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HYDROGEOCHEMICAL DYNAMICS OF ELEMENTS IN WATERSHEDS DRAINING SEDIMENTARY AND IGNEOUS ROCKS: CONTRIBUTION TO INORGANIC NUTRIENTS

A thesis submitted in partial fulfilment of the requirements for the degree of Master of Engineering (MEng) in **Environmental Engineering**

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DEDICATION

Dedicated with profound gratitude to Cameroonian's rural farmers.

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LIST OF ACRONYMS AND ABBREVIATIONS

- AfNet: Africa Network for Soil fertility
- AfSIS: Africa Soil Information Service
- AGRA: Alliance for Green Revolution in Africa
- ASHC: Africa Soil Health Consortium
- ASSS: Africa Soil Science Society
- BIW: Bidow igneous watershed
- BGR: Federal Institute for Geosciences and Natural Resources
- **CEA:** California Environmental Associates
- **CEC:** Cations Exchange Capacity
- CIA: Chemical Index of Alteration
- CIW: Chemical Index of Weathering
- **DLSW:** Douka Longo sedimentary watershed
- **DO:** Dissolved Oxygen
- **EC:** Electrical Conductivity
- FAO: Food and Agricultural Organisation
- FCFA: Franc de la Communauté Financière Africaine
- GIS: Geographic Information System
- **GPS:** Global Positioning System
- IFDC: Centre for Soil Improvement and Agricultural Development

IITA: International Institute of Tropical Agriculture

INRM: Integrated Natural Resource Management

INS: National Institute of Statistics

ISFM: Integrated Soil Fertility Management

IRGM: Institute for Geological and Mining Research

ITPS: Intergovernmental Technical Panel on Soil

LISA: Low Input Sustainable Agriculture

MINADER: Ministry of Agriculture and Rural Development

MINRESI: Ministry of Scientific Research and Innovation

NAIP: National Agricultural Investment Plan

NASPW: National Advanced School of Publics Works

NGO: Non-Governmental Organisation

OMAFRA: Ontario Ministry of Agriculture, Food and Rural Affairs

OSM: Open Street Map

PE: Polyethylene

PIA: Plagioclase Index of Alteration

ProSEP: Projet Sol-Eau-Plante

QGIS: Quantum Geographical Information System

RE: Weathering Index

REEs: Rare Earth Elements

RM: Relative Mobility

RUSLE: Revised Universal Soil Loss Equation

SDGs: Sustainable Development Goals

SSA: Sub-Saharan Africa

- **TDS:** Total Dissolved Solids
- UNESCO: United Nations Educational and Scientific Cooperation Organization

USD: US Dollars

USDA: United States Department of Agriculture

USLE: Universal Soil Loss Equation

WFP: World Food Program

- WHO: World Health Organization
- WIP: Weathering Index of Parker
- WRch: Rate of chemical weathering
- pH: Hydrogen ion potential
- Wt %: weight percentage
- Eh: redox potential

Myr: million years

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ABSTRACT

The Bidou - igneous and Douka Longo - sedimentary watersheds in the Cameroon's agrarian Adamawa and North regions, respectively, are characterised by poor nutrient soils and crop yields. Thus, hydrogeochemical investigations using major element oxides, major ions, silica (H₄SiO₄), δD and $\delta^{18}O$, and trace elements (TEs and REEs) in rocks and waters within the watersheds were conducted to contribute in proposing solution options. Accordingly, this study aimed at assessing (1) element generation, enrichment, depletion and relative mobility from the bedrocks, (2) elemental contents in waters and fluxes within the watersheds, and (3) inorganic nutrient availability in the sedimentary and igneous watersheds. 115 Shallow groundwater samples and 09 rock samples were collected on the field, sent to the laboratory for chemical analysis and the laboratory results were processed and interpreted. The obtained results were: Elements get released to water when carbonates and plagioclases were subject to weak, intermediate and strong chemical weathering that occurred at annual rates of 0.0006 mm, 0.0014 mm, 0.0006 mm, and 0.0005 mm, for granite, basalt, trachyte and sandstone, respectively; non-isochemical dissolution caused nutrient elements (Ca, Mn, Na, Cu, Zn, K, Ni and Fe) except Mo, to exhibit higher relative mobility compared to non-nutrient elements (Cr, Bi, Cs, Cu, Ga, Pb, Sn, Th, U, V, and Al); the groundwater that originated from rainwater through preferential flow have the chemistry Ca + Mg - NO₃ in Douka Longo sedimentary watershed, and Na + K -Cl, Ca + Mg- HCO₃, and Na + K - HCO₃ in Bidou igneous watershed; solutes flux followed the order HCO₃ > SiO₂ > Na > Ca > K > Mg > NO₃ Cl > Fe > Al > F > SO₄ > Zn > Sr > Ba > Mn > BO₂ > NH₄ > PO₄ > Br > Sr > Ba > Mn > BO₂ > NH₄ > PO₄ > Br > Sr > Ba > Mn > BO₂ > NH₄ > PO₄ > Br > Sr > Ba > Mn > BO₂ > NH₄ > PO₄ > Br > Sr > Ba > Mn > BO₂ > NH₄ > PO₄ > Br > Sr > Ba > Mn > BO₂ > NH₄ > PO₄ > Br > Sr > Sr > Ba > Mn > BO₂ > NH₄ > PO₄ > Br > Sr > Sr > Sr > Ba > Mn > BO₂ > NH₄ > PO₄ > Br > Sr > $NO_2 > Ti and HCO_3 > Na > Ca > SiO_2 > Fe > Mg > Cl > F > BO_2 > Mn > NH_4 > Zn > Al > Ba > Sr > SO_4 > K$ in the Douka Longo and Bidou watershed, respectively, with higher annual loss of nutrients from the DLSW than BIW. The poor nature of the soils could be due partly to deficiency in P, Fe and Mo in both watersheds, deficiency in NO₃, K⁺, B, REEs, in BIW, and excess of NO₃, K⁺, Ca, Mn, and REEs in DLSW. To improve soil nutrient content, water retention infrastructures and fertilizers enriched in N, K, B and REEs are recommended in Bidou watershed, while in Douka Longo watershed N, K, Ca, Mn, and REEs should be reduced.

Key Words: Chemical weathering, Relative mobility, Element flux, Water content, Soil nutrient.

Х

RESUME

Le bassin igné de Bidou et le bassin sédimentaire de Douka Longo qui se trouvent respectivement dans la région de l'Adamaoua et du Nord du Cameroun, sont soumis à des déficiences en éléments nutritifs et de faible productivité agricole. Pour cela, une étude hydrogéochimique à l'aide des ions majeurs, oxyde des éléments majeurs, silice, δD et $\delta^{18}O$, et éléments traces présents dans les roches et les eaux des bassins a été faite afin de contribuer à la proposition des solutions. Les objectifs de cette étude étaient d'évaluer (1) la génération des éléments, l'enrichissement, la dégradation et la mobilité relative de ceux-ci à partir des roches mères, (2) le contenu des éléments dans les eaux et leur flux dans le bassin, et (3) la disponibilité des nutriments inorganiques dans les bassins igné et sédimentaire. 115 échantillons d'eau et 09 échantillons de roche collectés sur le terrain ont été envoyés au laboratoire pour les analyses chimiques. Les résultats obtenus étaient les suivants : les éléments sont dissous dans l'eau quand les carbonates et les plagioclases sont soumis à des faibles, intermédiaires et fortes altérations chimiques qui se sont produits à des taux annuels de 0.0006 mm, 0.0014 mm, 0.0006 mm, et 0.0005 mm, respectivement pour le granite, le basalte, le trachyte et le grès ; l'altération chimique non iso-chimique permet aux éléments nutritifs (Ca, Mn, Na, Cu, Zn, K, Ni et Fe) à l'exception du Mo, de présenter une mobilité relative plus élevée par rapport aux éléments non-nutritifs (Cr, Bi, Cs, Cu, Ga, Pb, Sn, Th, U, V, et Al); les eaux souterraines provenant des eaux de pluies sont influencées par le passage des écoulements préférentiels et sont majoritairement de faciès Ca + Mg – NO₃ dans le bassin sédimentaire de Douka Longo et le mélange en diffèrent variation de Na + K - Cl, Ca + Mg- HCO₃ et Na + K - HCO₃ du bassin igné de Bidou ; le flux élémentaire était HCO₃ > SiO₂ > Na > Ca > K > Mg > NO₃ > Cl > Fe > Al > F > SO₄ > $Zn > Sr > Ba > Mn > BO_2 > NH_4 > PO_4 > Br > NO_2 > Ti pour le bassin sédimentaire de Douka Longo et HCO_3$ > Na > Ca > SiO₂> Fe > Mg > Cl > F > BO₂> Mn > NH₄> Zn > Al > Ba >Sr > SO₄> K pour le bassin igné de Bidou et qui présentait moins de perte de nutriments annuelles que le bassin de Douka Longo ; la nature non fertile des sols serait due en partie aux : déficiences du Phosphore, Fer et Molybdène dans les deux bassins ; déficiences en NO_3^- , K^+ , B, et les terres rares dans le bassin de Bidou ; et l'excès en NO_3^- , K^+ , Ca^{2+} , Mn et les terres rares dans le bassin de Douka Longo. Les techniques de lutte contre l'érosion, les infrastructures hydrauliques et les fertilisants organiques ont été proposé.

Mot clés : Altération chimique, Flux élémentaire, mobilité relative, teneur en eau, nutriment du sol

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GENERAL INTRODUCTION

This part of the work presents the context of the study, the problem statement, the research question, the hypothesis taken, the set objectives and the impacts of the research.

CONTEXT

An expanding world population and the urgency of eradicating hunger, malnutrition and poverty call for determining effective actions to ensure sustainable growth in agricultural productivity and production. According to Roy et al. (2006) every person has an inalienable right to be free from hunger and malnutrition since this proclamation on the World Food Conference in 1974. Therefore, production of food to satisfy the growing population needs become imperative. The present and future agriculture must not only meet the growing population needs but should be sustainable and resilient so as to resist external factors such as climate change, drought and urbanisation (Gram et al., 2020).

In addition, we cannot discuss about agriculture without mentioning about fertile soils and their availability. Global fertile soils are unevenly distributed and the entire African continent has less than 0.5% of the world's most fertile soils (CEA, 2013). Unfortunately, these limited resources are being depleted with time (Christophe et al., 2020; Tsozué et al., 2015). Experts estimate that roughly 40% of soil used for agriculture around the world is classified as either degraded or seriously degraded (CEA, 2013). The case of Africa is more alarming, low inherent soil fertility in the highly weathered and leached soils largely account for low and unsustain crop yield in most of Sub-Saharan Africa (SSA) (Basga et al., 2018a; Bationo et al., 2004; Gram et al., 2020; Joël et al., 2012; Nguemezi et al., 2020; Okalebo et al., 2006; Rotich & Kisinyo, 2018; Sneyd, 2014; Tsozué et al., 2014; Vanlauwe et al., 2017). African soils are highly weathered and acidic, which reduces yields by as much as 30% in some countries, resulting to an average crop yield of only 1 tonne/ha in SSA while most regions in the world have food grain yield range from 2.2 to 2.8 tonnes/ha (Bationo et al., 2006; Roy et al., 2006). Meanwhile prospection show that between now and 2050, food demand is expected to increase by 125% in SSA (CEA, 2013). Still in this light, soil fertility decline has been described as the single most important constraint on food production and food security in SSA, resulting in an annual loss of 6 000 kg of nitrogen, phosphorus, and potassium (NPK) per hectare in the semiarid, arid, and Sudano-Sahelian areas that are more

densely populated (FAO & ITPS, 2015). In addition, various studies have reported 'non-responsiveness' where the application of inorganic fertilisers does not lead to an increase in crop yield (Roobroeck et al., 2020), this could be probably due to the fact that the nutrients in need in that area were not included in the applied fertilisers. One of the main concerns is that agriculture is and will continue to be the backbone of the economy in SSA (Mutuku et al., 2020).

Therefore, maintaining soil fertility becomes a critical component of the crop production system to ensure economical profitability, food security, soil health and sustainable productivity. Soil fertility is the ability of a soil to supply essential plant nutrients in adequate amounts and proportions for plant growth and reproduction (OMAFRA, 2018). Plants require 17 essential elements for growth: carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), potassium (K), sulphur (S), calcium (Ca), magnesium (Mg), boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn) which are classified as macro-nutrients and micro-nutrients, based on their relative abundance in plants (Mahler, 2004; OMAFRA, 2018; Sharma et al., 2014). Nutrients are only available to plants when they are dissolved in soil water or in shallow groundwater (root absorption). Therefore, naturally available or applied nutrients which are not dissolved in groundwater or are not absorbed by plants are susceptible to leaching to downstream or out of the watershed during rainfall depending on the type of the soil and the watershed topography. Since crop production removes nutrients from soil, applying them back in some form is essential to the sustainability of agriculture. Fertilisers are applied to replace nutrients removed by harvest, improve yield, enhance nutrition, and increase quality and utility of crops.

The ongoing increase in crop prices, shrinking cropland areas, increasing fertiliser prices, food insecurity and environmental concerns associated with fertiliser application are triggering a rethink of our current principles of crop nutrition and soil fertility management practices. Precision agriculture is needed in terms of nutrients application, just as in precision irrigation where only necessary and needed amount of water is given to plants during irrigation, here too only necessary and needed quantity of inorganic fertilisers should be given to the soil. This can only be effective if farmers know the natural available inorganic nutrients and its mobility in the watershed.

A scientific paper published in 2003 titled 'Les enjeux du développement agricole dans le Grand Nord du Cameroun' by Barbier et al. (2003) revealed that the Northern part of Cameroon is suffering from low agricultural productivity with very low crop yield as compared to other parts of the world with the same soil type. This paper further revealed that the majority of farmers live below poverty line.

PROBLEM STATEMENT

The northern part of Cameroon constitutes the Sudano-Sahelian, Sub-humid and semi-arid zone of the country and bears two of the five agro-ecological zones (Sudano-Sahelian and Guinean Savana) of the country(Abdoul Aziz et al., 2008). Here, agriculture is the main activity in rural area and employs more than 90% of the rural population (World Food Program, 2016). Agriculture in this part of the country is facing some challenges such as flooding, drought, insecurity, low rainfall, lack of agricultural inputs, low productivity, climate change, agropastoral conflicts, low soil fertility and nutrients depletion (Barbier et al., 2003; Basga, et al., 2018a; WFP, 2016).

In addition, Herve et al.(2008) revealed that in the North Cameroon, the soil organic matter and available P contents had barely declined, while the soil cation exchange capacity (CEC) had sharply decreased along with the N, K, Ca and Mg soil mineral contents. This paper goes further to give some details concerning nutrients depletion on the top soil and revealed that for the 0-20 cm horizon, the soil potassium, calcium and magnesium contents decreased by 56%, 28% and 35%, respectively, in 14 years. Apart from having low crop yield at the level of farmers, research also indicates low mineral levels or mineral deficiencies in natural pastures in the Adamawa region (Njwe & Issa, 1990).

The consequences of this low soil fertility and nutrients decline to farmers varied from economic, social and environmental. Some of these include ; increase in poverty and hunger level, lack of access to basic needs such as children education and health, migration of young people in search for better life in urban areas or migration to more fertile lands, addition of more fertilisers which sometimes end up being transported downstream by rain, spending their money on renting more and more lands, poor farmers become rural labourers (Abina et al., 2002). One of the tremendous consequences of this is hunger where in 2016, Voufo & FOTIO (2016) revealed that the North and the Adamawa regions are the most exposed to food insecurity with 38.6% and 37.4% incidence of food insecurity respectively. According to World Food Programme (WFP), in early 2020, the Far North, North, Adamawa and East regions are the most affected regions in Cameroon as concern food insecurity and the net funding requirement for food assistance between July-December 2020 is USD 52.8 million.

In addition to these problems stated above, the Boko Haram insurgency in the Lake Chad Basin which continues to cause large-scale influx of refugees from Nigeria as well as the internal displacement of people and also refugees from the Central African Republic, the situation becomes an urgency and the dilemma today is how to feed a fertile population from a low fertile soil with significant nutrients decline in an insecure environment? For this reason, the government is putting efforts to manage the situation such as government programs and projects, an example being the adoption of the National Agricultural Investment Plan (NAIP) in April 2014 which aimed to invest 3.35 trillion FCFA in the development of agriculture between 2014-2020, involvement of national and international institutions, civil society organizations and national or international NGOs. On the effective investment to manage the situation, yet the scientific base information for managing soil fertility and prioritizing investments has been quite limited. But soil health being the main condition for food security, it's imperative that we explore soil chemistry and sustainable soil quality management practices to increase crop nutrient use efficiency. There exist before now, no comprehensive hydrogeochemical investigations linking elements derived from water-rock interaction to explaining nutrient availability behaviour in watersheds within the northern regions of Cameroon.

RESEARCH QUESTION

Taking into consideration the real-life situation of people in the study area (Bidou and Douka Longo watersheds) and the socio-economic and environmental impacts of soil health, it will be important to provide necessary scientific soil information. The following question is asked:

-Is the use of shallow groundwater chemistry and rocks chemistry an effective method for assessing soil fertility in watersheds, given that they are the main factors controlling the dynamic of nutrients in the soil?

OBJECTIVES

General objective

Characterise the hydrogeochemical properties of elements in Douka Longo and Bidou watersheds in order to assess the elemental provenance, relative mobility, fluxes and inorganic nutrient availability.

Specific objectives

- Evaluate the elemental provenance, enrichment, depletion and relative mobility from the bed rocks,
- Assess the elemental contents in waters, and fluxes within the watersheds, and
- Assess the inorganic nutrient availability in Douka Longo and Bidou watersheds.

CHAPTER ONE

LITERATURE REVIEW

In this chapter, key concepts and principles necessary to understand the above-mentioned problem, general methods developed to evaluate the problem and the proposed management practices in other regions of the world will be examined.

1.1. SOILS AND SOIL FERTILITY

1.1.1 Soil

Soils are the uppermost part of the earth's crust, formed mainly by the weathering of rocks, formation of humus and by material transfer. Soil is one of the furthermost essential natural resources and source of infinite life (OMAFRA, 2018). It is the most vital and treasurable natural non-renewable resource. From the agricultural perspective, soil supports the growth of plants which supply the world with food, biomass and renewable energy. For large-scale and low-cost crop production, there is no substitute for natural soils as a substrate for crops in the foreseeable future. A soil consists of mineral matter, organic matter and pore space, which is shared by air, water and life forms. About 45–50 percent of the volume of a normal soil consists of mineral matter, 1–5 percent is organic matter and the remaining 50 percent consists of open pore spaces that are shared by air and water (Sharma et al., 2014). In a very dry soil, most of these pores are full of air, while in a saturated soil, they are filled with water. Ideally, air and water occupy about equal spaces, the air residing in the larger pores and water in the smaller ones. Both are needed for the soil to serve as a medium for plant growth.

Well-developed soils generally show a distinct profile with different layers which are the uppermost layer called topsoil or A horizon, the subsoil or B horizon and the parent soil or C horizon. The topsoil is richest in organic matter, nutrients and various soil organisms. Major types of soils are formed from rocks by weathering processes over long periods extending to more than 1 000 years. During weathering, physical disintegration of rocks and minerals occur, and chemical and/or biochemical soil forming processes lead to their decomposition. Soils vary largely with respect to their natural fertility and productivity resulting in plant growth ranging from practically zero to abundant luxuriant growth of natural vegetation. Well-known fertile soils are deep alluvial soils formed from river mud, organic matter-rich soils on loose material, nutrient rich

Vertisols and volcanic soils. In most countries with large food demand, cropping cannot be restricted to the most fertile soils because of the large population and general shortage of usable land. Soils with medium fertility can be improved and naturally poor or degraded soils can also be restored to a satisfactory fertility level. Under poor management, soil fertility can be seriously depleted and soils may become useless for agriculture (Roy et al., 2006).

For the assessment of scientifical base soil information, many organisations and institutions such as FAO, UNESCO and USDA have classified world soil into different types based on developmental (pedogenic) aspects and resulting special soil properties. From their classification, the total land surface of the world is covered by the following major soils:

- Soils of humid tropics, e.g. Ferralsols (Oxisols), etc.: 20 percent;
- Soils of arid regions, e.g. Calcisols (Calcid), etc.: 18 percent;
- Mountainous soils, Leptisols (Umbrept): 15 percent;
- Soils of steppe region, e.g. Chernozems (Udolls): 7 percent;
- Podzols (Spodosols) and similar soils: 7 percent;
- Clay soils of subtropics, Vertisols (Vertisols): 3 percent.

As the need of food is increasing, more sophisticated agricultural technologies are being put in place and consequently the natural properties of soils, especially of the topsoils become more and more similar and adapted to crop requirements.

1.1.2. Soil fertility

Soil fertility is the ability or the quality of a soil that enables it to provide chemical elements (nutrients) in quantities and proportions for plant growth. It is a dynamic natural property of soil and it can be changed under the influence of natural and anthropogenic induced factors (Kannan et al., 2020). Many factors contribute to soil fertility and those factors are as follows:

- Ground water and infiltration

- Soil acidity (pH), active soil life

- Content of available nutrients
- Mineral content and organic mater

- Nature of parent soil and structure
- Exploitable soil depth

Many methods have been developed for the evaluation of soil fertility. These fall into several clusters (Kostov, 2018):

- Plant performance trials including field trials and pot cultures to assess growth, development, toxicity and nutrient deficiencies.
- Chemical analyses of plants, including total elemental analyses and plant tissue analyses.
- Chemical and biological analyses of soils: pH, ammonium and nitrate nitrogen, population of soil microorganisms such as nitrifying bacteria, free living nitrogen fixing bacteria, symbiotic N-fixers, bacteria and mycorrhizae.

1.2. PLANTS ESSENTIAL NUTRIENTS

In agriculture, optimal crop nutrition is an important prerequisite for obtaining high yields and goodquality produce. A plant contains more than 90 elements, out of which, 17 elements are known to be essential which are classified as macronutrients and micro-nutrients, based on their relative abundance in plants (Brataševec, 2013; Mahler, 2004; Roy et al., 2006; Sharma et al., 2014; Stubbs, 2016). The elements are as follows; carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), potassium (K), sulphur (S), calcium (Ca), magnesium (Mg), boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn). The first 03 elements are derived from air or water, while the remaining 14 elements are soil-derived nutrients. These soil derived nutrients are divided into macronutrients (N, P, K, S, Ca and Mg) and micronutrients (B, Cl, Cu, Fe, Mn, Mo, Ni and Zn).

Armon & Stout, (1939) proposed the following criteria of essentiality of mineral nutrients:

- A deficiency of the element in question results in failure to complete the life cycle,
- Deficiency of element in question can be corrected only by supplying that particular element, and
- The element must extend its effect directly on growth or metabolism and not by indirect effect such as antagonism of another element present at a toxic level.

These essential nutrients have different functions and uptake forms. Table 1 gives the various nutrients with their principal uptake forms and functions.

Nutrients	Principal forms for uptake	Functions in plant
Carbon	CO_2	carbohydrates, proteins, lipids and nucleic acids
Hydrogen	$\mathrm{H}_{2}\mathrm{O},\mathrm{H}^{+}$	Metabolism, ionic balance and reducing agent
Oxygen	H_2O, O_2^+	carbohydrates, proteins, lipids, and nucleic acids
Nitrogen	$\rm NH_4^+$, $\rm NO_3^-$	proteins, protoplasts, enzymes
Phosphorus	H ₂ PO ₄ ⁻ , HPO ₄ ²⁻ , PO ₄ ³⁻	ATP, ADP, basal metabolism
Potassium	\mathbf{K}^+	water relations, energy relations, cold hardiness
Calcium	Ca ²⁺	cell structure, cell division, cell elongation
Magnesium	Mg^{2+}	chlorophyll, enzymes
Sulphur	SO ₄ ^{2–} , SO ₂	proteins, protoplasts, enzymes
Iron	Fe^{2+}, Fe^{3+}	chlorophyll, metabolism, enzyme activation
Zinc	Zn^{2+}	protein breakdown, enzyme activation
Manganese	Mn ²⁺	chlorophyll, enzymes
Copper	Cu^{2+}	enzyme activation
Boron	$H_2BO_3^-, B_4O_7^{2-}, BO_3^{3-}$	sugar translocation, cell development, growth
Molybdenum	Mo04 ⁻	nitrogen fixation, nitrogen use
Chlorine	Cl ⁻	photosynthesis and osmo-regulation on saline
Nickel	Ni ⁺	SOIIS
		iron metabolism

Source:(Mahler, 2004)

Due to the essential nature of these nutrients, their deficiency in the soil have enormous consequences on crops appearance, crops growth and crops yield. Nutrient deficiency symptoms may be classified as follows (Sharma et al., 2014):

- Complete crop failure at the seedling stage.
- Severe stunting of plants.
- Specific leaf symptoms appearing at varying times during the season.
- Internal abnormalities such as clogged conductive tissues.
- Delayed or abnormal maturity.
- Obvious yield differences, with or without leaf symptoms.
- Poor quality of crops, including differences in protein, oil, or starch content, and storage quality.
- Yield differences detected only by careful experimental work.

For more information concerning nutrient deficiency symptoms related to a particular essential nutrient, table 2 gives the summary of each essential nutrient and its deficiency symptoms. Our focus here is on the 14 soil-derived essential nutrients and their relative deficiency symptoms.

Table 2: Essential soil-derived nutrient deficiency symptom	ns
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Nutrients	Deficiency Symptoms and Occurrence
	• Stunted, slow growing, chlorotic plants.
Nitrogen	• Reduced yield.
	• Plants more susceptible to weather stress and disease.
	• Some crops may mature earlier
	• Over-all stunted plant and a poorly developed root system.
Phosphorus	• Can cause purple or reddish colour associated with the accumulation of sugars.
	• Difficult to detect in field.
	• Commonly causes scorching or firing along leaf margins.

