Sveriges lantbruksuniversitet
Swedish University of Agricultural Sciences

Department of Soil and Environment

Groundwater quality of Malawi
– fluoride and nitrate of the Zomba-Phalombe plain

Anastasia von Hellens

Degree project in Biology
Agriculture Programme – Soil and Plant Sciences

Examensarbeten, Institutionen för mark och miljö, SLU 2013:10

Uppsala 2013

SLU, Swedish University of Agricultural Sciences
Faculty of Natural Resources and Agricultural Sciences
Department of Soil and Environment

Anastasia von Hellens

Groundwater quality of Malawi – fluoride and nitrate of the Zomba-Phalombe plain

Supervisor: Dr. Jonas Mwatseteza, Department of Chemistry, University of Malawi
Assistant supervisor: Ingmar Persson, Department of Chemistry, SLU
Examiner: Jan Eriksson, Department of Soil and Environment, SLU

EX0689, Independent project in Biology - bachelor project, 15 credits, Basic level, G2E
Agriculture Programme – Soil and Plant Sciences 270 credits (Agronomprogrammet – inriktning mark/växt 270 hp)

Series title: Examensarbeten, Institutionen för mark och miljö, SLU
2013:10

Uppsala 2013

Keywords: groundwater, quality, fluoride, nitrate, Malawi, East Africa

Online publication: http://stud.epsilon.slu.se

Cover: Field sampling with Dr. Jonas Mwatseteza, Alawesta village, 2012. Photo by author.

Abstract

Contamination of groundwater is a widespread issue around the globe and the water quality is highly dependent on the geology as well as anthropogenic interventions in the area. High (0.9 – 1.2 mg F^-/L) fluoride levels in groundwater can give rise to dental fluorosis and have been reported in several areas of Malawi. Further studies of groundwater contamination apart from fluoride are limited. The aim of this study was to investigate the fluoride and nitrate concentrations of groundwater in boreholes around Lake Chilwa and the origin of the contaminants. The hypothesis was that elevated concentrations of fluoride and low nitrate concentrations would be found in the area.

On average, most fluoride and nitrate values were non-measurable, however, on some sites elevated concentrations were measured. Around the village of Jali, levels ranging from 1.5 to 4.5 mg F^-/L were found. The village of Nine miles had elevated levels of nitrate in the water with 48.5 mg NO_3^-/L as the highest. The latter is an interesting result since levels greater than 50 mg NO_3^-/L have been correlated with blue-baby syndrome, a condition lethal for bottle-fed infants. Due to these findings, further studies of the area are recommended along with implementation of nitrate-contamination prevention measurements.

Table of contents

Abbreviations

AAS	Atomic Absorption Spectroscopy
APHA	American Public Health Association
BGS	British Geological Survey
CEC	Cation Exchange Capacity
EC	Electric Conductivity
FAO	Food and Agriculture Organization
FAOSTAT	Statistic division of the FAO
IC	Ionic Chromatography
IGRAC	International Groundwater Resource Association Centre
MBS	Malawi Bureau of Standards
NPK	Fertilizer containing nitrogen, phosphorus and potassium
OECD	Organization for Economic Co-operation and Development
SADC	Southern African Development Community
TDS	Totally Dissolved Solids
UN	United Nations
WHO	World Health Organization

1 Introduction

1.1 Background

Groundwater in Malawi is, according to a study made by groundwater consultants Bee Pee and SRK Consultants (SADC, 2002), estimated to supply about 3 million people in rural areas making out about 29 % of the rural domestic water supplies. As groundwater is transported through layers of sand and gravel it is normally clean from anthropogenic pollution. However, due to weathering processes, high contents of different chemical compounds might be accounted for depending on the geological constitution of the area (BGS, 2004).
Most of the water supplies of the rural areas of Malawi are derived from shallow hand dug wells or hand pumped boreholes. According to a study made by the BGS (2004), little documentation on the chemical parameters of aquifer groundwater has been done. However, FAO (2005) stated in a report that the areas around Lake Chilwa have saline waters and water consumption is limited due to high concentrations of iron, fluoride, sulphate, nitrate and TDS.

Fluorine is naturally occurring and when consumed in high levels on a daily basis, 0.9 – 1.2 mg F^-/L, it can lead to dental fluorosis in children (WHO, 2006). Such elevated levels have been reported in Southern Malawi in both Zomba and the Machinga area (UN, 1989; BGS, 2004; Sajidu et al., 2004, 2007 and 2008) and in some dispersed parts of alluvial aquifers of Malawi (UN, 1989).

The occurrence of chemical compounds in groundwater varies with type of rock the water flow through and the abundance of the chemical compounds in the rock (WHO, 2006). Due to this, the area around Lake Chilwa might be of interest for further investigation since the mineral fluorite has been discovered on Chilwa Island and south of the lake through a study conducted by Carter and Bennett (1973).

Groundwater is a source prone to high fluoride concentrations since the fluoride accumulates from rock dissolutions and geothermal sources. East African Rift Valley is a region, extending partially through Malawi, where a high concentration of fluoride in groundwater has been noticed (Edmunds and Smedley, 2005).

Groundwaters from alkaline granites are particularly sensitive to relative high fluoride concentrations (Brunt et al., 2004; Edmunds and Smedley, 2005). Rocks of such sort can be found in Precambrian basement areas (Brunt et al., 2004). This makes Malawi a country where finding fluoride contaminated water would be likely, since the country's geology consists of crystalline Precambrian basement granites according to a report conducted by IGRAC (Brunt et al., 2004) and additional older studies by Smith and Carington (1983). In a report by IGRAC (Brunt et al., 2004), the entire country is classified as being of a medium to low probability range regarding high fluoride levels in groundwater.

Occurrence of nitrogen in groundwater is generally low and high levels are usually present due to anthropogenic pollution, either by seepage from inorganic fertilizers or poorly sited latrines and septic tanks (WHO, 2006). Studies have shown that bottle fed infants consuming groundwater with levels of nitrate higher than 50 mg NO_3^-/L have been associated with blue-baby syndrome. The risk of the syndrome is also increased if the general health of the infants is low, with malnourishment, infections and vitamin C deficiency worsening the situation (WHO, 2006; who.int).

In Malawi, only relatively old studies are available regarding occurrence of nitrogen in groundwater and little information is available on what impact pollution from agricultural runoff might have on the groundwater quality. Denitrification may be an important process in some of the quaternary alluvial aquifers but probably has less significance in the basement aquifers where conditions are likely to be more commonly aerobic (BGS, 2004).

