which averaged 0.09 ± 0.20 and 0.14 ± 0.24 mg/l during dry and wet seasons, respectively, was highest relative to other sources (Fig. 2a). Borehole waters had the lowest

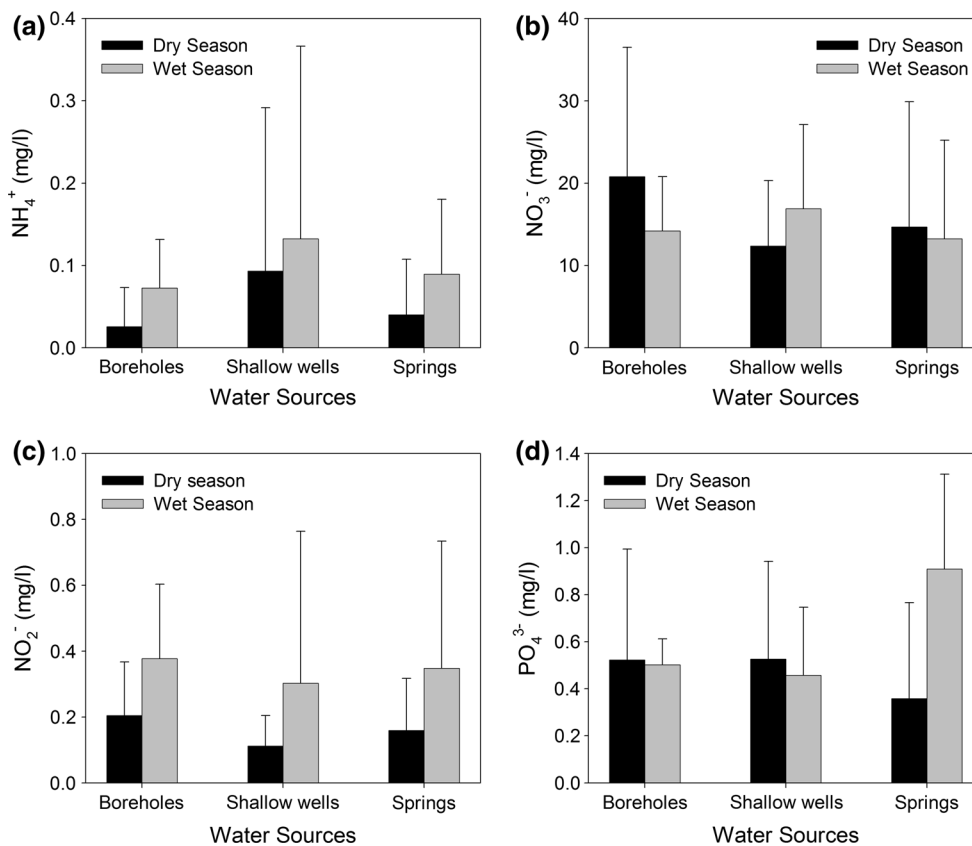


Fig. 2 Mean concentrations of various nutrients **a** NH_4^+ , **b** NO_3^- , **c** NO_2^- and **d** PO_4^{3-}

NH_4^+ concentration during both wet and dry seasons which averaged 0.03 ± 0.05 and 0.07 ± 0.06 mg/l, respectively (Fig. 2a). The NH_4^+ concentration for springs averaged 0.04 ± 0.07 mg/l during dry season and 0.06 ± 0.07 mg/l during wet season. The concentration of NH_4^+ in all water sources during the two seasons was very far below 6.1 mg/l, the maximum value recommended for irrigation water by FAO (Ayers and Westcott 1994). In the boreholes NH_4^+ concentration displayed a slight decreasing trend while in the shallow wells it displayed a slight increasing trend to about 15 m deep then started to decrease (Fig. 3a, b). Generally, concentration of NH_4^+ during the dry season in all water sources was relatively lower than respective concentration during wet season although such difference was not statistically significant ($p < 0.05$) (Fig. 2a; Table 1).

The NO_3^- concentration in water samples collected from all water sources during the two seasons ranged from below detection limit to above 50 mg/l, the maximum recommended value for drinking water according to WHO (2008). The highest average concentration of NO_3^- was observed in boreholes during the dry season (Fig. 2b). Concentration of NO_3^- for the boreholes averaged 20.77 ± 15.72 mg/l during dry season and 14.20 ± 6.57 mg/l during wet season, while for shallow wells it averaged 12.35 ± 7.94 and 17.41 ± 9.96 mg/l during dry and wet seasons, respectively (Fig. 2b). The NO_3^- concentration for spring averaged 14.68 ± 15.20 mg/l during dry season and 15.25 ± 21.93 mg/l during wet season. In general, the concentration of NO_3^- was high during the dry season in water samples collected from boreholes and springs (Fig. 2b). In contrast, the concentration of NO_3^- was high during wet season in water samples collected from shallow wells (Fig. 2b). Generally, most samples had NO_3^- concentration less than 50 mg/l except in one borehole (BH14) and two springs (S5 and S22) during the dry season and one spring (S5) during wet season which had higher values. Furthermore, most of water sources had NO_3^- levels higher than background concentration of 10 mg/l. Similar to NH_4^+ concentration, NO_3^- concentration in the boreholes displayed a slight decreasing trend while in the dug wells it displayed a slight increasing trend to about 15 m deep then started to decrease (Fig. 3c, d).