Nutrients	Deficiency Symptoms and Occurrence
Potassium	• Deficient plants grow slowly, have poorly-developed root systems, weak stalks; lodging is common.
Potassium	• Seeds and fruits are small and shrivelled.
	Plants possess low resistance to disease.
	• Deficiency most common on acid sandy soils and soils that have received large applications of Ca and/or Mg
Poor root growth: Ca deficient roots often turn black and rot.	
Calcium	• Failure of terminal buds of shoots and apical tips of roots to develop, causing plant growth to cease.
	• Most often occurs on very acid soils where Ca levels are low.
	• Other deficiency effects such as high acidity usually limit growth before Ca deficiency apparent.
Magnesium	• Leaves show a yellowish, bronze or reddish colour while leaf veins remain green.
	• Chlorosis of the longer leaves.
Sulphur	• If deficiency is severe, entire plant can be chlorotic and stunted.
	• Symptoms resemble those of N deficiency; can lead to incorrect diagnoses.
Boron	• Reduced leaf size and deformation of new leaves.
	• Interveinal chlorosis if deficiency is severe.
	• May cause distorted branches and stems.

Nutrients	Deficiency Symptoms and Occurrence	
	• Related to flower and or fruit abortion, poor grain fill, and stunted growth.	
	• May occur on very acid, sandy- textured soils or alkaline soils.	
Copper	• Reduced leaf size. • Uniformly pale-yellow leaves. • Leaves may lack turgor and may develop a bluish-green cast, become chlorotic and curl.	
	• Flower production fails to take place.	
	• Organic soils are most likely to be Cu deficient.	
Iron	• Interveinal chlorosis that progresses over the entire leaf. With severe deficiencies, leaves turn entirely white.	
	• Factors contributing to Fe deficiency include imbalance with other metals, excessive soil P levels, high soil pH, wet, and cold soils.	
	• Interveinal chlorosis.	
Manganese	• Appearance of brownish-black specks.	
	• Occurs most often on high organic matter soils and soils with neutral to alkaline pH with low native Mn content.	
	• Shortened internodes between new leaves.	
Zinc	• Death of meristematic tissue.	
	• Deformed new leaves.	
	• Interveinal chlorosis.	
	• Occurs most often on alkaline (high pH) soils or soils with high available P levels.	

Nutrients	Deficiency Symptoms and Occurrence
Molybdenum	• Interveinal chlorosis.
	• Wilting.
	• Marginal necrosis of upper leaves.
	• Occurs principally on very acid soils, since Mo becomes less available with low pH.
Chlorine	
	• Chlorosis in upper leaves.
	• Overall wilting of the plants.
	• Deficiencies may occur in well drained soils under high rainfall conditions.
Cobalt	• Causes N deficiency: chlorotic leaves and stunted plants.
	• Occurs in areas with soils deficient in native Co.
Nickel	• Symptoms and occurrence are not well documented but may include chlorosis
	and necrosis in young leaves and failure to produce viable seeds.

Source: (Roy et al., 2006)

The above essential nutrients are obtained by plants both from soil reserves (natural available nutrients) and external nutrient sources (fertilizers, organic manures, the atmosphere, etc). It is therefore important for farmers to be aware of the natural nutrients available in the soil so that they can choose an appropriate fertiliser necessary for plants growth and crops production.

1.3. FACTORS AFFECTING SOIL FERTILITY

1.3.1. Elements mobility

Many soils have vast reserves of plant nutrients but only a small portion of these nutrients becomes available to plants during a year or cropping season. Out of the total amount of nutrients in soils, more than 90

percent is bound in relatively insoluble compounds or is inaccessible within large particles and, therefore, is unavailable for crop use (Sharma et al., 2014). Nutrients are present in both organic and mineral forms and all forms must change themselves to specific mineral ionic forms in order to be available to plant roots.

The content of available nutrients and their degree of availability and accessibility is not a static condition for all situations but ever-changing and very dynamic because of the various inorganic and biochemical processes that take place in soils. These depend on temperature, water content, soil reaction, nutrient uptake, input and losses, etc. Most forms of a nutrient (in solution, adsorbed, fixed, sparingly soluble, etc.) are in a dynamic equilibrium. Nutrient uptake by plants, biological activity of soil organisms and external nutrient input can result in large or small fluctuations among the nutrient fractions, resulting in an ever-changing soil fertility status. To a certain extent, this can and should be controlled by appropriate management practices (Roy et al., 2006).

1.3.2. Chemical weathering

Chemical weathering and soil removal rates are responsible for the Earth's landscape, composition of surface and ground- water, soil development and buffering the composition of the atmosphere (Fernandes et al., 2020). In virtually all environments, weathering results in the neutralization of hydrogen ion (H⁺) and the production of soluble basic cations (Ca, Mg, K and Na), aluminium and silica (H4SiO4) and it is also a major sink for H⁺ in most natural systems (Johnson et al., 1994). The presence of water is required for chemical weathering to occur. Additionally, rate constants for weathering reactions are temperature-dependent.

Catchment budgets in agricultural systems are significantly influenced by major additional inputs of agrochemicals, which aim to produce and maintain an optimum environment for plant growth. Chemical applications are necessary in most agricultural systems, because natural weathering rates and nutrient pools are insufficient to maintain plant growth at the levels required in modem agriculture. In unfertilized/unlimed areas weathering rates would be expected to increase in response to cropping (Weller et al., 1986). According to Paces, (2018) fertilisers also accelerate chemical weathering and so chemical weathering can be estimated from the mineral depletion in the soil.

To determine the degree of rock weathering in a given drainage basin, Boeglin & Probst, (2019); Mortatti & Probst, (2003) calculated the molecular ratio Re from the concentrations of different dissolved species measured in the surface waters from granite and gneiss terrains:

Re is also equivalent to the molecular ratio $(SiO_2)/(Al_2O_3)$ of secondary mineral neoformation within the soil profile. The Re values are classified as such: if Re = 0, the dominant weathering process is the genesis of gibbsite, if Re = 2, kaolinite is essentially formed, if Re = 4, the weathering products are mainly smectites.

To determine the chemical weathering rate (WRch), Boeglin & Probst, (2019); Mortatti et al., (2003); Mortatti & Probst, (2003) considered WRch to be the ratio between the amount of silica to be removed S_L (kg/m³) to transform 1 m³ of granite into 1 m³ of kaolinite and the flux Q_{SiO_2} of dissolved silica (kgkm⁻² yr⁻¹.) measured in the river; note, $S_L = S_0 - S_S$, we have:

Where;

 Q_{SiO_2} is the specific flux of dissolved silica in the river.

 S_0 is the volumetric amount of silica in the unweathered mean parent rock and.

 S_S = is the volumetric amount of silica in the saprolite (weathered or altered rock)

From this, the WRch of the Niger river was found to be 4.44 m/Myr Boeglin & Probst, (2019) and the mean chemical weathering rate of silicate rocks (WRch) for the Piracicaba River basin was about 2.8 m/Myr, which means the silicate rock profile reduction and consequently soil formation (Mortatti et al., 2003). The chemical weathering rates of silicate rocks (rate of bedrock transformation into saprolite) calculated for the Amazon basin (8 m/Myr in the Shield to 24 m/Myr in the Andes, 15 m/Myr on average for the whole basin) is comparable to other estimations made for other humid tropical–equatorial river basins in Guyana and in Africa, but they are higher than weathering rates estimated for dry tropical environments like for the Niger river basin (Mortatti & Probst, 2003).

Chemical weathering also has indices which are commonly used to characterise weathering profiles: Weathering Index of Parker (WIP), Chemical Index of Alteration (CIA), Chemical Index of Weathering (CIW), and Plagioclase Index of Alteration (PIA). The Weathering Index of Parker (WIP) is the most appropriate for application to weathering profiles on heterogeneous parent rock and this is because it allows aluminium mobility (Price & Velbel, 2014). These indices are widely used in determining the weathering ability of rocks. An example is Ngueutchoua et al., (2017) who revealed that the PIA and CIW of sediment from Kumba area in the Douala sub-basin ranged from 79.63 to 99.90 and 87.57 to 99.92 respectively, suggesting that the sediments and their potential source rocks experienced intense weathering. In the same light, Saikia et al., (2015) revealed that the interrelation between CIA, PIA, Al/Na and K/Na reflects the silicate weathering intensity.

1.3.3. Solute flux

A steady flow of nutrients occur naturally with surface water or groundwater movement in hilly and mountainous areas as part of the natural erosion process, even under natural vegetation cover. The annual losses of nutrients in the soil solution from hilly parts of the landscape are often relatively small as are the gains for the low-lying land. It helps in evaluating the nutrients loss from a watershed. Many research papers had evaluated the base cations fluxes for short and long term. An example is the case of granitic till in northern Sweden where Land & Öhlander, (2000) the present and long-term average fluxes of base cations were 0.356–0.553 keq ha⁻¹ yr⁻¹ and 0.325 keq ha⁻¹ yr⁻¹. Additionally, Mortatti et al., (2003); Mortatti & Probst, (2003) revealed that the mean annual dissolved SiO₂ carried out by the Amazon river to the ocean is calculated to be $38.1*10^{6}$ tons, corresponding to a specific riverine transport of 8.3 tons km⁻² yr⁻¹.

1.3.4. Soil erodibility

Soil erodibility refers to the susceptibility of soil to erosion by water. The susceptibility of a soil to water erosion is primarily determined by the erosive potential of the rainfall, the slope of the land surface, the topography of the watershed, and the vegetative cover on the soil surface (Arif, 2020). Most clay-rich soils have a high resilience because they are resistant to detachment. Coarse textured, sandy soils are also resilient because of low runoff even though these soils are easily detached. Meanwhile medium textured soils, such as silt loam soils are only moderately resistant to erosion because they are moderately susceptible to detachment and they produce moderate runoff (FAO & ITPS, 2015). Soils having a high silt content are the most erodible of all soils due to the fact that they are easily detached and produce high rate of runoff.

The main model used to estimate soil loss by erosion is the Universal Soil Loss Equation (USLE), which unites the major factors that influence erosion into one equation. The USLE model defines annual soil loss (*A*) (t h⁻¹ y⁻¹) as a product of six main factors: rainfall erosivity (*R* factor), soil erodibility (*K* factor), slope length (*L* factor), slope angle (*S* factor), land cover (*C* factor) and conservation practice (*P* factor) (Ghosh et

al., 2013). The soil erodibility factor (K) is the component of the equation that represents soil physics, and is defined as the inherent capacity of the soil to withstand disintegration of its particles and their subsequent transport (Celestino et al., 2017).

$$K = \frac{0.1318 * 2.1 \text{M}^{1.14} (10^{-4}) (12 - 0\text{M}) + 3.25(\text{S} - 2) + 2.5(\text{P} - 3)}{100} \dots \dots \dots \dots \dots (3)$$

Where: M is the parameter related to the primary soil particles, S is the clay in percentage, OM is the organic matters and P is the parameter related to soil permeability.

Soil erodibility is reduced by organic matter and soil structure due to their ability to reduce soil detachment, increase infiltration, which reduces runoff and thus erosion. moreover, permeability of the soil profile affects erodibility because it affects runoff (FAO & ITPS, 2015). The loss of cropland is a serious problem because the World Health Organization (WHO) and the Food and Agricultural Organization reported that, two-thirds of the world population is malnourished and that soil is being lost from agricultural areas 10 to 40 times faster than the rate of soil formation, imperilling humanity's food security (Pimentel & Burgess, 2013). Soil erosion contributes to severe nutrients decline in SSA and is responsible for low productivity in most African countries. Along with the loss of soil is the loss of water, nutrients, soil organic matter, and soil biota. The soil system is severely harmed when soil erosion is allowed to occur. According to Pimentel & Burgess, (2013), 1 mm of soil is easily lost in one rain or wind storm, this gives 15 t/ha of soil loss over a hectare of cropland. Replenishing this amount of soil under agricultural conditions requires approximately 20 years, meanwhile the lost soil is not available to support crops.

1.3.5. Water resources

It refers to potential useful sources of water. It is useful in sustaining life. It can be divided into surface water (rivers, streams, wetlands) and groundwater (wells, boreholes and springs).

- Surface water
- Stream: A stream is a body of water, with a current, confined within a bed and banks.
- **River**: A river is a natural flowing watercourse, usually freshwater, flowing towards an ocean, sea, lake or another river.
- Wetland: A wetland is a land area that is saturated with water, either permanently or seasonally, including during the growing season.

• Groundwater

- **Spring:** A spring is any natural situation where water flows from an aquifer to the Earth's surface.
- **Well:** Water well is an excavation or structure created in the ground by digging, driving, boring, or drilling to access groundwater in underground aquifers.
- **Borehole:** A borehole is a narrow shaft bored in the ground, either vertically or horizontally made by a special tool or machine, especially one that is made in the ground when searching for oil or water.

Considering that water is a unique substance not only for the reason that it can occur in three phases (gas, liquid and solid) under the conditions of Earth's temperature and pressure, but also because its large dipole moment of 1.8×10^{-18} esu, gives it a great potential for dissolving matters (Kitano, 1975), it can dissolve rocks to form their altered equivalents (saprolites). Such dissolution releases, transports and distributes nutrients based on geographical and geochemical conditions that prevail within a watershed (e.g., Faure, 1991). The dissolution of primary and secondary minerals, which can occur either congruently or incongruently in rocks has been identified as a geochemical process that releases nutrients to soil horizons through water-rock interaction (Forth, 1984), and has become an important domain of investigation for hydrogeochemists within watersheds with or without agricultural activities (McLelland, 1950), and has led to litany of results in scientific literature. Examples of such results include: behaviour of elements in weathering profiles developed from Quaternary volcanic rocks (Quantin et al., 1991; Price et al., 1991; Nesbitt and Wilson, 1992; Cotten et al., 1995; Hill et al., 2000; Patino et al., 2003; Little and Aeolus Lee, 2006); behaviour of elements in soils developed from nephelinites at Mt. Etinde in Cameroon (Etame et al., 2009); solute generation during silicate weathering in Japan (Vuai and Tokuyama, 2007); mobility and fluxes of elements during basalt weathering at Mt. Etna (Aiuppa et al., 2000); trace metal modelling of groundwater-gas-rock interaction in a volcanic aquifer (Aiuppa et al., 2005); weathering rates of granitoids in humid tropical watersheds (Braun et al., 2005); implications of water-rock interaction on the failure of Lake Nyos natural dam (Fantong et al., 2015); compositions and mobility of elements at Benue River Basin in Cameroon (Fantong et al., 2020); enrichments and depletion of elements in altered rocks within hydrochemical systems (Brimhall and Dietrich, 1987); rare earth elements variation in agricultural fields from eroded granite hilly lands in southern China watershed (Chen et al., 2019), and bioaccumulation and translocation of rare earth elements in two forage legumes grown in soils treated with coal fly ash (He et al., 2019). Although the aforementioned results depict that chemical weathering of minerals from bed-rocks can contribute to the abundance and availability of nutrients in soil horizons, which in turn determines crop yields (Cruickkshank, 1972), there exist before now, no comprehensive hydrogeochemical investigation that links up elements derived from water-rock interaction to nutrients availability and behaviour, in watersheds within the northern regions of Cameroon.

1.3.6. Land use

Land use refers to the activity that occupies a geographical space. It is an important factor when dealing with resources management. Land use involves the management and modification of natural environment into built environment such as settlements and semi-natural habitats such as arable fields, pastures, and managed woods or arrangements, activities, and inputs that people undertake in a certain land cover type. Land use affects chemical weathering, soil erosion, nutrient content and soil fertility. Land use affects total clay (TC), water dispersible clay (WDC), clay dispersion ratio (CDR) and dispersion ratio (DR) in the northern Cameroon (Basga, et al., 2018b). Land use also affects the soil removal rate and Fernandes et al., (2020) revealed that in Brasilia, the soil removal rate in the Sorocaba River basin is almost 3-folds higher than the Cenozoic soil removal rates and it is due to the current land use.

1.3.7. Watershed

A watershed is a hydrologically defined area that is drained by a network of streams, which meet together in such a way that the water leaves through a common point. A watershed is made up of soil, vegetation and water along with the people and animals who are the integral part of the system. Sustainable management of a watershed thus entails the rational utilization of land and water resources for optimum production but minimum hazard to natural and human resources. Therefore, watershed management is the process of guiding and organizing land use and use of other resources in a watershed to provide desired goods and services to people while enhancing the resource base without adversely affecting natural resources and the environment (Sreedevi et al., 2004).

1.4. WATER QUALITY ANALYSIS

1.4.1. Major Ions

Major ions are positively charged cations and negatively charged anions which occur in water in higher concentrations. Their concentrations range from a few mg/L to several hundred mg/L. Major anions include; CI^- , NO_3^- and HCO_3^- while major cations include; Na^+ , K^+ and Ca^{2+} . In assessing the quality of water, the various major ions are taken into consideration: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , PO_4^{3-} , CI^- , NO_3^- , HCO_3^- , and F^- . These ions enable us to know the type of water we are dealing with in terms of classification, concentration, its

salinity, suitability for irrigation, suitability for domestic use and also it nutrient content. Testing for major ions gives the spatial variation and evolution of water chemistry, quality of water resources and the nutrient content.

Major ions are dissolved in groundwater through many processes, Rain water, as it passes through the air and through and over the land, dissolves many chemical species. Passing through the atmosphere, for example, it dissolves the gases which constitute air including nitrogen, oxygen and carbon dioxide. By the time that rain water has passed over and through land to become groundwater or surface water it has normally acquired many dissolved chemical species. Clearly, the precise chemical composition of the water will depend upon the types of rock and soils with which the water has been in contact and this can be used to characterise a particular water by determining its chemical make-up.

1.4.2. Trace Elements

Trace elements are elements which occur naturally in very low concentrations as compared to major ions. They can be divided into four categories; (1) alkali and alkaline-earth metals [barium (Ba) and lithium (Li)]; (2) transition metals [chromium (Cr), molybdenum (Mo), and vanadium (V)]; (3) metalloids [arsenic (As) and boron (B)] and the nonmetal selenium (Se); and (4) informally denoted heavy metals [cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn)]. Mineral precipitation, dissolution reactions, surface interactions, adsorption and oxidation-reduction reactions often govern the activities of trace elements in soil solutions. Mobility depends primarily on redox potential and pH and secondarily on surface interactions. Depending on geologic sources, high concentrations of these elements are often observed in arid and semiarid areas because of the typically oxidized and alkaline conditions. Any trace elements exist in more than one oxidation state (e.g., V, Cr, Se, As), and are therefore affected by electron transfer or oxidation-reduction (redox) reactions. An element's mode of occurrence is in turn, determined primarily by the pH and redox status of soil solutions and groundwater, and by the solid phase controlling solubility and distribution. According to Hem, (1985), Sedimentary rocks and soils are the solid-earth materials that must affect and determine the trace element chemistry of groundwater. Some of these trace elements constitute the soil derived micronutrients (Cu, Ni, Mo, B, Zn) while others contribute to soil phototoxicity (Cd, Cu, Ni, Hg, Pb, and Zn).

Evaluation of soil quality relative to inorganic trace element concentrations involves general consideration of the soil's capacity to perform its function within the ecosystem. Evaluation of uptake by plants requires comparison of trace element concentrations in the soil with levels known to be associated with harmful levels of plant uptake. Evaluation of all considerations require that the mode of

occurrence of the element or elements be determined and the effects of the various biogeochemical and physical processes be identified.

1.4.3. Rare Earth Elements (REEs)

The rare earth elements (REEs) comprise the elements scandium and yttrium, and 15 lanthanides with successive atomic numbers (Z) from 57 to 71. The name "rare earth elements" arises from minerals from which they were isolated, which were uncommon oxide-type minerals. The low atomic number elements of the series termed are light rare earth elements (LREE), those with the higher atomic number are referred to as heavy rare earth elements (HREE). According to Walters et al. (2010), light-rare earth elements (LREE) include; lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), and europium (Eu); and heavy-rare-earth elements (HREE) gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Rare earth elements are considered particularly informative on the conditions prevailing during the formation of rocks, and REE studies have important applications in igneous, sedimentary, and metamorphic petrology (Rollinson, 1993). The REE content strongly depends on the parent rocks. Application of phosphate fertilisers and phosphogypsum can supply REEs to the soil (Todorovsky et al., 1997). The light REEs La, Ce, Pr, Nd, Sm and Eu account for 90% of the total REE content in soils. They are applied to soils as fertiliser's materials or as contaminations of industrial sludges so that an assessment of their behaviour in soils is required for evaluating agro-environmental effects (Hu et al., 2006). Crop response to REE application depends on various factors, including soil properties. The increase in crop yield reported upon the application of REEs by workers from all parts of China range between 5% and 103%, with an average response of 8 to 15% (Xiong et al., 2000).

1.4.4. Hydrochemistry

That part of hydrology that deals with the chemical characteristics of bodies of water. The assessment of water quality and graphical representation is done with the following tools:

- **Stiff diagrams:** It is a graphical representation of chemical analyses, widely used by hydrogeologists and geochemists to display the major ion composition of a water sample.
- **Piper diagram:** It is a graphical representation of the chemistry of a water sample or samples. Some of its advantages are: many water analyses can be plotted on the same diagram, it can be used to identify mixing of waters and also to classify waters.

- **Bivariate plot:** It is one of the simplest forms of quantitative (statistical) analysis. It involves the analysis of two variables (often denoted as X, Y), for the purpose of determining the empirical relationship between them.
- Wilcox diagram: Wilcox salinity diagram help to recognize various hydrogeochemical types in a groundwater basin. Irrigation water containing a high proportion of sodium will increase the exchange of sodium content of the soil, affecting the soil permeability and texture.

1.5. INTEGRATED SOIL FERTILITY MANAGEMENT

The evaluation or assessment of soil fertility is perhaps the most basic decision- making tool for balanced and efficient nutrient management (Fairhurst, 2012). It consists of estimating the available nutrient status of a soil for crop production. A correct assessment of the available nutrient status before planting a crop helps in taking appropriate measures for ensuring adequate nutrient supply for a good crop over and above the amounts that the soil can furnish. Currently, soil fertility research and strategy focus on the new paradigm of Integrated Soil Fertility Management (ISFM) which is a holistic approach in soil fertility research that embraces the full range of driving factors and consequences of soil degradation – biological, chemical, physical, social, economic, health, nutrition and political. Soil fertility management is crucial for sustained production and requires inputs of nutrients to compensate those removed by crops and lost from the soil through various physical and biochemical processes. The recently developed soil fertility management options have targeted the efficient use of N and P by crops and the integrated nutrient management approach.

During the past three decades, the paradigms underlying soil fertility management research and development efforts in SSA have undergone substantial change. From the nutrient replacement paradigm to Low Input Sustainable Agriculture (LISA), AfNet adopted the Integrated Soil Fertility Management (ISFM) paradigm that forms an integral part of the Integrated Natural Resource Management (INRM) research approach with a focus on appropriate management of the soil resource (Bationo et al., 2004). Other organisations and associations were created to promote ISFM, such organisations include; ASHC, AGRA, ASSS, IFDC and IITA.

ISFM strategies include; soil conservation, water management, resilient germplasm /fertilizer, integrated pest management, ecosystem services, policies, good markets. ISFM embraces responses to the full range of driving factors and consequences, namely biological, physical, chemical, social, economic and

political aspects and requires an evolutionary and knowledge intensive process and participatory research and development (Vanlauwe et al., 2017). ISFM plays a critical role in both short-term nutrient availability and longer-term maintenance of soil organic matter and sustainability of crop productivity in most smallholder farming systems in the tropics. A two year result showed that the integrated application of organic and inorganic fertilizers improved productivity of wheat and tef as well as the fertility status of the soil (Agegnehu & Bird, 2014). Nevertheless, though ISFM is the notably preferred option in replenishing soil fertility and enhancing productivity, it is not yet widely taken up by farmers. The reasons for this are many, which include access or availability of inputs, use of organic resources for other purposes in place of soil fertility, nutrient balancing, collecting, transporting and management of organic inputs and economic returns of investments. These are the key challenges of adoption in the scaling up of such alternative soil fertility management practices to millions of small-scale farmers in the highlands of the country.
CHAPTER TWO

METHODOLOGY

In this chapter, the study area will be described, as well as the steps taken in order to achieve the objectives set in the introduction of this document. These steps include the means through which field survey was done, samples were collected, tools, difficulties faced during sample collection, and a statistical data analysis to obtain favourable results.

2.1- DESCRIPTION OF STUDY AREAS

This work was carried out in two different watersheds in the northern Cameroon. These watersheds include the Bidou igneous iatershed (BIW) located in the Ngaoundere III municipality (Adamaoua region) and the Douka Longo sedimentary watershed (DLSW) located in the Ngong municipality (North region). The watersheds selection were done while taking into consideration the climate type, geology, previous work, scientific publication, farmer experience and socio-economic situation.

2.1.1. Location

The Bidou watershed, which from here is referred to as Bidou igneous watershed (BIW), because its bedrock is dominantly igneous rocks (Figure 1c), covers a surface area of 61 km² with altitude ranging from 1064 m to 1387 m. BIW is administratively located in the Adamawa Region of Cameroon, Vina division, Ngaoundere III municipality and geographically located between latitudes 7.40 and 7.53 N and longitudes 13.52 and 13.58 E. It is constituted of 17 villages and 4 urban quarters and also bears the university of Ngaoundere (PCD, 2013).

The Douka Longo watershed, which is also referred to as Douka Longo sedimentary watershed (DLSW), because the dominant rock is sandstone, has a surface area of about 678 km² with altitude ranging from 203 m to 458 m. DLSW (Figure 1b) is administratively located in Cameroon's North Region, Ngong municipality and it is geographically situated between latitudes 8.80 and 9.10 N and longitudes 13.30 and 13.50 E (PCD, 2011). The figure 1 showed the located of the BIW and DLSW in Cameroon together with their respective geology and rivers network.



Figure 1: Locations of selected watersheds, in Cameroon (a), location of Douka Longo watershed-described here as Douka Longo Sedimentary watershed- (DLSW) (b), and Bidou watershed- described here as Bidou igneous watershed- (BIW) (c).

2.1.2. Climate

The climate of BIW is of Sudano-Guinean climate and moderated by altitude. It has an annual rainfall of 1500 - 2000 mm. a dry season of about 5 months and a rainy season of about 7 months between April and October. It has an average annual temperature of 23° C with an absolute maximum of 34° C in March (Njwe & Issa, 1990).

