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Tracking nitrate sources in groundwater and associated health risk for rural communities in the White Volta River basin of Ghana using isotopic approach ($\delta^{15}N$, $\delta^{18}O—NO_3$ and ^3H)

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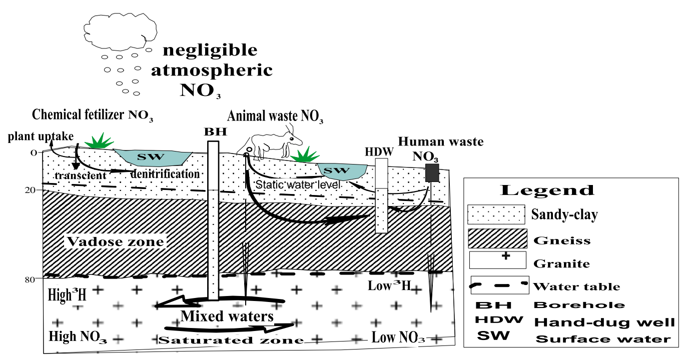
HIGHLIGHTS

- Groundwater, hand dug wells and surface water were analysed using dual isotope approach and hydrochemistry for nitrate source identification.
- Recent nitrate concentration and spatial distribution map of nitrate in drinking water in the area were evaluated and developed.
- Manure (animal and human waste) is main source of NO_3 in the Boreholes, hand dug wells and the surface water.
- Non carcinogenic health risk ($HQ_{nitrate}$) of nitrate to adults and children were evaluated.
- The study will help evaluate remediation efforts and groundwater management strategies in the area.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we present a first attempt on the use of integrated hydro-chemical and isotopic technique to trace the sources of groundwater nitrate contamination in the Upper East Region of Ghana to aid the sustainable management of this vital resource. The objectives of the study are (1) assess the present status and spatial distribution of the nitrate contamination (2) identify and distinguish the most likely sources of nitrate , (3) identify the relationship between ^3H and NO_3^- and F^-, and (4) ascertain the potential human risk from exposure to nitrate contamination. The results showed that, nitrate concentrations varied from 0.42 to 431.17, 0.83 to 143.94, 0.03 to 28.94 mg/l with mean values of 36.09, 21.54 and 5.01 mg/l for boreholes, hand dug wells and the surface water respectively. These values showed that, about 95% of boreholes and hand dug wells and 45% of the surface water have nitrate concentration above the baseline value in the area. The NO_3^-/Cl^- ratio showed that, 98.4%, 95% and 64% of the NO_3^- in the borehole, hand dug wells and the surface water are from anthropogenic activities. The $\delta^{15}N—NO_3$ and $\delta^{18}O—NO_3^-$ data confirmed that NO_3^- in the samples was predominantly derived from manure (human and animal waste) and denitrification occurring in some areas. The isotopic data further affirms the hydro-chemical interpretation that, chemical fertilizer and atmospheric deposition are unlikely sources of NO_3^- in the area. The relationship between ^3H and NO_3^- concentrations showed that, higher NO_3^- values are associated with younger waters. Non carcinogenic health risk for adults and children posed by oral ingestion of the NO_3^-

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contaminated water revealed some degree of health risk, especially to children whose risk is about 72% higher. The study provides a conceptual model of the NO_3^- dynamics and some recommendation for groundwater management in the area.

1. Introduction

Groundwater is of great importance for many countries in sub-Saharan Africa, where aquifers provide a safe and reliable source of drinking water (Foster et al., 1998; Reynolds-Vargas et al., 2006). The provision of groundwater can be associated with improvements in public health, food security and many other socio-economic benefits. Nonetheless, in recent years, this precious resource is facing the problem of salinity, fluoride and nitrate contamination in most countries of the world. Groundwater managers are faced with the challenge of attaining sustainable management of groundwater in places where the quality of the groundwater is threatened. Nitrate and fluoride contamination of groundwater has now become a global issue. Many studies in Africa (Ako et al., 2013; Boadu et al., 2008), Europe (Mattern et al., 2011; Lasagna et al., 2016; Lorenzo Di et al., 2012), Asia (Sharma et al., 2016; Reddy et al., 2009; Cao et al., 2012) and Australia (Barber et al., 1996) have reported high levels of nitrates in rivers, lakes and groundwater, primarily due to unregulated human activities that have adverse impact on surface and groundwater systems.

In nature, the nitrate ions exist as part of the nitrogen cycle. However, its rising trend in natural water has made it a contaminant of concern (Fenech et al., 2012). Groundwater nitrate concentration >3 mg/l is a sign of natural groundwater quality deterioration due to anthropogenic activities (Pastén-Zapata et al., 2014). However, most countries as well as the World Health Organization (WHO, 2004) have set the maximum admissible concentration (MAC) within the range of 45–50 mg/l, which is equivalent to 10–11 (mg/l) nitrate as nitrogen (Ako et al., 2013). Nitrate may originate from synthetic and natural fertilisation, bacterial production, atmospheric deposition and leaking septic systems (Fenech et al., 2012; Bordeleau et al., 2008). Other forms of nitrogen such as NO_2, NH_4, and NH_3 can also be transformed by some biogeochemical processes to NO_3 (WHO, 2004). Major human and environmental health risks of nitrate contamination in drinking water include methemoglobinemia/blue baby syndrome, potential carcinogenic effects, nitrate poisoning in animals, excessive plant and algae growth (Murgulet and Tick, 2009; Stadler, 2012).