NO_2^- concentration for boreholes averaged 0.20 ± 0.16 mg/l during dry season and 0.38 ± 0.23 mg/l during wet season. In the water samples collected from shallow wells, NO_2^- averaged 0.11 ± 0.09 and 0.31 ± 0.47 mg/l during dry and wet seasons, respectively, while for springs it averaged 0.16 ± 0.16 mg/l during dry season and 0.35 ± 0.57 mg/l during wet season. The concentration of nitrite was lower than 3 mg/l, the maximum recommended concentration for drinking water

according to WHO (2008). Concentrations of NO_2^- in all water sources were significantly higher ($p < 0.05$) during wet season than during dry season (Table 1; Fig. 2c). Similar to NH_4^+ and NO_3^- , concentration of NO_2^- in the boreholes displayed a slight decreasing trend while in the dug wells it displayed a slight increasing trend to about 15 m deep then started to decrease (Fig. 3e, f).

The PO_4^{3-} concentration for springs, which averaged 0.36 ± 0.41 and 0.84 ± 0.52 mg/l during the dry and wet seasons, respectively, was highest during the wet season and lowest during the dry season relative to other sources (Fig. 2d). The PO_4^{3-} concentration for boreholes averaged 0.52 ± 0.47 mg/l during dry season and 0.5 ± 0.11 mg/l during wet season, while it averaged 0.47 ± 0.29 mg/l during dry season and 0.53 ± 0.42 mg/l during wet season for shallow wells (Fig. 2d). The PO_4^{3-} concentration in the boreholes lacked variation with depth, while it displayed slight increase with depth for the shallow wells during both seasons (Fig. 3g, h). Multivariate analysis of variance displayed significant difference ($p = 0.01$) of PO_4^{3-} concentration in different water sources and different seasons (Table 1). Post hoc test showed that concentration of PO_4^{3-} was significantly higher ($p = 0.017$) in springs during wet seasons than during dry season (Fig. 2d; Table 1). Furthermore, the concentration of PO_4^{3-} was significantly higher ($p = 0.014$) in springs during wet seasons than in shallow wells during the same season (Table 1).

The $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ values of groundwater nitrate

The $\delta^{15}\text{N}\text{-NO}_3^-$ values in most of water sources were above 10 ‰, with shallow wells and boreholes having higher δ -values during dry season than during wet season (Figs. 4, 5a). High enrichment in $\delta^{15}\text{N}\text{-NO}_3^-$ values (higher than 18 ‰) was observed in W21 and S6 during the two seasons (Figs. 4, 6a, b). Furthermore, few samples plotted within a range indicating nitrification of soil N (Fig. 6a, b).

The theoretical $\delta^{18}\text{O}\text{-NO}_3^-$ values calculated as per Eq. 4 (Aravena and Mayer 2010) using $\delta^{18}\text{O}\text{-H}_2\text{O}$ values reported by McKenzie et al. (2010) in Kilimanjaro close to mount Meru and Pittalis (2010) around mount Meru ranged between +3.7 and +6.1 ‰. Most of observed $\delta^{18}\text{O}\text{-NO}_3^-$ values lied within the calculated values (Figs. 4, 5, 6). Exceptionally high $\delta^{18}\text{O}\text{-NO}_3^-$ values were observed in groundwater samples from BH13, W21, S1 and S6 during the two seasons and S9 during the dry season (Figs. 4, 6c, d). Most of groundwater samples with elevated NO_3^- concentration plotted in area consistent with nitrification (Fig. 6c, d).

A plot of $\delta^{15}\text{N}\text{-NO}_3^-$ (‰) versus $\delta^{18}\text{O}\text{-NO}_3^-$ (‰) showed that isotopic values of dissolved NO_3^- for all water sources during the dry and wet seasons were a result of

