UNIVERSITY OF SOUTHERN QUEENSLAND

Faculty of Health, Engineering and Sciences

Alkaline Soils in Libyan Sahara and Murray-Darling Basin, Australia: Characteristics, Carbon Geochemistry and Environmental Issues

A dissertation submitted by

Emohamed A. H. Maryol

BSc. (Environmental studies), M.Sc. (Marine Environment)

For the award of

Doctor of Philosophy

2015

Abstract

The geochemical characteristics of alkaline soils in the Fezzan Basin in the Sahara Desert (Libya) and the Murray-Darling Basin in Australia were studied with emphasis on carbon geochemistry and the environmental and agricultural implications of these soils. In addition, microcosm experiments were conducted to evaluate the potential of a highly alkaline soil for carbon sequestration through both soil carbonation and biomass production.

The results show that in the Fezzan area, 0.7% carbon was stored in the topsoil with approximately 1/3 being inorganic carbon and 2/3 being organic carbon. The fine-grained soil fraction contained 2.13% of iron and 252 mg/kg of phosphorus, suggesting that this area could be an important source of ocean iron and phosphorus. Manganese and strontium were identified as the major chemical pollutants that are likely to dominate in the dusts formed in this area. The soils were generally alkaline and saline, which require appropriate amendment in order to develop desert agriculture using the groundwater resources from the Man-made River Project.

In the Murray Darling Basin, the SiO_2/Al_2O_3 and most elements in the soils between the upper catchment and the lower catchment were similar, suggesting that the surface soil materials in the lower catchment tended to be of upper catchment origin. However, there were marked differences in pH, electrical conductivity, sodium adsorption ratio, exchangeable sodium percentage, inorganic carbon, and $^{87}Sr/^{86}Sr$ ratio of the acetic acid-extractable fraction between the upper catchment soils and the lower catchment soils.

This is attributable to the catchment processes, which drive the re-distribution of readily movable bicarbonates of basic metals within the catchment. The elevated pH in the lower catchment zone inhibits the growth of plants, resulting in lower soil organic carbon content, as compared to the upper catchment zone. Given the relatively low outward discharge rate, large amounts of carbonates were deposited within the lower catchment zone. The strontium isotopic signatures obtained from this study suggests a significant contribution of silicate rock-originated Sr towards the composition of soil strontium in these soils, inferring that silicate rock-originated

Ca might play an important role in the formation of carbonate minerals in the lower catchment zone, and consequently contribute significantly to CO_2 sequestration.

It appears that calcium and strontium behaved differently in the investigated highly alkaline soil system in the upper catchment of Murray Darling Basin. There was also a marked difference in geochemical behaviour between the two elements during the course of atmospheric transport from the ocean surface to the land surface. Therefore, $^{87}Sr/^{86}Sr$ provided no reliable indication of the Ca source to form pedogenetic carbonates in the investigated alkaline soils. This raises concerns over the suitability of strontium isotopic signatures in tracing Ca source for pedogenetic carbonation in alkaline soils.

The microcosm experiments showed that application of gypsum resulted in an increase in inorganic carbon and a decrease in organic carbon. The addition of talc did not significantly enhance carbonate formation. Soluble $CaCl_2$ and $MgCl_2$ did not have statically significant better effects on soil carbonation, as compared to gypsum. The one-year growth experiment using five widely cultivated pasture grasses revealed that accumulation of carbonates following gypsum application could be inhibited by plant growth; the organic acids secreted from plant roots were likely to facilitate soil carbonate dissolution. In comparison with pedogenic carbonation, carbon sequestration by biomass production was much more evident. However, the biomass carbon gain varied markedly among the five species with *Digitaria eriantha* showing the highest biomass carbon gain. This further enhanced the accumulation of soil organic carbon. At the end of the experiment, an estimated CO_2 sequestering capacity of 93 t/ha was achieved. The research findings have implications for cost–benefit analysis of alkaline soil reclamation projects.

List of Publications

The research contained in this dissertation is the full documentation of the research results that are published as

1. Maryol, E. & Lin, C. (2015). Evaluation of Atmospheric CO_2 Sequestration by Alkaline Soils through Simultaneously Enhanced Carbonation and Biomass Production. *Geoderma*, vol. 241, pp. 24-31.
2. Maryol, E. & Lin, C. (2015). Geochemical characteristics of soils in Fezzan, Sahara desert: Implications for environment and agriculture. *Journal of Geochemical Exploration*, vol. 158, pp. 122-131.

These articles have been/will be submitted to scientific journals:

1. Maryol, E., Lin, C. & Feng, Y. (submitted). Effects of Geomorphic Processes on Catchment-scale Soil Variation in a Semiarid-dominant River Basin: Land Degradation and Carbon Sequestration. *Geomorphology*
2. Maryol, E. & Lin, C. (to be submitted). Limitation of Strontium Isotopic Signatures for Inferring Calcium Sources to Form Pedogenetic Carbonates in Highly Alkaline Soils.

Certification of Dissertation

I certify that the ideas, experimental work, results, analyses, software and conclusions reported in this dissertation are entirely my own effort, except where otherwise acknowledged. I also certify that the work is original and has not been previously submitted for any other award, except where otherwise acknowledged.

ENDORSEMENT

Emohamed A. H. Maryol	Date
Dr Vasantha Aravinthan, Principal Supervisor	Date
Professor Chuxia Lin, Co-supervisor	Date

(Principal Supervisor during the period from October 2010 to December 2013)

Acknowledgment

I would like to extend my sincere gratitude to my supervisor Professor, Chuxia Lin for his full support, excellent supervision, encouragement and patience throughout the course of this thesis. His guidance made this research enjoyable and full of challenges, motivations and knowledge. I really obtained lots of experience which will help and support me through my scientific life. Thanks also go to my supervisor Dr Vasantha Aravinthan for her support and guidance.

My deepest appreciation goes to my wife, for her patience, encouragement, understanding and assistance despite being a mother of Retaj, Issra, Mohammed, Ibrahim and Ahmed. The same appreciation goes to them for being so brave and dealing with many cultural shocks during their childhood.

Financial support from my country is greatly appreciated. Thanks are also due to all my friends for their support especially my friends Dr Abdalhakim Ksheem, Dr Abdurazaq Amar, Dr Rajab Abousnina, Omer Abugila, and Mohamed Maryol. A special thanks to the staff in the Faculty of Health, Engineering and Sciences, USQ. The help of Dr Friederike Eberhard is highly appreciated for her support in the waste water laboratory and proof reading in some stages.

Last but not least, I would like to dedicate this work to my parents, especially my Mother who was my first teacher, and for her commitment to educate her children.

Table of contents

List of figures

List of tables

List of abbreviations

ESP	Exchangeable Sodium Percentage
EC	Electrolyte Concentration
SOM	Soil Organic Carbon
(Hc)	Hydraulic Conductivity
TSP	Total Suspended Particles
PM2.5	Particle with a diameter <2.5 µm
PM10	Particle with a diameter <10 µm
FAO	Food and Agriculture Organisation
AHP	African Humid Period
GAB	Great Artesian Basin
C	Carbon
dS m^{-1}	Decisiemens per meter
EC	Electrical Conductivity
MgCl	Magnesium chloride
CaCl	Calcium chloride
Na	Sodium
AAS	Atomic Absorption Spectrometer
SAR	Sodium adsorption ratio
TIMS	Thermal Ionization Mass Spectrometer
IC	Ion Chromatography
QMDSC	Queensland Department of Environment and Resource Management
MDB	Murray Darling Basin

Chapter 1 : Introduction

1.1 Background of the study

Alkaline soils are widely distributed around the world (Palandri et al. 2005; Silva et al. 2008; Zhang et al. 2011; Zhang et al. 2013). The formation of alkaline soils is linked to carbonic acid-driven weathering of rocks and accumulation of carbonate and bi-carbonate salts in arid and semi-arid areas (Berner et al. 1983; Pal et al. 2003; Richards 1954; Velbel 1993). Where sodium silicates dominate parent rocks in the erosional zone of a river catchment, soil alkalinity tends to develop, as shown in the following example chemical equations:

$$2NaAlSi_3O_{8(s)} + 2CO_{2\,(g)} + 11H_2O \rightarrow 2NaHCO_{3\,(aq)} + 4H_4SiO_{4\,(aq)} + Al_2Si_2O_5\,(OH)_{4(s)} \qquad (1.1)$$

$$2NaHCO_{3\,(aq)} \rightarrow NaOH_{(aq)} + CO_{2(g)} \qquad (1.2)$$

The elevated concentration of sodium in the soils can further alter soil characteristics, leading to formation of sodic soils, which have reduced water infiltration and results in waterlogging during and after rainfall events (Rengasamy & Olsson 1991).Where calcium or magnesium-bearing rocks dominates, the carbonic acid-driven chemical weathering defined in equations (1.3) and (1.4) in the erosional zone result in formation of soluble calcium or magnesium bicarbonates (Schlesinger & Bernhardt 2013), which are then transported from the erosional zone to the lower catchment area where precipitation takes place to form insoluble carbonate minerals i.e. calcium carbonate shown in Equation (1.5).

$$CaAl_2Si_2O_{8(s)} + 2CO_{2\,(g)} + 3H_2O \rightarrow Al_2Si_2O_5(OH)_{4(s)} + Ca(HCO_3)_2 \qquad (1.3)$$

$$CaCO_{3(s)} + H_2O + CO_{2\,(g)} \rightarrow Ca\,(HCO_3)_2 \qquad (1.4)$$

$$Ca\,(HCO_3)_2 \rightarrow CaCO_{3(s)} + H_2O + CO_{2\,(g)} \qquad (1.5)$$

The combination of Equations 1.3 and 1.5 is a process leading to sequestration of atmospheric CO_2 while the combination of Equations 1.4 and 1.5 does not result in fixation of atmospheric CO_2. The information on the abundance and distribution of soil carbonate-C has implications for a global carbon inventory, and understanding of the origin of pedogenetic carbonates can provide useful information for evaluating soil carbon sequestering capacity at catchment-scale.