According Young (1976) nitrogen is usually deficient in the tropics, one reason is field clearing by implementation of slash-and-burn, a technique that is known to diminishing the nitrogen status of the soil. Due to the prolonged weathering of tropical soils they generally have greater ANC and bind anions better then cations, thus nitrate is bound better than ammonium (Stevensson, 1982; Canter, 1992; Eriksson et al., 2011).

Ahn (1993) and Wambeke (1992) both states that the given soil types of the area (vertisols, gleysols and arenosols) have low organic matter content leading to a higher demand for fertilizers since they are deficient in nitrogen. This would however, not necessary lead to higher nitrogen leaching with greater ANC of the soils but rather that the amount nitrogen applied would be taken up better.

1.2 Objectives and scope

The objective of this study was to investigate chemical quality parameters of the groundwater in areas Lake Chilwa basin and Zomba – Phalombe Plain. Further the objective was to correlate the water quality with geological heritage and soil-properties of the study site to investigate the impact of minerals of the area as well as anthropogenic interventions. The chemical parameters examined were soluble fractions of nitrogen and fluoride in groundwater of 30 boreholes and when analysed to be compared with WHO (2006) as well as Malawian guideline values (MBS, 2005) (Appendix I).

1.3 Outline of the project

The initial part of the project was a literature study of the area defining soil type, geological heritage as well as anthropogenic interventions and through that determining the potential occurrence of the parameters to be analysed. Later a field campaign around the study area Lake Chilwa basin and Zomba – Phalombe Plain was executed and thereafter field sampling with borehole site marking by help of GPS technique. The GPS-measured sample sites were with the help of ArcGIS inserted in a map together with information of geological composition of the study area.

1.4 Hypothesis

As fluoritic minerals have been found in the areas around Machinga (Carter and Bennett, 1983; Sajidu et al., 2004, 2007 and 2008) the hypothesis was to find elevated levels of fluoride in the groundwater. Nitrate, generally not being a naturally occurring ion in groundwater was assumed only to be found in low concentrations. If nitrate was found, sources were assumed to be anthropogenic such as agricultural fertilizers or poorly sited latrines.

2 Study site

2.1 Climate and geography

2.1.1 Malawi

Malawi is a landlocked country situated in the southern part of Africa. It is bordered by Mozambique to the east, south and southwest, Tanzania to the north and northeast as well as Zambia to the west. The country is located between latitudes 9°22'S and 17°03'S and longitudes 33°40'E and 35°55'E and has a total area of 118 480 km^2 (FAO, 2006).

The climate in Malawi is tropical and the year is divided in two distinct seasons, a rainy season lengthening from November to April and a dry season stretching between May and October.
The dry season may further be divided in to two periods, May to July being cool and June to October being hot (FAO, 2006; metmalawi.com).

Figure 1. Malawi on the world map, framed area representing the study area.
Source; world map from Wikipedia and map of Malawi from ESRI world map.

The annual rainfall in the country ranges from approximately 725 mm to 2 500 mm per year. The annual temperatures range from 17°C to 27°C in the cool season and from 25°C to 37°C in the dry season (metmalawi.com). In the plateau areas they can vary from 10°C to 28°C, depending on the elevation (FAO, 2006).

2.1.2 Lake Chilwa and Zomba – Phalombe plain

The Lake Chilwa wetland is situated in the Southern Region of Malawi, east of the Zomba Plateau, being water fed mainly by the Shire River (FAO, 2006).
The study area is relatively hot and humid due to being low-lying at an altitude of 2 050 feet to 2 200 feet above sea level (Garson, 1960). Temperatures ranging from 18°C to 30°C and annual average rainfall of 1 433 mm in Zomba area (metmalawi.com).

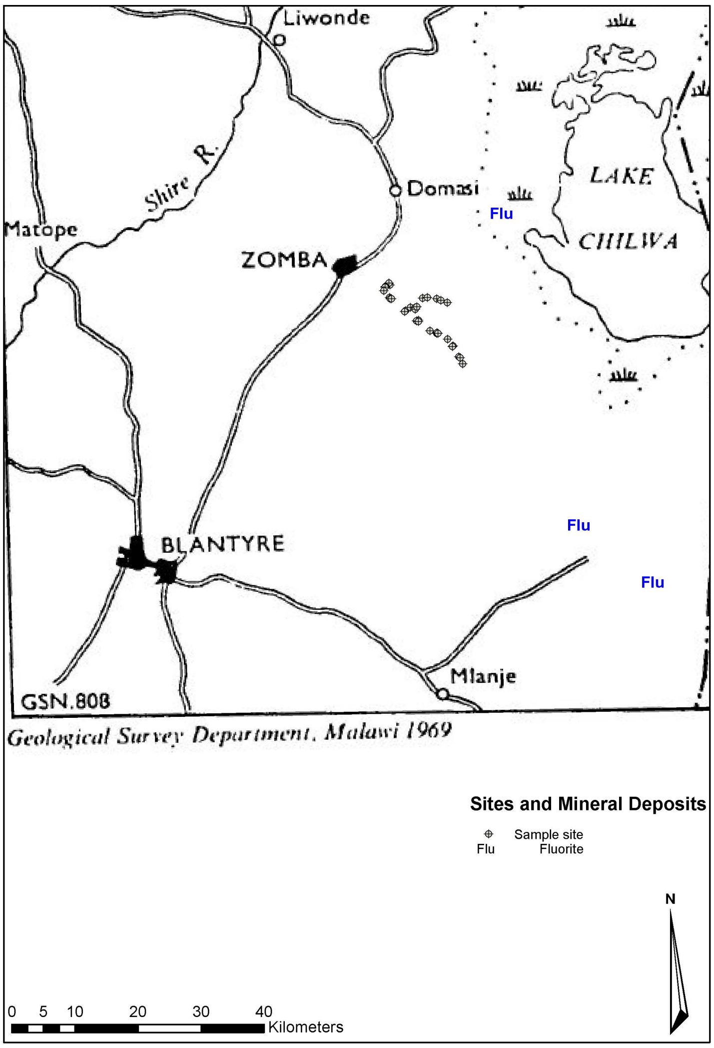

Figure 2. Map from Geological Survey Department representing study area with GPS-data showing the sample sites.
Source: Geo-referenced towards ESRIC world map by using ArcGIS. Fluorite data conducted from map by Carter and Bennet (1973).

