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RESEARCH ARTICLE

Seasonal water chemistry variability in the Pangani River basin, Tanzania

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Abstract The stable isotopes of $\delta^{18}O$, δ^2H, and $^{87}Sr/^{86}Sr$ and dissolved major ions were used to assess spatial and seasonal water chemistry variability, chemical weathering, and hydrological cycle in the Pangani River Basin (PRB), Tanzania. Water in PRB was $NaHCO_3$ type dominated by carbonate weathering with moderate total dissolved solids. Major ions varied greatly, increasing from upstream to downstream. In some stations, content of fluoride and sodium was higher than the recommended drinking water standards. Natural and anthropogenic factors contributed to the lowering rate of chemical weathering; the rate was lower than most of tropical rivers. The rate of weathering was higher in Precambrian than volcanic rocks. $^{87}Sr/^{86}Sr$ was lower than global average whereas concentration of strontium was higher than global average with mean annual flux of 0.13×10^6 mol year^{-1}. Evaporation and altitude effects have caused enrichment of $\delta^{18}O$ and δ^2H in dry season and downstream of the river. Higher d-excess value than global average suggests that most of the stations were supplied by recycled moisture. Rainfall and groundwater were the major sources of surface flowing water in PRB; nevertheless, glacier from Mt. Kilimanjaro has insignificant contribution to the surface water. We recommend measures to be taken to reduce the level of fluoride and sodium before domestic use.

Keywords Spatial · Seasonal · Water chemistry · Carbonate weathering · Strontium flux · Hydrological cycle

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Introduction

A river is the medium between land and sea, influenced by natural and anthropogenic activities taking place in the basin (Sun et al. 2010). Studies on how natural and anthropogenic activities influence water chemistry have been carried out in many rivers. Some feedbacks were agricultural and industrial activities have caused dramatic change to the chemistry of Nile River (Dekov et al. 1997; El-Sheekh 2016). Saline groundwater inflow, sewage treatment plants, and agricultural runoff were major factors for the change in the chemistry of Hawkesbury Nepean River (Markicha and Brown 1998; Pinto et al. 2013). Mining activities were the dominant factor for the chemistry of Upper Mara River basin with minor contribution from rock weathering (Kilonzo et al. 2014). In addition to that, mining and industrial activities were the main factors which control the chemistry of Tawa River (Mehto and Chakrapani 2013). It is clear that different rivers have different factors controlling their water chemistry, and in most cases, human effects override natural contribution and the impacts are severe to the basins dominated by extensive land use change (Kihampa et al. 2013).

Aquatic and terrestrial organisms thrive well under certain physical-chemical conditions of the water, and any change in the physical and/or chemical characteristics of the water from

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the desired one will have impacts to the aquatic and terrestrial organisms. Composition of major ions is among important factors determining suitability of water for aquatic and terrestrial organisms (Sharma and Subramanian 2008). Thus, detailed study of various physical-chemical parameters is required for better understanding of river systems and their suitability for various uses. Besides, knowledge of river's major ions and strontium (Sr) isotopes can not only help to understand suitability of water for human and aquatic ecosystem but also guide to understand chemical weathering processes, contribution from different minerals, and possible management measures to restore the problems.

Strontium is an alkaline earth element released into the rivers through rock weathering (Santos et al. 2015). It has four stable isotopes, namely, ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr. ^{87}Sr is radiogenically produced from decay of ^{87}Rb. The ^{87}Sr/^{86}Sr depends on age and Rb/Sr content available in the rocks (Chung et al. 2009). Each river has a certain ^{87}Sr/^{86}Sr value depending on weathering pattern and rocks of the basin (Pattanaik et al. 2007). Based on chemical weathering, there are two main sources of Sr isotopic ratio; these are silicate and carbonate weathering. Silicates weathering (from granite and gneiss basement) has low strontium content but high ^{87}Sr/^{86}Sr (> 0.710), while carbonate weathering have high strontium concentrations (up to 11.4 mmol/kg) and low ^{87}Sr/^{86}Sr (0.706–0.709) (Guilin and Congqiang 2001). On a global average, river water has Sr concentration of about 1 μM and ^{87}Sr/^{86}Sr of about 0.7111 (Peucker-Ehrenbrink et al. 2010), of which one third is from silicate weathering and two thirds from carbonate rocks (Gaillardet et al. 1999).