Strontium isotopic signatures have been used as primary evidence to support the hypothesis that Ca of atmospheric sources controls the pedogenetic carbonation in arid and semi-arid regions (Capo & Chadwick 1999; Chiquet et al. 1999; Dart et al. 2007; Hamidi et al. 2001; Van der Hoven & Quade 2002). The utilization of $^{87}Sr/^{86}Sr$ as a tracer for Ca sources in ecosystems is based on the following theoretical assumptions (Van der Hoven & Quade 2002): (a) There is no significant difference in fractionation between the strontium isotopic species as Sr passes through various phase transformations, such as precipitation or dissolution; (b) Because Sr and Ca have similar ionic radii, their chemical behaviours in the environments are also similar to each other. Therefore, Sr can be used as a chemical proxy for Ca. Nevertheless, there have so far been no serious efforts made to test the validity of these hypotheses in alkaline soil environments.

Alkaline soils in arid and semi-arid regions are also sources of aeolian soil dusts (Goudie 2014; Swap et al. 1996), which are likely to affect the global geochemical cycling and climate (Mahowald et al. 2010). For the past decades, concerns have been raised over the impacts of soil-derived dusts on air quality and possibly human health in the affected areas (Brunekreef & Forsberg 2005; Prospero 1999). An increasing number of studies have been conducted to evaluate the transport and deposition of aerosols from the arid and semi-arid areas (Barkan et al. 2005; Goudie & Middleton 2001). Most of these studies have used the concentration of total suspended particles (TSP), namely PM2.5 (particle with a diameter <2.5 μm) and PM10 (particle with a diameter <10 μm) with limited information on major chemical constituents to characterize the dusts (Alastuey et al. 2005; Rodrıguez et al. 2001). While these physical parameters give an indication of dust load and rough elemental signatures of the dusts, they provide no insight into the presence of potentially toxic elements, which is needed for better assessment of environmental risk from the dusts.

Traditionally, research into alkaline soils has focussed on its reclamation and agricultural utilization (Abrol et al. 1988; Mahmoodabadi et al. 2013; Mzezewa et al. 2003; Oster et al. 1996; Qadir, M et al. 1996; Richards 1954; Sheoran et al. 2010). Soil characterization is usually limited to determination of salinity, alkalinity, sodicity and phosphorus availability (Bertrand et al. 2003; Bresler et al. 1982;

Hayward & Wadleigh 1949; Holloway et al. 2001; Rengasamy 2006; Vorob'eva & Pankova 2008).

So far only a few studies on detailed elemental chemistry of alkaline soils have been published. In spite of some efforts, the available information is still far from sufficient for understanding the geochemical characteristics of arid and semi-arid soils. Substantial amounts of further work are required to accumulate knowledge that is needed to inform the development of strategies for minimizing the environmental impact and maximizing the beneficial uses of alkaline soils.

The maintenance of high pH in alkaline soils indicates that the supply of binding divalent metals to form stable carbonate minerals is limited. Therefore, artificial addition of substances containing soluble divalent metals into alkaline soils is likely to facilitate sequestration of atmospheric CO_2.

Application of gypsum and other calcium-containing materials is a common agricultural practice to ameliorate sodic soils by reducing the exchangeable sodium percentage (ESP) (Chawla & Abrol 1982; Hanay et al. 2004; Mace et al. 1999). Substantial amounts of research has been conducted to examine the effects of gypsum application on correcting soil sodicity and consequently enhancing crop growth (Abdel-Fattah 2012; Hamza & Anderson 2003). However, there have so far been no studies with a focus on atmospheric CO_2 sequestration associated with these agricultural practices. The application of gypsum or other Ca and Mg-bearing materials to alkaline soils could result in fixation of atmospheric CO_2 by both carbonate formation and organic matter production, which has implications for mitigating climate change. The potential carbon credit benefit from the amendment of alkaline soils may become a factor for consideration when developing plans for alkaline soil reclamation.

This is particularly relevant to situations where irrigation water becomes available from groundwater exploitation(Gijsbers & Loucks 1999) or where there is a need for groundwater disposal due to e.g. coal seam gas extraction operations (Hamawand et al. 2013). Evaluation of carbon credits from using improved alkaline soils for biomass production will provide useful information that can assist in performing cost-benefit analyses for alkaline soil reclamation projects.

1.2 Rationale for Selection of the Study Areas

This PhD work is a case study-oriented research project. Two large drainage basins were selected for the study: (a) the Fezzan Basin, Sahara Desert and (b) the Murray Darling Basin in Australia. The former represents a closed drainage system in the arid zone of northern Africa while the latter is an open drainage system located largely in the semi-arid zone of south-eastern Australia.

There has not been detailed research into the geochemical characteristics at catchment-scale level in these two drainage basins, especially in the Fezzan Basin of the Sahara Desert. The Sahara Desert is the world's largest source of aeolian soil dust (Goudie 2014; Swap et al. 1996). Another reason for selecting this area for the study is its relevance to desert irrigation agriculture. The construction of the man-made River in Libya, which draws water from four ancient water aquifers each with estimated capacities ranging between 4.8 and 20 thousand km^2, has provided the opportunities for agricultural production in its hyper-arid areas (Elhassadi 2008b; Gijsbers & Loucks 1999). To develop sustainable agricultural systems in these areas, there is a need to understand the soil properties of the potential agricultural areas.

The accessibility of sampling sites was also an important consideration for selecting these two areas. The Murray Darling Basin is in close proximity to the University of Southern Queensland while Fezzan is my hometown, which made it easy for me to get around and obtain assistance from local people.

1.3 Aims

This study aims to fill knowledge gaps regarding variations in geochemical characteristics of alkaline soils in catchment areas of two large drainage basins. Emphasis was placed on carbon geochemistry and the substances present in these soils that have environmental and agricultural implications. In addition, the carbon sequestration potential of the amended highly alkaline soils was evaluated.

1.4 Objectives

The following objectives were set to achieve the project goals:

1. To carry out catchment-scale investigations on soil geochemical characteristics in the Fezzan Basin, Sahara Desert in order to understand the

spatial variation in soil carbon stock, major chemical constitutes of fine soil materials that may contribute to Sahara-originated aeolian dusts, and soil conditions for sustainable agricultural development in irrigated areas using groundwater from the Man-made River project;

2. To carry out catchment-scale investigations on soil geochemical characteristics in the Darling Murray Basin in order to understand the influences of catchment processes on salinisation, alkalisation and carbonation in the depositional zone of the catchment;
3. To investigate highly alkaline barren soil patches in the upper catchment of the Murray Darling Basin in order to understand the factors controlling the formation of localized alkaline soil spots;
4. To investigate strontium isotopes in the alkaline soils to assist in explaining the origin of the pedogenetic carbonates in the study areas;
5. To conduct microcosm experiments to examine the effects of various Ca- and Mg-bearing materials on pedogenetic carbonation; and
6. To conduct a plant growth experiment to observe the effects of gypsum application on biomass production, and to compare the carbon sequestering capacity among the different plant species.

1.5 Thesis structure

This thesis is divided into seven chapters

- Chapter 1 provides necessary background information on the subject area. It highlights the importance and rationale for the selected research topic. It identifies the aims of the research and set objectives to achieve the research goals.
- Chapter 2 is a detailed review of the literature relevant to the research project. It includes alkaline soils definition, formation of the alkaline soils, chemical and physical characteristics, carbonate geochemistry, $^{87}Sr/^{86}Sr$ tracer geochemistry, dusts originated from arid and semi-arid area, global cycling of elements and conclusion.
- Chapter 3 presents the research findings obtained from the investigation of the Fezzan Basin, Sahara Desert.

- Chapter 4 presents the research results from the Murray Darling Basin, Australia by comparing the major geochemical characteristics of soils between the erosion-dominated upper catchment and the deposition-dominated lower catchment.
- Chapter 5 presents investigation results on localized alkaline soils at Yelarbon, upper Darling River catchment.
- Chapter 6 presents the results from the microcosm experiments to examine the effects of soil improvement on carbon sequestration.
- Chapter 7 draws general conclusions and makes recommendations for future research.

