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title: **Geochemical evolution of groundwater quality in shallow and deep wells of volcanic aquifer in Axum, Ethiopia**

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ABSTRACT

Water samples were analyzed to characterize the chemical and isotope signatures of the local groundwater and to identify the hydrogeochemical processes leading to groundwater quality deterioration in Axum. Hydrochemical data indicates that the anion composition is dominated by HCO_3^- and further modified by human activities as NO_3^- and Cl^- contents rise. The chemistry of the groundwater progressively evolved from $\text{Ca}^{2+}\text{-HCO}_3^-$ to $\text{Na}^+\text{-HCO}_3^-$ and $\text{Mg}^{2+}\text{-HCO}_3^-$ water types. The deep groundwaters evolve toward very high solute concentrations of variable cation contents owing to the influence of aquifer heterogeneity and degree of water-rock interaction.

The chemical composition of groundwater appear to be controlled by complex reactions involving uptake of gaseous CO_2 , dissolution and precipitation of silicates and carbonates as well as cation exchange between groundwater and clay minerals. The chemistry of the shallow groundwater is governed by the uptake of soil CO_2 . Calcium and bicarbonate is predominantly derived from the dissolution of carbonate minerals in the alluvial sediments. In contrast, in the deeper wells silicate weathering at high $p\text{CO}_2$, which is mainly derived from magmatic origin, is the dominating process. High content of NO_3^- and Cl^- in water samples highlights the impact of human activities on groundwater quality. Contamination of drinking water supply by sewage and farm waste is a major pollution concern from anthropogenic source. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data indicate that the solutions are of meteoric origin with apparent effect of evaporation and water-rock interaction.

INTRODUCTION

Groundwater from both shallow and deep aquifers is a significant drinking water supply for the town of Axum. The major concern in drinking water supply in Axum is the deterioration of groundwater quality due to geogenic origin and anthropogenic activities both in shallow and deep boreholes. The groundwater in the study area is hosted mainly by fractured basalt. The fractured and weathered rocks develop good permeability due to secondary porosity. However, the overlying alluvial sediment provides mostly poor condition of surface water infiltration. Hydrogeochemical characteristics of groundwater are of great interest in terms of water quality evolution, as the complex spatial distributions of volcanic rocks have led to extensive changes in groundwater composition. The chemistry of the groundwater primarily reflects the composition of host rocks and the intensity of water-rock interactions that greatly influence the ionic concentration starting from the recharge to discharge zone (Ayenew et al., 2008).

Hydrochemical and stable isotope composition of groundwaters provides information on evolution and source of groundwater and its components as well as on potential impact of human activities on groundwater quality. Knowledge on parameters that control groundwater chemistry is essentially required to develop tailored strategies for water resource management and sustainable drinking water supply for the population in Axum.

METHODS

Water samples were collected from springs, wells and boreholes at various depths. All samples were filtered through $0.45\ \mu\text{m}$ of Syringe Filters in the field and the samples were separated in different aliquots where the samples for cation analysis were preserved using diluted HNO_3 , while those used for anion analysis were not acidified. Electrical conductivity, pH, temperature and total alkalinity were measured in-situ. Laboratory analyses comprise dissolved major and

trace elements using a coupled plasma-optical emission spectrometry (ICP-OES, Perkin Elmer 4300) and ion chromatography (IC, Dionex 600). Stable isotopic composition ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of the water was analysed by Finnigan DELTA^{plus} Mass Spectrometer.

RESULTS

Hydrochemistry and water rock interaction

Distribution of major cations and anions in the sampled solutions is shown in Fig. 1 within a piper diagram. Data indicates that cations are mostly dominated by Ca^{2+} and to a lesser extent by Na^+ , and Mg^{2+} . However, relative amount of Ca^{2+} ranges from about 20 to 70%, whereas $(\text{Na}^+ + \text{K}^+)/\text{Mg}^{2+}$ ratio is rather constant at about 0.5 (see lines in Fig.1; $\text{Na}^+ \gg \text{K}^+$). Anions are obviously dominated by HCO_3^- , mostly about 50% and $(\text{NO}_3^- + \text{Cl}^-)/\text{SO}_4^{2-}$ ratio is close to 0.9. Accordingly, local groundwater is mainly of bicarbonate type that progressively evolved from $\text{Ca}^{2+}\text{-HCO}_3^-$ to $\text{Na}^+\text{-HCO}_3^-$ and $\text{Mg}^{2+}\text{-HCO}_3^-$ water types. Most shallow wells hosted within quaternary alluvial deposits and weathered basalt yield Ca^{2+} and HCO_3^- in the range from 0.9 to 2.5 mmol L^{-1} and from 2 to 8 mmol L^{-1} , respectively. Total dissolved solid (TDS) concentration indicates elevated water rock interaction in $\text{Mg}^{2+}/\text{Na}^+\text{-HCO}_3^-$ (mostly deep wells) versus $\text{Ca}^{2+}\text{-HCO}_3^-$ type solutions (mostly shallow wells). In deep groundwater a maximum TDS value of 2160 mg/L reflects strong uptake of cations from water-rock interaction especially for Mg^{2+} and Na^+ (Fig. 2a).