The climate of DLSW is of Sudano-Sahelian type, characterised by a unimodal variant precipitation ranging between 800 - 1300 mm. It has two seasons each lasting for a period of 6 months, the dry season (November - May) and rainy season (June - October). It has an annual average temperature of 28° C (PCD, 2011).

2.1.3. Soil

In general, the soils in BIW is of orthic and rhodic ferrals associated with orthic acrisols. The soil plateau of Ngaoundere originated from diverse ancient rocks essentially from ferritic formations. They are of red and brown colour, constituted of lateritic and clay horizons. Soil structure is highly altered on agricultural and pasture zones (PCD, 2013). The dominant soil types in the watershed are spodosols (composed of accumulation of oxides/hydroxides of Al and Fe that form "hardpan") and lateritic oxisols. Just before the downstream area, where the Bidou and the Dori rivers (flowing at the west and out of the watershed) meet to flow into the Bini River, is a constellation of cultivation activities by farmers who attest that over the years, yields of food crops are very poor at the sites labelled as "poor soil sites". Thus, they are bound to concentrate their agricultural activities within the low-lying alluvium in order to contribute in meeting the food demand from the one million inhabitants of the Adamawa Region and beyond.

The DLSW has different soil types. In the lowlands, the soil types are hydromorphs and vertisols near permanents river networks. In the highlands, the soil is lithosols. Moving towards living zones, there is a transition to vertilithomorps on planosols. The dominant soil types in the watershed are sandy arenosols that consist of patches of oxisols, aridosols, and vertisols (PCD, 2011).

2.1.4. Vegetation

The vegetation of BIW is dominated by 3 types of formations: savannah, forestry galleries and massive forestry. Constituted of trees such as; *Daniellia oliveri, Lophira lanceolota,*

Combretum spp., Ekebergia senegalensis, Terminalia spp., Parkia biglobosa et Vitellaria paradoxa and animals such as antelopes, reptiles and others.

The vegetation of DLSW is of Sudanian savannah shown degraded land near villages. Constituted of the following species: *Isoberlinia doka, l'Eucalyptus camadulensis, Borassus aethiopium, Isoberlina tomatosa, Anogeissus leiocarpus, Khaya senegalensis, Afzelia africana, Daniela oliveri, Terminalia marcroptera, Terminalia laxiflora, Acacia spp.* The zone 19 is protected and used for practical works by the school of Fauna of Garoua.

2.1.5. Hydrology

BIW is drained dendritically by the Dang, Madjinge, Maso and Bidou streams. The Dang stream and discharged groundwater accumulate to form the Dang Lake whose outlet meets with the confluence of Madjinge, Maso and Bidou tributaries downstream to form the Bidou River that empties into the Bini River (PCD, 2013).

DLSW is drained by the Mayo Douka and Mayo Mbangai, which are tributaries that dendritically drain the watershed to form the Douka Longo River. At the peak of dry season, these tributaries run dry with underflows at depths to about 0.5 m in the river channels, while at the peak of the rainy season, the monotonously low-lying topography of the watershed with altitudes range from 285 to197 m. asl get over flooded, and clay sized sediments clog inter-grain spaces rendering the top soil inadequate for agricultural production

2.1.6. Geology

The geology of BIW is mainly ancient granites and volcanic material (mainly recent basalt) (Njwe & Issa, 1990). It belongs to the Cameroon Volcanic Line and constitutes of 3 orography which is appeared in the form of steps moving the South towards the North:

- Bini Dang Malang plain ranging between 1069 1089 m.asl, consist of many flooding zones during the peak on rainy season.
- Wouro Soua Beka Mounguel plain, characterised by altitude ranging from 1128 1379 m.asl at Mounguel. This plain is constituted of acidic volcanic rocks (trachyte and phonolite).
- The Tchabal plateau with an altitude of 1388 m and which is the transition zone to the NGaoundere plain.

The topography of BIW drops drastically with valleys dividing gentle slopes of Tertiary basaltic domes from 1377 m.asl in the northern upstream. Southwardly, the basaltic flow terminates abruptly forming a clifflike feature that drops the topography to 1149 m.asl, and continuous monotonously with altitude ranging between 1149 and 1070 m. asl in the midstream, which is spatially covered by an alternation of lateritic duricrust and ferruginous soils, observed to be formed from the chemical weathering of granites and trachyte. The blanketing lateritic hard pan causes run-offs that wash off the overlying thin soil, which mixes and accumulates together with organic matter to form Quaternary alluvium at low-lying stream banks at the outlet of the watershed, where sporadic outcrops of Precambrian potassic-rich granites occur. Younger basaltic flows and trachytic domes with piedmont deposits resulting from weathering, intrude the older Formations.

For DLSW, and in the geological point of view, ca. 80 % of the watershed drains Cretaceous siliceous, ferruginous and arkosic sandstones, and poorly sorted immature polymict basal conglomerates, that megascopically consist of the mineral's quartz and feldspars. The intercalations of sandstones and conglomerates show graded bedding. The intra - and inter - rocks beds are separated by thin layers of iron oxides which form decimetric "sandstone ball" structures with cores that contain conglomerate and crust that contains sandstone. In some locations, mosaic of potholes occurs, which are relics of the coarser conglomerate cores that have undergone differential weathering by surface runoffs. Joints, fractures and faults with NW-SE and N-S trends intersect the rocks providing pathways for some runoffs to also infiltrate and recharge the groundwater that the inhabitants of the watershed exploit for various domestic uses through hand dug wells. Overlying the conglomerates and sandstones are Quaternary alluvial/fluvial gravel, sand and clay size sediments. The Quaternary and Cretaceous sediments and sedimentary rocks occupy the middle and downstream portions of the watershed, while at the southward upstream are outcrops of Precambrian granites, and intrusions of Tertiary syenite and basalt, from where the first order tributaries of Mbangai and Douka take their rise and together with other tributaries from sandstone hills that flank the west of the watershed (Figure 1b), collect into the Douka Longo stream. As a dominantly stream gaining system, the Douka Longo stream also collects direct runoffs during the rainy season and flows northwards into the Benue river.

2.1.7. Demography

According to the Municipal development plan of Ngaoundere 2013, the municipality has a total population of 38169 inhabitants with a population density of 60 inhabitants per km². The total population add up to 61 000 inhabitants when considered the Ngaoundere university student population. The population is constituted of Peulh, Kanouri, Dii, Haoussa, Mboum, Bamoun, Bamiléké, Toupouri, Moundang, Gbaya and others (PCD, 2013).

According to the Municipal development plan of Ngong 2011, the municipality has a total population of 147 385 inhabitants constituted of 43,7% males and 56,3% females. The population is constituted of Fulbes, Lames, Mousoys, Massas, Dabas, Lakas, Mafas, Moufous, Moundangs, Gabris, Kapsikis, Falis, Keras, Guidars, Namdjis, Hinas, Tchouvouks, Haoussas, Madas, Toupouris, Bamileke, Batas and others (PCD, 2011).

2.1.8. Economic activities

Economic activities in BIW includes agriculture, animal raring, selling and transport. The agricultural sector employed most of the population where diverse crops such as: potatoes, beans, maize are cultivated. While at the level of Tchabal Baouro and Tchabal Mounguel, cattle raring is predominated. The mixture of agriculture and cattle raring is at the origin of agropastoral conflicts. Corps productivity is limited here by low soil fertility and uncontrolled burning of lands (PCD, 2013).

The situation is not different in Ngong, where 72% of the population (about 106 000 farmers) and the others activities include raring, fishing, transport, selling, social economic and others informal activities. The main crops producing in Ngong include: maize, sorghum, groundnut, rice, onion, banana, soja beans, cotton and others (PCD, 2011).

2.1.9. Socio-environmental challenges

Both Ngaoundere III and Ngong are facing numerous global challenges which include: climate change, low soil fertility, nutrients depletion, food insecurity, social insecurity, flooding, water scarcity and water insecurity. For food insecurity, the World Food Program revealed that both areas are exposed to food insecurity of about 38.6%. This coupled with the fact that the area is suffering from Boko Haram war and has influx of refugees from other countries makes the situation to be become one of the most urgent situations for the country.

2.2- DESK STUDY

This involves the scooping of relevant documents to ensure that the objectives were actually issues that needed to be addressed in the study area, and has local and international significance for science and wellbeing of the society. It involves the use of documents obtained from the internet, books and journals from various authors enabled the layout of a good literature review which was used to orientate this work. A location map for the study areas were gotten from open street map and used to identify the names of the areas whereby water samples were collected. With this information, one was able to assess the roads and river network in the study area and identify zones for water sample collection. It also involved the establishment of a plan to collect samples from field during the rainy and dry seasons, and sites where watershed discharge is performed.

2.3- FIELD STUDY

In order to meet the objectives set up for this work, the field work is divided into 4 main parts which are;

- Field survey and sites selection, which include getting in contact with the local community,
- Rocks sampling
- Shallow groundwater sampling for both rainy and drying season,
- Stream flow discharge measurement.

2.3.1. Field survey and sites selection

This involved the use of our eyes (sight) as a parameter to evaluate the well-being of plants, identified rocks weathering and as well as the use of digital cameras and/or mobile phones to take pictures which served as proof of what was seen in our area of study. Also interviews and open-ended discussions with local authorities including farmers and agronomists to enable one get their views on the agricultural productivity, soil fertility and the social impacts on famers. A site visit was in sites where farmers have experienced poor yield of food crops, which are indicated on Figure 6 as poor soil sites, and confirmed that in the Adamawa Region (Figure 6a), the soils at the sites are dominantly lateritic, while in the North Region (Figure 6b), the soil at the sites are sandy and clogged with clay. The topographic maps were used to delineate the BIW in the Adamawa Region (Figure 6a) and the DLSW in the North Region (Figure 6b), both of which circumscribed the six selected poor soil sites.

2.3.2. Rocks and shallow groundwater sampling collection procedure and instruments

The various instruments that were used in the onsite/field data collection included: a GPS, EC meter, pH meter, a thermometer, 5L of distilled water, three coolers, hammer, 10L bucket, notebooks, pens, pencils, digital camera, cellulose filters, 100 ml syringes, 100 ml and 250 ml polyethylene plastic bottles, 50 ml glass bottles, total station, 1 M concentrated nitric acid, rope, a measuring tape, a stop watch, a marker and ice packs as shown in Figure 2. The table 3 gives a summary of all the materials used during field data collection and their related uses.

Instruments	Uses
GPS Garmin 64s	To get geographical coordinates (latitude, longitude and
	altitude) of water sample collection points
EC Meter	Measure electrical conductivity (EC, μ S/cm) and Oxidation-
	reduction potential (ORP, mV)
pH Meter, DO meter and	Measure the pH, dissolved Oxygen and temperature of water
thermometer	samples respectively.
250ml, 100 ml PE plastic	For anions, alkalinity and cations, trace elements and isotopes
bottles and 50 ml glass bottles	samples respectively
Coolers	Use to store samples at a conserve temperature of 4 °C
Hammer	For rocks sampling
100 ml Syringes and Cellulose	Use in filling, filtering of suspended particles and acidified
filters (0.45 μ m) and Acidified	cations and trace elements samples respectively.
Nitric acid	
Total station	To install hydrometric station and measure river discharge
Piezometers	Measure the water table level in wells
Digital camera	To take pictures of our area of study and samples sources

Table 3: Materials used during data collection and their uses
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Some of materials uses on the field are shown in figure 2.



(e) Multimeter kit



Sampling campaigns were conducted in the months of November 2019 to collect wet season samples and March 2020 to collect dry season samples. During both seasons a total of 115 water samples were collected from hand-dug wells, springs, rivers, boreholes and lakes. From both watersheds, the rainy season samples included 32 from open wells with depths to water varying between 13.7 (in BIW) to 1.3 m (in DLSW), 02 sealed wells and boreholes, 19 from rivers, 05 from springs and 01 from lakes. Whereas in the dry season, the number of samples included 33 from open wells, 02 from sealed wells and boreholes, 18 from rivers, 01 from springs, and 02 from lakes. Locations and altitudes of sample collection sites were recorded using a 3 m precision Garmin 64 Global Positioning System (GPS).

Open wells were sampled using buckets anchored by ropes. Hand pump wells and boreholes were pumped for 5-10 minutes before sample collection. The waters were collected into a collector after thorough rinsing with large volume of sample water. Water from the collector was filled into three new polyethylene bottles (100-ml and 250-ml in volume), and one new 50-ml glass bottles after rinsing with the sample. The first polyethylene bottle (250-ml) was filtered through 0.45 μm cellulose filters and preserved unacidified for the determination of the dissolved anions of SO₄²⁻, Cl⁻, F⁻, Br⁻, NO₃⁻, and PO₄³⁻ from each site. The second polyethylene bottle (100-ml) was filled with filtered and acidified water that was used for cations (Ca²⁺, Mg²⁺, Na⁺, K⁺, NH4⁺, and H4SiO₄) and trace elements (Fe²⁺, Mn²⁺, Al³⁺, Pb, Cd, Ni, Zn, Cu, Ti, Sn, Mo, As, Co, Sb, Ba, U, Sr, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) determination. Acidification was done to pH ca. 2 with supra-pure HNO₃ for the sampled water. The third bottle (250-ml) contained water that was used for alkalinity measurement and the 50-ml glass bottle used for ¹⁸O and ²H was properly corked to avoid evaporation.

In-situ parameters such as Electrical conductivity (EC), pH, Redox potential and water temperature were measured immediately in the field before sample collection, using a multi-meter 3320. Atmospheric temperature was measured with a custom CT-450WR thermometer (figure 3). Land use, human activities, and rock type were noted at each sampling site using the mobile Open Data Kit (ODK) smartphone application. Alkalinity measurements were carried out within 10 hours of sample collection by acid titration with 0.02 N HCl until reaching the end-point titration at a pH of 4.5. Samples for anions, cations and trace elements, and stable environmental isotope determination were labelled, preserved in ice chilled boxes prior to laboratory analyses. The figure 3 showed the measurement of in-situ parameters from different water sampling sources.



Figure 3: Images showing how some in-situ parameters (pH, temperature, electrical conductivity and redox potential) were obtained from the different water sampling sources; wells (a), rivers (b), springs (c), and boreholes (d).

Regarding rock sampling, a total of 9 samples, with 7 (fresh granite, altered granite, fresh basalt, altered basalt, fresh trachyte, altered trachyte, and laterite) from the Bidou heterolytic igneous watershed, and 2 (sandstone and clay) from the Douka Longo sedimentary watershed as shown in figure 4. The collected water and rock samples were dispatched to the Federal Institute for Geosciences and Natural Resources (BGR), Hanover-Germany, for laboratory analyses.

Figure 4 presented the different rocks and water samples that were collected from the up mentioned watersheds.



Figure 4: rocks and water samples collected from the watersheds

2.3.3. Stream flow discharge measurement

A current meter No. 19069 and helix No. 18475 were used to measure stream discharges for the 2019/2020 hydrological year at the outlets of each watershed. The watershed discharge measurement was evaluated at the watershed outlet during the peak of the dry season (March) and rainy season (September) in order to estimate the average annual flow rate of the rivers draining the watersheds. This also helps in calculating the average annual nutrients loss by river draining.

2.4- LABORATORY ANALYSIS

Major elements (anions and cations) were quantified using a Spectro Ciros ICP-AES and a DIONEX ICS 3000 ion chromatography. Silica (H₄SiO₄) was analysed by the molybdenum-blue method using spectrophotometry. Stable environmental isotope ratios were determined on a PICARRO cavity ringdown spectrometer (CRDS model L2120-i), following the procedures described by Brand et al. (2009) and Lis et al. (2008). Trace elements, including the REEs content, were measured on an Agilent 7500ce ICP-MS. Details on the analytical instrumentation and methods can be found in Birke et al. (2010). For the major elements, reliabilities of the chemical measurements were verified by using a charge balance equation (Appelo and Postma, 1993), and they were within the limit of less than \pm 7%, with a strong correlation of 0.98 between total cations and total anions (Figure 8) for all the investigated water samples. The obtained stable isotope ratios were given in the conventional delta (δ) expression in parts per mil (∞) relative to Vienna Standard Mean Ocean Water (VSMOW) with analytical precisions of \pm 1‰ for δ D and \pm 1.5‰ for δ ¹⁸O. For TEs, the analytical accuracy was checked from replicate measurement of several samples and by measuring the certified reference materials (CRM) standard of River Water (SLRS-4), produced by the National Research Council of Canada. The detection limits were 1ng/L for all REEs. Analytical precision for the REEs, except for Ce and Pr, was better than 5% relative standard deviation (RSD), with a 10 and 11% RSD precision for Ce and Pr, respectively.

Weight % oxide of major elements (Si, Al, Ti, Mn, Na, Ca, Mg, K, P) were measured with Energy Dispersive X-ray Spectrophotometer -700 HS from 4 g of rock powder. The detection limits (in wt.%) are 0.9 for SiO₂, 0.7 for TiO₂, 0.5 for Al₂O₃, 0.3 for Fe₂O₃, 0.05 for MnO, 0.6 for MgO, 0.6 for P₂O₅.

2.5- DATA ANALYSIS

All statistical analyses were performed with R software. Aquachem software was used to draw Pipers' diagram to identify water facies, and REE patterns and δD versus $\delta^{18}O$ space diagrams were drawn using Microsoft excel, while maps were established with ArcGIS version 10.2 and QGIS 2.18.X softwares. Although the distribution and geochemical behaviour of REEs in natural materials can be illustrated by plotting the relative abundances versus the atomic number, such a plot produces a saw tooth pattern (the Oddo–Harkins rule effects), with decreasing slope toward the highest atomic numbers. Thus, the REEs behaviour is better presented if the values are normalized and reported as a relative abundance plot on a logarithmic scale. This means that the concentrations of REEs found in the sample are normalized to their concentrations in a reference material such as Cl chondrite, the chondritic meteorite, and the Post Archean Australian Shales (PAAS) (Edet, 2004). The advantage of this process is that the Oddo–Harkins rule effect is eliminated, and any fractionation that has occurred among the REEs will be detected. Hence, the abundance of positive peaks and negative troughs in the normalized REE pattern reflects the geochemical history of the sample.

Generally, the abundance of REEs in natural waters is extremely low in comparison with the levels found in most rocks. In this investigation, the Post-Archean Average Australian Shale (PAAS) (McLennan, 1989) was chosen as a reference standard because "shales" are widely used in hypergene processes and environmental studies (Migaszewski et al., 2014) such as surface and shallow groundwater systems affected by weathering. Detection of anomalies is based on the presence of individual elements that are higher or lower than the corresponding shale-normalized patterns. For example, Eu and Ce anomalies were quantified, according to Noak et al. (2014), in which the geogenic value of each element was obtained by interpolation of the neighbor-normalized REE elements of Ce and Eu, by using the equations presented in Eqs. (4) and (5), respectively.

 $Ce/Ce^* = Ce_{PAAS}/(La_{PAAS} + Pr_{PAAS})^{0.5}.....(4)$ $Eu/Eu^* = Eu_{PAAS}/(Sm_{PAAS} + Gd_{PAAS})^{0.5}....(5)$

It is worth mentioning that the last two indexes could be influenced in some situations by anomalies in La and Gd. Nevertheless, their calculation can be useful in discriminating sampled water types. We equally employed calculations of normative minerals from water chemistry and mass balance calculations to evaluate elemental losses and gains in altered rocks equivalents. The procedure for identifying real gains and losses of elements as a result of chemical weathering is based on the assumption that one of the major-element oxides has

remained constant in amount even though its concentration may appear to have changed. The constituent chosen for this purpose is Al_2O_3 , consistent with the limited solubility of $Al(OH)_3$ (Faure, 1991). This choice is also consistent with the convention regarding the conservation of Al during incongruent dissolution of aluminosilicate minerals.

2.6- DIFFICULTIES

- Due to bad roads, mobility into the villages to collect samples was not easy. The only mode of transport in some zones was by foot which was very challenging especially with the sunlight intensity of the northern Cameroon;
- In the dry season, some rivers dry and to collect samples, holes were dug in the river bed in order to have water;
- Risk due to the insecurity in the villages coupled with the Boko Haram situation;

Conclusion

The materials and methods used as well as the steps taken towards data collection in

BIW and DLSW in order to affirm the hypothesis were clearly elaborated in this chapter as well as the difficulties faced on the field during data collection.

CHAPTER THREE

RESULTS, INTERPRETATION AND DISCUSSION

The results obtained from the procedures established and executed from the preceding chapter is presented here. These results are presented in tables, figures, maps and interpreted accordingly in the form of tables and figures with respect to the set objectives of this study

3.1- RESULTS PRESENTATION

Considering that cultivation of food crops is basically rain fed, the data presented in this study are only those from samples that were collected in the rainy season. Table 4 presents the descriptive statistics for the content of major cations and anions, stable environmental isotopes (δD , $\delta^{18}O$), SiO₂, in-situ values of electrical conductivity (EC), pH, water temperature, GPS records (locations and altitudes), and calculated values of partial pressure of carbon dioxide (pCO₂). Meanwhile, trace elements (TEs) in water, rare earth elements (REEs) in water, and elemental content (major oxides and TEs) in rocks are presented in Tables 5, 6 and 7 below, respectively.

In the DLSW, the measured values for EC, pH, and water temperature, ranged from 58-698 μ S/cm, 4.2-7.3, and 33.9 to 26.5 °C, respectively. Whereas in BIW, measured EC, pH, and water temperature, ranged from 9 -160 μ S/cm, 5.6 -7.4, and 26.1 to 19.5 °C, respectively. By comparing samples from both watersheds, those from DLSW showed higher values in water temperature, pH and EC than those from BIW, as shown in Figure 5. The average values of major ions in water samples in DLSW are in decreasing order as follows in mg/L : 51.6 (NO₃⁻) > 25.14 (HCO₃⁻) > 13.18 (K⁺) > 10.24 (Ca²⁺) > 8.36 (Cl⁻) > 6.64 (Na⁺) > 3.50 (Mg²⁺) > 0.81 (SO4²⁻) > 0.25 (Fe²⁺). While in BIW the values are 15.40 (HCO₃⁻) > 2.57 (Ca²⁺) > 2.41 (Na⁺) > 2.24 (NO₃⁻) > 1.14 (Cl⁻) > 1.02 (Mg²⁺) > 0.59 (SO4²⁻) > 0.51 (K⁺) > 0.26 (Fe²⁺). Stable environmental isotopes ratio range from -5.07 to -2.79 ‰ for δ^{18} O, and -30.7 to -21.3 ‰ for δ D in DLSW, and -4.51to -0.86‰ for δ^{18} O and -24.5 to -11.5 ‰ for δ D in BIW. By considering only nutrient trace elements (B, Cu, Mn, Mo, Ni, and Zn), their mean value in sampled waters in the DLSW range from 158 to 0.06 μ g/L, with decreasing order of Mn > Zn > B > Ni > Cu > Mo, against 45.49 to 0.06 μ g/L, with Mn > Zn > B > Ni > Cu > Mo in BIW. In DLSW, total REEs vary from 0.916 -1716.25 μ g/L, with Nd > Ce > La > Sm > Pr > Eu for LREEs, and Gd > Dy > Er > Yb > Tb > Ho > Tm > Lu for HREEs. In BIW, the total REEs range from 0.085-2.37 μ g/L, with Ce > Nd > La > Eu >

Sm > Pr for the LREEs and Gd > Dy > Yb > Er > Tb > Ho > Lu for the HREEs. The tables (table 4, 5 and 6) give the descriptive results obtained from the laboratory. It's therefore noted that the full analytical results are available in appendix I, II and III respectively.