Over long time period, climate has been changing; it is expected that these changes had impacts to water resources through increasing and/or decreasing rainfall frequency and intensity (Gizaw and Gan 2016). Furthermore, the stable isotopes of water (δ^{18}O and δD) are considered as an important tool in tracing natural water cycle (Deng et al. 2016). Precipitation, surface, and groundwater can have different isotopic compositions owing to fractionation when changing from one phase to another. Knowledge of spatial and temporal river flows is therefore an important step for planning and management of water resources (Jeelani et al. 2016). Additionally, an understanding of the relationship between river water chemistry, water cycle, weathering process, and basin characteristics will provide foundation in understanding how change in climate and land use will affect river water quality andquantity (Jarvie et al. 2002) as well as provide baseline knowledge needed in managing river water resources.

Despite possible changes in water chemistry as a result of human influences and geological process, studies on water chemistry in East African Rivers are few relative to Asia and Europe (Petersen et al. 2017). Some of the available studies have focused on few parameters, few sampling stations, and/or of short duration. This led to difficulties in getting baseline information for monitoring, management, and prediction for future change. Some of the available studies were conducted in the Pangani River Basin (Mckenzie et al. 2010; Kihampa et al. 2013), Wami-Ruvu Basin (Ngoye and Machiwa 2004), Sabaki River (Ongore et al. 2013), Mara River (Kilonzo et al. 2014), and Nile River Basin (Dekov et al. 1997; El-Sheekh 2016). Studies carried out in the Pangani River Basin have shown that quality of water for human and aquatic ecosystem health was threatened by anthropogenic activities (Mckenzie et al. 2010; Kihampa et al. 2013). However, these studies focused on one season and had few sampling stations respectively. In addition to that, findings from these studies highlighted the need of intensive study to broaden the existing baseline database and add new parameters which were not covered. Therefore, the present work was carried out to cover the basin from the upstream to the river mouth, including groundwater stations to investigate spatial and seasonal water chemistry variability, focusing on basin characteristics, hydrological process, chemical weathering and to predict their impacts in future. The study utilized concentration of major ions, Rb, and Sr, ^{87}Sr/^{86}Sr and the isotopic compositions of δ^{18}O and δ^{2}H in water to (i) understand water-rock interactions and determine the processes and factors controlling the river water chemistry; (ii) determine interrelationships between surface and groundwater in order to understand the hydrological cycle of the basin and (iii) estimate contribution of PRB to the coast of Indian Ocean so as to understand its impact at local, region, and global level; thereafter make comparison with other rivers in the region (African Rivers) and other global Rivers with similar setting. Findings from this study can be used to carry out possible management measures to ensure sustainable use of the water resource in terms of quality as well as quantity.

Methodology

Description of the study area

Pangani River Basin (PRB), which is located in the north-eastern part of Tanzania, is among the largest and important basins in East Africa. It is located between latitudes 3°03′S and 5°59′S and longitudes 36°23′E and 39°13′E (Fig. 1), encompassing an area of about 43,650 km^2, of which 95% is in Tanzania and 5% is in Kenya. This study concentrated on the part located in Tanzania. The river flows from Mt. Kilimanjaro (the highest Mountain in Africa with an altitude of 5895 m asl), Meru (4565 m asl), and Usambara to Indian Ocean having a length of about 500 km (Fig. 1). The basin is a source of livelihood to about 6.8 million people from Kilimanjaro, Manyara, Arusha, and Tanga regions (National Bureau of Statistics 2013). Activities carried out include farming, animal keeping, fishing, hydroelectric power generation,