Chapter 2 : Literature review

2.1 Overview of alkaline soils

Alkaline soils are salt-affected soils that have a high pH (Beek & Breemen 1973). There is currently no universally accepted definition for “alkaline soil”. The Collins Dictionary defines an “alkaline soil” as a soil with a pH >8.5 (Hazelton & Murphy 2007). Unlike saline soils that contain neutral salts such as chloride and sulphate of sodium, potassium, magnesium and calcium, alkaline soils have elevated levels of carbonate or bicarbonate salts, which can hydrolyse to produce hydroxyl ion (OH^-) and consequently raise soil pH.

Like other types of salt-affected soils, alkaline soils are commonly found in the low-lying areas with dry climatic conditions (Abrol et al. 1988). In these areas, the soils may receive net inputs of carbonate and bi-carbonate salts that are translocated from the upper parts of the catchment via both surface and sub-surface runoff (Abrol et al. 1988; Kelley 1934). Consequently, alkaline materials may be accumulated in the soils, resulting in elevated pH values. Because the available soluble Ca^{2+} is removed to form solid calcium carbonate, the proportion of soluble Na^+ in the sum of total soluble basic cations increases. This can lead to soil sodification and the formation of sodic soils (Brinkman 1988).

In the Australian soil classification system, a soil is considered sodic if the exchangeable sodium percentage (ESP) exceeds 6 (Adcock et al. 2007; Chartres 1993; Cochrane et al. 1994; Doyle & Habraken 1993). This is different from the USA soil classification system, which considers a soil as sodic only when the ESP exceeds 15 (Rengasamy & Olsson 1991). The lower ESP value set for defining sodic soils in the Australian soils takes into account the relatively lower content of soluble soil constituents in Australian continent. Calcium has a lower concentration in the soluble solution, which is important to maintain the electrolyte concentration during the leaching (Northcote & Srene 1972; Rengasamy & Olsson 1991).

Figure 2.1 shows the classification of sodic soils and the major chemical species present in different types of sodic soils (Rengasamy & Olsson 1991). Depending on the source of soluble salts, a diverse range of alkaline soils can be formed. Different aspects on alkaline soils are separately reviewed in the following sub-sections.

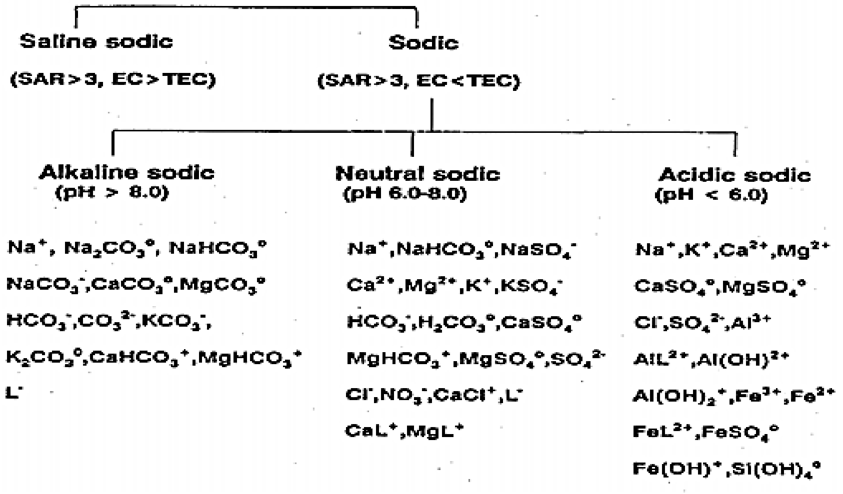


Figure 2.1: Classification of sodic soils and the predominant chemical species present in their solutions (Rengasamy & Olsson 1991)

2.1.1 Formation of Alkaline Soils

Salt-affected soils are formed due to accumulation of soluble salts in the soil profiles. The soluble salts are derived from chemical and biochemical weathering of rocks or from seawater as for the soils developed from marine sediments or sedimentary rocks of marine origins water (Shivakumar et al. 2013).

While salt-affected soils commonly occur in arid and semi-arid regions, in-situ generation of soluble salts may not provide sufficient amounts of salts to form salt-affected soils. The salts in these soils tend to originate from relatively humid areas in the upper catchment of a river basin (Abrol et al. 1988).

Acid sulphate weathering of rocks as a result of sulphide oxidation produces neutral salts and results in no alkaline materials being generated (Fitzpatrick et al. 1996). In contrast, carbonic acid-driven weathering of silicate rocks cause production of carbonates and bi-carbonates (Berner et al. 1983; Pal et al. 2003; Richards 1954; Velbel 1993), which could lead to alkalinisation if sodium dominates the basic cations in the runoff. However, formations of alkaline soils require favourable environmental conditions and are frequently induced by human activities.

2.1.1.1 Climate

The formation of salt-affected soils is generally controlled by climate (Abrol et al. 1988). Although humid climate causes rapid weathering of minerals and release of soluble salts, the salts released can be quickly leached out of the source of origins and therefore it is unlikely that saline and alkaline soils can be formed under such climatic conditions. Under semi-humid or semi-arid climatic conditions, mineral weathering and leaching of the released soluble slats are relatively weaker, as compared to humid climatic conditions. The soluble salts may be retained at some depth within the soil profile (Abrol et al. 1988). However, the amounts of soluble salts generated in-situ are rarely sufficient to reach a high level of salinity and alkalinity. Under arid and hyper-arid climatic conditions, the degree of mineral weathering is too weak and there is a lack of runoff to carry soluble salts to low-lying sites. Any saline and alkaline soils occurring in these areas are likely to be developed in the past when the climate was less dry (Brock & Buck 2009; Rech et al. 2006).

The role of climate in affecting formation of alkaline soils is more likely to enhance the evaporation and evapotranspiration, which allow upward movement of carbonate and bi-carbonate salts to the soil from the groundwater or to dry alkaline surface water to turn shallow lakes to alkaline soils (Beek & Breemen 1973). Many areas around the world are considered to be arid or dry (Table 2.1). Precipitation in such environments is rare, leading to higher relative evapotranspiration. Chartres (1993) stated that 70% of the Australian soils are located within areas with less than 500 mm annual rainfall, which means, that most of the continent is covered by arid landscapes where the salts have accumulated for hundreds of thousands of years. The sodification of Australian soils poses a significant problem. Pal et al. (2003) concluded that sodic soil can be formed when the soils in arid and semi-arid regions go through many cycles of wetting and drying as each cycle supplies new alkali bicarbonates and carbonates.

Table 2.1: Comparative distribution of areas of saline and sodic soils on several continents (10^3 km^2) (Chartres 1993; Rengasamy & Olsson 1991).

Continent	Saline	Sodic	Sodic/saline ratio
North America	**81.6**	**95.6**	**1.17**
South America	**694.1**	**595.7**	**0.86**
Africa	**534.9**	**269.5**	**0.50**
Asia	**1949.2**	**1218.6**	**0.63**
Australia	**386.3**	**1997.0**	**5.17**

2.1.1.2 Geomorphology, Geology and Hydrology

The formation of alkaline soil is also linked to topography. In low-lying areas, the accumulation of soluble salts which are swept to the top with shallow ground water is common. Therefore, it has been found that the older sediments are more likely to accumulate higher proportions of sodium and magnesium (Walker & Coventry 1976).

Many Australian rocks and non-combined deposits contain significant quantities of soluble salts and other sources of sodium such as feldspars (Kump et al. 2000). Researchers have extensively studied the salt content in both eastern and western Australian soils and rocks (Bettenay et al. 1964; Dimmock et al. 1974; Gunn & Richardson 1979). They indicate that salt (Na^+ and Cl^-) in soils was present in rocks of both terrestrial and marine origin.

Closed basins with an evaporation rate greater than precipitation allow accumulation of sodium carbonate and bi-carbonate in the soils (Beek & Breemen 1973; Eugster & Jones 1979). Groundwater usually contains elevated concentration of sodium carbonate and bi-carbonate, which could result in the formation of alkaline soils when the groundwater table occurs within the soil capillary zone (Eugster & Jones 1979).

Due to the tendency to form insoluble calcium and magnesium carbonates (Eugster & Jones 1979), ground water usually has a higher concentration of sodium relative to calcium and consequently develop sodicity (Rengasamy & Olsson 1991). Queensland (Australia) has a high use of groundwater with moderate to high level of salinity. Therefore, the risk of soil sodicity is high in this state. Breazeale (1927) mentioned that soil of the alluvial plain along the north bank of the Macintyre Brook shows sodicity and alkalinity problems which he attributes to upward leakage of Great Artesian Basin (GAB) groundwater along parts of a major fault.

It is believed that young volcanic areas that have very high rates of evapotranspiration are important sources of sodium carbonate and bi-carbonate-rich groundwater (Kovda & Samoilova 1969; Szabolcs 1989). The specific geochemical evolution of alkaline salt-affected soils is still unclear. As part of the carbonic acid-driven weathering of silicate minerals, smectite is typically the dominant clay mineral present (Kovda & Samoilova 1969; Szabolcs 1989) and silica commonly accumulates in considerable amounts (Kelley & Brown 1939; Szabolcs & Darab 1958) in alkaline salt-affected soils. Yang et al. (2011) examined the role of groundwater in alkalinisation and sodification of soils in the Songnen Plain, northeast China and they found that the development of soil sodicity and alkalinity was closely associated with the micro-topography with soils occurring in elevated patches having high salinity, sodicity and alkalinity. Ardahanlioglu et al. (2003) showed spatial variation of exchangeable sodium, electrical conductivity, soil pH in the Igdir plain, Turkey.