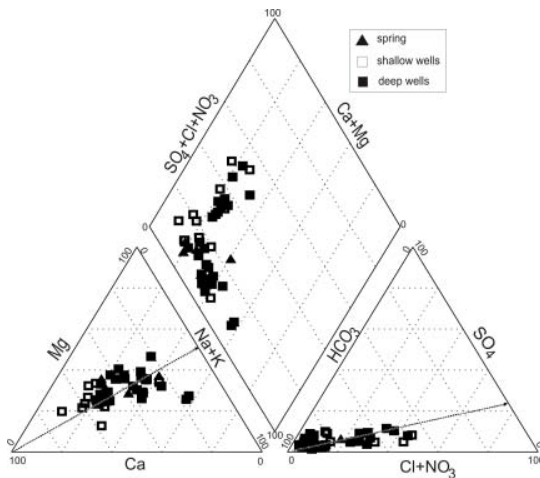


Figure 1. Piper diagram of hydrochemical data from Axum waters.

The calculated internal partial pressure of CO_2 ($p\text{CO}_2$) for all solutions is significantly higher than that of the Earth's atmosphere ($10^{-3.5}$ atm) (Fig. 2b). Groundwaters with $p\text{CO}_2$ values up to about $10^{-0.8}$ atm may be related to a CO_2 source different from soil carbon as soil CO_2 may usually contain $p\text{CO}_2 < 10^{-1.5}$ atm. Evidently; CO_2 -rich groundwaters (mostly deep wells) contain highest solute concentrations owing to degree of water-rock interaction. The apparent incongruent weathering of silicate minerals results in e.g. kaolinite formation and causes an increase of Na^+ , Mg^{2+} , Ca^{2+} , and HCO_3^- . The raise of Mg^{2+} and decrease of Ca^{2+} concentration could be explained primarily by incongruent weathering and leaching of Mg^{2+} from ferromagnesian silicates (Fig. 2c). $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$ vs. $[\text{Mg}^{2+}]+[\text{Ca}^{2+}]$ ratio displays that the shallow wells have lower

$[Mg^{2+}]/[Ca^{2+}]$ ratio at less absolute cation content. Thus, elevated $[Mg^{2+}]/[Ca^{2+}]$ ratios of deep groundwaters may represent strong weathering of mafic minerals, most likely attributed to progressive reaction of Mg-silicate dissolution caused by uptake of elevated content of gaseous CO_2 . $[Ca^{2+}]+[Mg^{2+}]$ and $[HCO_3^-]$ concentrations rise at a slope of 1:2 indication both silicate weathering and $CaCO_3$ dissolution in areas where carbonate minerals are present e.g. in the alluvial aquifer and calcite filling veins (Fig. 2d).

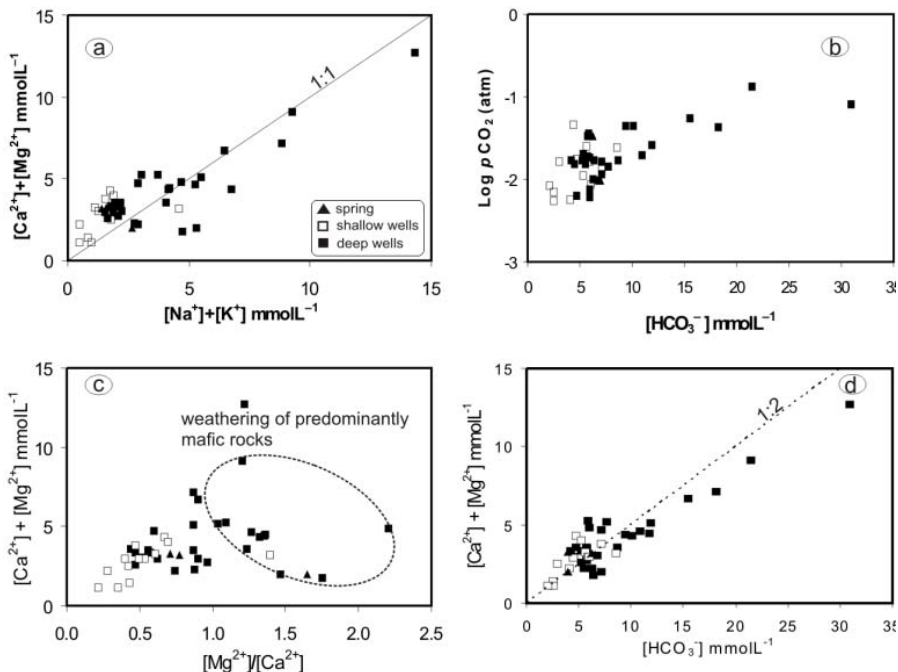


Figure 2. Plots of (a) $[Ca^{2+}]+[Mg^{2+}]$ vs. $[Na^{+}]+[K^{+}]$ (b) pCO_2 vs. $[HCO_3^-]$ (c) $[Ca^{2+}]+[Mg^{2+}]$ vs. $[Mg^{2+}]/[Ca^{+}]$ (d) $[Ca^{2+}]+[Mg^{2+}]$ vs. $[HCO_3^-]$ for Axum groundwaters.