	`		1	U	2				e
Parameter			Douka I	Longo waters	hed				
•	Unit	Min	Max	Average	Std.deviation	Min	Max	Average	Std. deviation
Temp	(°C)	26.5	34	30.2	1.4	19.5	26.1	23.5	1.4
PH		4.2	7.4	6.4	0.7	5.6	7.2	6.4	0.4
EC	(µS/cm)	58	698	183.7	110.1	9	160	30.67	21.4
HCO ₃	(mg/l)	1.7	55.5	24.81	16.41	3.3	36.8	10.26	5.612
K	(mg/l)	2.9	75.3	13.47	9.053	0	1.2	0.43	0.262
Na	(mg/l)	1.4	27	6.775	3.673	0.4	25	2.474	2.9
Cl	(mg/l)	0.8	43.2	8.56	7.644	0.01	16.9	1.375	2.250
Mg	(mg/l)	0.4	11.6	3.559	2.133	0.076	2.85	0.576	0.50
Ca	(mg/l)	1.34	24.6	10.39	5.157	0.4	6.03	1.723	1.094
Fe	(mg/l)	0.01	1.94	0.238	0.283	0	1.58	0.254	0.283
Mn	mg/l)	0.01	1.66	0.163	0.193	0	0.42	0.047	0.04
SO_4	(mg/l)	0.011	7.01	0.828	0.801	0.003	18.7	0.79	1.433
NO ₃	(mg/l)	0.506	266	53.4	46.91	0.012	37.9	2.724	3.82

0.004

0.01

0.018

8.7

-5.31

-30.7

0.002

1

(mg/l)

(mg/l)

(mg/l)

(mg/l)

(‰)

(‰)

(‰)

(atm)

Br

 NH_4

SiO₂

 $d^{18}O$

 d^2H

DE

 pCO_2

F

0.04

0.34

0.941

16.2

-2.79

-21.3

0.014

12

0.016

0.062

0.134

12.97

-4.5

-26.23

9.792

0.006

0.008

0.052

0.124

1.502

0.343

1.852

1.778

0.003

0.012

0.01

0.005

-4.51

-24.5

0.001

-5

2

0.067

0.88

0.091

10.1

-0.86

-11.5

13

0.009

0.04

0.102

0.025

4.193

-3.365

-16.09

10.88

0.005

0.028

0.11

0.016

1.407

0.312

1.436

1.494

0.002

Table 4: Descriptive statistics of major ions, SiO_2 , stable environmental isotopes, and pCO_2 of groundwater (n=36) and surface water (n=16), sampled during the rainy season in the Bidou and Douka Longo watersheds

		Douka Lon	go watershed		Bidou watershed				
Element	Min	Max	Average	Std.deviation	Min	Max	Average	Std.deviation	
Sc	0.138	0.609	0.279	0.094	0.000	0.206	0.095	0.040	
Y	0.115	484898	35237	63737	0.014	0.302	0.087	0.061	
Ag	0.003	0.033	0.017	0.009	-	-	-	-	
As	0.022	17744	1333	2453	0.010	0.108	0.038	0.020	
В	6351	64427	19717	8995	2393	20014	11353	3774	
Ba	164795	3921168	783758	648557	18929	141486	56859	17368	
Be	0.031	22885	1709	2823	0.007	0.298	0.071	0.048	
Bi	0.002	0.003	0.003	0.001	-	-	-	-	
Cd	0.003	0.214	0.025	0.028	0.002	0.032	0.006	0.003	
Ce	0.110	272674	18677	32269	0.025	2049	60	117	
Co	0.123	107929	9955	13790	0.062	6219	672	988	
Cr	0.058	1654	166	292	0.027	2001	133	242	
Cs	0.013	2413	187	344	0.004	0.129	0.015	0.011	
Cu	0.276	54535	4222	6024	0.071	1005	29.912	57	
Ga	0.028	40329	2916	5365	0.003	0.044	0.017	0.008	
Hf	0.003	0.159	0.032	0.032	0.003	0.004	0.004	0.001	
In	0.026	0.028	0.026	0.001	0.026	0.027	0.026	0.000	
Li	0.452	22166	3583	3441	0.108	1116	65.381	122	
Mn	6626	1755128	158037	191204	2032	406570	45492	39202	
Мо	0.022	0.260	0.066	0.043	0.056	0.068	0.062	0.006	
Nb	0.012	0.216	0.082	0.063	-	-	-	-	
Nd	0.180	658209	49452	88937	0.005	0.229	0.068	0.039	
Ni	0.652	72682	7560	8308	0.202	5891	651	946	
Pb	0.073	56304	3775	6303	0.020	0.260	0.055	0.024	
Pr	0.042	119478	8839	15913	0.002	0.053	0.016	0.009	
Rb	7196	83497	27916	15623	0.112	4083	1454	1223	
Sn	0.022	0.222	0.071	0.056	-	-	-	-	
Sr	36496	611105	185074	101834	4678	115395	30379	22672	
Та	0.001	0.031	0.009	0.008	-	-	-	-	
Те	0.020	0.061	0.031	0.007	0.010	0.042	0.020	0.007	
Th	0.008	0.213	0.072	0.047	0.005	0.005	0.005	0.000	
Ti	0.092	53832	9294	11535	0.064	2568	147	267	
T1	0.022	1228	49	94	0.003	0.053	0.009	0.004	
U	0.008	66695	3911	7196	0.001	0.018	0.006	0.003	
V	0.070	1391	486	583	0.017	1415	80	150	
W	0.104	0.139	0.123	0.013	-	-	-	-	
Zn	8444	138580	50419	27812	2482	70538	30785	10166	
Zr	0.006	1380	108	197	0.005	0.081	0.017	0.011	

Table 5: Descriptive statistics of trace element data of groundwater and surface water sampled during the rainy season in the Bidou and Douka Longo watersheds

		Douka Long	go watersnee	Bidou watershed				
	Min	Max	Average	Std.deviation	Min	Max	Average	Std.deviation
La	0.185	192772	14569	25122	0.009	38.200	1.144	2.117
Ce	0.110	272674	18677	32269	0.025	2049	61	115
Pr	0.042	119478	8839	15913	0.002	8.830	0.268	0.489
Nd	0.180	658209	49452	88937	0.005	33.900	1.034	1.878
Sm	0.036	139225	11085	20202	0.002	5.550	0.175	0.307
Eu	0.062	41615	3190	5869	0.008	1.080	0.052	0.059
Gd	0.041	121368	9480	17353	0.004	4.660	0.150	0.258
Tb	0.004	17870	1359	2501	0.000	0.770	0.024	0.043
Dy	0.024	95362	7121	13102	0.000	4.680	0.145	0.259
Но	0.003	15706	1149	2115	0.000	0.990	0.030	0.055
Er	0.010	43248	3114	5729	0.000	2.850	0.089	0.158
Tm	0.001	5760	415	764	0.000	0.410	0.012	0.023
Yb	0.007	32323	2337	4301	0.000	2.820	0.088	0.156
Lu	0.000	4882	361	664	0.000	0.430	0.013	0.024
∑REE	0.916	1716247	133184	234516	0.085	184773	5381	10251
LREE	0.634	1243133	92502	162088	0.041	160530	4650	8907
HREE	0.050	215151	16045	29145	0.002	12953	370	719
MREE	0.156	298455	23969	43390	0.017	11290	323	627
LREE/HREE	4499	17525	10818	2655	2389	71500	12632	6718
Eu/Eu*	1367	42665	7822	6393	1000	22112	8123	3906
Ce/Ce*	0.084	1143	46	88	0.331	11162	1264	916
La/Yb	4653	31137	17928	5283	0.929	31000	9201	4860
La/Sm	1110	8175	4389	1264	1182	12000	3755	1576
Gd/Dy	0.981	2167	1433	185	0.786	5000	1645	676

Table 6: Descriptive statistics of rare Earth elements content in groundwater and surface water sampled during the rainy season

	Fresh Granite	Altered Granite	Fresh Basalt	Altered Basalt	Fresh Trachyte	Altered Trachyte	Laterite	Sandstone	Clay
SiO ₂	70.55	74.86	45.32	62.31	56.54	55.72	8.81	95.22	83.07
TiO ₂	0.17	0.248	3.244	0.34	0.605	0.647	1.436	0.103	0.624
Al ₂ O ₃	15.72	13.71	16.11	18.21	19.02	21.1	9.11	3.09	7.61
Fe ₂ O ₃	1.2	0.97	12.04	4.3	3.57	3.8	64.88	0.09	1.29
MnO	0.027	0.019	0.241	0.068	0.245	0.204	0.098	< 0.001	0.036
MgO	0.17	0.11	4.92	0.18	0.52	0.55	0.03	0.01	0.1
CaO	0.788	0.264	8.529	0.642	2.395	1.571	0.031	0.049	0.116
Na ₂ O	3.78	2.73	2.27	6.12	7.35	3.83	< 0.01	< 0.01	0.12
K ₂ O	0.00	5.348	2.065	5.327	4.766	5.446	0.037	0.032	3.093
P2O5	6.555	0.026	1.289	0.146	0.165	0.208	1.648	0.013	0.029
(SO ₃)	0.035	< 0.01	< 0.01	< 0.01	0.08	< 0.01	< 0.01	< 0.01	< 0.01
(Cl)	0.02	0.005	0.014	0.002	0.017	0.005	0.002	0.004	< 0.002
(F)	0.003	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
LOI	<0.05	1.55	3.37	2.06	4.1	6.18	13.63	1.35	3.62
Sum	0.73	99.76	99.44	99.66	99.29	99.22	99.66	99.87	99.63
(As)	99.73	<3	<4	<3	7	4	<5	<3	<3
Ba	<3	159	1131	150	1464	2026	198	<62	843
Bi	485	<6	<7	<6	<6	<6	<10	<5	<6
Ce	<6	131	166	176	213	229	<57	<54	62
Co	126	8	32	<8	<8	<8	48	<7	<8
Cr	<8	<11	51	<12	<12	<12	543	<11	27
Cs	<12	<54	<60	<57	<57	<57	<54	<54	<54
Cu	<57	<6	19	<6	16	10	53	<6	8
Ga	8	20	22	28	25	25	<9	<5	10
Hf	26	<18	<22	<19	20	26	<34	<17	<18
La	<18	87	88	113	125	199	<49	<47	<47
Мо	64	<8	<8	<8	<8	<8	<8	<8	<7
Nb	<8	23	83	160	141	152	33	6	13
Nd	24	88	78	65	68	89	<52	<39	<39
Ni	58	<6	41	<6	<6	<6	56	<6	9
Pb	6	36	<8	8	13	<7	<11	</td <td>20</td>	20
Rb	48	261	38	112	127	151	</td <td><4</td> <td>86</td>	<4	86
Sb	339	<19	<23	<21	<21	<21	<33	<19	<20
Sc	<21	<26	<28	<26	<26	<26	<26	<26	<26
Sm	<26	<24	<26	<24	<25	<24	-21	<23	<24
Sn	<23	<1/	<21	<18	<18	<18	<31	<17	<1/
Sr	<18	41	1573	-12	-12	-12	80 <24	24	-11
Th	-12	26	10	~12	~12	~12	11	~11	-11
II	31	50	-7	21 <6	21	25 <6	<0	<6	15
V	51	<17	154	<17	<0	<0 10	208	<0	~0
V W/	<17	~1/	<12	~1/	~17	19 <11	570 <77	<10	24 ~11
w v	<11	25	-15	35	37	50	-22	~10	~11
7n	26	23	137	160	175	238	108	, <5	20 14
ZII 7.	45	187	324	812	1241	1250	1/12	152	805
Zr		10/	324	013	1241	1239	142	132	805

Table 7: Major element oxides and trace elements content in rocks sampled in the Bidou and Douka Longo watersheds.



Figure 5 gives the summary of the variation of in situ parameters such as temperature, pH and electric conductivity in water samples sources in Bidou Igneous watershed and Douka Longo sedimentary watershed.

Figure 5: Variations of temperature (a), pH (b), and EC (c) in water sample sources from the Bidou and Douka Longo watersheds.

Figure 6 gives the summary of spatially distributed map of sample collection point, different water sources from which each sample is collected, the sampling period and the selected sites (poor soil sites) in Bidou watershed and Douka Longo watershed.



Figure 6: spatially distributed map of sample collection point, different water sources from which each sample is collected, the sampling period and the selected sites (poor soil sites) in Bidou watershed and Douka Longo watershed.

From field observation, many geological phenomena were observed, out of which we have rocks dissolution (chemical weathering of sandstone) in Douka Longo sedimentary watershed. Figure 7 shows

differential weathering of the conglomeritic core, an erratic mosaic of potholes representing relics of weathered conglomerate.



Figure 7: Occurrence of "sandstone balls" (a), with conglomerate core and sandstone crust (b). Differential weathering of the conglomeritic core begins to form pothole (c), and an erratic mosaic of potholes representing relics of weathered conglomerate (d).

3.2- INTERPRETATION AND DISCUSSION

3.2.1. Ion balance

As mentioned in the previous chapter, the ion balance was calculated immediately to verify if the results obtained from the laboratory were acceptable. Hence the plot in Figure 8 shows a clear relation between the sum of anions and that of cations in BIW and DSLW with a linear correlation of:

y = 0.8187x + 0.229 With $R^2 = 0.98 \sim 1$

This correlation illustrated in Figure 8 proves that the results are acceptable.



Figure 8: Reliability of analytical technique of water samples measured by charge balance between total cations and anions.

3.2.2. Solute generation

The chemical composition of freshwater was used by Gibbs (1970) to identify major chemical weathering domains that control dissolved ions in water based on their total dissolved solids (TDS) values and their $(Na^+ + K)/(Na^+ + K + Ca^{2+})$ ratios (Figure 9a) and TDS vs Cl/(Cl+HCO₃⁻) (Figure 9b). The Gibbs diagrams show data points for the sampled water sources from both the DLSW and BIW distributed in the water-rock dominant domain (Figure 9). This suggests that incongruent weathering of silicate minerals (Faure, 1991) is a dominant contributing source of dissolved inorganic ions by the dissolution reaction of anorthite shown in eqn. 6 as an example that can occur for other primary and secondary rock forming minerals.

$$CaAl_{2}Si_{2}O_{8} + 6H_{2}O + 2H^{+} = 2Al (OH)_{3} + Ca^{2+} + 2H_{4}SiO_{4}....(6)$$

Figure 9 illustrated the distribution of the water-rock dominant domain in Bidou and Douka Longo watershed.



Figure 9: Gibbs plots indicating rock domain (water-rock interaction) as main process controlling groundwater chemistry in the watersheds.

The strength of the water-rock interaction was evaluated by the intensity of weathering, which is presented in this study using the weathering index of Parker (PI) (Parker, 1970) defined in eqn. 7 as

$$PI = \left(\frac{2Na_2O}{0.35} + \frac{MgO}{0.9} + \frac{2K_2O}{0.25} + \frac{CaO}{0.7}\right).$$
 (7)

And the chemical alteration index, CIA (e.g., Nesbit and Young, 1989), which is defined in eqn. 8 as

$$CIA = \left(\frac{Al_2O_3}{Al_2O_3 + CaO + Na_2O + K_2O}\right) \times 100 \dots (8).$$

The calculated CIA and PI values for the observed rock are presented in Table 8. The obtained values were plotted (Figure 10) to evaluate the intensity of chemical weathering in the watersheds. By considering the CIA-based classification of intensity of chemical weathering (e.g., Shao et al., 2012), Figure 10 indicates that the intensity of chemical weathering vary from intermediate category for clay (Cl), too strong for sandstone (SST), in the DLSW. Whilst in the BIW the intensity of chemical weathering vary between the weak (50 - 60 CIA unit) category for the altered granite (AG), altered trachyte (AT) and altered basalt (AB) to strong (> 85 CIA unit) in laterite (LT).

Table.8 illustrated the calculated values for the observed rocks.

	CIA (%)	PI	RE (SiO ₂ /Al ₂ O ₃)	K ₂ O/ Al ₂ O ₃	Fe ₂ O ₃ /Al2O3	Fe ₂ O ₃ /K ₂ O	Fe ₂ O ₃ /Na ₂ O	Fe ₂ O ₃ /TiO ₂
Fresh granite to altered granite	52	9.31	4.49	0.42	0.08	0.18	0.32	7.06
Fresh basalt to altered basalt	43	7.39	2.81	0.13	0.75	5.83	5.30	3.71
Fresh trachyte to altered trachyte	47	11.60	2.97	0.25	0.19	0.75	0.49	5.90
Laterite	99	0.05	0.97	0.00	7.12	1753.51	6488.00	45.18
Altered granite	56	7.17	5.46	0.39	0.07	0.18	0.36	3.91
Altered basalt	52	10.39	3.42	0.29	0.24	0.81	0.70	12.65
Altered trachyte	58	8.72	2.64	0.26	0.18	0.70	0.99	5.87
Sandstone to clay	96	0.05	30.82	0.01	0.03	2.81	9.00	0.87
Clay	68	2.80	10.92	0.41	0.17	0.42	10.75	2.07

Table 8: Calculated values of Chemical Index of Alteration (CIA) and Parker Index (PI) for rock samples from Bidou and Douka Longo watersheds

CIA: Chemical Index of Alteration, PI: Parker Index, RE: Weathering Index,

A plot of this chemical indices of rocks obtained from the watersheds is shown on the figure 10.



Figure 10: Correlation between the CIA and PI in fresh basalt, altered basalt, fresh granite, altered granite, fresh trachyte, altered trachyte, clay, sandstone, and laterite that were sampled from the watersheds.

To further elucidate the water-rock interaction process in the watersheds, the chemical weathering rate (WRch) of the observed rocks were calculated from the flux of dissolved silica in water. If the chemical composition of silica in parent rock (So) and of the alteration facies (Ss) are known, then WRch can be estimated using the formula of eqn. 2 reported by Vuai and Tokuyama (2007), and Boeglin and Probst (1998).

The chemical composition of silica (weight %) in the sample rocks from the watersheds are 70.6 % in fresh granite, 74.9% in altered granite, 45.3 % in fresh basalt, 62.3 % in altered basalt, 56.5 % in fresh trachyte, 55.7 % in altered trachyte, 95 % in sandstone and 83 % in clay. The density was taken as 2.6 ton/m³ for fresh granite, altered granite, fresh basalt, altered basalt, fresh trachyte, altered trachyte, sandstone, and clay (Dalai et al., 2002; Vuai and Tokuyama, 2007; Boeglin and Probst, 1998). These gave (So - Ss) values of 786 kg/m³, 306 kg/m³, 690 kg/m³, and 1313 kg/m³, for granite, basalt, trachyte and sandstone, respectively, and the specific flux of SiO₂ (QSiO₂) were 0.0073 mol/m² from the BIW and 0.01070 mol/m² from DLSW. The calculations from Eqn. 7, gave weathering rates of 0.0006 mm/y, 0.0014 mm/y, 0.0006 mm/y, and 0.0005 mm/y for granite, basalt, trachyte and sandstone, respectively, as shown in Table 9.

			Average	Chemical		QSiO ₂	
Roc	Rock type		density	composition S	So-Ss	(mol/y	WRch (mm/yr)
			(ton/m^{-3})	(Kg/m ⁻³)		m ²)	
	fresh	70.55	2.6	1834.30			
Granite	altered	74.86	1.4	1048.04	786.26		0.0006
	fresh	45.32	2.6	1178.32			
Basalt	altered	62.31	1.4	872.34	305.98	0.007324	0.0014
	fresh	56.54	2.6	1470.04			
Trachyte	altered	55.72	1.4	780.08	689.96		0.0006
	sandstone	95.22	2.6	2475.72			
Sandstone	clay	83.07	1.4	1162.98	1312.74	0.010701	0.0005

Table 9: Calculated values of chemical weathering rates for granite, basalt, trachyte and sandstone samples from Bidou and Douka Longo watersheds

For comparison, the results are lower than (0.0085, 0.078, 0.063, and 0.048 mm/y) observed for crystalline rocks by Nkounkou and Probst (1987), Nyos - Cameroon basalts (ca. 5 mm/y) (Fantong et al., 2015), sandstone (0.013 mm/y) and for granitoids in Nsimi humid watershed in southern Cameroon (2.8 mm/y) (Braun et al., 2005). The observed lower rates of chemical weathering could be attributed to the impermeable and inert characteristics of the already abundant strongly weathered lateritic duricrust and ferruginous sandstones in the watersheds that is subject to runoffs, short water-rock interaction time, and limited chemical weathering.

The weathering types (RE) that occur in the watersheds were determined by the molar ratios of SiO₂/Al₂O₃ remaining in the weathered equivalents (Pedro, 1966 in Boeglin and Probst, 1998). When weathering index (RE) value decreases, more silica is released and the chemical weathering stage of mineral increases. If the value of RE is either 4, 2, or 0, then it represents the genesis of smectite, kaolinite and gibbsite, respectively, during incongruent dissolution. For this study, the calculated values of weathering index ranged from 10.9 to 30.8 in DLSW, and 0.97 to 5.5 in BIW. The high values in DLSW may be due to the fact that the sandstone and clay there-in have very low susceptibility to chemical weathering, thus the formation of secondary clay minerals during incongruent dissolution is limited. Whilst in BIW, the igneous rocks are more susceptible to chemical weathering that result in forming gibbsitized kaolinite through the process of monosalitization. Boeglin and Probst (1998), established a link between type of weathering to the draining characteristics of the landscape, in that formation of gibbsite is common in a well-drained landscape, while smectite is formed a landscape that is poorly drained. The geological characteristics of the DLSW and BIW portray good drainage due to dominant porous and permeable sandstone and poorly drained lateritic duri-crust, respectively.

To verify the above phenomena in the watersheds under investigation, the Na and Ca systems stability diagrams (Figure 11a and b) further clarify the equilibrium states between the secondary minerals (clays) and the circulating water (Tardy, 1971; Appelo and Postma, 1993). For example, the stability of albite, anorthite, gibbsite, kaolinite, montmorillonite in the water was evaluated in this study by plotting log (aNa⁺/ aH⁺) versus Log (aH_4SiO_4), and Log ($aCa^{2+}/a2H^+$) versus log (aH_4SiO_4). The diagrams were drawn with the assumption that Al was preserved in the weathering product (Appelo and Postma, 1993; Faure, 1991). End-member compositions were also assumed using equilibrium relationship for standard temperature (25 °C) and pressure (1 atmosphere), which approximately reflect the groundwater conditions. Constituent activities computed using Phreeqc for Windows version 2.1 (Appelo and Postma, 1993) show that groundwater and surface water from the study area span the stability fields of gibbsite and kaolinite, which also correspond to the cluster of sample points within the plagioclase to gibbsite and plagioclase to kaolinite field of the Garrels (1967) plot of mole ratios of Na^+/Ca^{2+} against HCO_3^-/H_4SiO_4 (Figure 12). From the hypothesis that, well drained landscape usually result in gibbsite formation, while poorly drained soil is attributed to kaolinite and smectite formation (Vuai and Tokuyama, 2007). The indicators that gibbsite and kaolinite are common in the studied watersheds, concur with the good (sandy) and poorly (lateritic) draining soils in DLSW and BIW, respectively. The illustration of the stability diagram and the plot of mole ratios of Na^+/Ca^{2+} against HCO_3^-/H_4SiO_4 is shown on the figure 11 and figure 12.



Figure 11: Stability diagrams at 25° C. (a) Albite system, (b) anorthite system. In both systems the water samples are in equilibrium with gibbsite and kaolinite.



Figure 12: Mole ratio of Na^+ to Ca^{2+} plotted against mole ratio of HCO_3^- to H_4SiO_4 for waters from the studied watersheds.

Moreover, intensive mechanical erosion may partly influence such type of weathering as purported by Tokashiki (1993). Exposing fresh rocks containing minerals such as felspars, and subsequent reaction with weak carbonic acids, transforms the minerals into secondary kaolinite through incongruent dissolution of primary rock forming silicates and secondary carbonates in host rocks. This assertion was verified by plotting the ratios of Mg/Na versus Ca/Na (Figure 13), which suggests that waters circulating within the DLSW and BIW are dissolving silicates and carbonate minerals. Consequently, the chemical compositions of water presented in Table 4, were used to identify the silicate mineral (normative mineral) and to calculate their relative abundance following the procedure by Garrels (1967) based in part on preceding work of Feth et al. (1964), and to identify the carbonate(s) that was dissociated. The plot of the ratio of Mg/Na versus Ca/Na is illustrated on figure 13.



Figure 13: Plots of the ratios of Mg/Na versus Ca/Na in sampled waters suggest that waters circulating within the DLSW and BIW are dissolving silicates and carbonate minerals.

The incongruent dissolution of silicates and carbonates in the rocks of the watersheds must have led to elemental losses and gains in the altered forms of the rocks as explained by Etame et al. (2000). To demonstrate that the altered granite, basalt, trachyte and clay, which are exposed in the studied watershed have been subject to losses (depletion) and gains (enrichment) of elements, the results presented in Table 9 were examined and they show that the altered rocks have significant lower concentrations in MnO, MgO, CaO, Na₂O, K₂O, P₂O₅ and Fe₂O₃, and higher concentrations in Al₂O₃. The decrease and increase of the major - element oxides in the

altered rocks balance in such a way that the sum of the concentrations is equal to or close to 100. Therefore, the real losses of some of the oxide components that occurred during incongruent dissolution are partly compensated by apparent increases in the concentrations of other components. Similarly, real gains in some components caused apparent losses in others. When both gains and losses occur, the resulting chemical composition of the weathering products can only be interpreted by recalculating the analyses based on the assumption that one of the oxides remained constant in amount. In this study, Al₂O₃ is selected as the constant oxide despite its increase, because the concentration of a constituent expressed in weight percent is equivalent to an amount in gram per 100 gram of rock. Thus, by assuming that the amount of Al₂O₃ remain constant, the apparent increase in its concentration must be caused by a reduction in the weight of the rock from 100 g to some smaller amount derivable from the relation in eqn. 9.

Weight of constituent / weight of rock x100 = percentage concentration......(9)

The amounts of the other oxide constituents remaining in the altered rocks were then calculated by multiplying their percentage concentrations by a weight loss factor derived from the ratio of the concentrations of the constant oxide in the fresh and altered rocks. The actual gains and losses of each component was determined by following the systematic procedure explained in Faure (1991) and Fantong et al. (2015), and the obtained values and plots are presented in appendix IV and Figure 14. The plots for major-element oxides (Figure 14a) show the following trends: in altered granite, SiO₂ and TiO₂ are gained, while Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, and P₂O₅ are depleted; in altered basalt, SiO₂, Na₂O and K₂O are enriched, while TiO₂, Fe₂O₃, MnO, MgO, CaO, and P₂O₅ are depleted; in altered trachyte, K₂O, and P₂O₅ are gained, while SiO₂, TiO₂, Fe₂O₃, MnO, MgO, CaO, Na₂O are depleted. The plots for trace elements (Figure 15b) show that: for altered granite, Ce, La, Nb, Nd, Y, Th, and Zr are enriched, as against the depletion of Ba, Ga, Rb, Sr and Zn; in altered basalt, Ga, La, Nb, Rb, Th, Zn, and Zr are gained, while Ba, Ce, Nd, Sr, and Y are lost; in altered trachyte, Ba, La, Nd, Th and Y are enriched, while Ga, Nb, Sr, Zn and Zr are depleted; in clay Sr, Y, and Zr show enrichment, while Th and Zn show depletion. An interplay between the dissolutions of plagioclases, carbonates and the elemental gains and losses in the altered rocks within the watersheds, would influence the aqueous solutes contents.

The values of enrichment- depletion of rocks from the table (appendix IV) were further represented on figure 14. The trend of enrichment-depletion is well observed on this figure



Figure 14: Plots of gains (enrichments) and losses (depletion) of major-element oxides (a), and trace elements (b), after chemical weathering of rocks in the watersheds.

3.2.3. Elemental contents in waters

The waters that drain the watersheds have their origin from pristine rainfall, and the processes involved as the rainfall infiltrates the geologic Formation, can be deciphered by using the contents of stable environmental isotopes of oxygen and hydrogen (e.g., Fantong et al., 2010; Asai et el., 2010; Goni , 2006).

Stable environmental isotopes ($\delta^{18}O$ and $\delta D)$ content

The observed δ^{18} O and δ D values can be regarded as conservative during water–rock interaction reaction (e.g., Gat, 2010; Taylor and Howard, 1996). Thus, the δ -values of the groundwater would be expected to be almost similar to that of the recharging meteoric water. Factors that can affect the recharging rainfall are soil-zone processes and direct heterogeneous/diffuse or localized/focused rainfall infiltration (Taylor and Howard, 1996). The clustering of observed groundwater and surface water along the GMWL (Global Meteoric Water Line) with those from the BIW being relatively enriched than in the DLSW (Figure 15a) indicates that soil-zone evaporation prior to rainfall infiltration is not a significant process in the area.