2.1.1.3 Human Activities

The inputs of sodium carbonate and bi-carbonate into soils are often induced by human activities such as irrigation of farmlands with alkaline groundwater (Chen 1962; Marlet et al. 1998) or clearing of forests in semi-humid lowlands, which causes rise in water table (Radford et al. 2009; Ruprecht & Schofield 1991).

2.1.2 Physical characteristics of alkaline soils

Alkaline soils have a poor structure and a low infiltration capacity. They often have a hard calcareous layer at 0.5 to 1.0 meter. Alkaline soils’ unfavourable physico-chemical characteristics are due to high sodium carbonate concentration, which causes the soil to swell and difficult to clarify or settle.

Aggregate formation happens through the combination of mineral particles with organic and inorganic substances. High exchangeable sodium percentage (ESP) and electrolyte concentration (EC) have a significant impact on the formation of these secondary particles. An excess of sodium on the exchange sites can have marked consequence on soil aggregates. Sodic soils which disperse when they are wet lead to severe soil problems such as hardsetting, which is increased soil compaction due to blocking of pores, and surface crusting. This results in a decrease in drainage, infiltration and root expansion. The reduction of aeration is mainly due to decreased hydraulic conductivity (K) which is described as the ease of water movement through the pore space of soil.

2.1.2.1 Soil structure and texture

Stability of aggregates is highly associated with soil structure. The solidity of aggregates is used as an indicator of soil structure. It has a significant impact on plant growth by affecting their ability to take up nutrients and water (Mishra et al. 2004). The infiltration capacity of the alkaline soils and the water availability in them is significantly reduced. Therefore the runoff is increased which affects the seedling emergence and crop production and also fertilizer retention. Clay type and content of these soils is important as it physically affects aggregation through swelling and dispersion. The potential of swelling induced by disaggregation is reduced at low clay levels (Qadir, M et al. 2001). Even though high sodic soil can be used as filling material especially below dams to prevent leakage of water, agricultural productivity has been adversely affected by sodification.

2.1.2.2 Swelling

Swelling is mainly caused by imposing stress, like through osmotic forces and high ESP and EC levels. Swelling will increase significantly if ESP exceeds a threshold value. The process of swelling is mainly attributed to intra-crystalline swelling or osmotic swelling that leads to reduction in hydraulic conductivity through waterlogging, crusting, increased dispersive potential, and hardsetting (Qadir & Schubert 2002; So & Aylmore 1993).

2.1.2.3 Slaking

Slaking is mainly a sodic soils feature. Aggregates of sodic soils, when exposed to rapid wetting, break down to micro-aggregates, giving rise to a surface seal and reduction in infiltration rate (So & Aylmore 1993). This process could be related to either physical or chemical properties and may lead to poor workability of the soil and ultimately to a reduction in crop yields.

2.1.2.4 Soil strength, hardsetting and crusting

Soil strength is related to a soils' ability to resist external shearing forces. Soil strength can impact crop production if it is diminished. The soils' strength can be impacted by several causes, including ratio/type of cations and humidity content of the soil (Chan et al. 1999). Moreover, crusting, hardsetting and dispersion will contribute to a reduction in soil strength. Bronick and Lal (2005) stated that dispersion is one of the main characteristics of sodic soils. It renders soil unsuitable for most agricultural uses as the breaking up of soil aggregates eventually causes decomposition of available organic matter. Wet-dry cycles of the sodic/alkaline soils can be the main reason of dispersion and slaking (Bronick & Lal 2005). Rapid wetting of unstable soils result in slaking. Spontaneous swelling and dispersion could occur as well especially when the ESP is high and EC is low.

Rain drop impact on soils and formation of a crust is the main mechanical disturbance that affects the soil surface. Crusting is highly related to the dispersive potential of soils and can be inhibited through the presence of a surface mulch or through chemical reclamation (Keren & Shainberg 1981).

Hard-setting is considered to be the key feature of degraded soil (Dexter 2004). Sodic soils demonstrate the characteristics of hard-setting which is the formation of a massive apedal (i.e. structure less) formation in the top soil, that becomes very hard on drying (Mullins et al. 1990). For instance, large areas of the Australian wheat belt face this problem, as well as many other soils around the world. For example, about 12% of Zambian soils are hardsetting (Mullins et al. 1990). These physical features of sodic/alkaline soils can increase soil loss and erosion, and are the main cause of yield reduction (So & Aylmore 1993). For this reason and other environmentally related reasons, these soils need to be reclaimed.

2.1.3 Chemical properties of alkali soils

2.1.3.1 Alkaline soil solution

Sodic soils are referred to as soils that have an exchangeable-sodium-percentage (ESP %) greater than 15 and an electrical conductivity (EC) in saturation extract less than 4 mmhos/cm.

It is 100% K^+, Na^+, Cl^- and NO_3 ions in an alkaline soil solution which present as free species. About 89% of the total Ca^{2+} and 88% of the total SO_4^{2-} occur as free species as well (Essington 2004). In addition, a high percentage of bicarbonate exists in an alkaline soil solution, which mainly contains the inorganic carbon species bicarbonate and carbonate (Figure 2.2). A major problem in alkaline soils is reduced nutrient, and specially micronutrient, availability.

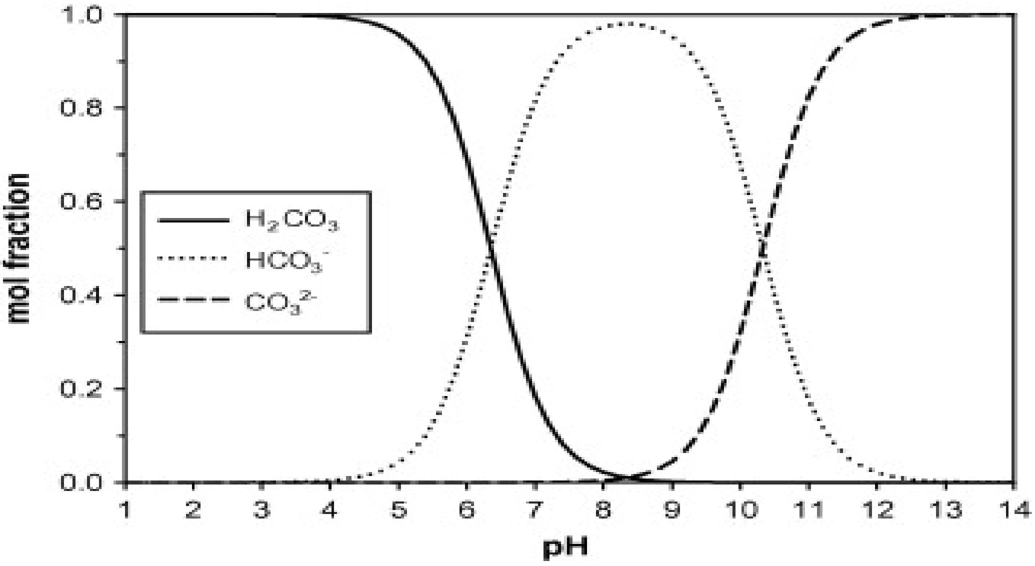


Figure 2.2:distributions of carbonate species as a portion of total dissolved carbonate in relation to solution pH(Steel et al. 2013)

2.1.3.2 Nutrient deficiency

In alkaline soils, especially in calcareous soils a deficiency in nutrients is common. Especially microelements such as phosphorus, zinc and iron are impacted due to their reaction with calcium. This results in insoluble complexes which cannot be taken up by plants. Formation of magnesium and calcium phosphate in most calcareous soil can lead to phosphorus deficiency which may result in light green coloration of leaves and reduced growth rate.

Worldwide, Zinc (Zn) is considered to be the micronutrient which causes the most significant problems, especially in Mediterranean regions where alkaline calcareous soils are abundant. Zinc deficiency caused by high pH, low soil organic matter and zinc-free fertilizer was reported in wheat and barley in Anatolia, Turkey (Rashid & Ryan 2004; Yau & Ryan 2008).

Research in the recent past has revealed that sodic stress on plants disturbs plant growth in many plant species, such as wheat (Millar et al. 2007) and rice (Yang et al. 1994). Iron deficiency is the second most important micronutrient disorder worldwide in alkaline soils. Plants are severely affected by iron deficiency because it is highly immobile in fractionation and is therefore difficult for plants to absorb. (Campbell & Nishio 2000; Rashid & Ryan 2004).

Rashid and Ryan (2004) concluded that micronutrient problems in Mediterranean-type soils cause considerable losses in productivity, with possible health hazards to the human population. Soil sodicity issues are present in both irrigated and non-irrigated cropping areas. Therefore, in order to sustain human life on earth, finding effective ways to control and utilize these widespread saline sodic soils for agricultural purposes, are vital and urgent. In the next section the reclamation process will be summarized.