2.2 Geology and soils

2.2.1 Geology

Intrusions of carbonarities have been found around the Chilwa Alkaline Province and most of these intrusions have formed the features making out the topographic ring complex Zomba and Mount Mulanje (Swanzie and Stubbs, 1972). A map conducted by Swanzie and Stubbs (1972) show that the carbonatite deposits contains rare earth elements, apatite, limestone and marble and pyrochlore.

In a study conducted by Carter and Bennett (1973) occurrence of fluorite on Chilwa Island has been found, as well as 11 km south of Lake Chilwa. Fluorite has also been discovered in the northern part of Mulanje Districts, Tundulu. Apatite containing 'high' levels of fluoride has been found northwest of Tundulu (Carter and Bennet, 1973; BGS, 2009). Bloomfield (1965) states that the major rock types of the area are charnockitic gneiss and granulite. As well, a study conducted by the Ministry of Energy and Mines of Malawi (2009) states that the mineral deposits of the area Lake Chilwa – Phalombe are fluorite, limestone, nepheline syenite and niobium.

The areas around the Lake Chilwa basin are swampy, dambo areas consisting of fine-grained quaternary alluvial sediments. The sediments are thought to have been deposited in a low energy environment thus the fine-grained particle size of them gives low yielding aquifers (Smith-Carington and Chilton, 1983).

2.2.2 Soil

The soils of Malawi are divided in to four major categories; latosols, lithosols, calciomorphic and hydromorphic soils. Hydromorphic black cotton soils, vertisols, in mixture with gleysols constitute the main soil types surrounding the Lake Chilwa basin (Smith-Carington and Chilton, 1983; Macmillan Malawi, 2001; FAO, 2006). This is also shown by a soil map of Malawi (Swanzie and Stubbs, 1972), which indicates that the soils around Lake Chilwa are calciomorphic alluvial soils, locally called "makande soils" (Wambeke, 1992). Further "dambos" have been found around the lake (Smith-Carington and Chilton, 1983), a local chi-chewan name for hydromorphic gleys (Young, 1976). In a more detailed study of the area, Venema (1991) concluded that the soil around Jali (a village located within the study area) is surrounded by cambic arenosols.

2.3 Fertilizer consumption

In Malawi 72 % of the population belongs to the agricultural sector (FAOSTAT, 2012). In Sub Saharan Africa, Malawi is one of the countries that use most fertilizer with an average of 28 kg NPK/ha of arable land (FAO, 2012, Data provided by FAOSTAT 2010).

Between the years of 2001 and 2004 severe food insecurity arose in Malawi due to poor rainfalls and droughts (Gockel and Gugderty, 2009; Dorward and Chirwa, 2011; OECD, 2012). These food shortages lead to an implementation of a large-scale subsidy programme in 2005/06, initiated by the Malawian Government and the World Bank. The subsidy programme targeted around 50 % of the farmers in the country that received fertilizers for maize production. The fertilizer-vouchers given out were for 50 kg of NP 23:21 + 4S and 50 kg of urea along with seeds from different maize varieties (Dorward and Chirwa, 2011). The subsidy programme for fertilizers has led to an overall increase in fertilizer use intensity in the country, as viewed in figure 3.

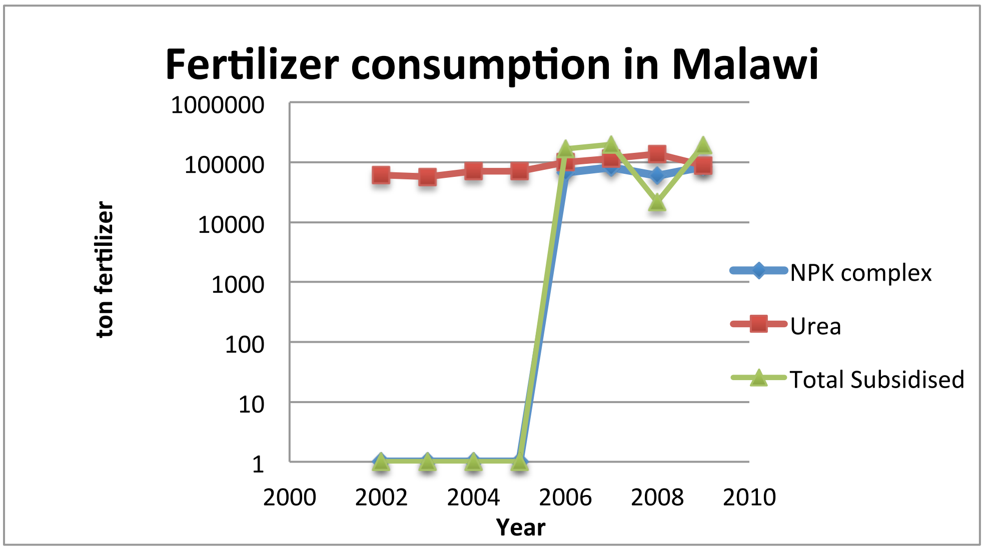

Figure 3. Fertilizer consumption in Malawi 2002 – 2009.

Source: Data for NPK complex and Urea, FAOSTAT 2002-2009. Data for Total subsidized (NP bags), Dorwa and Chirwa (2011).

Theory

Mineral weathering is a naturally occurring activity involving physical, chemical or biological processes (Essington, 2004; Dahlin et al., 2011). Chemical weathering is a process where matter is converted from a less stable mineral phase to a more stable or insoluble phase. Weathering is also an important dissolution process where various ions are released into the soil solution. For any weathering to occur water is an important transport medium since water molecules and protons react to form new minerals or clays through the process of hydrolysis.
The most important chemical reactions regarding weathering are hydrolysis and oxidation. These two generally occurs in cooperation with each other, where primary silicates are altered to secondary ones. An example of a hydrolysis and oxidation reaction, where olivine is hydrolysed and iron(II) is oxidised to form goethite, is shown in the equation below (Essington, 2004).

$$MgFeSiO_4\ (s) + 0.25\ O_2\ (g) + 1.5\ H_2O + 2\ H^+ \rightarrow FeOOH\ (s) + Mg^{2+} + H_4SiO_4^0$$

Chemical weathering is driven by several factors such as temperature, soil moisture content, pH in the soil and the composition and structure of the mineral particles. In humid tropical regions where high temperatures and high precipitation are common, the chemical weathering of minerals is intense (Eriksson et al., 2011).