In Ghana, various authors have studied groundwater quality and geochemistry in almost all the river basins (Gibrilla et al., 2011; Kortatsi et al., 2009), Ahialey et al., 2010, Tay and Kortatsi, 2008; Yidana et al., 2012; Loh et al., 2012). Focused study on nitrate in groundwater in the Upper East Region dates back to late the 1950s. Mallari (1959) compiled a list of nitrate contents of groundwater prior to 1959 in the Upper Region of Ghana. The nitrate values were generally low with an average value of 1.5 (mg/l). He also observed an isolated high nitrate value of about 9 mg/l in one borehole. In 1977, almost two decades later, studies by Akiti (1982) showed similar nitrate values ranging from 0.4 to 10.6 with average value of 1.76 mg/l. However, three years later, nitrate levels in the same boreholes ranged from 0 to 65 mg/l with average value of 12.2 mg/l (Akiti, 1982). The study further concluded that, the observed change in nitrate values from 0.3 to 54 mg/l was due to contaminants entering the aquifer. Other studies on nitrate pollution in Ghana include Badu et al., 2013; WRC, 2003; Karikari and Bosque-Hamilton, 2004; Fianko et al., 2010. One major limitation of these studies is that, the source of nitrate is not clearly identified. Agricultural activities, animal excrement (resulting from cattle rearing) and nitrogen fixation by certain plants were, however, hypothesised as possible sources of nitrate.

These previous studies and findings which constitute the basis for many groundwater management plans, strategies and policies are based on repeated sampling and analysis of physico-chemical parameters. These only provide information on the temporal trends in solute concentration and the extent of groundwater contamination within an aquifer. Undoubtedly, such management decisions were good and served some purpose, but for a long term sustainable management of the groundwater system additional and vital information, towards understanding the potential threat to groundwater, is required. Clearly, sustainable management of groundwater resources requires different perspectives, including available data, economic consequences and applicability of the management approach. Identification of the sources and variability of nitrate is, therefore, an important step in the improvement and management practices associated with maintaining the groundwater quality.

A fast growing and popular approach in resolving these issues is the use of nitrogen and oxygen isotopes ($^{15}N—NO_3^-$ and $^{18}O—NO_3^-$). Stable isotopic compositions of nitrate can provide useful information that can be used to track the sources of nitrate in groundwater via $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- at natural abundance levels (Xue et al., 2009). The combination of $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- can discriminate the various sources of nitrate (NO_3^- derived from fertilizer, animal manure, atmosphere and septic leachate from animal waste). Several authors (Cao et al., 2012; Pastén-Zapata et al., 2014; Zhang et al., 2012; Fenech et al., 2012; Zhang et al., 2014; Liu et al., 2006; Mattern et al., 2011; Reynolds-Vargas et al., 2006; Shomar et al., 2008; Wong et al., 2015; Xu et al., 2015) have used the distinct isotopic charasteristics and values of $\delta^{15}N$ and $\delta^{18}O$ in NO_3^- to assess sources of nitrate in groundwater. Tracking the origin of nitrate contamination in groundwater and understanding the processes responsible for localized nitrate concentrations are important for groundwater management strategies and remediation of contaminated sites. This could help enforce the polluter pay principle aimed at preserving water quality (Fenech et al., 2012).

Currently, there is a lack of data, information and understanding of the origin of nitrate and the relationship between groundwater age and nitrate concentration in the Upper East region. This paper intends to bridge the knowledge gap and present the first attempt at using dual isotopes of $\delta^{15}N—NO_3$ and $\delta^{18}O—NO_3$ and tritium (^3H) to: (1) assess the present status and spatial distribution of the nitrate contamination (2) identify and distinguish the most likely sources of nitrate (3) identify the relationship between ^3H and NO_3^- and F^- and (4) ascertain the potential human risk from exposure to nitrate contamination using USEPA risk assessment model. The study will also seek to highlight the effectiveness of the combined use of isotopes and hydro-chemical data for nitrate source identification in order to improve management and remediation efforts.

2. Materials and methods

2.1. Study area

The study area is boarded on the north by Burkina Faso, west by Upper West Region and east and south by the Republic of Togo and Northern Region respectively (Fig. 1a). The area is drained by the Black Volta, White Volta, Red Volta, Tamne, Siisili and Tono rivers. The region is characterized by two seasons, a long dry season and a very short rainy season between May and August. The mean annual rainfall