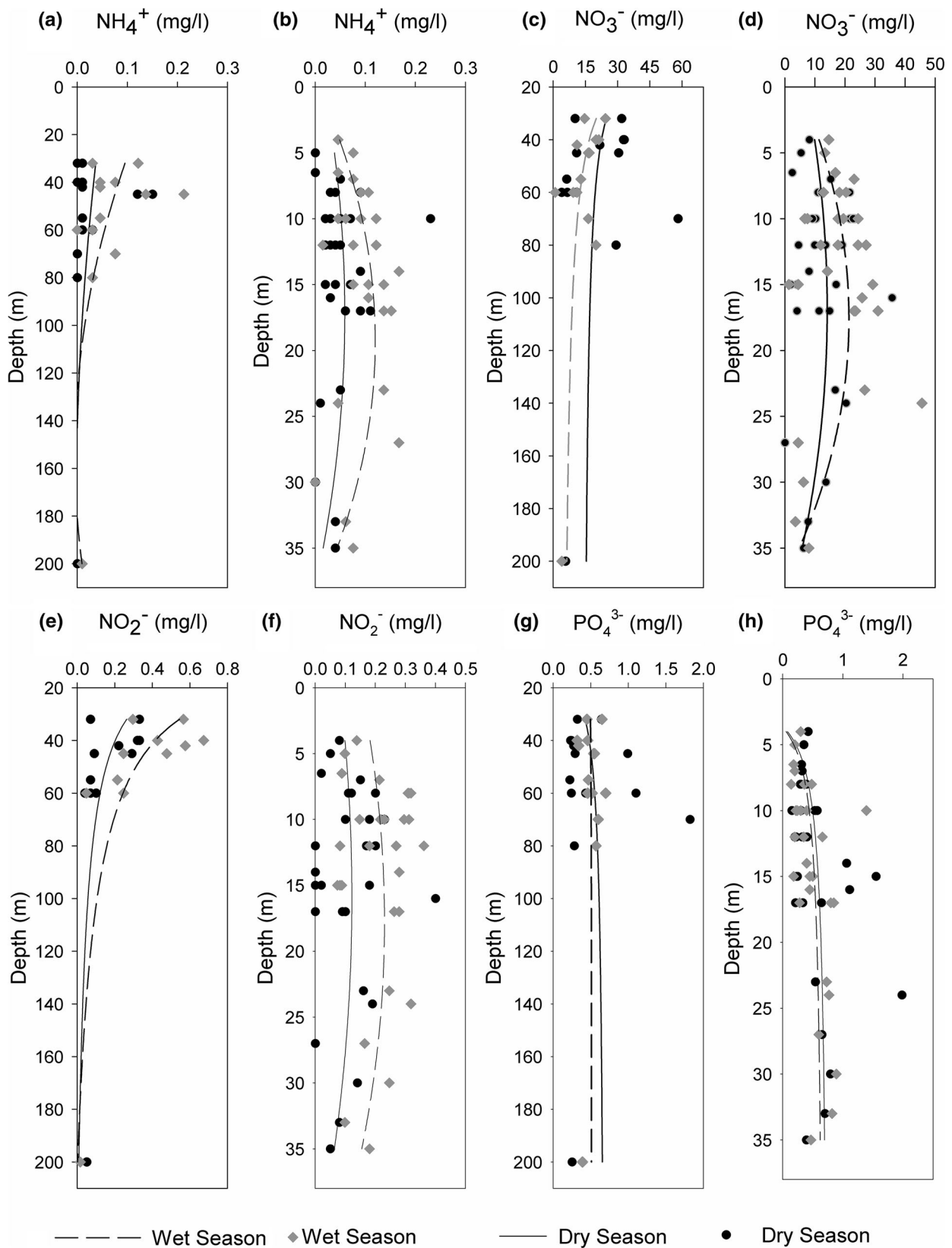


Fig. 3 Variation of depth (m) against concentration of (a) NH_4^+ (mg/l) in boreholes, (b) NH_4^+ (mg/l) in the shallow wells, (c) NO_3^- (mg/l) in boreholes, (d) NO_3^- (mg/l) in shallow wells, (e) NO_2^- (mg/l) in boreholes, (f) NO_2^- (mg/l) in shallow wells (g) PO_4^{3-} (mg/l) in boreholes and (h) PO_4^{3-} (mg/l) in shallow wells

Table 1 Main effects and interactions of the independent variables (seasons and water sources) on studied parameters in multivariate analysis of variance tests

Parameter	Water sources					Seasons					Water sources × seasons				
	<i>df</i>	<i>SS</i>	<i>F</i>	<i>p</i>	S/NS	<i>df</i>	<i>SS</i>	<i>F</i>	<i>p</i>	S/NS	<i>df</i>	<i>SS</i>	<i>F</i>	<i>p</i>	S/NS
NH ₄ ⁺	2	0.07	1.64	0.20	NS	1	0.06	2.98	0.09	NS	2	0.02	0.42	0.66	NS
NO ₃ ⁻	2	204.27	0.82	0.44	NS	1	27.11	0.22	0.64	NS	2	626.03	2.52	0.09	NS
NO ₃ ⁻	2	0.24	3.40	0.04	S	1	0.56	16.21	0.00	S	2	0.02	0.24	0.79	NS
PO ₄ ⁴⁻	2	0.61	1.76	0.18	NS	1	0.54	3.09	0.08	NS	2	1.60	4.61	0.01	S

S significant, NS not significant, *df* degree of freedom, *SS* sum of squares, *F* *F* value, *p* *p* value

nitrification of manure and/or sewage-derived nitrate (Fig. 7). The groundwater sample from BH3 and S14 showed to be influenced by nitrification of NH₄⁺ from soil N during the two seasons (Fig. 7). Furthermore, groundwater samples from the BH2 during dry and wet season and S14 during the wet season showed mixing of water NO₃⁻ resulting from nitrification of NH₄⁺ from soil N and sewage/manure (Fig. 7). Similarly, groundwater samples from S1 and S9 during the dry season and S1 and BH13 during the wet season showed mixing of water contaminated with NO₃⁻ fertilizers and that resulting from nitrification of NH₄⁺ from soil N and/or sewage/manure (Fig. 7). Only two groundwater samples from W21 and S6 during the dry and wet season fell into a denitrification zone (Fig. 7) and showed a slope of about 0.5.

Discussion

Concentration of nutrients in the groundwater

The very low total concentration of ammonia (NH₃ and NH₄⁺) and NO₂⁻ observed in this study (Fig. 2) can be attributed to the nitrification process owing to existing oxic conditions of the groundwater. Rapid nitrification in the aquifers normally proceed until DO is about 0.3 mg/l (Aravena and Mayer 2010; Pastén-Zapata et al. 2014). Furthermore, in acidic to neutral water condition, the equilibrium reaction favours dominance of NH₄⁺ over NH₃ species (USEPA 2013). Therefore, the prevailing near-neutral pH in all groundwater samples collected from the study area, favoured occurrence of NH₄⁺ species. This is good news since dissolved NH₃ is toxic to aquatic organisms at very low concentration relative to NH₄⁺ which is relatively harmless.

Concentration of NH₄⁺ in the shallow wells was generally higher than in springs and boreholes probably due to proximity of shallow wells to contaminant sources (pit latrines, farms and cowsheds) compared to other sources. It is very likely that more contaminants like NH₄⁺ took less

time to reach the shallow wells before being oxidised. Furthermore, groundwater concentration of NH₄⁺ and NO₂⁻ increased with rise in water levels during the wet season and decreased with receding water levels during the dry season. Generally, during wet season, the groundwater is rapidly recharged and hence, there is an increased propensity for NH₄⁺ and NO₂⁻ leaching. The rising of groundwater level leads to dissolution of nitrogenous compounds such as NH₄⁺, NO₂⁻ and NO₃⁻ accumulated in the organic wastes like manure heaps and pit latrines during the preceding dry season, therefore, elevating their concentration during wet season.