Clay minerals are built up by silica tetrahedra and aluminium hydroxyl octahedra units making out sheets in the silicate structure. The silica tetraheders can then be linked together by various cations or oxygen ions depending on the type of mineral.

Isomorphic substitution in the minerals where aluminum substitutes silicate and magnesium and reduced iron(II) substitutes aluminium lead to a deficit of positive charge, giving rise to a net negative layer charge. This is called the *permanent clay charge*, which always is negative. The other one is a *variable charge*, which is a result of protonation and deprotonation of the hydroxyl groups on the surfaces and the charge can be negative, positive or neutral. This varies with the pH, for example the variable charges of goethite are shown in equation 3.1 and 3.2 (Essington, 2004)

$$FeOH + H_3O^+ \rightarrow FeOH_2^+ + H_2O \tag{3.1}$$

$$FeO^- + H_3O^+ \rightarrow FeOH + H_2O \tag{3.2}$$

The negative charge of a tropical soil usually diminishes with age since permanently charged 2:1 clays disappear, while aluminium and iron(III)oxides that under acidic conditions has a surplus of positive variable charges, accumulate. This gives tropical soils lower cation exchange capacity but higher anion exchange capacity (Eriksson et al., 2011).

2.4 Fluoride

2.4.1 Geological source

During weathering and other chemical processes affecting rock and soil, such as percolation of water, fluoride has a potential to leach out and dissolve in the groundwater. Thus, the origin and type of rock the groundwater flows through affects the fluoride content of it (Wedepohl, 1972).

Being a naturally occurring element, fluorine is present in minerals as the anion fluoride (Edmunds and Smedley, 2005). Since the fluoride ion and the hydroxide ion almost share the same ionic radius and valence, fluoride can replace the hydroxide ion by isomorphic substitution in many rock-forming minerals (Wedepohl, 1972; Saxena and Ahmed, 2001; Edmunds and Smedley, 2005). The most common fluorine bearing compounds are fluorite (CaF_2), apatite ($Ca_5(PO_4)3F$) and micas ($K_2Mg_5Si_8O_{20}F_4$) (Edmunds and Smedley, 2005). Wedepohl (1972) states that the most abundant of them is fluorite, often forming fluorite veins in the rocks. However, Saxena and Ahmed (2001) state that fluorite is not readily soluble in water under normal pressure (100kPa) and temperature (25°C) (Saxena and Ahmed, 2001).

Other factors that affect the fluoride content of the groundwater apart from the geology are climate and contact time (Brunt et al., 2004). Groundwater with long residence time in the aquifer allows prolonged dissolution time between rock and water, making it likely that deep boreholes and aquifers with slow groundwater movement contain higher concentrations than surface waters. Wedepohl (1969) found the average fluoride content in granitic rocks to be 810 mg/kg, leading to increased fluoride content in groundwater due to weathering. This has further been confirmed by Brunt (2004) and Edmunds and Smedley (2005) who found that crystalline rocks and especially alkaline granites could generate groundwater with high fluoride concentrations.

2.4.2 Transport in the soil profile

Fluoride transport in aqueous solutions is controlled mainly by the solubility of fluorite and fluorite apatite (Wedepohl, 1972; Allmann et al., 1974), which is dependent upon various factors. Edmunds and Smedley (2005) found that the solubility of fluoride is very temperature dependent; it decreases with decreasing temperature.

Groundwater with high fluoride content often also contains sodium bicarbonate and low calcium concentrations (<20 mg/L), accompanied by a moderately to high pH value in the range 7 to 9 pH (Brunt et al., 2004; Edmunds and Smedley, 2005).

$$CaF_2\,(s) + Na_2CO_3^{2-} \rightarrow CaCO_3\,(s) + 2\,F^- + 2\,Na^+$$

$$CaF_2\,(s) + 2\,NaHCO_3^- \rightarrow CaCO_3\,(s) + 2\,F^- + 2\,Na^+ + H_2O + CO_2\,(g) \qquad (3.3)$$

$NaHCO_3$ affecting the concentration of fluoride in groundwater (Saxena and Ahmed, 2001)

A study by Saxena and Ahmed (2001) indicated that the pH-range favouring the dissolution is 7.6 to 8.6 and that the specific conductivity that favours dissolution is within the range of 750 to 1750 µS/cm. They also found that bicarbonate affects the solubility when within the range of 350 to 450 mg/l.

Arid regions are prone to high fluoride concentrations due to slow groundwater flow, which is prolonging the reaction time between rock and water.

2.5 Nitrate

2.5.1 Source of nitrate in groundwater

There are four categories into which the nitrate sources in groundwater can be divided; natural sources, waste materials (industrial sludge or badly sited pit latrines), row crop agriculture and irrigated agriculture. The latter two are connected to application of nitrogen fertilizers. Nitrogen from chemical fertilizers is commonly inorganic and applied in the form of ammonium and nitrate ions. The amount of leaching from fertilizers varies with timing and method of fertilizer application, vegetative cover, soil porosity, amount fertilizer added and rate of irrigation. Nitrogen from human waste or treated wastewater is applied in organic form or as ammonium as well as urea. These are the main sources of biogenic pollution (Canter, 1996).

2.5.2 Transport from topsoil to groundwater

Transport of nitrogen in the soil profile down to groundwater level is generally a result of its movement through the unsaturated zone, where transformation processes such as nitrification regularly take place. The unsaturated zone is an aerated zone where ammonia (NH_4^+) can be oxidized and converted to nitrate (NO_3^-) by nitrification. There are various transport processes of which nitrogen, in organic or inorganic form, can enter the subsurface environment; diffusion of ammonium and nitrate and movement of both in the water phase (Canter, 1996). Other transformation processes apart from nitrification that enable losses of nitrogen from the soil profile are; ammonification where organic nitrogen is converted to ammonium nitrogen and ammonia volatilization where ammonium nitrogen is converted to gaseous ammonia and is lost through diffusion.

Nitrogen can also be lost in the system if biological denitrification occurs, since this is a reaction where nitrate is reduced to various gaseous nitrogen products (Stevensson, 1982; Canter, 1992; Eriksson et al., 2011).