2.1.4 Distribution of sodic alkaline soils

Soils with a high pH (> 8.5), with an electrical conductivity of less than four ($dS.m^{-1}$), and more than 15% exchangeable sodium are referred to as alkaline soils in the US. These soils commonly occur in the arid or desert regions around the world (Dart et al. 2005; Rengasamy & Olsson 1991; Vorob’eva & Pankova 2008).

Arid areas of the world have soils with high alkalinity and abundant exchangeable sodium (Holloway et al. 2001). Alkaline soils make up more than 30% of the world soils; a large part of it is used for agriculture. In Australia, the calcareous soils are widely spread throughout the enormous agricultural area covering about 23.8% of Australian land. Northcote and Srene (1972) have shown that the area affected by sodic soils is about 33% of the Australian continent. This is approximately 340 million hectares which is considered the largest affected land mass in the world. In southern Australia, about 8 million hectares within the cropping zone are alkaline soils.

The salt affected soils and their extent and distribution in different continents have been extensively studied (Chartres 1993; Rengasamy & Olsson 1991). Figure 2.3 shows the distribution of the world's alkaline soils where the blue areas represent the alkaline soils distribution worldwide. The map shows that both the intensively developed southern and eastern parts of the continent and the sparsely grazed lands of Queensland and Western Australia consist mainly of sodic soils (Rengasamy & Olsson 1991). About eight million ha of the southern Australian cropping zone is alkaline. Approximately 25% of the soils in Queensland are considered to be strongly sodic and another 20% are variably sodic (Doyle & Habraken 1993; Shaw et al. 1994). Figure 2.4 shows distribution of soil pH values where symbols from green to dark blue represent the alkaline soils.

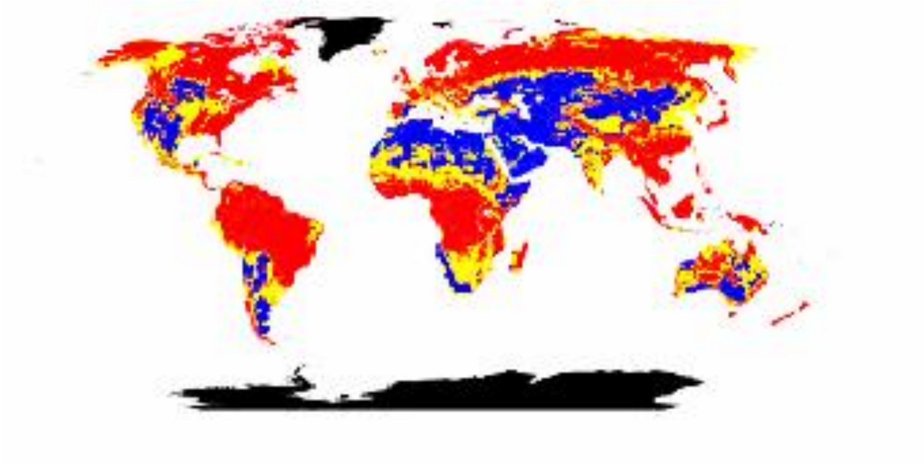


Figure 2.3: Extent of the world's alkaline soils (blue area) source: http://en.wikipedia.org/wiki/Soil_pH (reviewed 26 March 2014).

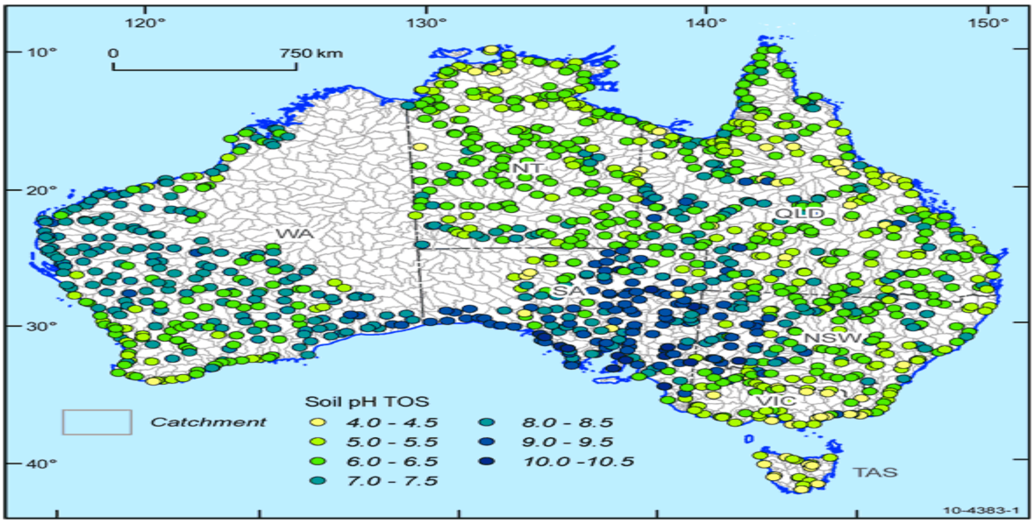


Figure 2.4: distribution of soil pH values determined in top outlet sediments. The symbols are coloured according to the pH recorded at the sampling site http://www.ga.gov.au/ausgeonews/ausgeonews201003/soil.jsp (reviewed 01May 2014)

2.1.5 Management of alkaline soils

Alkaline/sodic soils have become global environmental problems and are limiting the agricultural productivity, including adversely affecting the physical and chemical properties of soil. As has been mentioned previously, high pH > 8.4 is likely to impair the quality of these soils. They have typically low quality soil structure and low water infiltration capacity. Low availability of many essential nutrients is a common problem significantly linked with alkaline soils.

2.1.5.1 Chemical amendments

The sodic/alkaline soils can sometimes be reclaimed by chemical or by biological amendments. Chemical amelioration includes amending of soils with various reagents: gypsum, calcium chloride, limestone, sulphuric acid, sulphur, iron sulphate, or electro reclamation (treatment with electric current) (David & Dimitrios 2002; Ilyas et al. 1997; Mahmoodabadi et al. 2013; Mzezewa et al. 2003; Qadir & Oster 2004; Qadir, M et al. 1996). The chemical method based on removal of sodium (Na^+) from the exchange sites on the colloid, is usually the application of gypsum ($CaSO_4$). Gypsum provides a source of calcium which may take the place of Na^+ which is leached out of the root zone during subsequent rain fall or irrigation(Ilyas et al. 1997;

Mahmoodabadi et al. 2013). In South Africa, amelioration experiments were conducted with sulphur, gypsum, molasses meal, potassium sulfate and farmyard manure. The results indicate that sulphur, gypsum and molasses meal are efficient ameliorants. However, potassium sulfate did not hold much promise as saline-sodic ameliorant and farmyard manure and did not successfully enhance the soil condition (Mzezewa et al. 2003; Van Rooyen & Weber 1977). Mahmoodabadi et al. (2013) concluded that application of sulphuric acid in irrigation water has a significant effect on soil sodium adsorption ratio (SAR) and eventually the electrical conductivity could significantly decrease.

Sodic soil can also be reclaimed by application of both gypsum and synthetic polymers as soil conditioners as the synthetic polymers improve the soil permeability and improve the action of gypsum (Mzezewa et al. 2003). However, chemical amelioration becomes more and more cost-intensive as amendment agents get more expensive. Efficient, inexpensive, and environmentally acceptable management is essential. Calcareous sodic/alkaline soils with adequate drainage can be ameliorated with phytoremediation (Qadir, M. et al. 2001). The mechanism of biological reclamation is mainly based on increasing the partial CO_2 pressure in the soil. CO_2 is produced by plant roots and microorganisms in the root zone and dissolve the calcite. The growth of plant roots improves soil physical properties.

Many studies have been conducted in order to prove the usefulness of phytoremediation (Qadir & Oster 2002; Qadir & Oster 2004). Root respiration is not the only mechanism manipulating the partial pressure of CO_2. It is also influenced by organisms associated with plant roots which can also alter rhizosphere pH via redox-coupled reactions. CO_2 also oxidises plant root exudates and produces organic acids. Root-mediated pH changes help dissolve the native calcium carbonate (Hinsinger et al. 2003; Qadir & Oster 2004; Qadir, M. et al. 1996). In addition to aqueous CO_2 that eventually results in the formation of H^+ and HCO_3^- in the root zone, another source of H^+ may occur in soils if cropped with N_2-fixing leguminous plant species (Hinsinger 1998; Smith et al. 2009). Qadir et al. (2003) concluded that the N_2-fixing species Alfalfa (*Medicago sativa L.*) could increase the rate of Na^+ removal from calcareous sodic soils. Attempts made to reclaim these soils with forestation have indicated sustainable improvement. These methods are a cost effective and ecofriendly approach compared to the chemical methods.