In the study area, the main source of PO₄³⁻ identified was anthropogenic activities such as detergents, inorganic fertilizers and manure. Significantly high concentration of PO₄³⁻ in springs during wet season than dry season was likely a result of mixing of groundwater with rain water infiltrating through soils enriched with industrial fertilizers during the growing season. Most springs are located in the northeastern part of the study area where small-scale farming with intense fertilizer utilisation is practiced (Fig. 1). However, very low concentrations of PO₄³⁻ in the wells and boreholes (Fig. 2d) could be attributed to adsorption and precipitation. PO₄³⁻ are retained in soil by adsorption on clays and metal oxides particularly iron oxide. Adsorption of dissolved PO₄³⁻ by iron oxides is facilitated by aerobic condition of water and low pH (<7). General aerobic conditions and slightly low pH observed in all water sources probably favoured adsorption of PO₄³⁻. However, composition of iron oxide in the soil and aquifer material was not determined. Furthermore, PO₄³⁻ can be precipitated as FePO₄ at low pH, AlPO₄, around neutral pH and apatite Ca₅(PO₄)₃(OH) at high pH (Agca et al. 2014).

There is no WHO maximum permissible recommended for PO₄³⁻ mainly because of its low solubility (Agca et al. 2014). The Food standard Agency (2003) recommended 6.75 mg/l as a maximum drinking water concentration for PO₄³⁻. Conversely, FAO recommended maximum limit for irrigation water of 6.13 mg/l (Ayers and Westcot 1994). However, similar to findings by Ağca et al. (2014), all

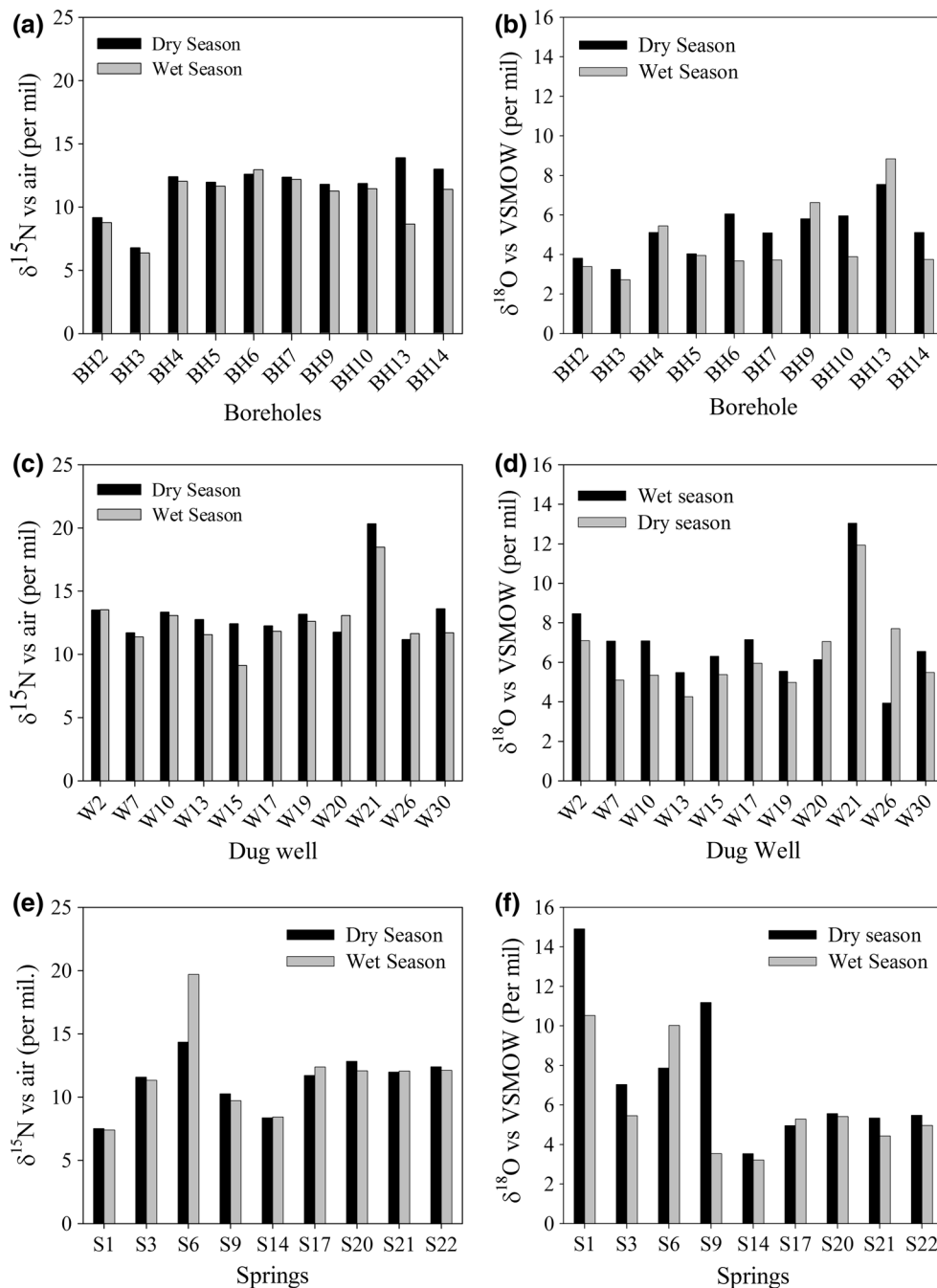


Fig. 4 The $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ values in groundwater samples collected from boreholes, shallow wells and springs during the wet and dry seasons

groundwater samples were very far below these maximum limits. Furthermore, if groundwater discharged to surface water can raise a PO_4^{3-} concentration of the surface water to 30 $\mu\text{g/l}$ or higher, eutrophication will occur (Jørgensen 2000).