Nitrogen loss by leaching from topsoil to deeper soil layers and into groundwater is mainly in form of nitrate, rather than ammonium (Stevensson, 1982). Nitrate remains soluble, as it is normally not easily adsorbed to the negatively charged clay mineral surfaces. Due to this it can be transported long distances away from the input areas when it has reached the groundwater (Canter, 1996).

2.6 Soils

2.6.1 Vertisols

Vertisols are formed in areas with distinguished wet and dry climate with variation in the soil moisture content, giving the minerals specific characteristics like strong swelling and shrinking capacity. The soil is rich in smectite with gives the clay higher specific surface area leading to more weathering (Young, 1976; Wambeke, 1992; Schaetzl and Andersson, 2005; Eriksson et al., 2011).

Vertisols have high cation exchange capacity, high amounts of calcium carbonates and low permeability with standing water during wet season. The nitrogen content in the soils is usually low due to low organic content. However, Young (1976) states that vertisols can be highly productive with moderate nitrogen levels and that the fertilizers added are retained due to the high CEC and slow permeability. Difficulties in root penetration might lead to reduced nutrient uptake from plants.

The main nitrogen losses from vertisols are ammonia volatilization since moist conditions in the vertisols leads to reduction of nitrates, transforming them to gaseous nitrogen. On waterlogged soils denitrification is rapid since denitrification requires an anaerobe environment, which occurs when the soil is water saturated (Wambeke, 1992).

2.6.2 Gleysols

Gleysols are formed during extensive wetness being periodically saturated during times of the year. They often occur in valley floors and marches and are being characterized as dambo clays in the Malawian language chi-chewa (Macmillan Malawi, 2001; Young, 1976). Wambeke (1992) refers to dambo clays as aquults, which are soils with fair nutrient supplying power.

Young (1976) describes the difference between temperate and tropical gleysols where in seasonally wet tropics the gleysols dry out completely during the dry season hence iron mottles develop. Further more Young states that on poorly drained sites, salinization is likely to occur additional to gleying.

2.6.3 Arenosols

Arenosols are sandy soils and according to Ahn (1993) immature soils which are agriculturally unproductive due to lack of colloids and low water and nutrient holding capacity. In a study conducted by Venema (1991) cambic arenosols were found to cover the area around Jali.

3 Methods and materials

3.1 Collection of water samples

The samples were collected from boreholes using the single grab or catch method according to Standard Methods for Examination of Water and Wastewater (APHA, 1976). This method is used when source is known to be fairly constant over a period of time. Samples were collected with 0.5 and 1 L polythene bottles, thoroughly cleaned with deionized water prior to collection.

The boreholes where pumped for approximately one minute before sample was collected, the sample bottles were rinsed three times with sample water before filled up to the edge.

3.2 Sample analysis

All samples were analysed for main chemical properties using standard methods and they were analysed according to Standard Methods for Examination of Water and Wastewater (APHA, 1976). Since temperature, pH and EC change over time, they were analysed in the field according to Standard Methods for Examination of Water and Wastewater (APHA, 1976) with a portable Oakton Instrument, Eco Tester, Model pH2. The rest of the parameters (Na^+, $Ca^{2+,}$ $Mg^{2+,}$ K^+, Cl^- , SO_4^{2-} , NO_3^-, F^-) were determined at the Chemistry Department laboratory, Chancellor College, University of Malawi.

The total concentrations of cations calcium, potassium, sodium and magnesium were determined using atomic absorption spectrophotometry (Buck Scientific Model 200A). The anions chloride, nitrate, sulphate and fluoride were analysed by an ion chromatography system composed of a Dionex CDM-1 conductivity detector, an Ionpac AS14 anion exchange column and Data Apex Clarity chromatography software.

3.3 Treatment of samples for laboratory analysis

All samples were treated according to reglement's from Standard Methods for Examination of Water and Wastewater (APHA, 1976) apart from not being acidified already on site due to risk of contaminating the samples.
In the lab all samples were filtered with 0.45 µg filters and the samples for analysing cations were and acidified with nitric acid. The samples for measuring nitrate, sulphate and fluoride were stored at 4˚C and analysed within 24 h according to Standard Methods for Examination of Water and Wastewater (APHA, 1976).

4 Results

Upon arriving to Malawi, a fuel crisis was occurring in the country disabling any kind of sampling or fieldwork for the first sex weeks of the project time. When fuel finally came, not much was available and there was no certainty for how long it would stay. Decisions were thus taken that the sampling sites could not be as spread out as we originally planned for thus, the sites were concentrated around and not far from Zomba town.

The values of fluoride were generally of non-measurable concentrations but some elevated values were obtained. High values of fluoride, 1.5 – 4.5 mg F^-/L, were measured in Chande, Jali police station, Jali epicentre and Jali Anglican; these sample sites were all in the same area situated around the rural village of Jali. The sample points Khwiliro and Mamphanda were also situated in the same area; this however can not be seen on the map shown in figure 2, due to the low resolution. It is viewed as strange that non-measurable concentrations of fluoride or nitrate were obtained in these two villages since the others of Jali-area had at least some elevated values of both the ions. These exceptions might be explained by contamination of the sample bottles or erroneous measurement by the IC.

On average, most nitrate values were of low or of non-measurable concentrations. However, around the area of the village Nine miles, high values of nitrate, 48.5 and 14.5 mg NO_3^-/L, were obtained. The value of 48.5 mg NO_3^-/L obtained at one sample site in the centre of the village Nine miles, was exceeding the MBS maximum limit (45 mg NO_3^-/L) for nitrate content in potable water.

Table 1. Chemical quality parameters measured in field and laboratory analyses. Values of the ions are given in mg/L and temperature in °C and EC in µS.

The results for the anions are given in values by the accuracy of ±0.5 due to the fact that no narrower precision could be given from the IC. The values for the cations are stated by the accuracy of ±1. The values for pH, temperature and EC were measured by a precision of ±0.1 units.

The values written in bold type represent elevated values of nitrogen and fluoride. The values written in italic represent concentrations that are believed to be erroneous since the villages Khwiliro and Mamphanda are situated very close to the Chande – Jali area, where elevated values where obtained.