2.2 Carbon Geochemistry

Arid and semi-arid regions contain a lot of soil carbonate. Pedogenic carbonate has been studied with respect to its importance to carbon sequestration, plant nutrition, landscape age and paleoclimatology. Soil carbonate dissolution is shown in Equation 2.9. It may be either pedogenic i.e. pertaining to processes that add, transfer, transform, or remove soil constituents; or geogenic, i.e resulting from geological processes in the parent material. Carbonate is mainly dissolved by weak acids like carbonic acid represented by dissolved CO_2. In wet regions, available Ca^{2+} and HCO_3^- will leach out of the soil the reaction is then determined to the right by plant Ca^{2+} uptake, evaporation of $2HCO_3^-$, increased CO_2 and H_2O.

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{+2} + 2HCO_3^- \tag{2.9}$$

However, formation of soil carbonate in arid soils is shown in Equation 2.10. In this case, Ca^{2+} sources either from chemical weathering or atmospheric deposition combine with $2HCO_3^-$ from dissolved CO_2 produced by root respiration. In contrast to the carbon incorporated into organic matter, this involves a one-step process whereby carbon is absorbed by green leaves as CO_2 (g) and converted to carbon compounds by photosynthesis, carbon in pedogenic carbonate ($CaCO_3$) requires three additional steps. After the carbon has been fixed by photosynthesis, it passes from organic matter back to CO_2 (g) by plant respiration, then to HCO_3^- (aq) via dissolution in water, and then to $CaCO_3^-$.

$$Ca_2+ +2HCO_3- \leftrightarrow CaCO_3 +H_2O + CO_2 \tag{2.10}$$

Carbon sequestration (in millions of years) takes place by chemical weathering of rocks composed of Ca-Al silicates (Equation 2.11).

$$CO_2+2H_2O+CaAl_2Si_2O_8 \leftrightarrow Al_2Si_2O_5 (OH)_4 + CaCO_3 \tag{2.11}$$

This is the main process whereby the atmospheric carbon dioxide is removed and transferred as bicarbonate from rivers to oceans and stored as calcite in marine ecosystems (Berner 1964). A large amount of carbonate, 48.000.000 Pg, is therefore stored in marine sediments such as limestone (Monger 2001).

On the short-term geologic time scale, based on the source of calcium, the formed carbonate could lead to an increase in the net carbon sequestration if the Ca^{2+} source stems from the Ca-silicate or/and other primary minerals. However, if the calcium source is from recycled carbonate, no net carbon sequestration will occur. This is because CO_2 is already used to dissolve the pre-existing carbonate. Equation 2.12 shows another form of carbon sequestration.

$$
\begin{array}{l}
CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO^{3-} \\
\qquad\qquad\qquad\qquad \downarrow\uparrow \text{ (precipitated in soil)} \\
Ca^{2+} + 2HCO_3 \leftrightarrow CaCO_3 + CO_2
\end{array}
\qquad (2.12)
$$

This carbon sequestration takes place if bicarbonate ($2HCO_3^-$) leaches into ground water instead of precipitating in the soil. This means the atmospheric carbon is transferred from soil to the hydrosphere for storage (Kraimer et al. 2005; Mikhailova et al. 2013). In pedogenic carbonation, the source of calcium is the limiting factor especially in the alkaline soils where the available calcium is very low. Therefore, strontium isotopic signatures have been used as primary evidence of calcium sources that control the pedogenetic carbonation in arid and semiarid regions.

2.2.1 Soil Carbon Sequestration

Carbon sequestration involves capturing or moving the atmospheric CO_2 into long-term carbon pools where it is stored. Therefore, increasing both organic (SOC) and inorganic carbon (SIC) in soils by following judicious land use and recommended management practices results in significant soil improvement (Lal 2004). A very recent project by the Commonwealth Science and Industrial Research Organization (CSIRO) resulted in a nationwide soil carbon map of Australia (2014). This map provides the first map of soil carbon content in Australian soils. The total organic carbon concentration ranged from 0.02 Gt (Gigatonnes) which was recorded in the Australian Capital Territory (ACT) to 7.09 Gt recorded in Western Australia with a total amount of carbon of 24.98 Gt (Figure 2.5).

A higher sequestered carbon content could lead to improved soil properties by storing more organic material and adding calcite to remove soil alkalinity and eventually mitigating the atmospheric carbon dioxide.

As the atmospheric carbon has increased, the importance of soil carbon mitigation efforts is vital in order to stabilize or reduce it. Soil management is considered one of the more effective way to achieve this, as soils store twice as much carbon as vegetation, and two thirds as much as the atmosphere (Smith 2004). Introducing organic carbon into the soil will not only sequester atmospheric carbon dioxide but will also increase the agricultural productivity and nutrient and water retention. Potential economic and climate change mitigation and other positive environmental impacts are considered the main benefits (Anderson-Teira et al. 2009).

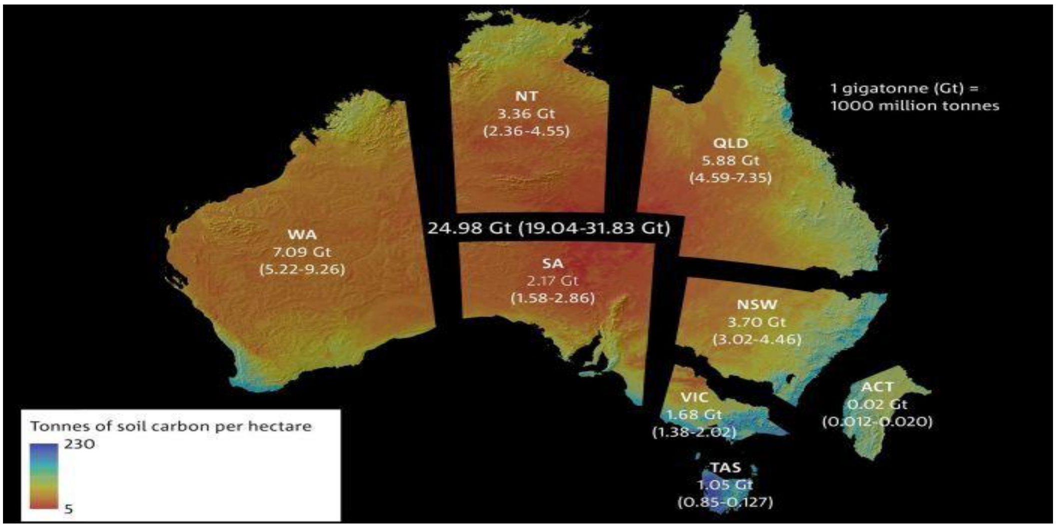


Figure 2.5: Australian soil organic carbon map digital photography 2014 Source: (http://www.abc.net.au/news/csiro-carbon-map/5331368) [Accessed 27/03/2014]

2.2.1.1 Soil organic carbon

Soil organic carbon (SOC) is comprised of plant, animal and microbial residues in all stages of decomposition. An estimation of the worlds' carbon content for terrestrial ecosystems is 1500 Gt of organic carbon which is twice the carbon content in the atmosphere (Baker et al. 2007; Kirschbaum 1995; McCarl et al. 2007; Pan et al. 2004; Post & Kwon 2000; Qiguo et al. 1997). The biotic carbon plays the main role in terrestrial ecosystems, as it is usually greater than the amount of living vegetation. It is hence essential to understand its role in the terrestrial carbon balance and the global carbon cycle (Post and Kwon 2000; Baker et al. 2007). Because of the abundance and importance of organic carbon stored in the soils, many studies have been done on this topic (Jobbágy & Jackson 2000; Watson 2000). Human land use activities influence both carbon storage and soil organic carbon and increase turnover times significantly (Davidson & Ackerman 1993; Mann 1986).

Early in the previous century, land use changes including cultivation and deforestation resulted in the release of about 1.6 ± 0.7Gt of carbon annually (Houghton 1995) wheras fossil fuel combustion added more than 6.0 Gt carbon per year in the same period of time (Battle et al. 2000). Agricultural activity accounted for about 14% of these fossil fuel emissions in the same period (Lal & Kimble 1997). The large contribution of the soil organic carbon to the total of released carbon is due to agricultural practices. In China and Indonesia, organic carbon is significantly lower in the cultivated and unirrigated soils than in the irrigated and the undisturbed soils. Therefore, the conversion of primary forests to plantations and cultivated land can cause a decline of the SOC by as much as 40% in temperate regions and more than 60% in the tropics. However, irrigation seems to be benefical for the soil organic matter content (Minasny et al. 2011; Wu et al. 2003).

Soil carbon has been significantly depleted due to intensification of cultivation in the past, but it is believed that the improved management of forests and agricultural land increases the sequestered carbon in soils. Forest ecosystems afforestation,conversion of tree species, thining, drainage, fertilisation, liming, site prepartion and harvest management could lead to an increase in the SOC and to a high potential for soil carbon sequestration (Wiesmeier et al. 2014). Lai et al. (2013) found that adding fresh organic matter and water does not have a large impact on the SOC pool. In addition, Kätterer et al. (2012) in a long term study clearly showed that SOC can be raised if the time between planting, i.e the time when the soil is without cover, is minimised. This can also be achieved with break crops. The application of nitrogen fertilisers also contributes to high SOC as it induces a higher amount of organic material.