There is no known geological source of NO_3^- in the study area; therefore, its detection in the groundwater samples at a level higher than the background

concentration ($>10\text{ mg/l}$), probably resulted from anthropogenic activities. In the study area, elevated nitrate concentration in the groundwater was likely a result of high density of pit latrines and manure application in small farms observed in the study area (Elisante and Muzuka, under preparation). The NO_3^- concentration in BH14 (58.1 mg/l) and S22 (58.4 mg/l) during the dry season, and S5 during dry season (56.7 mg/l) and wet season (102 mg/l)

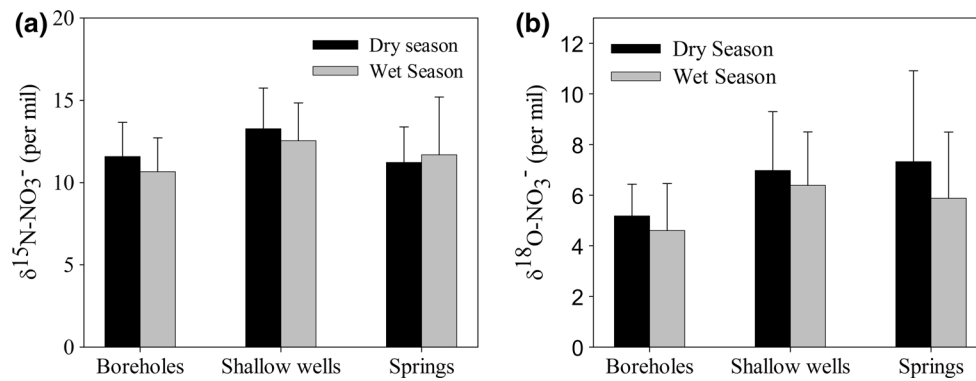


Fig. 5 Seasonal variability in the levels of (a) $\delta^{15}\text{N-NO}_3^-$ (‰) and (b) $\delta^{18}\text{O-NO}_3^-$ (‰), in various water sources

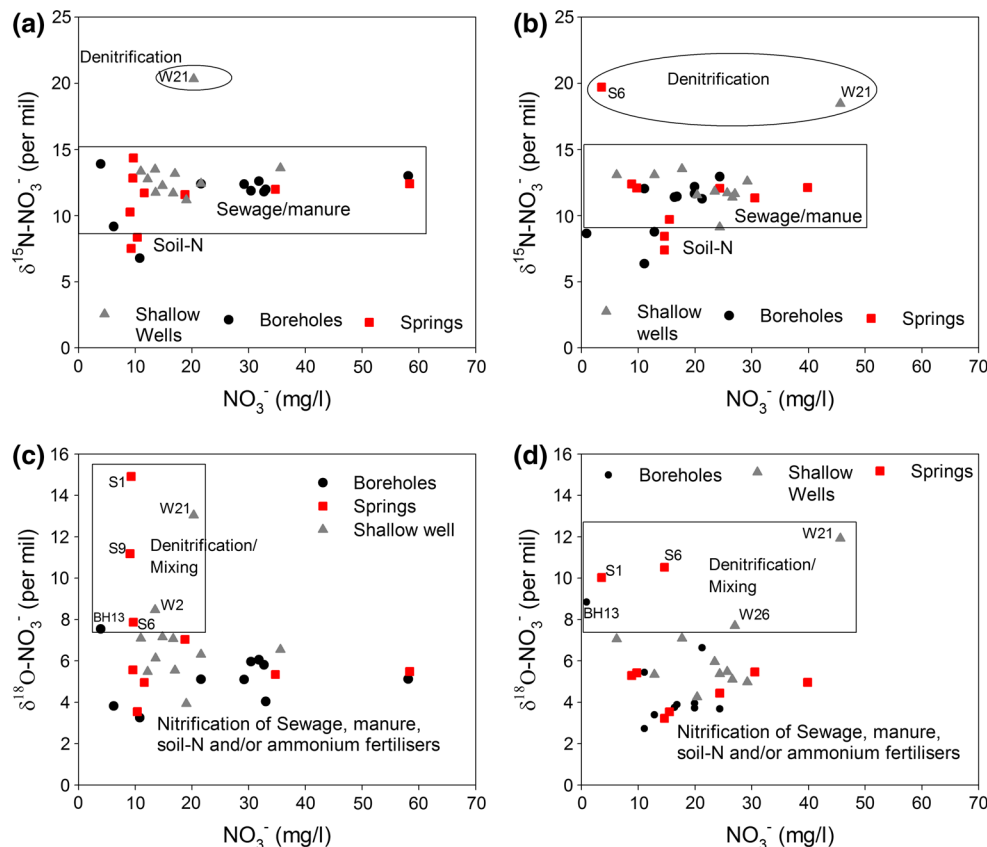


Fig. 6 Isotopic values of dissolved NO_3^- against nitrate concentration during the dry and wet season

l) was higher than 50 mg/l indicating not suitable for drinking. The spring, S5 was surrounded by commercial horticultural production where commercial fertilizers are highly used while BH14 and S22 were located downstream of highly populated residential areas (Fig. 1). Such NO_3^- -rich waters were very likely discharged into surface water reservoirs possibly distressing aquatic ecosystems.

Although the concentration of NO_3^- in groundwater from the study area was elevated due to human activities, it was lower than values reported in other areas of Tanzania.