Sample site	pH	Temp	EC	F^-	NO_3-	Cl^-	SO_4^{2-}	Ca^{2+}	Na^+
Chichiri	6.5	25.2	192	0	9.5	8.0	10.0	9	4
Nambesa	6.7	25.9	186	0	5.5	4.0	3.0	8	4
Elliot village	6.9	25.7	257	0	0.5	3.0	1.5	7	13
Chipoola	6.8	25.7	164	0	4.5	2.0	0	5	7
Mingu a)	6.7	25.4	426	0	0	57	0.5	18	13
Mingu b)	7.0	25.4	239	0	4.0	1.5	0	11	9
Nsomba	6.9	25.4	191	0	4.0	2.5	0	9	8
Nine miles a)	6.8	26.1	405	0	**48.5**	21	0	14	18
Nine miles b)	6.9	26.0	516	0	**14.5**	16.5	0	20	17
Bongwe	6.9	26.0	302	0	2.0	7.0	0.5	8	12
Mbidi	6.8	26.7	207	0	4.0	4.5	0	5	15
Chipera	6.8	26.6	223	0	1.0	3.0	0.5	8	13
Tambala	6.9	27.1	301	0.5	0	4.0	0.5	9	17
Kumbewe	6.8	26.1	222	0	1.5	2.5	0	8	10
Mpinda	6.8	26.4	126	0	5.0	1.5	0	4	9
Phulusa	7.0	26.1	224	0	8.5	5.0	0	7	12
Gomani	7.0	26.2	354	0	0.5	3.0	0	17	13
Lomoni	6.6	26.9	196	0	0.5	0	0	5	11
Mpokwa	6.5	26.2	214	0	0.5	0	0	7	9

Mpokwa agri	6.7	26.0	196	0	1.0	0	0	6	8
Samanwa	6.7	26.9	322	0	0	1.0	0	12	13
Mandota	6.6	26.9	358	0	0.5	1.5	0	14	11
Pirimiti	6.7	26.6	314	0	0	0.5	0	10	10
Pirimiti hosp	6.7	26.3	343	0	0	0.5	0	10	12
Chande	7.0	26.1	704	**4.0**	2.0	3.5	0	30	11
Jali police station	7.2	26.4	865	**4.5**	3.5	6.5	0	32	34
Jali epicenter	6.9	25.1	810	**4.0**	2.5	4.5	0	25	41
Jali Anglican	6.9	26.1	1161	**1.5**	1.5	3.0	0	37	47
Khwiliro	6.9	25.5	1806	*0*	*0*	36.5	2.5	47	50
Mamphanda	6.8	26.2	1630	*0*	*0*	40.5	2.5	47	53

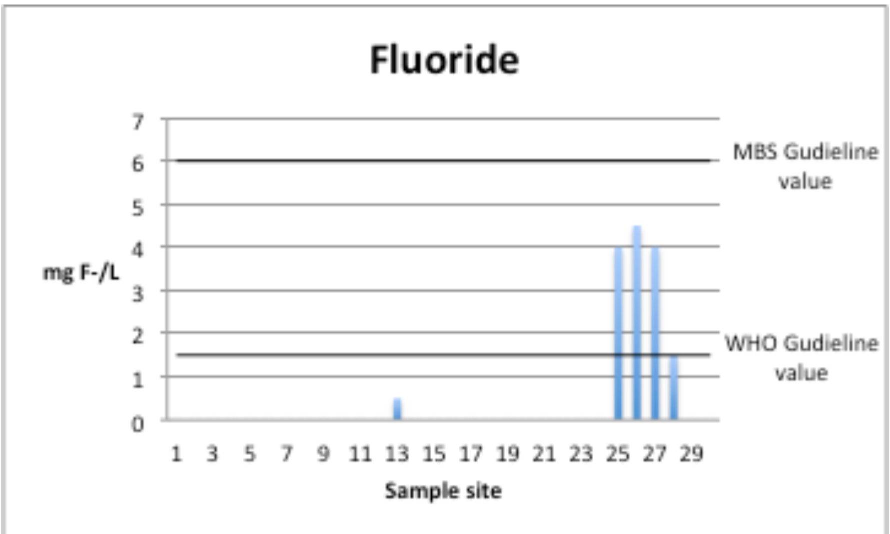

Figure 4. Fluoride concentration for every sample point compared to WHO and MBS guideline values, showing that a majority of the sites had non-measurable values of fluoride.

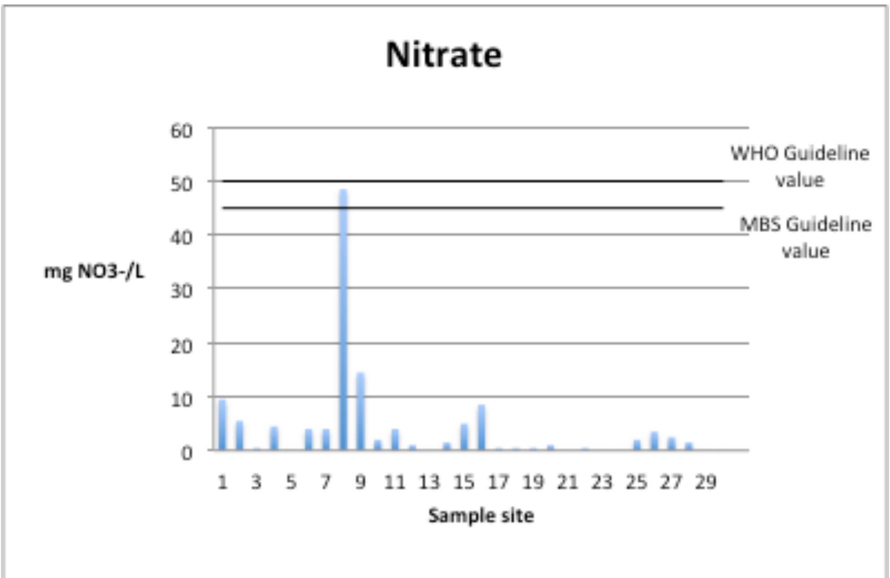

Figure 5. Nitrate concentration for every sample point compared to WHO and MBS guideline values, showing that only one sample site was within the risk of nitrate contamination.

5 Discussion

5.1.1 Fluoride

Brunt et al. (2004) found that due to the Precambrian basement of the area, there is a possibility that occurrence of alkaline granites may lead to a high fluoride concentration in the groundwater due to weathering. With this in mind and the fact that the minerals fluorite and apatite found around the study site (Carter and Bennett, 1973) fluoride was expected to be found in elevated levels in the groundwater.