2.2.1.2 Soil inorganic carbon

Compared to SOC, soil inorganic carbon (SIC) has not been studied extensively. Soil inorganic carbon is the most common form of carbon in arid and semi-arid regions, and has a very long turnover time. The SIC exists in soils as primary and secondary minerals. Parent rock material is considered to be a primary source of carbonates. Secondary carbonate is directly inherited from the parent material. When the primary carbonates dissolve and are translocated by water with organic acids and/or CO_2 from the soil and atmosphere, the secondary carbonates form dissolved atmospheric carbon with availability of divalent cations calcium and magnesium (Bronick & Lal 2005). The estimation of global (SIC) varies from 695– 1738Gt of carbonate in the top one meter of soil (Mikhailova et al. 2013). Carbonates (calcite, aragonite, dolomite and siderite) present in soil are formed due to lithogenic or/and pedogenic processes. Whereas the lithogenic process results from debris of parent material and therefore has no effect on carbon budget, pedogenic carbonate forms as a chemical process by which atmospheric CO_2 is sequestered. Formation of new carbonate minerals in soils (pedogenic carbonate) requires atmospheric carbon, an external source of calcium and magnesium such as wet deposition, and may also include fertilisation and irrigation.

2.2.2 Strontium isotopes in earth surface materials

2.2.2.1 The strontium cycle

Weathering can release strontium (Sr) in rocks, which is cycled through plants, animals and eventually enters oceans mainly through rivers. The ocean is considered the main dissolved strontium reservoir; some of the strontium leaves the ocean water mostly by deposition in marine carbonate. Small quantities of strontium are transferred directly from the ocean to the continents via precipitation.When using strontium isotopes as an ecosystem tracer, the isotopic composition of all strontium sources to the system and the amount of isotopic differences within each source should be determined. Determining of the isotopic composition of the soil parent, local rain and dust, ground and surface water is essential if characterisation of the soil-plant ecosystem is needed (Capo et al. 1998).

Strontium (Sr) has a chemical similarity to calcium. Strontium is a divalent alkaline earth element, and can substitute calcium in minerals like carbonate including calcite, dolomite and especially aragonite. Pedogenetic carbonates, which develop in soils especially in arid regions, contain a significant amount of calcium. Calcium resources can come from the primary material of the soil, atmospheric deposition (dust) and weathering of silicates (Dart et al. 2005; Van der Hoven & Quade 2002). Understanding the link between carbon and calcium and their biogeochemical cycles is important as the calcium source provides essential information about global significance of carbon sequestration in calcrete. The idea that calcium is derived from atmospheric deposition was first brought up by Crocker (1946). He hypothesised that calcareous material throughout South Australia was deposited either by wind erosion from material exposed at the time of the eustatic sea level retreat and/or during the reworking of coastal calcareous dunes (Hesse & McTainsh 2003).

2.2.2.2 ^{87}Sr/^{86}Sr tracer geochemistry

Each chemical element normally has one or more alternative isotopes. This means that they have the same number of protons but vary in neutron number. Stable, naturally occurring isotopes of the alkaline earth metal strontium (Sr) are: ^{84}Sr, ^{88}Sr, ^{86}Sr and ^{87}Sr. ^{87}Sr is the only one which is radiogenic, which means it is produced by a process of radioactive decay of the alkali metal ^{87}Rb, yet all other isotopes of strontium are stable (Capo et al. 1998; Hess 1989) (Figure 2.6). Varieties of calcium resources need to be monitored and identified. The strontium isotope can be an effective tool in regard to studying the chemical weathering, soil genesis and cation origin and mobility (Capo et al. 1998). The ^{87}Sr/^{86}Sr ratio of the coastal soil fall between 0.7094 and 0.7098, showing that the ocean is the principal source of calcium to nearly all the soils near the coast, and that contributions from bedrock are generally small (Quade et al. 1995). Jacobson (2004) mentioned that an estimation of the ^{87}Sr/^{86}Sr ratio of sea water is about ~0.0709. Figure 2.7 shows the strontium isotope expressed as ^{87}Sr/^{86}Sr. The upper region of the picture shows the atmospheric (rain and dust) samples, and the lower portion shows the soil samples plotted against depth in the profile (Capo & Chadwick 1999). The strontium isotopes techniques has been utilized extensively to trace the sources and to constrain the timing of generation of digenetic cement, particularly of carbonate type (Banner 1995; Bickle et al. 2001; Emery et al. 1987).

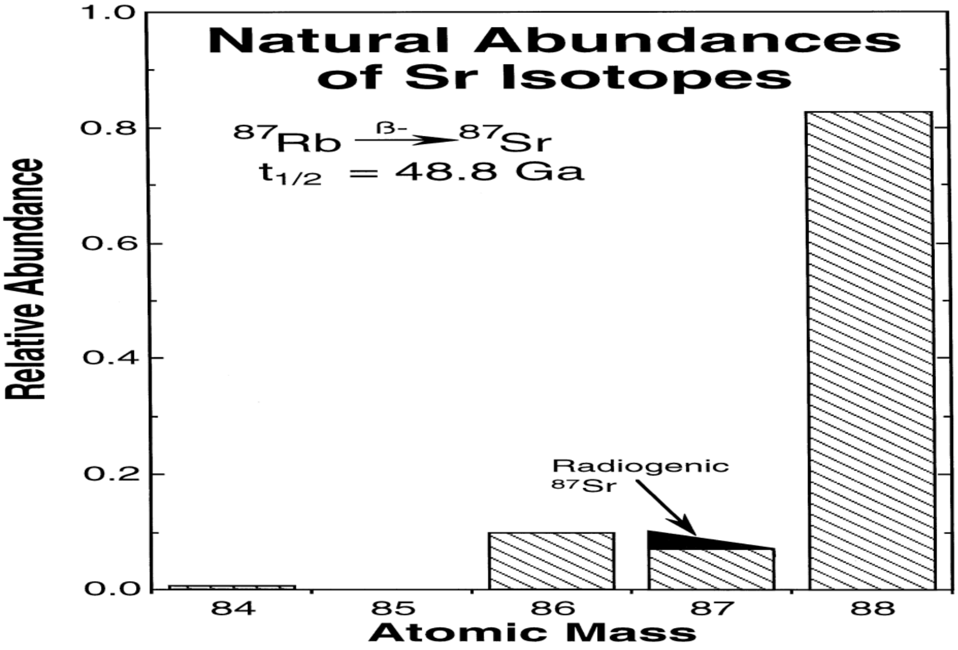


Figure 2.6: Isotopes of strontium. Strontium has four naturally occurring stable isotopes (Capo et al. 1998).

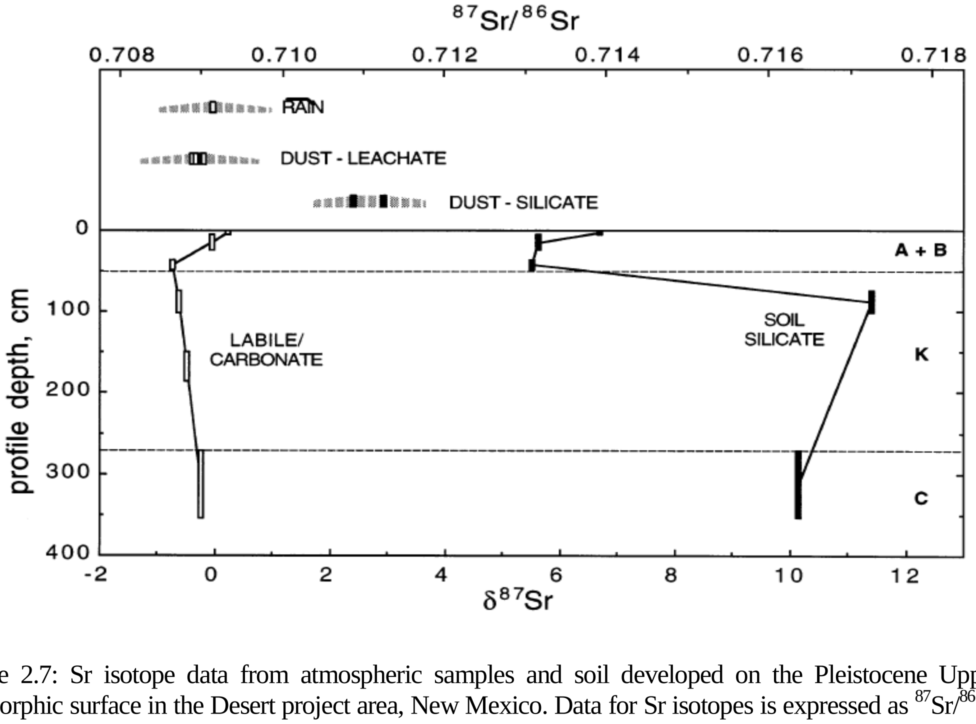


Figure 2.7: Sr isotope data from atmospheric samples and soil developed on the Pleistocene Upper La geomorphic surface in the Desert project area, New Mexico. Data for Sr isotopes is expressed as $^{87}Sr/^{86}Sr$ and in terms of ∂ 87. The upper region shows the atmospheric (rain and dust) samples, and the lower portion shows the soil samples plotted against depth in the profile. Open symbols are the acetic acid soluble leaches of dust and soil, which represent both carbonate and labile Sr. the solid symbols, are the HF C nitric C perchloric acid-soluble residues that represent the silicate fraction of dust and soil. Error bars are smaller than the size of the symbol (Capo & Chadwick 1999).