However, a few surface water samples from springs and lakes plot to the right of the GMWL, indicating the incidence of evaporation prior to groundwater recharge was not totally absent. Such a pattern for δ^{18} O and $^{\delta}$ D in the study area, suggest that the mechanism of preferential flow pass (e.g., Tsujimura et al., 2007; Asai et

al., 2010) dominates groundwater recharge after localized evaporation (Edmunds et al., 2002; Tsujimura et al., 2007; Fantong et al., 2010). The suggestion of a preferential flow pass hypothesis indicates local occurrences of effective porosity in the sand-rich sediment (in the case of DLSW) and joints and fractures (in the case of BIW), which favour rapid infiltration of rainwater into the aquifer. Similar recharge mechanism was identified in part of the study area by Njitchoua et al. (1995), and in the Lake Chad (Fantong et al., 2010), coastal (Fantong et al., 2016) sedimentary basins of Cameroon, and also in the semiarid sediments in Mongolia (Tsujimura et al., 2007). The high d-excess values in surface and groundwater (with ca. 80 % and 100 % of the water samples from DLSW and BIW, respectively, having values above 10 ‰) (Figure 15b) not only confirm direct infiltration of rainwater into the shallow aquifer (Kebede et al., 2005), but also suggest that groundwater recharge occurred under low relative humidity conditions (Kendall and Doctor, 2011). The implications from the δ -space diagram (Figure 15a) and d-excess (Figure 16b) indicate hydraulic connectivity within the shallow aquifer that does not only favour mixing between surface and the shallow groundwater, but also influence major ions and trace elements content in waters within. The graph of δ^{18} O and δ^{0} values for water samples in the watersheds is shown in figure 15.



Figure 15: A δ^{18} O - δ D relationship of groundwater, surface water, and rainfall in the watersheds.

Major ions and trace element content in water

The values of major ions (anions and cations) show that concentrations are higher in water samples from DLSW than in BIW. Such observation depicts that the sampled waters in DLSW might have interacted more with rocks than those in BIW. Piper's diagram (Piper, 1944) plots (Figure 16) suggest that the hydrochemical facies are predominantly Ca + Mg - NO₃ type in DLSW, whereas in BIW the groundwater show mixing trend between Na + K - Cl and Ca + Mg- HCO₃ facies, while springs and rivers vary between facies of Ca + Mg- HCO₃ and Na + K - HCO₃. By considering only the major ions that are plant nutrients (Figure 17a) for DLSW; and (Figure 17b) for BIW, their average concentrations were plotted for groundwater and surface water. The trend in the plots show that in DLSW, groundwater contains more major ion nutrients than surface water, with a descending order of NO₃ > K > Cl > Ca > Na > Mg > Fe SO₄ > PO₄ in groundwater and NO₃ > Ca > K > Na > Cl > Mg > Fe > SO₄ > PO₄ in surface water. On the other hand in BIW, surface water contains more major ion nutrients than groundwater, with a descending order of Ca > Na > NO₃ > Cl > Mg > SO₄ > K > Fe > PO₄ in both groundwater and surface water. Figure 16 shows a Piper's diagram plot of water samples in the watersheds.



Figure 16: Pipers' plots of observed water samples in the watersheds.

The salient information from these trends are that in DLSW the top soil may be depleted of major ion nutrients by infiltration through it permeable sediments to the aquifer, while in BIW the soil loses nutrient

through runoffs to the rivers, especially as it is covered by impermeable lateritic hard pan. As for trace elements that are nutrients their average concentrations were plotted for groundwater and surface water in DLSW (Figure 17c), and BIW (Figure 17d). Although the elements show similar patterns in both watersheds, they differ in that in DLSW surface waters contain higher concentrations than groundwater with a decreasing order of Mn > Zn > B > Ni > (Cu, Mo and Co that are almost absent), while in BIW the concentrations are higher in groundwater than in surface water, with decreasing order similar to that in DLSW. Unlike the scenario with major ion nutrients, the top soil in DLSW could be losing trace element nutrients through the process of surface run-offs into rivers, and in BIW the soil may be depleted in trace element nutrients through infiltration into shallow groundwater aquifers. The plots of the trace elements concentration in the water samples were shown in Figure 17.



Figure 17: Variations of average concentrations of major ion nutrients in groundwater and surface water in DLSW (a), BIW (b), average concentrations of trace elements nutrients in groundwater and surface water in DLSW (c), and BIW (d).

Using a similar approach, the average concentrations of LREEs were plotted for groundwater and surface waters in (Figure 18a) for DLSW and (Figure 18c.) for BIW. Likewise the mean concentrations for HREEs were plotted in (Figure 18b) for DLSW and (Figure 18d) for BIW. From the plots in both watersheds

we observe similar variations in LREEs and HREEs, but with the following peculiarities: the REEs content is higher in DLSW than in BIW; in DLSW the low and the high REEs fractionate with preference for groundwater than surface water; in BIW the REEs shows no fractionation between groundwater and surface water; summarily in DLSW groundwater is a favourable geochemical sink of REEs than surface water. The trend for the average concentrations of REEs in the watersheds were shown in Figure 18.



Figure 18: Plots of average concentrations of LREEs for groundwater and surface waters in DLSW (a), BIW (c), and mean concentrations for HREEs in DLSW (b) and in BIW (d).

The nutrients released from rocks and contained in water become bio-available partly as a result of their relative mobility (RM).

3.2.4. Relative Mobility of elements

The extent to which major and trace elements enter the aqueous phase during weathering is called relative mobility (RM) which was computed from Eqn. 10 (Meybeck, 1997; Gislason et al., 1996; Fantong et al., 2020).

 $RM = (X/Mg)_w / (X/Mg)_r....(10)$
Where w and r refer to water and the rock, respectively. Considering that this approach has been successfully applied to rivers draining basaltic terrains in Iceland (e.g., Louvat, 1997), Mt. Etna-Sicily (Aiuppa et al., 2000), Mount Vesuvius volcanic aquifer in Italy (Aiuppa et al., 2005), and sandstone terrain in Benue River Basin-Cameroon (Fantong et al., 2020), in this study, the relative mobility of elements was calculated for 5 samples from the BIW and 5 samples from DLSW. The preference to the selected samples was based on proximity to the poor crop yield soil sites. Their water/rock concentration ratio were normalized to magnesium, because of its strong chemical mobility during weathering. The results, which are presented as plotted in Figure (19 a and b), reveal the following information:

-The zig-zag pattern of the plots reveals a similar non-isochemical dissolution of rocks in DLSW (dominated by sandstone sedimentary rocks) and BIW (dominated by trachyte, basalt and granite igneous rocks). The patterns do not differ from that obtained by Fantong et al. (2020) in a Benue River basin that consist of both sedimentary and igneous rocks.

- Except for Mo, the nutrient elements (Ca, Mn, Na, Cu, Zn, K, Ni and Fe) exhibit high relative mobility compared to non-nutrient elements (Cr, Cs, Ga, Pb, Th, U, V, and Al) in both watersheds.

-The mean mobility sequence for alkalis is Na > K > Rb, and that for alkaline earth elements is Ca > Ba. In agreement with the observation of Aiuppa et al. (2005) and Fantong et al. (2020), both sequences are similar to the Hofmeister series, which refer to the relative affinity of cations for clay minerals and oxides (e.g., Stumm and Morgan, 1996). Thus, water - rock interaction is a controlling factor for the distribution of these elements between the aqueous and solid phase in BIW and DLSW.

- Manganese, Ca, Na, K, Ti, Rb and Cu are among the most mobile elements in BIW and DLSW.

- Aluminium exhibits remarkable immobility, probably because it is retained in the product of incongruent dissolution products of kaolinite and gibbsite clay minerals. Contrary to the results in Benue River Basin by Fantong et al. (2020), Sn, Mo, Cs, and Sn are among the least mobile elements in BIW and DLSW. Figure 19 illustrates the relative mobility of trace elements (nutrients) from the water samples obtained in the selected poor soil sites in Bidou and Douka Longo watersheds.



Figure 19: Relative mobility (RM) of elements in selected water samples in BIW (a) and DLSW (b). RM values were normalized to magnesium and computed from Eq. 10 (see text).

To evaluate the amount of the generated and mobilized elements that the Douka Longo and Bidou rivers transport away from the watersheds, we calculate elemental fluxes.

3.2.5. Elemental fluxes in the watersheds

In order to assess the relative flux of the dissolved ions in the watersheds, the solute flux was calculated (e.g., Vuai and Tokuyama, 2007). The solute flux (Qi) for an individual component (i) was calculated by using the following procedure:

$$Q_i (mol \ km^{-2} \ y^{-1}) = C_i V_t / A_{.....(11)}$$

Where C_i is the mean concentration (mol/L) of ions in rivers Bidou and Douka Longo at their outlets. The locations of the outlets are indicated and situated with the installed hydrometric stations in Figure 1b for DLSW and Figure 1c for BIW. V_t , which is annual average stream discharge that were measured at the outlets shown in Fig. 1, has values of 0.98 m³/s and 0.34 m³/s for DLSW and BIW, respectively. A is the surface area in km², of the watersheds. By using the values of concentrations of ions in the river waters and the stream discharges at the outlets, the obtained annual fluxes of chemical species through the watersheds (Tables 10 and 11) show the following trends in decreasing order.

 $HCO_3 > Na > Ca > SiO_2 > Fe > Mg > Cl > F > BO_2 > Mn > NH_4 > Zn > Al > Ba > Sr > SO_4 > K$, for Bidou watershed, with annual nutrients loss of Na > Ca > Fe > Mg > Cl > B > Mn > N > Zn > Al > S > K from BIW. Whereas $HCO_3 > SiO_2 > Na > Ca > K > Mg > NO_3$, $Cl > Fe > Al > F > SO_4 > Zn > Sr > Ba > Mn > BO_2 > NH_4 > PO_4 > Br > NO_2 > Ti, for Douka Longo watershed, with annual nutrients loss of Na > Ca > K > Mg > NO + SIO_2 > Na > Cl > Fe > Al > S > Zn > Mn > B > PO_4. Comparatively, the BIW losses less nutrients in a year than DLSW, probably because the large surface areas of Douka Longo watershed. The calculated values for flux of elements in Bidou and Douka Longo are presented on Tables 10 and 11 respectively.$

	concentration		
Element	mg/L	mol/L	mole/y m ²
Κ	0	0	0
Na	1.1	4.7826E-05	0.00841
Cl	0.381	1.0732E-05	0.0019
Mg	0.318	0.00001325	0.00233
Ca	1.88	0.000047	0.0083
SO ₄	0.003	3.125E-08	0.0000055
HCO ₃	10.8	0.00017705	0.03112
Fe(II)	1.58	2.8214E-05	0.005
Mn	0.041	7.4545E-07	0.00013
NH4	0.01	5.5556E-07	0.000098
F	0.021	1.1053E-06	0.0001943
Al	0.013	4.8148E-07	0.000085
BO ₂	0.04	9.3023E-07	0.000164
Ba	0.039	2.8467E-07	0.00005
SiO ₂	2.5	4.1667E-05	0.007324
Sr	0.015	1.7123E-07	0.00003
Zn	0.033	5.0382E-07	0.00009

Table 10: Values of calculated flux of elements from Bidou watershed

	concentration		flux
Element	mg/l	mol/l	mole/y m ²
Κ	4.6	0.00011795	0.005371
Na	5.4	0.00023478	0.01069
Cl	2.11	5.9437E-05	0.00271
Mg	2.4	0.0001	0.0046
Ca	8.62	0.0002155	0.0098
SO ₄	0.396	4.125E-06	0.00019
HCO ₃	48.7	0.00079836	0.03636
Fe(II)	0.589	1.0518E-05	0.00048
Mn	0.068	1.2364E-06	0.0000563
NH4	0.01	5.5556E-07	0.0000253
NO ₂	0.002	4.3478E-08	0.00000198
Br	0.01	1.25E-07	0.0000057
NO ₃	4.52	7.2903E-05	0.00332
F	0.094	4.9474E-06	0.00023
PO ₄	0.03	3.1579E-07	0.0000144
Al	0.162	0.000006	0.000273
BO ₂	0.04	9.3023E-07	0.0000424
Ba	0.196	1.4307E-06	0.0000652
SiO ₂	14.1	0.000235	0.0107
Sr	0.135	1.5411E-06	0.0000702
Ti	0.001	2.0833E-08	0.00000095
Zn	0.121	1.8473E-06	0.000084

Table 11: Values of calculated flux of elements from Douka Longo watershed

Flux of elements from a watershed contributes in determining their spatial aqueous concentration variation, which may have implications on soil nutrients availability and amelioration options. For more appreciations of these results for flux in the two watersheds, a graphical illustration below is done to show the trend of flux of elements in the watersheds. Figure 20 shows the trend of flux of elements in the watersheds.



Figure 20: Trend of flux of elements in the DLSW and BIW. The trend showed more nutrients lost in the DLSW than the BIW.

With regards to the above graphical illustration of flux of elements, it's seen clearly that the curve of flux in Douka Longo Sedimentary watershed is always above the curve for Bidou igneous watershed for almost all the elements. This is a clear evident that the DLSW loses more nutrients than the BIW. This can be explained by the large surface areas of the Douka Longo Sedimentary watershed and equally its gentle topography.

It was therefore important to evaluate the spatial distribution of inorganic nutrients in the watersheds. To do this, intensification of sampling collection points were needed and this was an expensive task. The problem was overcome by considering samples collected near the selected sites (sites which are considered as poor agriculture yields sites). Further analysis were done as explained in the section below.

3.2.6. Spatial distribution of nutrients and REEs in waters close to selected sites with poor agricultural yields within the watersheds and water chemistry based improvement options

The poor agriculture yield sites that were identified are indicated as S1, S2 and S3, for Douka Longo watershed and S4, S5, and S6 for Bidou watershed (Figure 21). The shallow water wells (GW001, GW005, GW013, NW014, NW005, and NW001) that are located on these sites as shown on the same Figure 20, were selected to assess nutrients and REEs contents at the sites, based on water chemistry. The assessment was done by plotting concentrations in wells at each site for major anion nutrients (NO_3^- , SO_4^{2-} and PO_4^{2-}) (Fig. 22a), major cation nutrients (K^+ , Ca^{2+} , Na^+ , Mg^{2+} , Fe^{2+}) (Figure 22b), trace element nutrients (Cu, Ni, Mn, Mo, B, and Zn) (Figure 22c), and total low and high REEs (Figure 22d). The salient information from the plots are that:

-In the sites (S1-S6) within both watersheds shallow groundwater contains very low concentrations of PO_4^{2-} , Fe^{2+} , and Mo, indicating that their poor soil nature could be due partly to deficiency in phosphorous, iron and molybdenum;

- Nitrate (NO₃⁻), K⁺, B, TLREEs, and THREEs show tendencies of deficiency in the sites S4, S5 and S6 in BIW, whereas in DLSW (S1, S2, S3), the NO₃⁻, K⁺, Ca, Mn, TLREEs, and THREEs suggest tendency of toxicity, especially at site S1;

-Groundwater that circulates within the sites in BIW is comparatively poorer in all the nutrients and REEs than in the DLSW sites;

- The low TREEs concentrations in Bidou igneous watershed, contradicts the findings of Chen et al. (2019) that LREEs and HREEs concentrations are high in granitic watersheds in Southern China.

Figure 21 and Figure 22 illustrate the selected poor soil sites and their nutrients variation in concentration respectively.



Figure 21: Locations of poor agriculture yield sites (S1, S2 and S3) for Douka Longo watershed and (S4, S5, and S6) for Bidou watershed. The shallow water wells (GW001, GW005, GW013, NW014, NW005, and NW001) that are located on these sites are shown.



Figure 22: Plots of concentrations of major anion nutrients (a), major cation nutrients (b), trace element nutrients (c), and total low and high REEs (d) in wells at each site with poor agricultural yields.

CHAPTER FOUR

PROPOSITION OF SOLUTIONS AND RECOMMENDATIONS

From the previous chapter, it resulted that there is deficiency in somme nutrients and also nutrients loss by elemental fluxes in both watersheds. The question that remains in the mind is how can we improve soil nutrient availability and reduce nutrient loss in both watersheds. In a more sustainable development vision, the challenge is how to increase agricultural productivity while simultaneously reducing the cost of fertilisers and nutrient loss.

In order to overcome this challenge, locally adapted solutions are needed, and these solutions should be implemented in collaboration with the farmers. Therefore in order to spark the framers interest to preserve their land, it seems necessary to answer their immediate problems first: how to increase income and reduce production risks by improving first nutrients management on their productive fields? An Integrated nutrient management approach is then needed (Fairhurst, 2012). Then to do this, an agricultural ecosystem will be considered as a system where its equilibrium is governed by input and output factors as shown in Figure 23. The main input factors include; application of fertilisers, natural available nutrients (from geochemical generation), land management and nutrients mobility. While the output factors include; plants uptake (agent of crops production yields) and nutrients loss (mainly by erosion). Our main goal here will be to manage the impacts of each of these factors in a way as to increase productivity, reduce production costs and nutrient loss. This involves proper management of fertiliser application, enhance natural soil nutrients release and soil erosion control techniques.

Figure 23 illustrate the agricultural ecosystem with its main input and output factors that are responsible for soil fertility of a particular soil. The combination of these factors will help in an efficient management of nutrients in the soil.



Figure 23: Agricultural ecosystem showing main input and output factors governing its equilibrium (soil fertility).

In agricultural ecosystems, plants absorb nutrients from the soil and plant products are constantly removed and exported together with the nutrients they contain. As a result, the amount of nutrients in the system is reduced at every harvest. Apart from nutrients uptake by plants, some nutrients are also lost by soil erosion and leaching, probably due to the natural geology of the soil and/or due to poor land management. This is not good for agriculture since it does not contribute to increase in crops productivity. To maintain a constant soil fertility, the application of fertiliser is needed to overcome the absorbed nutrients from the soil by plants and by other unwanted phenomena such as leaching and runoff.

In the following section, different strategies concerning efficient use of fertilisers, proper land management approaches to reduce soil erosion and nutrients leaching, techniques for soil nutrient conservation are explained to help farmers and local community in BIW and DLSW.

4.1- Fertiliser use efficiency

The application of fertiliser is one of the most effective means to increase nutrient uptake in crop plants and improve yields. Fertilisers produce direct benefits by increasing crop yields and indirect benefits by increasing the amount of crop residues available to replenish soil organic matter. To use fertiliser in a sustainable manner, management practices must aim at maximizing the amount of nutrients that are taken up by the crop and minimizing the amount of nutrients that are lost from the soil. The efficiency of mineral fertilisers can be improved by using the right techniques for applying fertiliser. These techniques are often called the '4Rs' of fertiliser use (Fairhurst, 2012). The four best management practices, commonly referred to as the 4Rs or four 'rights' of fertiliser management are to apply the right source of nutrient at the right rate, at the right time and in the right place to meet crop demand. These 4Rs help to improve the recovery fraction of fertiliser and therefore contribute to improve agronomic efficiency.

a) Right fertiliser product

The right fertiliser product means matching the fertiliser source and product to the crop's needs and the properties of the soil. In the studied areas where numerous crop species are cultivated, the main concern here is to provide chemical fertilisers that is only needed by the soil to satisfy the fertility conditions. Only fertilisers containing some particular deficient nutrients in the soil are used. This process is analogous to smart irrigation method used in arid zone in developed countries, where only a needed quantity of water is given to plants.

In this light, farmers or local communities in the Bidou watershed are encouraged to use artificial chemical fertilisers rich in N, K, B and REEs. While those in the Douka Longo watershed are encouraged to use chemical fertilisers having lower content in N, K, Ca, Mn, and REEs. Adding to these nutrients deficiency in particular watershed, both watersheds need chemical fertilisers enriched in phosphorous, iron and molybdenum. Taking into consideration the fertiliser cost, it will be more sustainable to use fertilisers produced from local products. Therefore the use of vivianite as a local available fertiliser is an option. Vivianite is a very rich iron and phosphorus (Fe₃ (PO₄)₂8H₂O) from which iron and phosphorus are greatly released from its crystal lattice and be dissolved in the soil and be available for plant nutrition. The fertilising effect of vivianite from Hangloa on the growth and yield of the bean plant *Phaseolus vulgaris* on oxisoils from Ngaoundere was assessed and results showed that vivianite has a total dissolution rate of 53.48% at the end of experiment and also that its application has a positive effect on the growth and the yield of the bean plant in the oxisoils from Ngaoundere and this can therefore be used as natural phosphate fertilizer alternative to chemical fertilizers commonly used (Fodoué et al., 2015).

b) Right fertiliser rate

The right fertiliser rate means matching the amount of fertiliser applied to the crop's needs. Note that applying too much fertiliser leads to waste of nutrients not taken up by the crop and possible contamination of

the environment. On the other hand, applying too little fertiliser results in less yield, crop quality and less crop residues to protect and build the soil. Here scientific base information about the soil and crops health are needed in order to evaluate the right fertiliser rate. The collection of these data involved information from fertiliser trials, field history, crops for signs of nutrient deficiency symptoms, crop stunting and retarded development. With these data, an optimum amount of fertiliser application is calculated. A ratio of 4:2:1 of N:P₂O₅:K₂O is ideal for maximum use efficiency. A calibrated measure should always be used to apply fertiliser. To apply fertiliser uniformly at the right rate in a large field, soft-drink-bottle tops can be used to measure the amount of fertiliser applied to each plant.

c) Right time for fertiliser application

The right time for fertiliser application means making nutrients available when the crop needs them. Nutrients are used most efficiently when their availability is synchronized with crop demand. Basal fertiliser application is done at or just after planting to supply N, P, K and other nutrients required for early crop growth (Fairhurst, 2012). Leaf colour charts or chlorophyll meters are available on the market to guide the application of N, based on crop demand. Fertiliser N is highly mobile and easily lost from the soil due to leaching so some fertiliser N should be applied as a 'top dressing' at key stages during crop development, usually when the crop is growing fastest. The use of slow-release N fertilisers and deep placement of fertiliser N improve the match between nutrient release and crop demand.

d) Right placement of basal fertiliser

The right placement of fertiliser means applying fertiliser where the crop can access the nutrients contained in the fertiliser. Application methods should be selected based on the particular crop or cropping system and soil properties. It is usually best to incorporate basal fertiliser in the soil at or before planting to achieve efficient fertiliser use. Conservation tillage, buffer strips of non-crop vegetation around crop plants and irrigation management are measures that will help keep fertiliser nutrients where they were placed and accessible to growing crops.

There are four main fertiliser placement methods:

- **Broadcasting:** Fertilisers are applied uniformly to the soil surface. This is done either before sowing or in the standing crop. The method is easy to implement and has low labour requirements. N fertiliser top dressings are usually broadcast in irrigated rice fields.

- **Banding:** Fertilisers are placed in a band at a depth of 5–8 cm below the soil surface and covered by the soil. Seeds are planted above the covered fertiliser. Banding is the most common method of placement for basal fertiliser applications.
- **Spot application:** Fertilisers are applied in small amounts either at planting in each plant hill together with the seed or close to each plant station during the crop growing season. Spot application is preferred where plants are widely spaced and where soil and climate conditions increase the risk of nutrient losses due to leaching. Spot application is becoming popular among farmers because it is more cost effective than broadcasting.
- **Deep placement:** Slow-release N fertilisers are placed in the soil in flooded fields.

4.2- Nutrient loss reduction approach

Nutrient loss in watersheds is mainly due to soil erosion and leaching. These nutrients leached into water bodies and are drained out of the basin. To overcome this situation of nutrients loss, a two steps approach is needed. The first involved the reduction of erosion and runoff mechanism in the watersheds. The second step involved the use of an appropriate method to retain leaching nutrients into the watersheds. This involves reduction of nutrients draining out of the watersheds. More information on each step of the above approach is given below.

a. Reduction of soil erosion, runoff and leaching mechanism

Erosion is a term governing many processes varying very much in time and space. Consequently, soil conservation strategies must be adapted from one area to another to ecologic and socio-economic conditions. Soil erosion results not only in nutrient loss but also in reduction of topsoil depth and water holding capacity. Leaching is the movement of crop nutrients beyond the root zone mainly due to excessive drainage in coarse textured soil. A range of practices include zero tillage, cover cropping, crop rotation, mulching. The aims are to simultaneously improve soil quality, increase water infiltration, reduce water runoff and nutrient losses, save energy, reduce inorganic fertiliser application. Erosion can also be reduced by the practices of contour ploughing, terraces, contour farming and contour strip cropping depending on the topography of the agricultural field. The use of stone lines along agricultural fields to catch sand during the dry season and runoff during the rains and the use of stone walls after bringing earth from the sandy plains in order to build new soils on sandstone flag can be used as a soil conservation system in the watersheds. Reforestation of steep slopes and higher areas of watersheds is also an efficient approach.

The above mentioned solutions need a well-adapted strategy to be successful. This is because most project failure is the consequence of improper strategy. Therefore a three phase strategy is proposed below for the success of the above mentioned erosion, runoff and leaching reduction mechanisms. The three phase strategy involves the diagnostic phase, the experimentation phase and finally the general plaining phases.

- Dialogues and diagnosis: Preliminary dialogues between farmers, researchers and technical services.
 This phase begins with two inquiries in order to localise problems (type of erosion, beginning of runoff, when during the season, where on the hillslope), to assess damages, their importance, their causes and the factors with which it will be possible to reduce runoff and soil degradation.
- Experimentation and demonstration: Simple experiments have to take place in farmers' fields to quantify and compare feasibility, efficiency, yield, runoff and erosion risks under various farming techniques and management systems mentioned above. An evaluation of the relative efficiency of various management systems must be done by farmers and by specialists before the end of this experimental phase.
- General planning: An overall management plan of the watersheds must then be drawn up after years of dialogue in order to improve the use of the land, the structure of the landscape and to correct unwanted feedback with simple methods easily controllable by the farmers. Nothing can be done without the farmer's agreement, who have to learn to manage their own environment and to maintain it.

b. In watershed nutrients retention mechanisms

After the implementation of soil erosion, runoff and leaching reduction mechanisms, it is also important to propose nutrients retention mechanisms which will help in retaining the remaining nutrient loss from upstream or high lands into the watersheds. Water retention infrastructures can be used in the watersheds to avoid loss of nutrients. For a more sustainable approach, an earth dam is more appropriate, due to its least environmental impacting nature. These water retention infrastructures are more needed in DLSW where results show that nutrients loss is higher there than in BIW.