The results show that fluoride was to some extent found in elevated levels; however, most of the fluoride concentrations were very low or non-measurable and as shown in figure 4, not many sample sites did exceed the WHO and MBS guideline values. This could be an indicator that there may not be an excessive problem in the area as such, rather that one village is having this issue.

The elevated fluoride concentrations were found around the Jali-area. Chande village, Jali police station and Jali epicenter had values exceeding WHO guide line values of 1.5 mg F^-/L. None of the boreholes sampled had higher values than MBS guideline values for fluoride of 6.0 mg F^-/L. It could be viewed as positive that the values did at least not exceed Malawis own limits for potable water, however, in a study conducted by IGRAC, Brunt (2004) mentions that a lot of developing countries have no choice than to set higher maximum values than the WHO guidelines, otherwise there would be no water to drink. It is therefore feasible to say that Jali-area have too high values for the water to be potable.

Saxena and Ahmed (2001) stated in a study that the pH value favouring the solubility of fluorite was within the range of 7.6 to 8.6. Jali epicentre and Anglican had pH-levels below 7 but still elevated levels of fluoride. However, the values were within the range of 7 to 9, which are the pH-ranges that Brunt (2004) stated are common for groundwater with high fluoride content.
In the range of 750 to 1750 μS/cm, solubility increases fluoride dissolution (Saxena and Ahmed, 2001). Elevated levels of fluoride could be correlated with solubility since the most of the villages with high fluoride concentrations had conductivity levels higher that 750 μS/cm, apart from Chande that had a value of 704 μS/cm.

5.1.2 Nitrate

As expected and shown in figure 5, most of the boreholes did not show high nitrate levels accept for Nine miles a) which with a value of 48.5 mg NO_3^-/L is exceeding the MBS guideline values for nitrate of 45 mg NO_3^-/L (Appendix I). However, it does not exceed the general WHO guideline values of nitrate in potable water of 50 mg NO_3^-/L (Appendix I). The concentration is in any case close to the limit of nitrate levels in potable water and the sample site was located in the centre of a village. This is an interesting finding since concentrations exceeding the guideline values of nitrate have been correlated with the blue-baby syndrome. This however, does not state that there is a major health problem in the area, merely that the might be a risk and further investigation would be of interest. Nine miles b) also had slightly elevated levels of nitrate with 14.5 mg NO_3^-/L; with the sample site being very closely located to Nine miles a), this was expected.
The borehole of Nine miles a) is situated in the centre of the village Nine miles and with no agricultural activity in the sampled area the high nitrate values most likely derives from poorly sited latrines. However, since nitrogen can be transported long distances in the groundwater (Canter, 1996) the source point of pollution might be hard to trace.

With the nutrient poor soils surrounding the area (Smith-Carington and Chilton, 1983; Venema, 1991; Macmillan Malawi, 2001; FAO, 2006) and a potential overload of fertilizers (Wambeke, 1992; Ahn, 1993), the elevated levels might origin from fertilizers. The amount of leaching from fertilizers varies with timing, application method and amount.

Thus, if fertilizers are given out with no training in correct practices a high risk of excessive broadcasting is present with leaching as a potential consequence.

Since denitrification may be an important process in the quaternary alluvial aquifers that can be found around the Chilwa area (BGS, 2004), that could be a reason to why only two boreholes have high levels of nitrate. However, since depth and residence time of the water flow in the aquifers of the various boreholes could not be established, occurrence of anaerobic conditions is hard to determine and occurrence of denitrification is hard to predict.

Denitrification might also occur in the other boreholes if the soils surrounding the area would get the waterlogged. Some of the added fertilizers, in the form of urea might be lost by ammonification and thereafter ammonia volatilization.

6 Conclusions and recommendations

Elderly equipment, power shortages and lack of completely distilled water can have affected the results and might explain some abnormalities. Due to the short time frame of this study only one sample was taken and no follow up was possible. Regarding the nitrate in particular sampling of it could be spread out over the year and be made both during the dry and during the rainy season, maybe sampling two times during the rainy season. The overall sample area could as well have been more spread out.

Not enough data could be obtained regarding depth and age of wells, due to lack of studies performed in the area and data storage. This influences the evaluation of the data.

Since no current geological study could be found, the information obtained regarding mineral occurrence of the area was scarce. As well, no detailed maps of the study area could be found which lead to an imprecise georeferencing of the study sites.

Information regarding the use of fertilizers in the area was hard to find. No such data was available at the Malawian Bureau of Statistics in Zomba and therefore general consumption data for the entire country was used. This might have led to a false interpretation that the usage of fertilizer has increased which might not be accurate for the given area. As well the agricultural activity of the area would have been a factor interesting to include, however no such up-to-date data could be found.

Since some elevated values for both nitrate and fluoride were found, with nitrate being a potential risk for bottle fed infants in the village of Nine miles, I would wish for and recommend further studies of the area using the more modern equipment currently available at Chancellor College.

Acknowledgements

First, I as the author, would like to acknowledge my supervisor Dr. Jonas Mwatsetesa and the exchange coordinators Dr. Samson Sajidu and Dr. Timothy Biswick for a warm reception. As well, acknowledgements to the additional helpful staff at Chancellor College, especially all the lab technicians at the Department of Chemistry for providing much help and guidance.

Further acknowledgements to the exchange coordinators Ingmar Persson and Daniel Lundberg at the Department of Chemistry at SLU, that with the help of the Linneaus-Palme board enabled this fantastic exchange. I would also like to acknowledge the examiner, Jan Eriksson from SLU for his numerous but truly helpful comments on this paper.

As well, I would like to acknowledge Anders Larsolle at the Department of Energy and Technology at SLU for lending GPS-equipment and providing helpful guidance on map construction. A special acknowledgement to professor Gunnar Jacks from the Royal Technical University of Sweden, KTH, who provided much guidance on the subject of fluoride.

Last but not least I would like to acknowledge my colleague Johanna Schütz for all the long hours in the lab and also for sharing the various experiences we have encountered.

Reference

Ahn, P., M (1993). *Tropical soils and Fertiliser Use* .Longman group UK Limited

Allmann, R. and Koritnig, S., (1974) Fluorine. In: Wedepohl, K.H. (editor) Handbook of Geochemistry, vol. II/1. Berlin, Heidelberg: Springer Verlag

APHA (1976). *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association 14th edition, New York, DC, USA.