For example, NO_3^- concentration of up to 441.1 mg/l was reported in Dodoma (Nkotagu 1996; Rwebugisa 2008), up to 477.6 mg/l reported in Dar es Salaam (Mtoni, et al. 2013), above 100 mg/l reported in Tanga (GITEC and WEMA 2011) and about 180 mg/l in Manyara (Bowell et al. 1997). However, in this study, most of groundwater samples had NO_3^- concentration lying between 6.2 and 33.14 mg/l, the range reported by Panno et al. (2001) in Illinois, USA. The concentration of NO_3^- in deep or protected water sources which ranged from below detection to

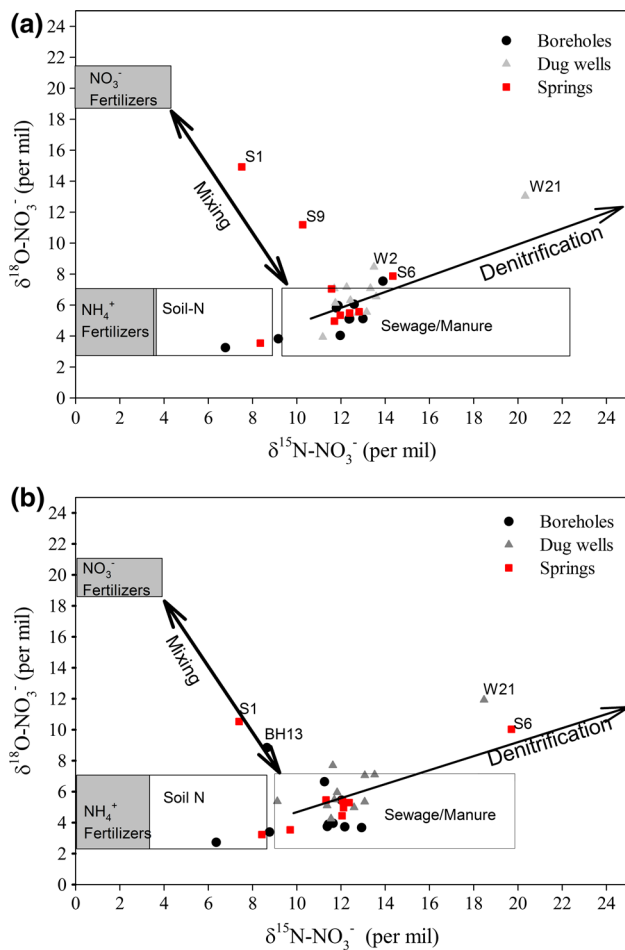


Fig. 7 $\delta^{15}\text{N-NO}_3^-$ vs $\delta^{18}\text{O-NO}_3^-$ values for groundwater samples collected from boreholes, shallow wells and springs during (a) dry and (b) wet seasons

<5 mg/l during dry and wet seasons was lower than values reported by Choi et al. (2007) for the uncontaminated natural area in rural areas of Korea which ranged from 1.33 to 20.77 mg/l. Concentrations NO_3^- in groundwater samples from shallow wells was generally higher during wet season than during dry season similar to results reported by Pittalis (2010) in northern side of Mount Meru. However, values reported in this study during wet season were generally lower than those reported by Pittalis (2010) during the same season. While in this study, 3 and 1 out of 67 groundwater sources during dry and wet seasons, respectively, exceeded 50 mg/l, the maximum recommended level for drinking water (WHO 2008), Pittalis (2010) reported that 2 out of 26 sources exceeded this level. The average concentration of NO_3^- in groundwater sources in the study area was higher than the values reported by Ağca et al. (2014) in Amik Plain (Turkey) which averaged 2.9 mg/l where concentration of NO_3^- in 12 out of 92 groundwater sources was higher than values recommended by WHO. In the study by Kiptum and Ndambuki (2012) in

Langas, Kenya, concentration of NO_3^- in more than 60 % of groundwater sources exceeded permissible values recommended by WHO.

The $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ have been used to identify various sources of groundwater NO_3^- and to elucidate its transformation pathways (Böttcher et al. 1990; Komor and Anderson 1993; Aravena and Robertson 1998; Panno et al. 2001; Alva et al. 2006; Pastén-Zapata et al. 2014). The $\delta^{15}\text{N-NO}_3^-$ values varied from 6.8 to 20.3 ‰ and from 6.4 to 19.7 ‰ during dry and wet seasons, respectively (Figs. 4, 5) probably suggest more than one source of groundwater NO_3^- contamination. Elevated NO_3^- concentration (>10 mg/l) was associated with relatively high $\delta^{15}\text{N-NO}_3^-$ values that ranged between +9.1 and +20.3 ‰ (Fig. 6a, b). These values fall within the $\delta^{15}\text{N-NO}_3^-$ values for nitrate from manure (+10 to +20 ‰) and sewage (+9 and +19 ‰) (Kendall 1998; Aravena and Mayer 2010). Furthermore, elevated NO_3^- concentration was associated with $\delta^{18}\text{O-NO}_3^-$ values in most of groundwater samples ranging within the values reported for nitrate-rich groundwater beneath residential areas (Koh et al. 2009; Pastén-Zapata et al. 2014).

Groundwater samples from S14, BH2 and BH3 were characterised by a relatively low concentration of NO_3^- accompanied with relatively low $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values (Fig. 6, 7) indicating nitrate from soil N (Kendall 1998). Samples from BH3 and S14 with low NO_3^- concentration had relatively low $\delta^{15}\text{N-NO}_3^-$ values between +6 and +8 ‰ (Fig. 6), similar to a range reported for NO_3^- from soil N (Kendall 1998; Kendall et al. 2007; Aravena and Mayer 2010; Pastén-Zapata et al. 2014). Contribution of synthetic nitrogenous fertilizers that has $\delta^{15}\text{N-NO}_3^-$ values ranging from -4 to +4 ‰ (Kendall 1998) in this study is considered to be minimum owing to relatively observed higher $\delta^{15}\text{N-NO}_3^-$ values (Fig. 6). Human activities were limited close to these sources. The spring (S14), one of water supply sources was well protected and located more than 500 m radius from human activities while boreholes (BH2 and BH3) are located in sparsely populated areas, therefore less contaminated.