Stable isotope composition of groundwater

δ^2H and $\delta^{18}O$ values of shallow and deep groundwaters as well as surface water from Axum area are given in Fig. 3. Most of the values scatter close to the global meteoric water line (GMWL) of Craig (1961) and the regional line of Addis Ababa (RMWL). In two samples a positive $\delta^{18}O$ shift is likely caused by isotopic exchange with the rock mass through water-rock exchange. The presence of isolated aquifer and high mineralization supports the possibility that such fluids may interact with surrounding rocks more strongly. Most of groundwater from deep aquifers is from semi-confined aquifers, suggesting vertical infiltration of evaporated waters. The δ^2H and $\delta^{18}O$ values for several surface water and spring water are isotopically different from the other solutions which may be caused by evaporation during precipitation and infiltration (see Fig. 3; evaporation line). The $\delta^{13}C$ of dissolved inorganic carbon (DIC) has been analysed for carbon evolution and the values range between +1 and -12‰ indicating magmatic CO_2 and soil CO_2 as predominant sources. The uptake of magmatic CO_2 at higher pCO_2 results in elevated major cations, dissolved SiO_2 and HCO_3^- -contents due to strong silicate weathering.

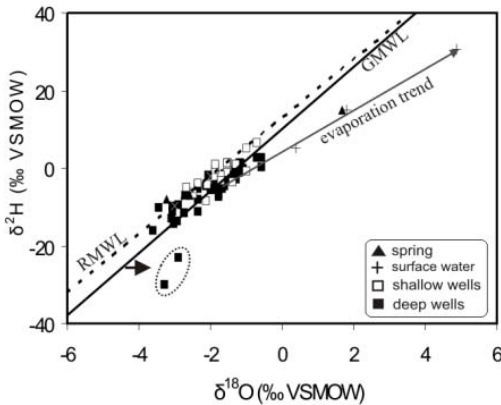


Figure 3. $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ values of H_2O for all sampled solutions. GMWL (solid line) refers to global meteoric water line of Craig (1961) whereas RMWL denotes the regional meteoric water line for Addis Ababa ($\delta^2\text{H} = 7.5 \delta^{18}\text{O} + 12.9$) using data from IAEA (2008).

Impact of human activities

Elevated NO_3^- and Cl^- content are indicative for anthropogenic impact. Naturally, NO_3^- concentration in crystalline rocks is very low and, therefore, high concentrations of NO_3^- in some groundwater within the study area indicates that human activity is increasingly impacting the water quality. The influence of human activities is evident in some municipal deep wells as well as shallow wells. The maximum nitrate concentration in the study area is 1.5 mmol L^{-1} , (mean concentration 0.4 mmol L^{-1}). In several solutions the nitrate concentration has exceeded WHO recommended value of 50 mg/L for drinking water. High levels of nitrate accompanied with high content of chloride are suspected to come from human and animal waste effluent. However, there exist no significant overall correlation between NO_3^- and Cl^- (Fig. 4), which is probably due to the non-conservative behavior of NO_3^- . In shallow wells, the origin of high NO_3^- is likely a consequence of farming practices such as manure application that can be introduced into the groundwater systems via infiltration through the soil horizon. The deep wells close to the town are vulnerable to pollutants from sewage, including septic tanks and leaking sewer lines.

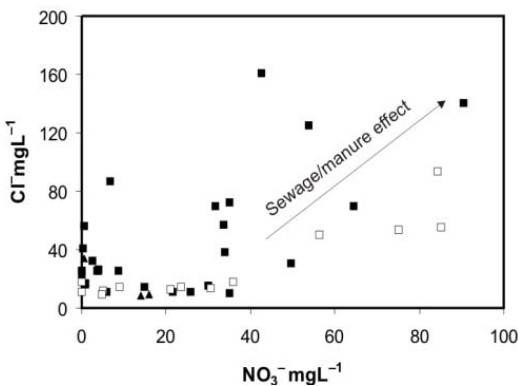


Figure 4. NO_3^- vs. Cl^- concentrations in deep and shallow wells. Symbols are given in Figure 1.

CONCLUSION

Hydrochemical data indicates that the anion composition is dominated by HCO_3^- and further modified by human activities. The influence of human activities in the groundwater quality is evident in wells located close to the town. The sign of quality deterioration highlights the need for water quality monitoring and management. The chemistry of the shallow groundwaters is controlled by the uptake of soil CO_2 while weathering of silicate at higher $p\text{CO}_2$ dominates in the deeper aquifers. The incongruent weathering of silicate mineral at high $p\text{CO}_2$ generally enriches the groundwater in HCO_3^- and Ca^{2+} , Na^+ , Mg^{2+} and dissolved SiO_2 .

Stable water isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$) show that the waters are derived from meteoric origin with apparent effect of evaporation and strong water–rock interaction in few sampled solutions. The groundwater recharge into deeper aquifer is either from base flow of infiltrating rainfall in recharge zone or from directly vertical infiltration of evaporated waters.

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