For a proper design, implantation and maintenance of these water retention infrastructures, some steps should be considered. Here data on the annual soil loss rate and its spatial distribution in the watersheds are estimated using Revised Universal Soil Loss Equation (RUSLE) model into Geographic Information System (GIS) framework (Ghosh et al., 2013). This model takes into consideration the combination of five factors

namely geology, soil, relief, climate and vegetation. Such factors presented in a more useful way are; rainfall erosivity (R), soil erodibility (K), topography (LS), crop management (C) and supporting conservation practice (P).

After obtaining the rate of annual soil loss and a spatially distributed map of soil erosion in the watersheds, the design, the implantation sites and the number of water retaining infrastructures can be evaluated from the map analysis. This means that the water retention infrastructures are designed and implanted according to the draining surface area and the soil loss intensity upstream. For the maintenance of these water retention infrastructures, it's extremely important to promote capacity building which aims to train local communities on the functioning of the infrastructures. This is to ensure sustainability of the project which is just one out of thousands of agricultural watersheds that need such that project in order to promote sustainable management of agricultural lands in Cameroon.

The next step after obtaining the number and geographical position of water retention infrastructures, was to choose the type of infrastructure and then design it according to the need. The possible water retention infrastructures were the small farm dams and the semi artificial (lakes created on the river network). Based on the topography on the watersheds, the semi artificial lakes were the most appropriate options. In order to design a hypothetical semi artificial lake in the watersheds, some initial parameters were assumed, such parameters include: the geology is that of Douka Longo, the semi artificial will be able to irrigate 20 hectares of farmland for 02 months while taking into account the evaporation and infiltration, which is 25 percent of the total carrying capacity of the lake. With these assumptions, a hypothetical semi artificial lake was designed with the dimensions and storage capacity as found in the table 12.

DESCRIPTION	DIMENSION
Embankment height include 10% settlement (m)	2.2
Embankment length (m)	48
Crest width (m)	2.5
Batter slopes (up and downstream)	3:1
Bywash/spillway (m)	1.5
Spillway width (m)	2
Foundation depth (m)	0.6
longitudinal length of the lake (m)	100
lake surface areas (m ²)	5000
lake depth (m)	3
geometry	trapezoid
Estimates of embankment volume an	d total storage volume
EMBANKMENT DESCRIPTION	DIMENSION
Volume (m ³)	2563
Earthfill in batters (m ³)	1392
Core volume (m ³)	935
Cut-off trench volume (m ³)	50
Topsoil stripping volume (m ³)	236
Total storage volume (m ³)	13650

Table 12: Assumed dimensions for a hypothetical, semi artificial lake at a favourable site

With the use of these parameters, the different profile of the lake with its embankment were produced and illustrated on the figure below. Figure 24 illustrates the different profile of the designed lake (transversal profile of lake and embankment, the 3D view).



Figure 24: illustrating transversal view of the lake (A), transversal view of the embankment (B) and the 3D view of the designed semi artificial lake (C).

After the design of the above water retention infrastructure (semi artificial lake), the budget was estimated and the estimated budget was found to be thirty millions CFA francs (see Appendix V)

The combined implementation of the fertiliser use efficiency and the nutrient loss reduction mechanism is part of an integrated sustainable soil fertility management vision of the Alliance for Green Revolution in Africa (AGRA) which aimed at promoting sustainable production approach, reduction of agriculture impact on the environment and elimination of food insecurity. A global analysis of the solution approaches presented in this chapter is illustrated in Figure 25.



Figure 25: ISFM involves the combined use of appropriate interventions on fertiliser use, soil erosion mitigation and nutrient loss management to drive the main output of crops production yields and productivity.

With respect to the problems discussed above, the following recommendations were developed in order to ameliorate the situation of agricultural productivity and improve living standards in the watersheds in the Northern Cameroon. The well application of these recommendations will extremely improve the agricultural practices in the Northern part of Cameroon.

On the part of the government,

- The Ministry of Agriculture and Rural Development (MINADER) in collaboration with its partners should provide scientific base information on the soil chemistry, geology and hydrology of the

watersheds. These data will help farmers to know which type of fertiliser is efficient in a particular agricultural field.

- The government should put in application the Abuja Declaration of 2006 (Africa Fertiliser Summit). The Declaration included the following objectives: Increase the level of use of fertiliser nutrients from the current average of 8 kg/ha to an average of at least 50 kg/ha by 2015; Reduce the cost of fertiliser procurement at national and regional levels; Improve farmers' access to fertilisers by developing and scaling up input dealers and community-based networks across rural areas; Address the fertiliser needs of farmers, especially women, and develop and strengthen the capacity of youth, farmers' associations, civil society organizations and the private sector; Improve farmers' access to fertiliser by granting targeted subsidies in favour of the fertiliser sector, with special attention to poor farmers.
- Make different types of fertilisers accessible to local communities.
- Trained local communities on different strategies of adaptive nutrient management and reduction of nutrients loss.
- Establish integrated watersheds management and soil fertility monitoring programs.

On the part of the decentralised territorial collectivities,

- Provide short training programs on fertiliser application to farmers.
- Being in constant collaboration with the farmers to follow up their agricultural needs. This permits the decentralized territorial collectivities to have more information on the agricultural problems in their different localities.
- Establish regular sustainable agricultural practice programs.
- Provide rural roads which helps in reducing fertiliser transport costs.

On the part of the local community (farmers),

- Before planting, they should consult the soil chemistry data. This will help them in choosing the type of crops appropriate in that agricultural field.
- Apply fertiliser use efficiency approach.
- Proper management of lands. This involves putting in place mechanism to mitigate soil erosion, runoff and nutrient leaching in their agricultural fields.
- Participate in all activities initiated by the decentralized territorial collectivities and or the government with the aim of improving agricultural productivity in the watersheds.

- Establish agricultural associations with the aim to share techniques, experiences and knowledge on agricultural soil management. This is also useful in requesting for aids and subventions from the governments.

For further research

- An extensive evaluation of the hydrogeochemical dynamics of nutrients in BIW and DLSW should be studied while taking into consideration the shallow groundwater, the soil and the plants.
- The evaluation of the actual uptake of essential nutrients by different crops in BIW and DLSW should be done.

IMPACT OF THE RESEARCH

Promotion of Sustainable Development Goals (SDGs) "Agenda 30" and African Union 2063 vision. This implies;

- Achieve food security in the Northern Cameroon.
- End poverty or improving living conditions of farmers in the Northern Cameroon.
- Reduce land degradation and nutrients decline in Ngong and Ngaoundere III.
- Promote sustainable agriculture, contributing to socio-economic and environmental well-being of the population.
- Contributing to global economic growth of Cameroon.

Contribute to the Integrated Africa Soil Information Service (AfSIS) initiative

GENERAL CONCLUSION

The present research work was centred on the use of shallow groundwater chemistry and rocks chemistry for assessment of soil fertility and nutrient decline in the BIW and DLSW. The main objective was to characterise the hydrogeochemical properties of elements in Douka Longo and Bidou watersheds. More specifically it consisted of: Identifying chemical weathering types and rates; evaluating elemental enrichment, depletion and relative mobility from the bed rocks; assessing elemental contents in waters, and fluxes within the watersheds and comparing hydrogeochemical processes in watersheds that drain sedimentary and igneous rocks.

The methodology order achieve mentioned research used in the above to objectives consisted generally of hydrogeochemical analysis of shallow groundwater samples and rock samples, interviews, documentary research and analysis, and field observations. This methodology permitted the identification and collection of 115 water samples from various water resources in BIW and DLSW ranging from surface to ground water samples such as rivers, streams, springs, wells and boreholes and 09 rock samples.

From the research activities, the following conclusions were attained:

- For elements to get released to waters in the watersheds, secondary carbonates (strontianite, dolomite and calcite) and primary plagioclases (dominantly andesine) in rocks were subject to three intensities of chemical weathering: weak for altered granite, trachyte and basalt; intermediate for clay; and strong for sandstone and laterite.
- The chemical weathering, which occurred at the rates of 0.0006 mm/year, 0.0014 mm/year, 0.0006 mm/year, and 0.0005 mm/year, for granite, basalt, trachyte and sandstone, respectively, are close to, but lower than those for crystalline rocks, basalts and sandstones.
- With the chemical weathering being dominantly incongruent and non iso-chemical in character, the nutrient elements (Ca, Mn, Na, Cu, Zn, K, Ni and Fe) with the exception of Mo, exhibit higher relative mobility compared to the non-nutrient elements (Cr, Bi, Cs, Cu, Ga, Pb, Sn, Th, U, V, and Al). The most mobile elements in the Bidou igneous and Douka Longo sedimentary watersheds were Mn, Ca, Na, K, Ti, Rb and Cu, with a mean mobility sequence of Na > K > Rb for the alkalis and Ca > Ba for alkaline earth elements.

- The water-rock interaction and relative mobility of the elements influence the groundwater that originated from rainwater through preferential flow pass to have the dominant chemistry of Ca + Mg NO₃ in the anthropic- affected Douka Longo sedimentary watershed, and Na + K Cl and Ca + Mg-HCO₃ mixing- affected variation, and Ca + Mg-HCO₃ and Na + K HCO₃ in Bidou watershed, probably due to cation exchange between springs and rivers within the Bidou igneous watershed.
- At the outlet of DLSW the relative elemental flux is $HCO_3 > SiO_2 > Na > Ca > K > Mg > NO_3 > Cl > Fe > Al > F > SO_4 > Zn > Sr > Ba > Mn > BO_2 > NH_4 > PO_4 > Br > NO_2 > Ti and HCO_3 > Na > Ca > SiO_2 > Fe > Mg > Cl > F > BO_2 > Mn > NH_4 > Zn > Al > Ba > Sr > SO_4 > K from the BIW.$
- The annual loss of nutrients from the Douka Longo watershed is in the order of Na > Ca > K > Mg > N > Cl > Fe > Al > S > Zn > Mn > B > PO₄ and Na > Ca > Fe > Mg > Cl > B > Mn > N > Zn > Al > S
 > K from the Bidou igneous watershed, which losses less nutrients in a year than the Douka Longo Sedimentary watershed, probably due to the large surface areas of Douka Longo watershed.
- Based on water chemistry, the poor soil nature could be due partly to: (1) deficiency in phosphorous, iron and molybdenum in both watersheds; (2) deficiency in NO₃⁻, K⁺, B, REEs, in BIW; and (3) Excess in NO₃⁻, K⁺, Ca²⁺, Mn, and REEs in DLSW.
- Water retention infrastructures should be constructed in Bidou watershed to avoid loss of nutrients,
- Artificial chemical fertilizers for soils in BIW should be enriched in N, K, B and REEs, while in Douka Longo watershed the soils may need fertilizers with lower content in N, K, Ca, Mn, and REEs.
- Erosion mitigation technics should be implemented in watersheds and especially in Douka Longo watershed to reduce soil erosion.

CONCLUSION GENERALE

Le présent travail de recherche a été centré sur l'utilisation des analyses chimiques des eaux superficielles et les roches pour évaluer la fertilité des sols et les pertes de nutriments dans les bassins versants de Bidou et de Douka Longo. L'objectif général était donc de caractériser les propriétés hydrogéochimiques des éléments dans les dites bassins versants. Plus précisément, il s'agissait: d'identifier les types et niveaux d'altération chimique des roches dans les bassins ; d'évaluer l'enrichissement, la dégradation et la mobilité des éléments à partir des roches mères ; d'évaluer le contenu des éléments dans les eaux, ainsi que leur flux dans les bassins versants ; enfin de comparer les processus hydrogéochimiques se produisant entre les deux bassins.

La méthodologie de recherche utilisée pour atteindre les objectifs mentionnés ci-dessus consistait généralement en une analyse hydrogéochimique des échantillons des eaux superficielles, des échantillons de roches, des entretiens, des recherches et des analyses documentaires et des observations sur le terrain. Cette méthodologie a permis l'identification et la collecte de 09 échantillons de roches et 115 échantillons d'eau provenant de diverses ressources en eau dans les bassins versants de Bidou et Douka Longo, allant des échantillons des eaux de surface aux eaux souterraines tels que les rivières, les cours d'eau, les sources, les puits et les forages.

Les activités de recherche ont permis de tirer les conclusions suivantes :

- Pour que les éléments soient dissout dans l'eau dans les bassins versants, les carbonates secondaires (strontianite, dolomite et calcite) et les plagioclases primaires (principalement andésine) présent dans les roches ont été soumis aux différents intensités d'altération chimique : faible altération du granite, trachyte et basalte ; altération intermédiaire pour l'argile ; et forte altération de la latérite et le grès.
- L'altération chimique qui s'est produite aux rythmes suivants : 0.0006 mm/an, 0.0014 mm/an, 0.0006 mm/an, et 0.0005 mm/an, respectivement pour le granite, le basalte, le trachyte et le grès, est proche mais inférieur à celle des roches cristallines, le basalte et le grès en générale.
- Avec l'altération chimique étant principalement incongrue et non iso-chimique de caractère, les éléments nutritifs (Ca, Mn, Na, Cu, Zn, K, Ni et Fe) a l'exception du Mo, manifestent une grande mobilité relative par rapport aux éléments non-nutritifs (Cr, Bi, Cs, Cu, Ga, Pb, Sn, Th, U, V, et Al). Les éléments les plus mobiles dans les bassins de Bidou et Douka Longo étaient Mn, Ca, Na, K, Ti, Rb

et Cu, avec une mobilité relative moyen séquentielle de Na > K > Rb pour les alcalis et Ca > Ba pour des éléments de terre alcaline.

- L'interaction roche-eau et les mobilités relatives des éléments influencent les eaux souterraines provenant des eaux de pluies par le passage préférentiel d'écoulement pour avoir une chimie dominée par Ca + Mg NO₃ dans les zones anthropiquement affectées du bassin sédimentaire de Douka Longo et le mélange en diffèrent variation de Na + K Cl, Ca + Mg- HCO₃ et Na + K HCO₃ du bassin igné de Bidou, probablement due à l'échange cationique entre les sources et les rivières dans le bassin igné de Bidou.
- A la sortie des bassins, le flux élémentaire était HCO₃ > SiO₂ > Na > Ca > K > Mg >NO₃ >Cl > Fe > Al > F > SO₄ > Zn > Sr > Ba > Mn > BO₂ > NH₄ > PO₄ > Br > NO₂ > Ti pour le bassin sédimentaire de Douka Longo et HCO₃ > Na > Ca > SiO₂ > Fe > Mg > Cl > F > BO₂ > Mn > NH₄ > Zn > Al > Ba >Sr > SO₄ > K pour le bassin igné de Bidou.
- Les pertes de nutriments annuelles étaient d'ordre Na > Ca >K > Mg > N > Cl > Fe > Al > S > Zn > Mn > B > PO₄ pour le bassin de Douka Longo et Na > Ca > Fe > Mg > Cl > B > Mn >N > Zn > Al > S > K pour le bassin de Bidou et qui présentait moins de perte de nutriments annuelles que le bassin de Douka Longo, probablement dû à la grande superficie du bassin de Douka Longo.
- En se basant sur la chimie de l'eau, la nature non fertile des sols seraient due en partie aux : déficiences du Phosphore, Fer et Molybdène dans les deux bassins ; déficience en NO₃⁻, K⁺, B, et les terres rares dans le bassin de Bidou ; et l'excès en NO₃⁻, K⁺, Ca²⁺, Mn et les terres rares dans le bassin de Douka Longo.
- La construction des infrastructures hydrauliques principalement dans le bassin versant de Bidou pour réduire la perte des nutriments.
- L'application des fertilisants chimiques riches en N, K, B et terre rare pour les sols du bassin de Bidou et les fertilisants ayant une faible concentration de N, K, Ca, Mn et terre rare dans le bassin de Douka Longo.
- Les techniques de protection des sols contre l'érosion doit être mise en place dans les bassins versants et principalement dans le bassin de Douka Longo.

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APPENDICES

Sample ID GW001	Long (dd.dd) 13.404659 13.403722	Lat (dd.dd) 9.069337	Temp (°C)	PH	EC (uS/cm)	HCO ₃	К	Na	CI	Ma	Ca	F۵	Mn	SO₄	NO ₂	Br	NH₄	F	SiO ₂	s180	<mark>8</mark> 2н	DE	nCO2
GW001	13.404659 13.403722	9.069337			(µ0,0)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(‰)	(‰)	(‰)	(atm)
	13.403722		30.4	4.2	623	-	38.0	14.4	27.50	11.6	24.6	0.04	0.64	0.347	249	-	0.34	0.941	10.2	-4.43	-25.4	10	
GW002		9.068414	30.4	4.3	698	-	75.3	27.0	43.20	8.29	19.6	0.05	0.4	2.69	266	-	0.04	0.809	8.7	-3.98	-21.9	10	
GS001	13.398551	9.069614	32.3	6.9	189	12.4	12.0	6.4	12.60	4.23	12.0	0.05	0.05	0.011	59.7	0.023	0.05	0.031	12.8	-4.60	-27.3	10	0.002
GR001	13.397299	9.070506	28.9	7.3	100	48.7	4.6	5.4	2.11	2.40	8.62	0.59	0.07	0.396	4.52	0.010	0.01	0.094	14.1	-4.26	-24.1	10	0.003
GW003	13.389630	9.056756	29.9	6.7	80	40.5	6.8	1.7	1.42	1.29	7.78	0.04	0.01	0.444	1.02	0.010	0.03	0.085	15.8	-4.90	-28.0	11	0.009
GW004	13.391245	9.061435	29.4	5.6	65	4.9	8.9	2.9	3.17	0.400	1.34	0.02	0.04	0.083	19.8	0.009	0.17	0.024	11.6	-4.61	-25.7	11	0.014
GS002	13.384551	9.052257	33.9	6.9	82	15.7	8.2	4.6	4.70	1.37	4.78	0.44	0.04	0.314	16.4	0.016	0.05	0.089	16.2	-3.51	-23.3	5	0.002
GR002	13.384553	9.052258	28.9	7.4	106	50.3	4.6	5.9	2.22	2.56	9.12	0.48	0.04	0.405	4.53	0.010	0.02	0.100	14.1	-4.42	-26.6	9	0.002
GW005	13.390569	9.044049	30.4	6.4	80	14.1	5.4	2.5	2.91	1.37	6.74	0.13	0.01	1.02	19.2	0.012	0.04	0.042	11.7	-5.31	-30.7	12	0.006
GW006	13.422484	9.037825	31.1	5.2	122	1.7	11.8	9.0	4.85	0.788	2.36	0.02	0.07	0.033	45.8	0.012	0.05	0.036	14.7	-4.54	-24.4	12	0.012
GB001	13.424827	9.036211	34.0	6.7	170	19.9	19.2	5.9	5.98	4.70	5.13	0.06	0.05	0.203	54.3	0.010	bdl	0.075	12.3	-4.71	-28.4	9	0.005
GS003	13.413819	9.033756	34.0	6.8	68	24.5	2.9	4.0	1.57	1.70	5.81	0.14	0.02	0.635	8.83	bdl	0.11	0.085	12.0	-4.73	-30.4	7	0.005
GR004	13.398575	9.085263	27.2	7.3	82	41.1	5.8	2.9	1.10	2.06	7.00	0.65	0.27	0.299	2.04	0.008	0.01	0.088	13.9	-4.18	-25.5	8	0.002
GR005	13.398614	9.085513	27.3	7.3	99	48.1	4.9	5.4	2.03	2.41	8.67	0.53	0.08	0.382	4.12	0.009	0.01	0.093	14.0	-4.47	-26.7	9	0.003
GW007	13.422984	9.088572	29.8	6.1	332	10.0	18.1	15.3	22.00	5.72	22.1	0.02	0.15	0.755	118	0.040	0.06	0.032	11.5	-4.34	-24.2	11	0.009
GW008	13.425094	9.093570	30.2	6.5	221	31.0	19.7	8.2	12.10	3.20	14.9	0.01	0.06	2.20	57.0	0.029	0.02	0.112	15.4	-5.07	-29.8	11	0.011
GR006	13.391867	9.067199	26.5	6.9	132	55.5	5.5	4.8	0.80	2.55	9.03	1.94	1.66	0.511	0.506	0.004	0.01	0.136	12.6	-2.79	-21.3	1	0.007
GR007	13.432431	8.973531	28.6	7.4	110	55.1	4.5	6.6	1.92	2.60	9.80	0.43	0.07	0.356	4.15	0.011	0.02	0.100	12.8	-4.53	-26.9	9	0.002
GW009	13.436909	8.978741	31.0	6.3	273	7.1	15.3	6.8	16.90	7.21	19.1	0.01	0.04	0.648	98.4	0.026	0.05	0.019	14.1	-4.84	-26.7	12	0.004
GW010	13.459058	8.994897	29.8	6.7	227	33.5	17.3	10.8	15.50	4.21	14.3	0.02	0.02	7.01	46.8	0.033	0.03	0.118	14.8	-4.71	-26.9	11	0.007
GW011	13.469292	9.003684	30.2	6.6	228	15.5	12.5	4.5	10.40	6.38	17.6	0.01	0.02	0.730	80.0	0.019	0.05	0.037	10.9	-4.55	-24.3	12	0.004
GW012	13.436425	9.009940	29.7	5.9	58	5.0	5.7	1.4	0.80	1.08	2.91	0.01	0.03	0.036	21.4	0.008	0.01	0.018	12.6	-4.77	-27.0	11	0.007
GW013	13.416880	9.003815	29.1	5.7	106	4.0	9.7	3.0	3.63	2.01	4.90	0.01	0.05	0.251	38.9	0.020	0.23	0.019	10.9	-4.95	-27.8	12	0.009
GW014	13.403423	9.003431	30.6	6.2	158	7.2	6.5	3.2	6.02	5.29	11.2	0.01	0.02	0.103	61.1	0.025	0.01	0.025	13.6	-4.79	-26.2	12	0.005
GR008	13.435463	9.012744	28.1	7.2	85	32.4	6.3	3.3	3.71	2.00	6.70	0.65	0.04	0.334	7.13	0.010	0.02	0.066	14.2	-4.62	-26.8	10	0.002
NW001	13.575147	7.441163	23.4	6.5	12	5.4	0.2	0.4	0.12	0.180	1.15	0	0.01	0.012	0.071	bdl	bdl	0.015	3.0	-3.65	-16.5	13	0.002
NR001	13.568552	7.422618	19.5	6.3	15	7.6	0.1	0.5	0.03	0.277	0.92	0.77	0.03	bdl	bdl	bdl	0.01	0.016	3.3	-3.42	-15.7	12	0.004
NR002	13.561354	7.427649	21.0	6.9	31	18.1	0.4	1.1	0.06	1.37	3.02	0.21	0.03	0.024	0.246	bdl	bdl	0.060	5.3	-3.52	-16.4	12	0.002

Appendix I: Results of major ions, SiO_2 , stable environmental isotopes, and pCO_2 of groundwater (n=36) and surface water (n=16), sampled during the rainy season in the Bidou and Douka Longo watersheds

APPENDIX

13 0.008 -5 0.006 0.009
-5 0.006 0.009
0.009
0.000
12 0.002
11 0.006
10 0.007
11 0.002
10 0.002
10 0.008
12 0.002
12 0.001
11 0.006
13 0.001
11 0.009
10 0.005
11 0.007
12 0.007
11 0.006
13 0.006
12 0.005
12 0.001
12 0.005
11 0.004
11 0.002
10 0.009

First letter of ID represents G= Ngong, N= Ngaoundéré III. Second letter of ID represent B= borehole, W= dug-well, R =river, L=lake, S=spring. Temp= Temperature, EC= electrical conductivity, n= number of samples, bdl= below detection limit. In addition, mean value of rain water and pCO₂ are included. - = not determined

Appendix II: Trace element data of groundwater and surface water sampled during the rainy season in the Bidou and Douka Longo watersheds