Mixing of waters of different concentrations and sources of NO_3^- , not only affects the nitrate concentrations but also it alters the isotopic values of nitrate in the predictive manner (Kendall 1998; Kendall et al. 2007; Aravena and Mayer 2010). For example, Rivett et al. (2008) reported that $\delta^{15}\text{N-NO}_3^-$ values between +6 and +10 ‰ indicated that a mixture of chemical fertilizers and manure was responsible for groundwater NO_3^- contamination. In this study, $\delta^{15}\text{N-NO}_3^-$ values probably indicating mixing of water with different sources of NO_3^- were observed in groundwater samples from the BH2 and BH14 during dry and wet season and BH13 during the wet season (Fig. 6a, b). In this study, the observed $\delta^{15}\text{N-NO}_3^-$ values between

+8 and +9.5 ‰ observed for BH2, BH13 and BH14 was likely a result of a mixing of waters with NO_3^- from sewage/manure and soil N. Furthermore, high $\delta^{18}\text{O}-\text{NO}_3^-$ values probably indicating mixing of waters with NO_3^- from different sources were observed in few samples (Fig. 6c, d). A plot of $\delta^{18}\text{O}-\text{NO}_3^-$ against $\delta^{15}\text{N}-\text{NO}_3^-$ can be used to identify mixture of water bodies with NO_3^- from different sources (Aravena and Mayer 2010). Groundwater samples from S1 and S9 during the dry season, and S1 and BH13 during wet season had relatively low $\delta^{15}\text{N}-\text{NO}_3^-$ and relatively high $\delta^{18}\text{O}-\text{NO}_3^-$ values (Fig. 7), indicating mixture of waters contaminated with sewage/manure and nitrate fertilizers. Such water sources were surrounded by coffee plantations and commercial horticultural production probably releasing nitrate fertilizers and sewage contaminated water to the underlying aquifers.

Biogeochemical transformation of NO_3^-

According to Aravena and Mayer (2010), the concentration of NO_3^- in water can be affected by several biogeochemical processes. Such processes can be divided into those which depletes nitrate like assimilation of NO_3^- by bacteria, denitrification, and dissimilatory nitrate reduction to NH_4^+ ; those which increases nitrate in water (e.g. nitrogen fixation and nitrification). Occurrence of dissimilatory nitrate reduction to NH_4^+ and assimilation of NO_3^- into bacterial biomass occurs at insignificant level in the subsurface environment (Rivett et al. 2008; Aravena and Mayer 2010). Similarly, uptake and assimilation by plants does not change significantly the isotopic composition of NO_3^- (Aravena and Mayer 2010).

Nitrification

Elevated levels of NO_3^- in most of water sources relative to other nitrogenous species such as $\text{NH}_3/\text{NH}_4^+$ and NO_2^- suggests that nitrification was a dominant process. Occurrence of nitrification can further exhibited by very low concentration of Mn and Fe and the observed oxic condition where DO level ranged from 1.7 to 7.2 mg/l (Elisante and Muzuka, under preparation). Nitrogenous organic compounds from different sources are firstly mineralised to NH_4^+ which is then oxidised (nitrified) by bacteria to nitrate (Casciotti et al. 2010). Such aerobic condition, may lead to accumulation of NO_3^- in the groundwater to a toxic level if there is no other processes which can attenuate its concentration. Elevated concentration of NO_3^- can be observed in aquifer systems underneath or in close proximity to anthropogenic activities such as agriculture, sanitation and/or waste disposal sites (Nishikawa et al. 2003). Nitrification process is

summarised by Eqs. 1–3 according to Casciotti et al. (2010). Nitrification can proceed rapidly even if DO is as low as 0.3 mg/l in groundwater (Aravena and Mayer 2010). Due to prevailing aerobic conditions, NO_3^- was the dominant nitrogen species in all groundwater sources in the study area (Fig. 1) owing to nitrification process. Similar observations have been reported elsewhere (Koh et al. 2009; Pastén-Zapata et al. 2014).

The $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ have been used elucidate NO_3^- transformation pathways (Böttcher et al. 1990; Komor and Anderson 1993; Aravena and Robertson 1998; Panno et al. 2001; Alva et al. 2006; Pastén-Zapata et al. 2014). The NO_3^- resulting from nitrification process is usually enriched in $\delta^{15}\text{N}-\text{NO}_3^-$ values owing to volatilisation of ammonia during the process (Kendall 1998). In the study area, elevated concentration of NO_3^- was associated with relatively high $\delta^{15}\text{N}-\text{NO}_3^-$ values that ranged between +9.1 and +20.3 ‰ (Fig. 6a, b). These values falls within the $\delta^{15}\text{N}-\text{NO}_3^-$ values for nitrate resulting from nitrification of NH_4^+ from manure (+10 to +20 ‰) and sewage (+9 and +19 ‰) (Kendall 1998; Aravena and Mayer 2010). Groundwater samples (BH3 and S14) with low NO_3^- concentration had relatively low $\delta^{15}\text{N}-\text{NO}_3^-$ values ranging between 6 and 8 ‰ (Fig. 6), which was within a range reported for NO_3^- resulting from nitrification of soil organic nitrogen (+3 to +8) (Heaton 1986; Pastén-Zapata et al. 2014). Additionally, nitrate resulting from nitrification of organic and ammonia fertilizers has low $\delta^{18}\text{O}-\text{NO}_3^-$ values which are variable depending on elevation, climate and distance from the ocean (Aravena et al. 1993; Aravena and Mayer 2010). In this study, most samples had low $\delta^{18}\text{O}-\text{NO}_3^-$ which indicated nitrification (Figs. 6, 7).