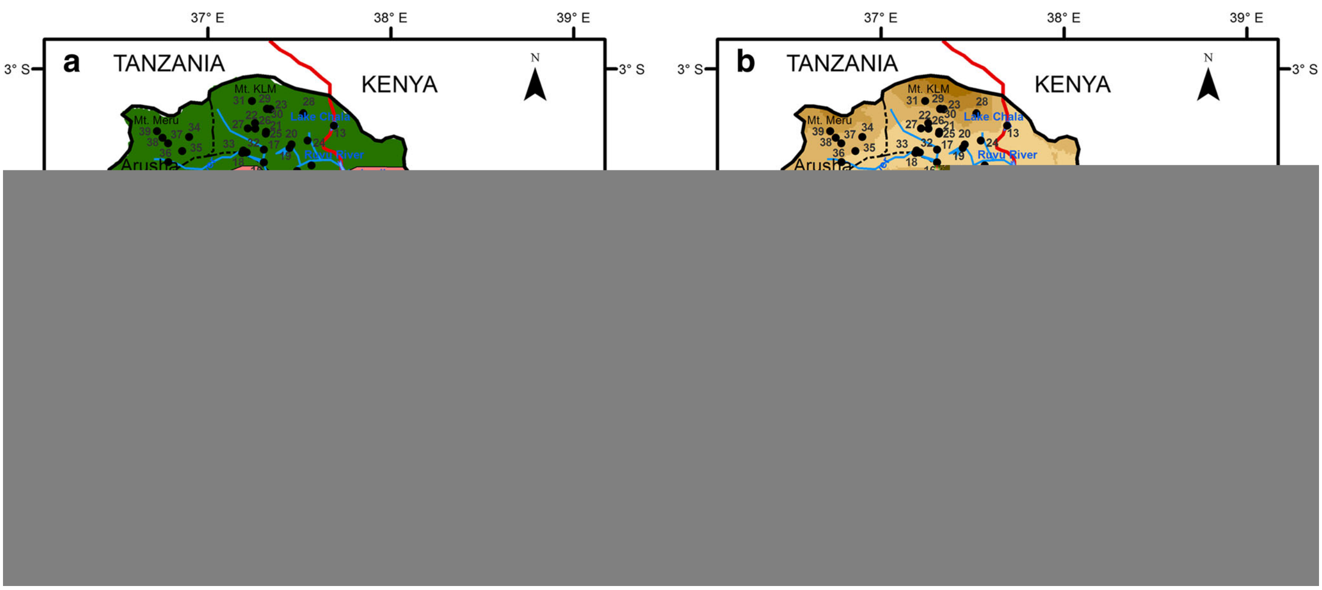

Fig. 1 A map of PRB showing (**a**) geology of the basin and (**b**) sampling stations numbered relevant to Table 1; four regions compose the basin, their elevation, and tributaries. Mt. KLM is abbreviation of Mount Kilimanjaro, Mt. Meru is Mount Meru

mining of various minerals including gemstones, and industrial and domestic activities.

Vegetation cover varies based on the climate of the areas. Along the coastal where rainfall ranges from 850 to 1050 mm per year, there is mangrove with scattered coastal forest. Mountain forests are found in mountain ranges of Kilimanjaro, Meru, Pare and Usambara; in this region, rainfall ranges from 1500 to 3000 mm per year. Grasses with scattered Miombo woodland occupy the areas with low rainfall < 850 mm per year (IUCN Eastern and Southern Africa Programme 2009). Temperature decreases with increase in elevation giving a lapse rate ranging from − 0.51 to − 0.56 °C per 100 m rise (Hemp 2006). Generally, the highest temperature of 32–35 °C occurs in January/February while the lowest temperature of 14–18 °C occurs in July/August (PBWB/IUCN 2008). The basin enjoys bimodal type of rainfall, short rains occur from October/November to December while long rains occur around March to May. These rains are associated with north-south movement of inter-tropical convergence zone (PBWB/IUCN 2008). Sufficient amount of moisture is brought to the area from Indian Ocean by southeast monsoon winds to cause long rainy season whereas short rains are associated with little moisture brought by north-east monsoon winds (McClanahan 1988).