Ref. code	Sc	Y	Ag	As	В	Ba	Be	Bi	Cd	Ce	Со	Cr	Cs	Cu
Douka Lon	go watershe	ed												
GW001	0.265	484898	0.017	15581	16421	3921168	22885	< 0.002	0.214	168041	107929	0.389	2413	54535
GW002	0.165	382287	0.018	17744	21944	3037584	15166	< 0.002	0.152	272674	70717	0.102	2262	29213
GS001	0.174	0.206	< 0.003	0.104	10900	834656	0.141	< 0.002	0.019	0.424	1557	0.180	0.315	0.548
GR001	0.496	1174	< 0.003	0.187	15251	197546	0.102	< 0.002	0.005	2623	0.664	0.443	0.028	1055
GW003	0.337	0.799	0.024	0.110	15734	246050	0.105	< 0.002	0.012	0.979	0.123	0.666	0.151	0.748
GW004	0.198	0.366	< 0.003	0.032	6596	282772	0.512	< 0.002	0.012	1174	4413	0.232	0.168	1381
GS002	0.609	3227	0.033	0.231	24438	255421	0.609	< 0.002	0.012	8607	1182	1263	0.060	3884
GR002	0.317	0.483	< 0.003	0.185	11654	184633	0.077	< 0.002	0.005	1616	0.305	0.535	0.031	1129
GW005	0.499	3949	< 0.003	0.200	21479	191690	0.210	0.003	0.005	1832	0.236	1238	0.135	1689
GW006	0.138	0.557	< 0.003	0.038	6785	1246914	2361	< 0.002	0.013	1435	16310	0.065	0.436	3754
GB001	0.272	0.115	0.004	0.023	20127	1434251	0.893	< 0.002	0.014	0.224	3564	0.216	0.310	0.711
GS003	0.484	2950	0.003	0.251	64427	292043	0.343	0.002	0.008	3064	0.482	1654	0.060	2034
GR004	0.271	0.226	< 0.003	0.160	8796	181023	0.035	< 0.002	< 0.002	0.603	0.932	0.157	0.023	0.394
GR005	0.266	0.407	< 0.003	0.184	19441	169399	0.062	< 0.002	0.004	1562	0.463	0.415	0.025	1248
GW007	0.192	2443	< 0.003	0.075	8933	2069113	1229	< 0.002	0.041	0.686	17236	0.218	0.634	1489
GW008	0.271	0.659	< 0.003	0.117	19368	726985	1084	< 0.002	0.008	0.998	5715	0.210	0.167	1346
GR006	0.295	0.628	< 0.003	0.524	48597	289733	0.079	< 0.002	0.008	2718	7503	0.475	0.034	1731
GR007	0.212	0.189	< 0.003	0.129	8776	164795	0.031	< 0.002	0.005	0.575	0.304	0.214	0.013	0.566
GW009	0.221	0.348	< 0.003	0.037	18617	957330	0.504	< 0.002	0.009	0.229	3548	0.256	0.129	0.390
GW010	0.246	0.530	< 0.003	0.080	17814	468542	0.301	< 0.002	0.014	0.763	0.213	0.237	0.068	0.853
GW011	0.142	0.412	< 0.003	0.043	6351	876008	0.075	< 0.002	0.009	0.338	0.942	0.058	0.201	0.276
GW012	0.162	0.143	< 0.003	0.022	11889	315003	0.288	< 0.002	0.004	0.217	2640	0.092	0.136	0.338
GW013	0.152	0.794	< 0.003	0.084	47300	469292	0.537	< 0.002	0.009	0.968	5122	0.184	0.104	0.732
GW014	0.216	0.473	< 0.003	0.035	19412	518896	0.232	< 0.002	0.008	0.110	1423	0.151	0.100	0.968
GR008	0.368	0.608	< 0.003	0.174	21864	263113	0.074	< 0.002	0.003	1560	0.453	0.291	0.032	1044
Bidou wate	rshed													
NW001	0.025	0.042	< 0.003	< 0.01	8017	23696	0.056	< 0.002	0.005	0.076	0.472	0.033	0.006	0.263
NR001	0.073	0.019	< 0.003	0.080	15935	54018	< 0.007	< 0.002	0.003	0.076	0.581	0.104	0.004	0.224
NR002	0.069	0.032	< 0.003	0.042	13416	64441	< 0.007	< 0.002	0.002	0.145	0.245	0.108	< 0.003	0.462
NW002	0.098	0.302	< 0.003	0.020	9506	141486	0.071	< 0.002	0.018	0.202	2285	0.031	0.129	0.251
NL001	0.098	0.041	< 0.003	0.045	12947	45726	< 0.007	< 0.002	0.003	0.116	0.137	0.105	0.005	0.452
NW003	0.034	0.150	< 0.003	0.018	20014	55940	0.060	< 0.002	0.007	0.050	0.894	0.252	0.007	0.665
NR003	0.151	0.085	< 0.003	0.027	8011	36934	< 0.007	< 0.002	< 0.002	0.236	0.884	0.134	0.007	0.280
NR004	0.073	0.014	< 0.003	0.053	2393	21754	< 0.007	< 0.002	< 0.002	0.085	0.344	0.027	0.005	0.071
NW004	0.034	0.038	< 0.003	0.019	15399	52298	0.036	< 0.002	0.006	0.048	0.468	0.074	0.006	0.408
NW005	0.049	0.052	< 0.003	0.041	16609	61349	0.049	< 0.002	0.006	0.113	0.700	0.077	0.011	0.281
NR005	0.132	0.059	< 0.003	0.056	15537	57262	< 0.007	< 0.002	0.003	0.181	0.601	0.120	0.007	0.350
NW006	0.054	0.032	< 0.003	0.018	19869	65425	0.077	< 0.002	0.005	0.025	0.441	0.113	0.005	0.343
NR006	0.068	0.015	< 0.003	0.108	4918	18929	< 0.007	< 0.002	0.006	0.083	0.420	0.035	0.015	0.160
NR007	0.098	0.034	< 0.003	0.075	17487	54460	< 0.007	< 0.002	0.002	0.171	0.249	0.099	0.025	0.474
NW007	0.073	0.243	< 0.003	0.030	10240	84575	0.007	< 0.002	0.005	0.150	0.992	0.041	0.038	0.453
NR008	0.088	0.047	< 0.003	0.085	8787	44184	< 0.007	< 0.002	< 0.002	0.299	0.062	0.102	0.014	0.399
NS001	0.122	0.148	< 0.003	0.030	12604	74534	0.096	< 0.002	0.005	0.366	0.946	0.070	0.011	0.406
NR009	0.156	0.081	< 0.003	0.056	3643	35114	0.010	< 0.002	0.002	0.234	1122	0.180	0.010	0.296
NW009	0.049	0.051	< 0.003	0.010	14173	71537	0.173	< 0.002	0.006	0.076	0.316	0.178	0.043	0.337
NW010	0.000	0.078	< 0.003	< 0.01	17885	75397	0.134	< 0.002	0.006	0.107	1947	0.136	0.005	0.289
NS002	0.103	0.035	< 0.003	0.016	11027	62068	0.040	< 0.002	0.004	0.128	0.482	0.205	0.006	0.258
NW011	0.069	0.046	< 0.003	< 0.01	13794	84811	0.113	< 0.002	0.004	0.034	3016	0.209	0.007	0.399
NW012	0.113	0.063	< 0.003	0.018	11849	55680	0.094	< 0.002	0.008	0.066	2627	0.165	0.007	0.485
NW013	0.132	0.098	< 0.003	0.011	10747	60333	0.053	< 0.002	0.003	0.036	1604	1332.000	0.014	0.220
NR010	0.206	0.059	< 0.003	0.044	7898	43281	0.007	< 0.002	< 0.002	0.173	0.802	0.236	0.016	0.245
NR011	0.191	0.050	< 0.003	0.055	<2	26858	0.009	< 0.002	< 0.002	0.090	0.330	0.172	0.009	0.381
NW014	0.098	0.018	< 0.003	< 0.01	10330	47699	0.110	< 0.002	0.003	0.036	2512	0.550	0.004	0.406
NW015	0.108	0.248	< 0.003	0.026	10746	44535	0.014	< 0.002	0.002	0.323	0.133	2001	0.008	0.716
NW016	0.029	0.122	< 0.003	0.023	8055	113250	0.298	< 0.002	0.032	0.042	6219	0.125	0.020	0.206
NW017	0.059	0.031	< 0.003	0.011	12528	42741	0.036	< 0.002	0.005	0.043	0.318	0.055	0.005	1005
NW018	0.133	0.217	< 0.003	< 0.01	13875	74824	0.038	< 0.002	0.014	2049	1509	0.530	0.011	0.457
NW019	0.177	0.175	< 0.003	0.022	6005	31308	0.022	< 0.002	0.010	0.260	0.477	0.300	0.023	0.544
NR012	0.172	0.207	< 0.003	0.033	7414	52965	0.017	< 0.002	0.006	0.617	0.938	0.229	0.010	0.570
NB001	0.084	0.033	< 0.003	< 0.01	2998	53800	0.146	< 0.002	0.006	0.046	0.822	1172	0.014	0.242

Appendix II: Continued

Ref. code	Ga	Hf	In	Li	Mn	Мо	Nb	Nd	Ni	Pb	Pr	Rb	Sb	Sn
Douka Lor	igo watersh	ed												
GW001	32563	0.159	0.026	22166	626811	< 0.02	< 0.004	552413	72682	56304	97117	83497	0.066	0.025
GW002	40329	0.159	0.026	21004	378308	0.048	< 0.004	658209	44519	29730	119478	64946	0.029	0.117
GS001 GB001	0.050	< 0.002	0.026	4170	43657	0.022	< 0.004	0.275	4345	0.129	0.067	40170	0.010	<0.02
GW003	0.252	0.003	0.027	1011	9112	<0.040	0.038	1346	1039	0.350	0.418	18086	0.015	0.02
GW003 GW004	0.125	0.020	0.026	3487	42242	<0.02	0.032	0.666	3311	0.540	0.171	26085	0.010	0.022
GS002	0.830	0.034	0.026	3518	46777	< 0.02	0.216	4543	2948	1761	1174	21497	0.006	0.222
GR002	0.236	0.022	0.027	0.751	41019	0.044	0.113	0.778	0.963	0.447	0.207	8466	0.011	< 0.02
GW005	0.747	0.036	0.026	1050	6626	< 0.02	0.187	6820	1553	0.568	1660	13118	0.008	0.049
GW006	0.081	< 0.002	0.026	8068	62206	< 0.02	< 0.004	0.711	6958	2485	0.203	41578	0.018	< 0.02
GB001	0.029	< 0.002	0.027	4148	46119	< 0.02	< 0.004	0.180	1280	0.554	0.045	60916	< 0.005	< 0.02
GS003	0.796	0.026	0.027	0.921	22015	< 0.02	0.160	5924	2045	0.946	1541	7781	0.005	0.039
GR004	0.047	< 0.002	0.026	0.970	261951	0.048	< 0.004	0.408	0.652	0.138	0.096	13026	0.007	< 0.02
GR005	0.154	0.006	0.027	0./44	//845	0.045	0.041	0.769	1186	0.457	0.190	8/90	0.014	< 0.02
GW007	0.140	<0.007	0.026	4515	55083	0.02	0.004	1142	9087 6184	0.310	0.308	32174	0.018	<0.02
GR006	0.206	0.002	0.026	0.452	1755128	0.260	0.079	1102	3078	0.758	0.282	8108	0.038	<0.02
GR007	0.075	0.005	0.027	0.513	66100	0.048	0.014	0.304	0.933	0.176	0.079	7196	0.014	< 0.02
GW009	0.034	< 0.002	0.026	3277	37084	< 0.02	< 0.004	0.332	7805	0.073	0.069	43221	< 0.005	< 0.02
GW010	0.062	0.005	0.026	0.838	16731	< 0.02	0.020	0.807	2318	0.215	0.189	26162	0.011	< 0.02
GW011	0.039	< 0.002	0.027	0.922	21154	< 0.02	< 0.004	0.515	3265	0.135	0.130	33239	0.011	< 0.02
GW012	0.028	< 0.002	0.026	2441	30579	< 0.02	< 0.004	0.214	1764	0.101	0.042	19272	< 0.005	< 0.02
GW013	0.121	0.004	0.026	3730	49575	< 0.02	0.013	1300	6859	4080	0.330	30265	0.158	< 0.02
GW014	0.039	< 0.002	0.027	1902	14887	< 0.02	< 0.004	0.539	4478	0.354	0.138	22055	0.012	< 0.02
GR008	0.094	0.005	0.026	1204	35459	< 0.02	< 0.004	0.949	1178	0.536	0.242	15467	0.006	< 0.02
Bidou wate	ershed													
NW001	0.008	< 0.002	0.026	0.308	5098	< 0.02	< 0.004	0.050	0.315	0.028	0.018	0.572	0.007	< 0.02
NR001	0.006	< 0.002	0.026	0.149	24392	< 0.02	< 0.004	0.025	0.291	< 0.02	0.005	0.205	< 0.005	< 0.02
NR002	0.019	< 0.002	0.027	0.125	28649	< 0.02	< 0.004	0.037	2048	0.030	0.009	1138	< 0.005	< 0.02
NW002	0.023	< 0.002	0.027	0.325	406570	< 0.02	< 0.004	0.092	0.582	0.043	0.024	4083	0.014	< 0.02
NL001	0.019	< 0.002	0.026	0.213	40280	< 0.02	< 0.004	0.045	0.552	0.146	0.009	0.112	0.011	< 0.02
NW003	0.003	< 0.002	0.026	0.460	4939	<0.02	< 0.004	0.051	0 505	0.057	0.013	0.379	< 0.005	< 0.02
NR003	0.020	<0.002	0.020	0.168	29997	<0.02	<0.004	0.030	<0.2	<0.082	0.020	1522	<0.008	<0.02
NW004	<0.002	< 0.002	0.026	0.292	13461	< 0.02	< 0.004	0.056	3361	0.049	0.004	0.749	0.009	< 0.02
NW005	0.010	0.003	0.027	0.302	35512	< 0.02	< 0.004	0.091	0.850	0.054	0.018	1988	0.009	< 0.02
NR005	0.032	< 0.002	0.027	0.210	55900	< 0.02	< 0.004	0.068	0.423	0.040	0.019	1399	< 0.005	< 0.02
NW006	< 0.002	< 0.002	0.027	0.602	25795	< 0.02	< 0.004	0.005	0.302	0.035	0.002	0.505	0.017	< 0.02
NR006	0.010	< 0.002	0.026	0.184	41178	< 0.02	< 0.004	0.020	0.202	< 0.02	0.006	1816	< 0.005	< 0.02
NR007	0.024	< 0.002	0.026	0.299	33660	< 0.02	< 0.004	0.049	1168	0.066	0.010	3128	0.010	< 0.02
NW007	0.015	< 0.002	0.026	0.253	28660	0.056	< 0.004	0.229	0.335	0.036	0.053	2264	0.005	< 0.02
NR008	0.024	< 0.002	0.026	0.154	12926	<0.02	< 0.004	0.074	0.899	0.074	0.018	4012	< 0.005	<0.02
NR000	0.025	<0.002	0.026	0.580	55052 110977	<0.02	<0.004	0.205	0.510	0.048	0.041	2499	0.008	<0.02
NW009	0.027	<0.002	0.020	1116 000	14387	<0.02	<0.004	0.101	0.393	0.028	0.022	1540	<0.000	<0.02
NW010	0.009	< 0.002	0.026	0.531	17555	< 0.02	< 0.004	0.093	0.936	0.047	0.018	0.428	< 0.005	< 0.02
NS002	0.014	< 0.002	0.026	0.342	4714	< 0.02	< 0.004	0.030	0.231	0.037	0.009	0.680	< 0.005	< 0.02
NW011	0.009	< 0.002	0.027	0.568	17948	< 0.02	< 0.004	0.023	2175	0.040	0.009	0.680	< 0.005	< 0.02
NW012	0.016	0.004	0.026	0.537	26138	< 0.02	< 0.004	0.056	0.867	0.037	0.012	0.644	0.018	< 0.02
NW013	0.009	< 0.002	0.026	0.271	2114	< 0.02	< 0.004	0.040	1800	0.020	0.009	1381	< 0.005	< 0.02
NR010	0.020	< 0.002	0.026	0.165	42747	< 0.02	< 0.004	0.054	0.529	0.031	0.016	2581	0.008	< 0.02
NR011	0.018	< 0.002	0.026	0.223	24671	0.068	< 0.004	0.046	0.361	0.051	0.009	3649	0.009	< 0.02
NW014	0.005	< 0.002	0.026	1031	7340	< 0.02	< 0.004	0.026	2517	0.021	0.006	0.396	0.005	< 0.02
NW015	0.039	< 0.002	0.026	0.241	2032	< 0.02	< 0.004	0.161	0.847	0.053	0.030	0.897	0.005	< 0.02
IN WU16	0.003	<0.002	0.026	0.894	52970	<0.02	< 0.004	0.026	0.228	0.069	0.005	0.712	<0.005	<0.02
NW017	0.004	<0.002	0.027	0.572	32870 19159	<0.02 <0.02	<0.004 <0.004	0.018	1112	0.047	0.003	1648	<0.007	<0.02 <0.02
NW019	0.024	< 0.002	0.027	0.396	22795	<0.02	< 0.004	0.079	0.257	0.007	0.020	3669	< 0.005	<0.02
NR012	0.044	< 0.002	0.026	0.108	83183	< 0.02	< 0.004	0.180	0.653	0.049	0.048	2242	< 0.005	< 0.02
NB001	0.010	< 0.002	0.026	0.699	2683	< 0.02	< 0.004	0.019	1391	0.260	0.006	1810	< 0.005	< 0.02

Ref. code	Sr	Ta	Te	Th	Ti	Tl	U	v	W	Zn	Zr
Douka Longo	watershed										
GW001	611105	0.031	0.030	< 0.004	0.228	0.949	66695	0.070	0.104	93062	0.061
GW002	356773	0.024	< 0.01	< 0.004	0.197	1228	31074	0.186	0.127	88024	0.055
GS001	220437	< 0.001	< 0.01	0.008	0.244	0.257	0.025	0.279	< 0.05	33163	0.038
GR001	132564	0.003	< 0.01	0.075	6177	0.024	0.240	1377	< 0.05	118377	0.199
GW003	79096	0.011	< 0.01	0.116	30796	0.114	0.095	1248	< 0.05	29361	0.801
GW004	36496	0.003	< 0.01	0.020	6731	0.185	0.085	0.495	< 0.05	13870	0.176
GS002	88849	0.019	0.020	0.141	53832	0.057	0.504	1391	< 0.05	62720	1380
GR002	134412	0.007	< 0.01	0.096	19535	0.026	0.112	1111	< 0.05	24544	0.599
GW005	82353	0.016	0.020	0.213	43759	0.072	0.166	1042	0.139	44024	1205
GW006	159899	< 0.001	< 0.01	< 0.004	0.092	0.338	0.722	0.095	< 0.05	17285	< 0.005
GB001	325499	< 0.001	< 0.01	< 0.004	0.170	0.349	0.376	0.186	< 0.05	73847	0.006
GS003	86005	0.013	0.030	0.167	42742	0.027	0.295	1363	< 0.05	138580	0.938
GR004	91566	< 0.001	< 0.01	0.057	0.588	0.022	0.052	0.366	< 0.05	21846	0.020
GR005	115190	0.003	< 0.01	0.061	7496	0.029	0.094	1197	< 0.05	33081	0.195
GW007	441153	< 0.001	< 0.01	< 0.004	0.372	0.312	0.094	0.285	< 0.05	25457	0.024
GW008	211248	0.001	< 0.01	0.017	2051	0.189	0.351	0.790	< 0.05	38162	0.060
GR006	119484	0.005	0.061	0.069	8372	0.030	0.111	1385	< 0.05	100247	0.428
GR007	162823	0.001	0.030	0.020	4629	0.022	0.062	1036	< 0.05	8444	0.118
GW009	321836	< 0.001	0.020	< 0.004	0.187	0.207	0.020	0.215	< 0.05	43293	0.024
GW010	207439	0.002	< 0.01	0.026	4299	0.094	0.045	0.559	< 0.05	37862	0.193
GW011	243104	< 0.001	0.030	< 0.004	0.282	0.134	0.008	0.341	< 0.05	13553	0.024
GW012	62129	< 0.001	0.041	< 0.004	0.345	0.143	0.015	0.139	< 0.05	36858	0.012
GW013	81895	0.003	0.031	0.012	1932	0.120	0.042	0.253	< 0.05	76146	0.084
GW014	162196	<0.001	0.031	< 0.004	0.252	0.062	0.011	0.113	<0.05	46262	0.006
GR008	93303	<0.001	<0.01	0.057	0.536	0.042	0.065	1006	<0.05	42416	0.077
Bidou waters	hed										
NW001	8868	< 0.001	0.020	< 0.004	0.079	0.004	0.005	0.022	< 0.05	12785	0.010
NR001	12385	< 0.001	0.010	< 0.004	0.095	< 0.003	0.002	0.056	< 0.05	35417	0.006
NR002	34084	< 0.001	0.010	< 0.004	0.317	< 0.003	0.003	0.093	< 0.05	31851	< 0.005
NW002	99744	< 0.001	0.021	< 0.004	0.174	0.053	0.003	0.106	< 0.05	13960	0.009
NL001	14942	< 0.001	< 0.01	< 0.004	0.206	< 0.003	0.003	< 0.007	< 0.05	37170	0.006
NW003	4678	< 0.001	0.031	< 0.004	0.111	< 0.003	0.007	0.024	< 0.05	42654	< 0.005
NR003	79362	< 0.001	0.041	< 0.004	0.239	0.008	0.018	0.361	< 0.05	12036	< 0.005
NR004	13414	< 0.001	0.021	< 0.004	0.064	0.007	0.003	0.017	< 0.05	4630	< 0.005
NW004	6607	< 0.001	0.010	< 0.004	0.080	< 0.003	0.008	0.022	< 0.05	36758	0.007
NW005	9505	< 0.001	0.021	< 0.004	0.096	0.008	0.013	0.064	< 0.05	41064	0.039
NR005	33305	< 0.001	0.010	0.005	0.145	0.005	0.007	0.176	< 0.05	32030	0.024
NW006	12/45	<0.001	<0.01	< 0.004	0.081	0.004	0.004	0.034	<0.05	48233	0.019
NR006	12683	<0.001	<0.01	< 0.004	0.080	0.008	0.002	0.018	< 0.05	/866	< 0.005
NK007	12834	<0.001	< 0.01	< 0.004	0.209	0.009	0.008	0.036	< 0.05	33/83	0.010
NW007	49524	< 0.001	0.021	<0.004	0.192	0.016	0.006	0.042	< 0.05	38203	0.007
NS001	22524	<0.001	0.021	<0.004	0.064	0.007	0.012	0.048	<0.03	27845	0.003
NR009	84596	<0.001	<0.010	<0.004	0.527	0.010	0.009	0.406	<0.05	6835	0.007
NW009	11905	<0.001	0.021	<0.004	0.271	0.010	0.007	0.076	<0.05	40272	0.012
NW010	8280	<0.001	0.021	<0.004	0.318	0.006	0.008	0.060	<0.05	41442	0.015
NS002	20016	<0.001	<0.021	<0.004	0.223	0.004	0.005	0.163	<0.05	31672	0.008
NW011	9823	<0.001	0.031	<0.004	0.318	0.005	0.003	0.088	<0.05	34805	0.020
NW012	8369	<0.001	0.042	<0.004	0.365	0.006	0.004	0.063	<0.05	34830	0.063
NW013	24543	<0.001	<0.01	<0.004	0.158	0.006	0.003	0.041	<0.05	33301	0.013
NR010	55585	< 0.001	< 0.01	< 0.004	0.206	0.009	0.013	0.427	< 0.05	22677	0.007
NR011	115395	< 0.001	0.010	< 0.004	0.253	0.005	0.010	1415	< 0.05	2482	0.006
NW014	14091	< 0.001	0.011	< 0.004	0.236	0.003	0.004	0.036	< 0.05	36763	< 0.005
NW015	24709	< 0.001	0.021	< 0.004	0.803	< 0.003	0.007	0.825	< 0.05	33447	0.014
NW016	13194	< 0.001	< 0.01	< 0.004	0.173	0.009	0.001	0.021	< 0.05	35365	0.008
NW017	6467	< 0.001	0.011	< 0.004	0.204	0.005	0.002	0.041	< 0.05	36584	0.017
NW018	50932	< 0.001	0.011	< 0.004	1144	< 0.003	0.005	0.140	< 0.05	40983	0.020
NW019	51366	< 0.001	0.021	< 0.004	2568	0.004	0.003	1221	< 0.05	27722	0.081
NR012	65703	< 0.001	0.021	< 0.004	1266	0.005	0.011	0.160	< 0.05	26965	0.017
NB001	26238	< 0.001	0.021	< 0.004	0.234	0.005	0.003	0.052	< 0.05	70538	0.006