Denitrification

Denitrification is the main mechanism which consumes nitrate in the subsurface environment (Rivett et al. 2008). Limited DO, presence of electron donors such as organic carbon, sulphides, Fe^{2+} , Mn^{2+} and suitable bacteria, are the main preconditions for denitrification (Korom 1992; Hiscock 2005; Tesoriero and Puckett 2011). Generally significant rate of denitrification occurs when DO concentration in the saturated zone is below 1 mg/l (Korom 1992; Pastén-Zapata et al. 2014). The generally high dissolved oxygen (DO > 1.5 mg/l) in all groundwater samples from all sources during the two seasons indicated insignificant denitrification (Kaown et al. 2009). However, denitrification process was localised to few sites that had high enrichment in $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ (Fig. 7).

High concentration of NO_3^- in groundwater may lead to health and environmental problems (WHO 2008; Rivett et al. 2008). Denitrification and dilution are the main

processes which can significantly lower the concentration of NO_3^- in the water sources (Aravena and Mayer 2010). Absence of denitrification may result into accumulation of nitrate in groundwater and/or discharge of nitrate-rich groundwater to the surface water, therefore, threatening aquatic ecosystems (Rivett et al. 2008).

Denitrification which occurs in a reducing condition (Panno et al. 2001; Rivett et al. 2008; Aravena and Mayer 2010) is associated with high fractionation factor leading to enrichment in the residue dissolved NO_3^- . Denitrification produces consistent enrichment in $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ values, and this trend has been used to evaluate denitrification in aquifers (Böttcher et al. 1990; Aravena and Robertson 1998; Panno et al. 2001; Silva et al. 2002; Alva et al. 2006). The chemical data (Elisante and Muzuka, under preparation) which showed high DO (>1.5 mg/l) and very low concentrations (<0.2 mg/l) of Mn and Fe in all groundwater samples generally preclude the occurrence of denitrification in the aquifers. Similar observations have been reported in groundwater beneath shrub-land and residential areas by some authors (Pastén-Zapata et al. 2014) but different from observation reported from strong reducing conditions (Panno et al. 2001).

Denitrification may occur under local reducing conditions in nitrate sources proximate to the water sources (Kaown et al. 2009; Pastén-Zapata et al. 2014). Relatively high $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ values (Figs. 6, 7) in groundwater samples (S6 and W21) were likely a result of local denitrification. The shallow well, W21 was located close (<10 m) to a soak away pit receiving organic carbon-rich wastewater from a commercial laundry and dry cleaner while S6 was located very close and downstream of manure heap. Due to closeness of sources of organic-rich wastes, probably local denitrification may have occurred at these two sites, leading to enriched isotopic values (Fig. 5). Additionally, this study observed that $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ values were relatively high during dry season than wet season in all water samples (Figs. 4, 5). Similar high isotopic values during dry season than during wet seasons were reported by Pastén-Zapata et al. (2014). Such slight enriched values are likely a result of local denitrification and/or volatilisation of ammonia during the dry season.

Conclusions

Results for 67 groundwater samples collected in two wards of Akeri and Kikwe, and Usa River Township, during dry and wet seasons showed that concentrations of NH_4^+ and NO_2^- were very low as a result of oxidation to NO_3^- . Concentration of NO_3^- in more than 80 % of the groundwater samples was above background level with few

samples exceeding 50 mg/l, the WHO permissible level for drinking water. Such concentration is caused by human activities particularly animal husbandry, application of animal manure in farms and use of onsite sanitation facilities like pit latrines.

Concentrations of PO_4^{3-} in all groundwater sources during the two seasons were very low owing to precipitation and adsorption. The isotopic compositions of $^{15}\text{N}-\text{NO}_3^-$ and $^{18}\text{O}-\text{NO}_3^-$ suggest that the sources of NO_3^- in most groundwater sources were predominantly soil N and sewage/animal manure with nitrification of ammonia/ammonium being the major transformation process of groundwater NO_3^- . Furthermore, there were some few water sources whose isotopic composition were influenced by NO_3^- fertilizers from coffee and/or flower farms, therefore, making the $\delta^{18}\text{O}$ values of the dissolved nitrate heavier than would otherwise be expected. Denitrification process was inhibited by presence of predominantly aerobic condition for all the groundwater sources during all seasons. However, local denitrification cannot be ignored as exhibited by the two sites that were located in close proximity to the heaps of manure and pit latrine. The study recommends protection of groundwater quality by prohibiting human activities close to water supply sources. Also further studies on the source of groundwater in the aquifers around the study area are required so as to establish their pathways before groundwater quality protection measures can be applied.

Acknowledgments This research was funded by the Government of Tanzania through The Nelson Mandela, African Institution of Science and Technology (NM-AIST). The authors wish to extend their sincere thanks to Mr. Trashias Kagenzi, District Executive Director (DED), Meru District Council for granting permission for conducting this study, Mr. Saruni (Natural Resource Officer), Ms. Angella Ndelwa and Mr. Fred Kuwese (Forest Officers) for assisting the fieldwork. Also sincere gratitude is extended to Dr. Katharine Pecsok Ewert and Emily Ngo Schick of UC Davis Stable Isotope Facility, Department of Plant Sciences Mr. Godfrey Mkongo and Masumbuko Godwin of Ngurdoto Defluoridation Water Research laboratory (NDWRL), Arusha for their technical advice and assistance during analysis of water samples. Last but not least, we wish to extend our sincere gratitude to the Village Chairmen, Village Executive Officers (VEO) of the villages in Akeri, Kikwe and Usariver and boreholes and well owners in these areas for allowing this study be conducted in their area.

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