Geology of the Pangani River basin

A simplified study map shows that the basin has a different geology varying from upstream to downstream (Fig. 1a). Generally, the basin falls within the Pangani graben which inclines in a NW-SE direction. The basin has Neogene and quaternary volcanic rocks in the northern part mainly due to Kilimanjaro and Meru volcanic mountains. The volcanic rocks in this area are younger than 40 Ma (Dawson 2008). A large part of the basin is covered by the Usagaran/Mozambican orogenic belt rocks, whose pyroxene granulite rocks from Pare Mountain aged 645 ± 10 Ma (Muhongo and Lenoir 1994). Close to the coast, the area is studded by the Jurassic limestone (Fig. 1a).

Field and laboratory methods

Surface and groundwater samples were collected from rivers, boreholes, springs, and reservoirs, making a total of 39 selected stations (Table 1). These stations were sampled twice, during dry season (Oct, 2014) and rainy season (May–June 2015) with an exception of three stations which were only sampled in dry season. A GPS (global positioning system) was used to locate sampling sites. Pre-cleaned polyethylene bottles of 1L size were used for sampling. Samples were collected from the center of the rivers and reservoirs so as to avoid local anthropogenic influence in the river/reservoir banks. This was made possible by using boat or fetching samples from the top of the bridge. Prior to sampling, the sampling device was rinsed at least three times with the water to be sampled. To minimize fractionation of stable isotopes of oxygen and hydrogen, amber glass bottles of 10 ml size were used. The bottles were also rinsed at least three times before filling samples, then filled and capped in water to avoid gas bubbles.

Electrical conductivity (EC) (μS/cm), temperature (°C), pH, dissolve oxygen (DO)(mg/L), and salinity were measured in situ by multi-parameter probe (Multi 350i Set 5 model from

weathering such as Zaire, Orinoco, and Tocantins have lower HCO_3^- level than PRB (Gaillardet et al. 1999).

PRB has various rocks from upstream to downstream, since there was no published work which measured concentration of Na^+, Mg^{2+}, Ca^{2+}, and K^+ from carbonate and silicate rocks. It was uncertain to estimate silicate and carbonate weathering rate in PRB. In order to compare with other rivers, we estimated total rate of chemical weathering (including both carbonate and silicate weathering) and compared with other rivers. Rate of weathering = Q/A. ($Na^+ + Mg^{2+} + Ca^{2+} + K^+ + SiO_2$) where Q is discharge ($m^3$/s), and A is area ($km^2$). The concentration of Na^+, Mg^{2+}, Ca^{2+}, and K^+ was taken after sea salt correction. Rate of chemical weathering was 229 kg/km^{-2} $year^{-1}$ in dry season and 191 kg/km^{-2} $year^{-1}$ in wet season. Since high concentration of most major ions increased in dry season compared to wet season, even rate of weathering was high in dry season compared to wet season. Increase in major ions in dry season has possibly been caused by increased weathering with temperature or evaporation effect. On the other hand, decrease of major ions in wet season can be caused by dilution effect. Even though PRB is located in the tropical region, it encompasses Mt. Kilimanjaro and Meru which receive the highest amount of rainfall with mean annual rainfall of more than 2000 mm per year (PBWO/IUCN 2006). Its rate of weathering was lower than other tropical rivers including Irrawady River (125,000 kg/km^{-2} $year^{-1}$), Brahmaputra River (46,000 kg/km^{-2} $year^{-1}$), Narmada (43,000 kg/km^{-2} $year^{-1}$), and Congo River (6000 kg/km^{-2} $year^{-1}$); the same case applied to rivers from mid and high latitudes such as Khatanga River (15,000 kg/km^{-2} $year^{-1}$) and Limpopo River (6000 kg/km^{-2} $year^{-1}$) (Gaillardet et al. 1999). Anthropogenic activities including hydroelectric power production and irrigation might be some of the factors reducing runoff value to less than 0.01 mm/year (Selemani et al. 2017). Climatic factors such as increasing temperature which increase rate of evapotranspiration and natural factors such as soil permeability and slope of the catchment might also play role in reducing rate of weathering.