Appendix III: Rare Earth elements content in groundwater and surface water sampled during the rainy

season

Ref. code	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
Douka Lor	igo watershe	d												
GW001	150396	168041	97117	552413	135472	41615	121368	17870	95362	15706	43248	5760	32323	4882
GW002	192772	272674	119478	658209	139225	38134	114498	16114	82651	13030	34593	4623	26109	4137
GS001	0.205	0.424	0.067	0.275	0.076	0.280	0.069	0.008	0.038	0.007	0.014	0.002	0.014	0.002
GR001	1307	2623	0.418	1846	0.371	0.153	0.381	0.049	0.257	0.042	0.110	0.015	0.098	0.014
GW003	1186	0.979	0.346	1346	0.267	0.132	0.227	0.030	0.156	0.027	0.083	0.010	0.056	0.012
GW004	0.548	1174	0.171	0.666	0.147	0.118	0.135	0.012	0.091	0.014	0.030	0.005	0.037	0.006
GS002 GR002	4/8/	8607	11/4	4543	0.924	0.271	0.943	0.125	0.621	0.105	0.300	0.041	0.238	0.032
GW002	5498	1832	1660	6820	1265	0.088	1125	0.155	0.098	0.137	0.395	0.007	0.045	0.007
GW006	1	1435	0 203	0.711	0 166	0.422	0.154	0.018	0.087	0.015	0.043	0.008	0.036	0.004
GB001	0.185	0.224	0.045	0.180	0.050	0.462	0.052	0.004	0.024	0.004	0.010	0.001	0.007	0.000
GS003	6134	3064	1541	5924	1161	0.341	0.895	0.116	0.611	0.101	0.261	0.036	0.197	0.035
GR004	0.328	0.603	0.096	0.408	0.082	0.075	0.078	0.010	0.050	0.007	0.019	0.003	0.019	0.003
GR005	0.745	1562	0.190	0.769	0.146	0.080	0.128	0.016	0.093	0.015	0.048	0.006	0.032	0.004
GW007	0.954	0.686	0.368	1659	0.431	0.720	0.468	0.058	0.332	0.063	0.170	0.025	0.129	0.020
GW008	0.818	0.998	0.279	1142	0.237	0.292	0.214	0.027	0.156	0.024	0.069	0.008	0.050	0.006
GR006	1068	2718	0.282	1102	0.182	0.135	0.210	0.022	0.135	0.023	0.051	0.009	0.047	0.008
GR007	0.292	0.575	0.079	0.304	0.036	0.062	0.058	0.005	0.038	0.006	0.024	0.002	0.017	0.002
GW009	0.300	0.229	0.069	0.332	0.070	0.314	0.053	0.007	0.054	0.010	0.025	0.004	0.024	0.002
GW010	0.601	0.763	0.189	0.807	0.181	0.194	0.166	0.020	0.106	0.019	0.062	0.008	0.050	0.010
GW011 CW012	0.597	0.338	0.130	0.515	0.092	0.287	0.086	0.011	0.070	0.012	0.035	0.004	0.022	0.004
GW012 GW013	1080	0.217	0.042	1300	0.058	0.100	0.041	0.003	0.029	0.003	0.015	0.005	0.014	0.002
GW013	0.654	0.908	0.330	0.539	0.303	0.204	0.234	0.033	0.184	0.033	0.080	0.015	0.007	0.010
GR008	0.835	1560	0.242	0.949	0.192	0.124	0.202	0.025	0.142	0.020	0.059	0.007	0.045	0.008
Bidou wate	ershed													
NW001	0.062	0.076	0.018	0.050	0.015	0.010	0.010	0.000	0.006	0.000	0.003	0.000	0.002	0.000
NR001	0.021	0.076	0.005	0.025	0.009	0.016	0.007	0.001	0.000	0.000	0.002	0.000	0.003	0.000
NR002	0.038	0.145	0.009	0.037	0.015	0.024	0.016	0.001	0.007	0.000	0.004	0.000	0.005	0.000
NW002	0.089	0.202	0.024	0.092	0.032	0.055	0.043	0.005	0.028	0.006	0.022	0.003	0.007	0.002
NL001	0.043	0.116	0.009	0.045	0.010	0.017	0.015	0.000	0.003	0.001	0.004	0.000	0.003	0.000
NW003	0.027	0.050	0.013	0.051	0.016	0.022	0.022	0.005	0.020	0.004	0.011	0.001	0.011	0.002
NR003	0.082	0.236	0.020	0.086	0.020	0.014	0.019	0.003	0.012	0.003	0.006	0.001	0.005	0.001
NW004	0.024	0.085	0.004	0.056	0.002	0.009	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000
NW005	0.025	0.113	0.011	0.091	0.015	0.020	0.009	0.001	0.003	0.001	0.007	0.000	0.003	0.000
NR005	0.054	0.181	0.019	0.068	0.022	0.022	0.013	0.002	0.013	0.002	0.006	0.000	0.006	0.002
NW006	0.009	0.025	0.002	0.005	0.005	0.021	0.004	0.001	0.005	0.000	0.003	0.000	0.005	0.000
NR006	0.016	0.083	0.006	0.020	0.004	0.008	0.005	0.000	0.003	0.000	0.003	0.000	0.001	0.000
NR007	0.040	0.171	0.010	0.049	0.016	0.019	0.015	0.001	0.006	0.001	0.002	0.000	0.003	0.000
NW007	0.206	0.150	0.053	0.229	0.042	0.039	0.044	0.007	0.029	0.005	0.014	0.002	0.012	0.002
NR008	0.069	0.299	0.018	0.074	0.026	0.017	0.014	0.003	0.008	0.001	0.007	0.000	0.008	0.000
NS001	0.147	0.366	0.041	0.205	0.049	0.033	0.036	0.005	0.031	0.004	0.019	0.002	0.021	0.003
NR009	0.077	0.234	0.022	0.101	0.020	0.014	0.019	0.003	0.014	0.002	0.005	0.000	0.009	0.001
N W009	0.030	0.076	0.011	0.044	0.013	0.028	0.011	0.002	0.014	0.002	0.007	0.000	0.007	0.001
NS002	0.049	0.107	0.018	0.030	0.015	0.027	0.020	0.002	0.018	0.002	0.007	0.000	0.000	0.000
NW011	0.025	0.034	0.009	0.023	0.000	0.029	0.010	0.001	0.007	0.002	0.004	0.000	0.004	0.001
NW012	0.028	0.066	0.012	0.056	0.005	0.021	0.012	0.002	0.010	0.002	0.006	0.000	0.006	0.000
NW013	0.045	0.036	0.009	0.040	0.005	0.021	0.011	0.002	0.009	0.003	0.007	0.002	0.004	0.000
NR010	0.064	0.173	0.016	0.054	0.009	0.018	0.020	0.002	0.011	0.002	0.004	0.000	0.003	0.000
NR011	0.035	0.090	0.009	0.046	0.018	0.011	0.013	0.002	0.006	0.002	0.005	0.000	0.004	0.000
NW014	0.015	0.036	0.006	0.026	0.009	0.016	0.006	0.001	0.002	0.000	0.002	0.000	0.003	0.000
NW015	0.109	0.323	0.030	0.161	0.048	0.021	0.038	0.006	0.038	0.006	0.026	0.002	0.016	0.003
NW016	0.013	0.042	0.005	0.026	0.011	0.040	0.007	0.001	0.005	0.001	0.008	0.002	0.014	0.005
NW017	0.012	0.043	0.003	0.018	0.010	0.016	0.008	0.000	0.003	0.001	0.004	0.000	0.005	0.001
NW018	0.069	2049	0.026	0.079	0.018	0.027	0.027	0.003	0.021	0.005	0.019	0.003	0.024	0.002
NW019	0.063	0.260	0.019	0.092	0.021	0.016	0.022	0.004	0.019	0.004	0.016	0.003	0.025	0.003
NR012	0.135	0.617	0.048	0.180	0.031	0.029	0.039	0.007	0.032	0.006	0.020	0.003	0.020	0.002
PASS	38 200	79 600	8 830	33 900	5 550	1 080	4 660	0.000	4 680	0.000	2.850	0.000	2 820	0.000
	50.200	, , , , , , , , , , , , , , , , , , , ,	0.000	22.700	2.220	1.000		0., / 0		0.220	2.000	0.110	2.020	0

Appendix III: Continued

Ref. code	∑REE	LREE	HREE	MREE	LREE/HREE	Eu/Eu*	Ce/Ce*	La/Yb	La/Sm	Gd/Dy
Douka Longo	watershed									
GW001	1481573	967967	215151	298455	4499	1528	0.321	4653	1110	1273
GW002	1716247	1243133	181257	291857	6858	1422	0.415	7383	1385	1385
GS001	1481	0.971	0.085	0.425	11424	18207	0.835	14643	2697	1816
GR001	7684	6194	0.585	0.905	10588	1916	0.819	13337	3523	1482
GW003	4857	3857	0.374	0.626	10313	2525	0.353	21179	4442	1455
GW004	3154	2559	0.195	0.400	13123	3944	0.885	14811	3728	1484
GS002	22711	19111	1462	2138	13072	1367	0.838	20113	5181	1519
GR002	4067	3455	0.233	0.379	14828	2848	0.887	19860	5770	1459
GW005	20474	15810	1902	2762	8312	1468	0.140	21646	4346	1293
GW006	4089	3136	0.211	0.742	14863	12428	0.828	21861	4741	1770
GB001	1248	0.634	0.050	0.564	12680	42665	0.566	26429	3700	216/
GS003	2041/	10003	1357	2397	12279	1575	0.230	31137	5285	1405
GR004	1/81	1435	0.111	0.235	12928	4416	0.784	1/203	4000	1360
GR005	3834	3200	0.214	0.354	15262	2756	0.958	23281	2212	13/0
GW007	4320	2227	0.797	0.743	4001	6105	0.207	16260	2213	1272
GR006	5002	5170	0.340	0.527	17525	3252	11/13	22723	5868	1572
GR000	1500	1250	0.094	0.156	13298	6389	0.873	17176	8111	1526
GW009	1493	0.930	0.126	0.437	7381	24275	0.367	12500	4286	0.981
GW010	3176	2360	0.275	0.541	8582	5270	0.522	12020	3320	1566
GW011	2203	1580	0.158	0.465	10000	15193	0.280	27136	6489	1229
GW012	0.916	0.660	0.071	0.185	9296	12646	0.565	13357	4921	1414
GW013	4841	3678	0.420	0.743	8757	3596	0.374	16119	3541	1272
GW014	1971	1441	0.165	0.365	8733	9248	0.084	27250	8175	1544
GR008	4410	3586	0.306	0.518	11719	2965	0.801	18556	4349	1423
Didan matanah	.d									
NW001	0.252	0.206	0.011	0.025	19727	2845	0.525	21000	4122	1667
NR001	0.165	0.127	0.006	0.032	21167	9492	1711	7000	2333	1007
NR002	0.301	0.229	0.017	0.055	13471	7295	1809	7600	2533	2286
NW002	0.610	0.407	0.073	0.130	5575	6982	1008	12714	2781	1536
NL001	0.266	0.213	0.011	0.042	19364	6536	1361	14333	4300	5000
NW003	0.255	0.141	0.054	0.060	2611	5522	0.616	2455	1688	1100
NR003	0.508	0.424	0.031	0.053	13677	3382	1345	16400	4100	1583
NR004	0.162	0.143	0.002	0.017	71500	12234	2002	-	12000	3000
NW004	0.196	0.140	0.014	0.042	10000	8707	0.668	8333	1923	1125
NW005	0.369	0.289	0.024	0.056	12042	7119	0.751	16750	4786	2000
NR005	0.410	0.322	0.031	0.057	10387	6126	1304	9000	2455	1000
NW006	0.085	0.041	0.014	0.030	2929	22112	1360	1800	1800	0.800
NR006	0.149	0.125	0.007	0.017	17857	8423	1955	16000	4000	1667
NR007	0.333	0.270	0.013	0.050	20769	5775	1973	13333	2500	2500
NW007	0.834	0.638	0.071	0.125	8986	4272	0.331	17167	4905	1517
NR008	0.544	0.460	0.027	0.057	17037	4196	1958	8625	2654	1750
NS001	0.962	0.759	0.085	0.118	8929	3700	1088	7000	3000	1161
NR009	0.521	0.434	0.034	0.053	12765	3382	1312	8556	3850	1357
NW009	0.246	0.161	0.033	0.052	4879	11026	0.965	4286	2308	0.786
NW010	0.362	0.267	0.035	0.060	/629	/885	0.831	8107	5/69	1111
NW011	0.233	0.197	0.019	0.039	5252	13982	0.522	/300	3000	1429
NW012	0.133	0.162	0.017	0.045	6721	17205	0.323	4107	5600	1200
NW012	0.220	0.102	0.020	0.037	4815	12700	0.412	4007	9000	1200
NR010	0.194	0.150	0.027	0.037	13055	6318	1247	21333	7111	1222
NR011	0.241	0.180	0.022	0.047	9474	3386	1170	8750	1944	2167
NW014	0.122	0.083	0.008	0.031	10375	10253	0.876	5000	1667	3000
NW015	0.827	0.623	0.097	0.107	6423	2315	1303	6813	2271	1000
NW016	0.180	0.086	0.036	0.058	2389	21465	1202	0.929	1182	1400
NW017	0.124	0.076	0.014	0.034	5429	8423	1654	2400	1200	2667
NW018	2372	2223	0.077	0.072	28870	5767	11162	2875	3833	1286
NW019	0.567	0.434	0.074	0.059	5865	3505	1734	2520	3000	1158
NR012	1169	0.980	0.090	0.099	10889	3927	1768	6750	4355	1219
NB001	0.130	0.090	0.010	0.030	9000	12657	0.994	4750	3800	2667
PASS	184773	160530	12953	11290	12393	1000	1000	13546	6883	0.996

Appendix IV: Calculated enrichments (gains) and depletion (losses) of major element oxides and trace element during water-rock interactions in Bidou and Douka Longo watershed.

Oxides	Fresh Granite	Altered granite	Amount remaining, g	Gain + or loss -, g	Gain + or loss -,%
SiO ₂	70.55	74.86	85.84	15.29	21.67
TiO ₂	0.17	0.25	0.28	0.11	67.27
Al_2O_3	15.72	13.71	15.72	0.00	0.00
Fe ₂ O ₃	1.20	0.97	1.11	-0.09	-7.32
MnO	0.03	0.02	0.02	-0.01	-19.31
MgO	0.17	0.11	0.13	-0.04	-25.81
CaO	0.79	0.26	0.30	-0.49	-61.59
Na ₂ O	3.78	2.73	3.13	-0.65	-17.19
K_2O	6.56	5.35	6.13	-0.42	-6.45
P_2O_5	0.04	0.03	0.03	-0.01	-14.82
(Cl)	0.00	0.01	0.01	0.00	91.10
Sum	99.00	98.29	112.70	13.70	-
Al	83220.00	72600.00	83220.00	0.00	0.00
Ва	485.00	159.00	182.85	-302.15	-62.30
Ce	126.00	131.00	150.65	24.65	19.56
Ga	26.00	20.00	23.00	-3.00	-11.54
La	64.00	87.00	100.05	36.05	56.33
Nb	24.00	23.00	26.45	2.45	10.21
Nd	58.00	88.00	101.20	43.20	74.48
Rb	339.00	261.00	300.15	-38.85	-11.46
Sr	118.00	41.00	47.15	-70.85	-60.04
Th	31.00	36.00	41.40	10.40	33.55
Y	26.00	25.00	28.75	2.75	10.58
Zn	45.00	27.00	31.05	-13.95	-31.00
Zr	115.00	187.00	215.05	100.05	87.00
Oxides	Fresh Basalt	Altered Basalt	Amount remaining, g	Gain + or loss -, g	Gain + or loss -,%
SiO ₂	45.32	62.31	55.12	9.80	21.63
TiO ₂	3.24	0.34	0.30	-2.94	-90.73
Al ₂ O ₃	16.11	18.21	16.11	0.00	0.00
Fe ₂ O ₃	12.04	4.30	3.80	-8.24	-68.40
MnO	0.24	0.07	0.06	-0.18	-75.04
MgO	4.92	0.18	0.16	-4.76	-96.76
CaO	8.53	0.64	0.57	-7.96	-93.34
Na ₂ O	2.27	6.12	5.41	3.14	138.51
K ₂ O	2.07	5.33	4.71	2.65	128.22
P_2O_5	1.29	0.15	0.13	-1.16	-89.98
(CI)	0.01	0.00	0.00	-0.01	-87.36
Sum	96.04	97.65	86.38	-9.66	-
Al	85300.00	95900.00	85300.00	0.00	0.00
Ba	1131.00	150.00	133.50	-997.50	-88.20
Ce	166.00	176.00	156.64	-9.36	-5.64
Ga	22.00	28.00	24.92	2.92	13.27
La	88.00	113.00	100.57	12.57	14.28
Nb	83.00	160.00	142.40	59.40	71.57
Nd	78.00	65.00	57.85	-20.15	-25.83
Rb	38.00	112.00	99.68	61.68	162.32
Sr	1573.00	19.00	16 91	-1556.09	-98.92
Th	10.00	21.00	18.69	8 69	86 90
Y	36.00	35.00	31.15	-4.85	-13 47
Zn	137.00	160.00	142.40	5 40	3 94
7r	324.00	813.00	722.57	390 57	123 32
Ovides	524.00 Fresh Trachute	Altered Trachyte	A mount remaining g	Gain + or loss - a	Gain + or loss - %
SiO	56 54	55 72	50.23	-6 31	_11 17
TiO	0.61	0.65	0.58	-0.01	-11.17
	10.01	21 10	10.00	-0.02	-5.00
A12O3	19.02	21.10	19.02	0.00	0.00

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5 6 37)3) 3 49
MID 0.25 0.20 0.18 -0.06 $-24.$ MgO 0.52 0.55 0.50 -0.02 -4.6 CaO 2.40 1.57 1.42 -0.98 $-40.$ Na ₂ O 7.35 3.83 3.45 -3.90 $-53.$ K ₂ O 4.77 5.45 4.91 0.14 3.0 P ₂ O ₅ 0.17 0.21 0.19 0.02 13.6	94 6 37)3) 3 49
MgO 0.52 0.55 0.50 -0.02 -4.6 CaO 2.40 1.57 1.42 -0.98 $-40.$ Na ₂ O 7.35 3.83 3.45 -3.90 $-53.$ K ₂ O 4.77 5.45 4.91 0.14 3.0 P ₂ O ₅ 0.17 0.21 0.19 0.02 13.0	6 37)3) 3 49
CaO2.401.571.42-0.98-40.Na2O7.353.833.45-3.90-53. K_2O 4.775.454.910.143.0 P_2O_5 0.170.210.190.0213.0	37 03 0) 3 49
Na2O7.35 3.83 3.45 -3.90 $-53.$ K2O 4.77 5.45 4.91 0.14 3.0 P2O5 0.17 0.21 0.19 0.02 13.0)3) 3 19
K_2O 4.775.454.910.143.0 P_2O_5 0.170.210.190.0213.0) 3 19
$ P_2O_5 0.17 0.21 0.19 0.02 13.0$	3 19
	19
(Cl) 0.02 0.01 0.00 -0.01 -73.	
Sum 95.19 93.08 83.91 -11.29 -	
Al 100700.00 117100.00 100700.00 0.00 0.0)
Ba 1464.00 2026.00 1742.36 278.36 19.0	1
Cu 16.00 10.00 8.60 -7.40 -46.	25
Ce 213.00 229.00 196.94 -16.06 -7.5	4
Ga 25.00 25.00 21.50 -3.50 -14.	00
La 125.00 199.00 171.14 46.14 36.9	1
Nb 141.00 152.00 130.72 -10.28 -7.2	9
Nd 68.00 89.00 76.54 8.54 12.3	6
Rb 127.00 151.00 129.86 2.86 2.2	5
Sr 1128.00 1135.00 976.10 -151.90 -13.	17
Th 21.00 25.00 21.50 0.50 2.3	3
Y 37.00 50.00 43.00 6.00 16.2	2
Zn 175.00 238.00 204.68 29.68 16.9	6
Zr 1241.00 1259.00 1082.74 -158.26 -12.	75
Oxides Fresh Granite (%) Laterite Amount remaining, g Gain + or loss -, g Gain + or	loss -,%
SiO ₂ 70.55 8.81 15.20 -55.35 -78.	15
TiO_2 0.17 1.44 2.48 2.31 1357	60
$A_{1_2O_3}$ 15.72 9.11 15.72 0.00 0.0)
Fe ₂ O ₃ 1.20 64.88 111.96 110.76 9229	62
MnO 0.03 0.10 0.17 0.14 526.	32
MgO 0.17 0.03 0.05 -0.12 -69.	55
CaO 0.79 0.03 0.05 -0.73 -93.	21
K_2O 6.56 0.04 0.06 -6.49 -99.)3
P_2O_5 0.04 1.65 2.84 2.81 8025	00
(Cl) 0.00 0.00 0.00 15.0	4
Sum 95.22 86.08 148.54 53.32 -	
A1 83220.00 48230.00 83220.00 0.00 0.0)
Ba 485.00 198.00 342.54 -142.46 -29.	37
Cu 8.00 53.00 91.69 83.69 1046	13
Ga 26.00 9.00 15.57 -10.43 -40.	2
Sr 118.00 80.00 138.40 20.40 17.2	9
Th 31.00 11.00 19.03 -11.97 -38.	51
Y 26.00 34.00 58.82 32.82 126.	23
Zn 45.00 108.00 186.84 141.84 315.	20
Zr 115.00 142.00 0.00 -115.00 -100	00
Oxides Sandstone Clay amount remaining, g Gain + or loss -, g Gain + or	loss -,%
S1O ₂ 95.22 83.07 33.73 -61.49 -64.	58
110_2 0.10 0.62 0.25 0.15 145.	, ,
$A_{12}O_{3}$ 3.09 7.61 3.09 0.00 0.0)
Fe_2O_3 0.09 1.29 0.52 0.43 482.	00
MgO 0.01 0.10 0.04 0.03 306.)4
$1 \text{ CaU} \qquad 0.05 \qquad 0.12 \qquad 0.05 \qquad 0.00 \qquad -3.8$	8
K ₂ O 0.03 3.09 1.26 1.22 3824	68
P_2O_5 0.01 0.03 0.01 0.00 -9.4	2
Sum 98.61 95.93 38.95 -59.65 -	
AI 16358.82 40288.24 16358.82 0.00 0.0)
Nb 6.00 13.00 5.28 -0.72 -12.)2
Sr 24.00 118.00 47.91 23.91 99.0	4
Th 7.00 15.00 6.09 -0.91 -12.	99
Y 7.00 28.00 11.37 4.37 62.4	2
Zr 152.00 805.00 326.87 174.87 115.)4

DESCRIPTION	Unit	Quantity	Unitary Cost	Total Cost					
PRELIMIN	NARY WO	RKS							
Geotechnical studies: Diagnostic and compliance monitoring missions of the installation		5	300000	1500000					
Site clearing and demolishing	m ²	9100	500	4550000					
Mobilisation and de-mobilisation of machinery		2%	1.2E+07	231354					
Sub Total 1		6281354							
EARTHWORKS COST ESTIMATE									
Trenching to desired depth	m ³	1910	3000	5730000					
compacted clay	m ³	935	2500	2337500					
Earth fill and topsoil	m ³	1628	2150	3500200					
Sub Total 2	00			11567700					
CIVI	L WORKS								
Reinforced Concrete	m ³	22	190000	4180000					
Application fee for operational work		1.50%		173515.5					
Investigation, design and Consultant fee		5%		578385					
Preparation and certification of EIA		2%		231354					
Sub Total 3	00		L	5163254.5					
TOTAL AMOUNT EXCLUDI	NG VAT		2301	2308.5					
LABOUR		20%	460	2461.7					
UNEXPECTED EXPENSES		10%	230	1230.9					
TOTAL ESTIMATED BUI	00 000								

Appendix V: Budget estimate for the construction of a semi artificial lake

This budget estimate gives a sum of thirty millions CFA francs.

			BGR	Bundesanstalt für Geowissenschaften und Rohstoffe
Prove PROSE	Ρ			
Federal Institute for Geosciences P.O. Box 51 01 53, 30631 Henov	and Natural Resources er			
Monsieur Chouna Yem - Yaoundé-	ele Gergino			
			Bearbeitet von	
			Gereon Heller	
Reference 54.49/2019/03/DRIPROREP.VDF	Your Meanage		Phone Mr.: =237 688677212	Yacundé
		;	-Mui Gereon.Heller@bgr.de	30.10.2019
Objet : Lettre d'Invitat l'Adamaoua	tion à la mission d	ie terrain du projet PR	OSEP/BGR dans la Régi	on de
Monsieur Chouna,				
J'ai l'honneur de vous i coopération technique de l'Adamaoua et du N Le Projet. Ladite mission se derou les caractéristiques hys	nviter de prendre p germano-camerour lord <i>Cameroun</i> (PR ulera dans les régio drauliques du sol et	art à la mission sur le te naise Conseils sur la ge OSEP), qui aura lieu du ns du Nord et de l'Adam échantillonner les point	errain dans le carde du Pro stion duvable des sols dar i 17 novembre au 03 dece aoua respectivement et vi ts d'eau.	ojet de Is <i>les Régions</i> Imbre, 2019. se à déterminer
Veuillez agréer, l'expre	ssion de mes senti	ments distingués.		
P.O. Gereon Heller, BC	3R B2.4 – Soil as a	Resource - Properties	and Dynamics	
Suppléant temporaire of	du responsable de p	projet ProSEP		
C.Udl				
Developfisher DEDUCTION DUTING DUTINO	Telefice OST1540-0 Telefice S-Mail Postsorie[fog:ds internet internet internet	Bashweitesbeig Burdesbeite Hans Bostatstei Bundesbann – Filse Lei Iden Bosto Bost 008 006 0010 40 (SMIT 260) Iddatage/Filse	Stevenewanner Stevenewanner bein Finanza 2000/1159 084.–0Normen: DE.81-039802	m Hamowe Nord

Appendix VI: Field works invitation letters for rainy and dry seasons

	Projet PROSE	Ρ		BGR	Bundesenstatt for Geowissenschaften und Rohstolfe
	Pedinal Inditute for Gamacianosa P.G. Bez 51 81 53, 30531 Hamov	and Natural Recources in			
	Monsieur Chouna Yemi - Yaoundé-	ile Gergino			
				Bearbeiter von Claire Carlier	
-	Relevence 24.02.302889G8.998G6EP-HOE	Your Message		Phone Ro. +237 680617312	Yaouniki 21.02.2010
				E-Mai Claire. Carlier@bgr.de	
	Objet : Lettre d'Invitati l'Adamaoua	ion à la mission d	e terrain du projet Pl	ROSEP/BGR dans la Régio	vi de
	Monsieur Chouna.				
	J'ai Monneur de vous in coopération technique p de l'Adémacua et du No	witer de prendre pa jermano-cameroun ard' Cameroun (PRS	et à la mission sur le l aise Conseils sur la g OSEP), qui aura lieu d	terrain dans le carde du Proj estion durable des sols dans lu 29 février au 21 mars 202	et de s <i>les Régions</i> 0.
	Ladite mission se derou les caractéristiques hyd	lera dans les région rauliques du sol et	is du Nord et de l'Adar échantillonner les poi	naoua respectivement et vis nts d'eau.	e å déterminer
	Veuillez agréer, l'expres	ision de mes sentin	rents distingués.		
	Claire Carlier				
-	Supplearne chef de pro	et ProSEP			
	Dismologistikusia (2002) SYIR AR ISAARKONE IK Distorengi 2002 - Alemanikusi Titadiisateetina 7 Ion Pappolaesee Disabilisateetina 7 Ion Pappolaesee	Falakan Stat SHD-8 Heldes SD11400-20 DH Heldes Research Research High Jacob Systems (Second Second High Jacob Systems) (Second Se	Businestrationag Durobahasis Hale Down Lin Bundenbark - Pase Li Roll Base cost cost an Switt Base cost of the cost at Switt Base 2000 - 0000 - 0000 - 00 Switt Base 2000 - 0000	Stavenumeer Stavenumer benntrivaulant spog UBL-ID-Manaer DE VICINED	Stannisse Navil

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Appendix VII: Pictures illustrating difficulties encountered on the field.





River dry up



Poor road's network



Car tyre down

Bridge failure



High temperature



State of roads near wetlands

Appendix VIII: Pictures illustrating agricultural activities in the watersheds

- Bidou watershed





Papaya farm

Soya beans farm



Irrigated vegetable farm



Lowlands potatoes farm



Wetland farm activities



Vegetable farm

- Douka Longo watershed



Cotton farm



Farm ready for planting



Onion farm



Irrigated crops seeds



Maize farm in fallow



Rice production after haversting

Appendix IX: SCIENTIFIC ACHIEVEMENT

Copy of a scientific paper to be submitted to the Journal of ENVIRONMENTAL RESEARCH