Bloomfield, K., (1965). *The geology of the Zomba Area*. Geological Survey Department, Bulletin Zomba, Malawi 16, 1–193.

BGS (2004). *Groundwater Quality: Malawi*. NERC 2004.

BGS (2009). *Mineral potential of Malawi.* Ministry of Energy and Mines. UK

Brunt, R., Griffioen, J. and Vasak, L., (2004). *Fluoride in groundwater: Probability of occurrence of excessive concentration on a global scale*. IGRAC, International Groundwater Resource Assessment Centre. Report No. SP 2004-2. Utrecht, The Netherlands.

Carter, G. S. and Bennett, J. D., (1973). *The geology and mineral resources of Malawi*. Geological Survey Department Bulletin, Zomba, Malawi 6, 1–62.

Canter, W. L., (1996). *Nitrates in Groundwater*. Florida: CRC Press Inc

Eriksson. J., Dahlin, S., Nilsson. I., Simonsson. M (2011). *Marklära*. Lund, Sweden: Studentlitteratur AB

Dorward, A. and Chriwa, E., (2011). *The Malawian agricultural input subsidy programme: 2005/06 to 2008/09*. International Journal of Agricultural Sustainability 9(11) 2011.

Edmunds, M. and Smedley, P., (2005) in: *Essentials of Medical Geology.* Elseveiser Inc. Chapter 12, Oxford: BGS, NERC

Essington, M. E., (2004). *Soil and Water Chemistry: an integrative approach.* Chapter 1 and 3. Boca Raton, Florida: CRC Press

FAO (2005). *Irrigation in Africa in Figures*. AQUASTAT Survey 2005.

FAO (2006). Country profile: Malawi. AQUASTAT Survey. Water report 29
Accessed on [27.05.2012] from
http://www.fao.org/nr/water/aquastat/countries_regions/MWI/index.stm

FAO (2012). *Fertilizer subsidies in sub-Saharan Africa.* Barreiro-Hurie, J. and Druilhe, Z.

Garson, M. S., (1960). *The geology of the Lake Chilwa Area*. Geological Survey Department Bulletin, Zomba, Malawi 12.

Gockel, R. and Guckerty, M. K., (2009). *Political Economy of Fertilizer Subsidies: Malawi.* Evans School of Public Affairs, University of Washington.

Macmillan Malawi (2001).*Senior secondary atlas*. Blantyre: Macmillan Malawi.
MBS (2005). *Borehole and shallow well water quality – Specification*. Malawi Standards Board. Blantyre, Malawi.
Consultants, Bee Pee (Pty) Ltd & SRK Consultans (Pty) Ltd. Water Sector Coordination Unit (2002). *Complication of the hydrogeological map atlas in the SADC Region. Situation Analysis Report: Malawi.*. SADC (2002*)*. Lesotho.
Ministry of Energy and Mines of Malawi. (2009) Mineral potential of Malawi. BGS
OECD (2010). *The Use of Input Subsidies in Developing Countries.* OECD. Paris.
Saxena, V. K. and Ahmed, S., (2001) *Dissolution of fluoride in groundwater: a water-rock interaction study*. Environ. Geol. 40, 1084–1087.
Sajidu S.M., Makhumula P., Masamba W.R.L., Mwatseteza J.F. (2004). *Fluoride Content and Chemical Water Quality in Borehole Water in Selected Rural Areas of Southern Malawi*. **Unpublished.**
Sajidu, S. M. I., Masamba, W. R. L.1,2, Thole, B. and Mwatseteza, J. F. (2008). *Groundwater fluoride levels in villages of Southern Malawi and removal studies using bauxite*. International Journal of Physical Sciences Vol. 3 (1), pp. 001-011 (2008)
Sajidu, S. M. I,, Masumbu F. F. F., Fabiano, E. and Ngongondo. C. (2007) *Drinking water quality and identification of fluoritic areas in Machinga, Malawi*. Malawi Journal of Science & Technic. Vol 8, 042-056 (2007).
Schaetzl, R. J. and Anderson, S., (2005). *Soils: genesis and geomorphology*. Cambridge: Cambridge University Press
Schmidt, E. L., (1982). *Nitrification in Soil in: Nitrogen in Agricultural Soils.* Agronomy; no. 22. American Society of Agronomy, Wisconsin.
Smith-Carington, A. K. and Chilton, P. J., (1983*). Groundwater Resources of Malawi*. Departments of Lands, Valuation and Water; Republic of Malawi, Lilongwe.
Stevenson, F. J., (editor) (1982). *Origin and Distribution of Nitrogen in Soils in: Nitrogen in Agricultural Soils.* Agronomy; no. 22. American Society of Agronomy, Wisconsin.
Swanzie, A. and Stubbs, M., (1972). *Malawi in Maps*. Hodder & Stoughton Ltd
UN (1989). Malawi. In: *Ground Water in Eastern, Central and Southern Africa*. Natural Resources/Water Series No. 19, United Nations, New York.
Venema, J. H., (1991). *Soil families of Malawi (Blantyre, Karonga, Lilongwe, Liwonde, Mzuzu and Ngabu ADDs)* Ministry of Agriculture and Husbandry branch, Malawi Government, Lilongwe
Accessed on [07.11.2012] from http://library.wur.nl/isric/index2.html?url=http://library.wur.nl/WebQuery/isric/28736
Wambeke van, A., (1992). *Soils of the tropics: properties and appraisals*. New York: McGraw-Hill Inc
Wedepohl, K. H., (editor) (1972). *Fluorine and Nitrate in: Handbook of geochemistry II/3.* Berlin, Heidelberg: Springer-Verlag
WHO (2006). *Guidelines for drinking water quality*. 3rd edition, Vol. 1, Recommendations, World Health Organization, Geneva
Young, A., (1976). *Tropical soils and soil survey*. Cambridge: Cambridge University Press

Internet references

http://www.metmalawi.com/ Accessed [29.04.2013]
http://www.who.int/water_sanitation_health/diseases/methaemoglob/en/ Accessed [03.05.2013]

Appendix

Appendix I. Guideline values in potable water derived from WHO (2006) and MBS (2005). All parameters being stated in mg/L

Parameter	Guideline values, WHO	Guideline values, MBS
Nitrate (NO_3^-)	50	45
Fluoride (F^-)	1.5	6.0
Sulphate (SO_4^{2-})	None stated	800
Chlorine (Cl^-)	None stated	750