The strontium ratio in water mainly relates to chemical weathering, and thus, the $^{87}Sr/^{86}Sr$ can reflect the nature of the soil and rocks (Bakari et al. 2013). The $^{87}Sr/^{86}Sr$ in PRB is in comparable level to most of the rivers draining the volcanic basin including rivers from Kurile Island (0.7034) and Chile (0.7057) among others (Bailey et al. 1987; Fiege et al. 2009). Normally, overall mean of $^{87}Sr/^{86}Sr$ from volcanic region is 0.70400 ± 0.00066 (Schopka et al. 2011); nearly all stations in PRB were in this range signifying that these isotopic signatures were from weathering of volcanic rocks. One station had 0.70642, and possibly, there was influence of rain water since the station is surrounded by volcanic rock and no limestone rock. This is because most $^{87}Sr/^{86}Sr$ values from rain water samples are higher than the ratio from volcanic rocks (Han and Liu 2006). Since, the concentration of elemental strontium and $^{87}Sr/^{86}Sr$ varies depending on the age and chemical composition of the bed rock (Brennan et al. 2014). The variation of $^{87}Sr/^{86}Sr$ and Sr in PRB from upstream to downstream was possibly caused by different geologies with different age and composition from upstream to the river mouth (Liu et al. 2016). Downstream, the PRBs there are Precambrian/Usagaran metamorphic rocks which caused $^{87}Sr/^{86}Sr$ to be higher (average 0.70301) than upstream dominated by Neogene volcanic rocks (average 0.70212). Usagaran rocks are older than Neogene rocks displaying high isotopic ratio while Neogene rocks are young displaying low isotopic ratio and vice versa; this is the case for elemental strontium (Santos et al. 2015). There was significant difference when comparing mean value of $^{87}Sr/^{86}Sr$ between PRB dominated by carbonate weathering and those rivers dominated by silicate weathering such as Brahmaputra (0.71970), Ganges (0.72490), Congo (0.71918), and Niger (0.71400) (Gaillardet et al. 1999).

Seasonal flux of Sr from PRB to the Indian Ocean was 0.12×10^6 and 0.13×10^6 mol $year^{-1}$ in dry and wet seasons, respectively. Contribution of PRB was lower than most of the rivers globally including 143.99×10^3 and 157.93×10^3 mol $year^{-1}$ from Beipan and Hongshuihe Rivers, respectively (Liu et al. 2017).

Conclusion

This research investigated spatial and seasonal water chemistry variability in PRB, and the study reveals that there was both seasonal and spatial water chemistry variability. Most of the major ions increased in dry season and downstream compared to wet season and upstream, and their order of abundance were $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ for cation and $HCO_3^{2-} > Cl^- > SO_4^{2-} >$ for anion.

Rock weathering was the main factor determining chemistry of PRB dominated by carbonate weathering with small atmospheric input. Weathering of igneous rock was of first priority and led to higher content of strontium and lower content of $^{86}Sr/^{87}Sr$ than global average. High concentration of strontium and low $^{86}Sr/^{87}Sr$ gave an inverse relationship between these two parameters. Chemical weathering in PRB was lower than most of tropical rivers with the same setting as PRB.

Altitude and temperature were the main factors regulating hydrological cycle in the basin. The basin relies on streams near the peak of Mt. Kilimanjaro, groundwater, and rainfall for surface water recharge. There was no significant contribution from the glacier; we therefore recommend sustainable use of water during rainy season and where possible, water should be stored in order to be used in dry season due to the expected increase in temperature, evaporation and decreasing rainfall due to climate change.

The study has also shown that Chemka spring, Themi River at lokii Mnadani and Maji ya Chai have higher fluoride than recommended level for drinking water. We recommend that the community should be treating water from these stations before consumption. Furthermore, even though most of the stations had water quality standards within recommended limits for human consumption (Tanzania Bureau of Standards 2005), there was localized enrichment of some parameters such as the observed highest level of TDS in Lake Jipe. Anthropogenic activities such as runoff from agricultural areas and domestic wastes were cause of concern. Therefore, there is a possibility of deteriorating quality of water in the future since human population and activities are expected to increase with time. We recommend regular water quality checking to understand the status of water so as to take appropriate measures where needed.

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