2.3 Dusts originated from arid and semi-arid area

2.3.1 Definition

In the glossary of Atmospheric Chemistry Terms, Dust is generally defined as small, dry, solid particles projected into the air by natural forces, such as wind, volcanic eruption and by mechanical or man-made processes (IUPAC 1990). Dust particles are usually in the size ranging from about 1 to 100 micrometre in diameter and they slowly settle under the impact of gravity.

2.3.2 Source areas of dust particles

Land use conversion has been identified as having potential impact on air quality especially in arid and semi-arid regions which comprise about 33% of the earth's surface (Huang et al. 2008). Aeolian landforms exist in regions where wind is the primary agent of transport (erosion and deposition) such as in arid and semi-arid regions. The result of turbulent winds which raise large quantities of dust from desert surface that can be transported over thousands of kilometres and deposited downwind by wet and dry processes (Choobari et al. 2014; Goudie 2014; Ravi et al. 2011). Some areas are major generators of dust particles to the atmosphere. However, other areas are much less active. The most important sources of dust aerosols are located in the Northern Hemisphere, primarily over the Sahara and Sahel in North Africa, the Middle East and Southwest and East Asia. Dust emissions estimates in different parts of the world are varied. However, in general, the Sahara, China and Central Asia, Arabia and Australia are major sources of the dust emissions. The importance of their dust emission strenght are: The Sahara > China and Central Asia > Arabia > Australia. In contrast, southern Africa and Americas are relatively minor sources with about 5% of the global total. (Choobari et al. 2014; Miller et al. 2004; Tanaka & Chiba 2006) (Figure 2.8).

The Sahara Desert is the world's largest source of aeolian soil dusts with over 50% of the global total (Goudie 2014; Prospero et al. 2002; Swap et al. 1996). Miller et al. (2004) concluded that based on Total Ozone Mapping data (TOM), The Bodélé depression, an area covering eastern Mauritania, western Mali and southern Algeria are the major source of dust particles. It also suggests that the Horn of Africa and the

Nubian Desert in southern Egypt and Northern Sudan are important sources. The second major source is China and Central Asia. The Taklimakan Desert of the Tarim Basin in north-western China and the Gobi Desert, east of the Tarim Basin in southern Mongolia and north central China, are two strong sources (Choobari et al. 2014; Goudie 2014; Prospero et al. 2002). Despite that most of the dust particles sources are from the Northern hemisphere, South America and Australia are the major dust particles source in the Southern hemisphere (Goudie 2014). These dust particles have been shown to have important ecological, environmental and health-related consequences (Merino-Martín et al. 2014).

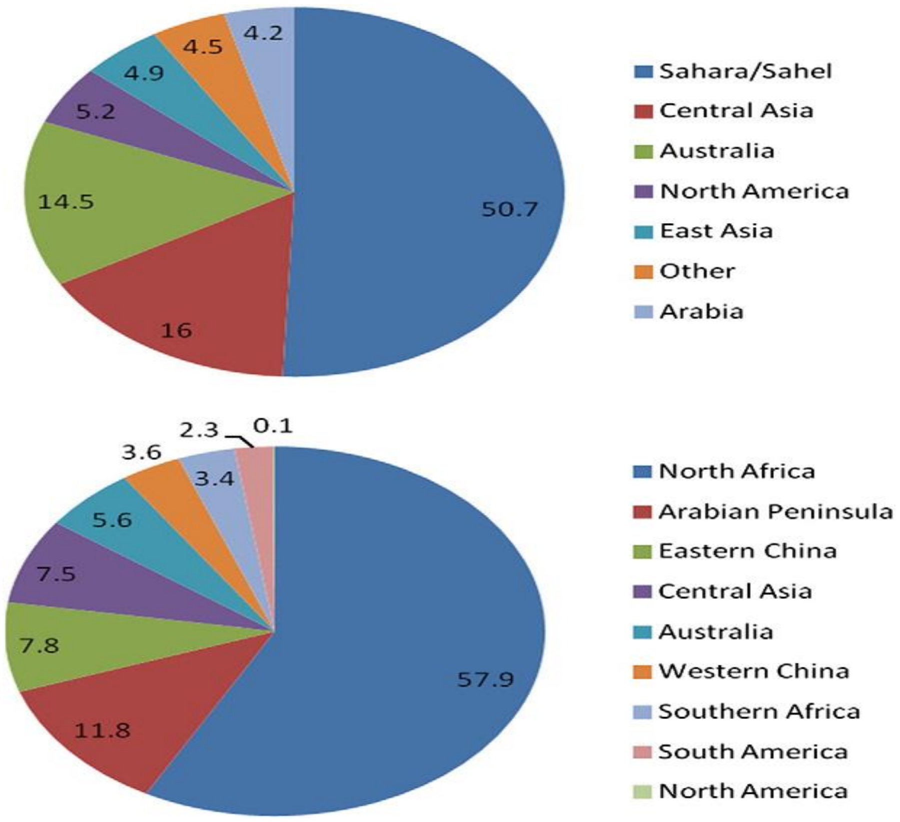


Figure 2.8: Estimates of the relative strength of dust emissions for different parts of the world (Miller et al. 2004) (top) and (Tanaka & Chiba 2006) (bottom).

2.3.3 Global cycling of elements

These Sahara dusts are likely to affect the global geochemical cycling and climate (Mahowald et al. 2010). For the past decades, concerns have been raised over the impacts of Sahara Desert dusts on air quality and possibly human health in the affected areas (Brunekreef & Forsberg 2005; Prospero 1999).The elements content of dust particles from different dust source regions influences biogeochemical cycles as iron-containing mineral provide an important nutrient for aquatic life (Krueger et al. 2004). Despite that the soluble iron in soils represent 0.5% of the total iron, the solubility range is higher in aerosols which can significantly affect the biogeochemical cycles in oceans (Mahowald et al. 2005). For instance, Goudie (2014) suggested that the nutrients carried in dust storms in Arabian gulf, including iron, can stimulate the algal blooms in coastal environments epically. The dust particles that carried high carbonate content may be a factor in the formation of carbonates (Goudie & Middleton 2001). Moreover, there is more powerful effect of dust deposition. Ridgwell and Kohfeld (2007) stated that nutrients delivered by dust do not appear to be a particularly important source of phosphate to the biota, in contrast iron, with aeolian deposition play a fundamental controlling role in the ocean carbon cycle. Capo and Chadwick (1999) mentioned that in most arid environments, atmospheric additions of calcium are believed to control rates of calcrete accumulation because weathering rates are low and the cycling of dust between the atmosphere and soil is high.

2.3.4 Human health impacts

These Sahara dusts are likely to affect the global geochemical cycling and climate (Mahowald et al. 2010). For the past decades, concerns have been raised over the impacts of Sahara Desert dusts on air quality and possibly human health in the affected areas (Brunekreef & Forsberg 2005; Prospero 1999; Salameh et al. 2015). For instance, there are a range of studies in East Asia, which is considered to be the second largest source of the dust particles, which have sought to relate Asian Dust events to respiratory problems such as asthma, pneumonia and tracheitis (Goudie 2014). Tao et al. (2012), working in China found that dust storms led to increased respiratory hospitalizations, particularly for those aged over 65. The effects of

African Sahara on asthma and other respiratory problems in Southern Europe have gained more attention. Jiménez et al. (2010) working in Madrid found a marked association between PM10 (particle with a diameter <10 µm levels) and mortality of elderly on Saharan Dust days.

Chapter 3 Geochemical Characteristics of Soils in Fezzan, Sahara Desert: Implications for Environment and Agriculture

3.1 Introduction

The Sahara has experienced alternate humid and dry periods at least for the past seven million years (Schuster et al. 2006). The latest wet/dry cycle commenced about 15,000 years BP with the peak African Humid Period (AHP),which lasted from approximately 5,000 to 10,000 years BP when the low-lying areas were covered by a layer of water, forming the so-called mega-lakes (Demenocal et al. 2000; Drake et al. 2008). The subsequent drying processes led to the disappearance of the mega-lakes, allowing soils to develop on the lake sediments. Due to the present hyper-arid conditions, modern paedogenesis is expected to be very weak. Therefore, the Sahara soils are, to a large extent, of relict nature. On the other hand, the characteristics of the relict soils could have been significantly modified due to wind. A reduction of these soils is possible under current climate conditions.

Detailed information on geochemical characteristics of the Sahara Desert soils is useful for a few reasons. First, the Sahara Desert is the world's largest source of aeolian soil dusts (Goudie 2014; Prospero et al. 2002; Swap et al. 1996). These Sahara dusts are likely to affect the global geochemical cycling and climate (Mahowald et al. 2010). For the past decades, concerns have been raised over the impacts of Sahara Desert dusts on air quality and possibly human health in the affected areas (Brunekreef & Forsberg 2005; Prospero 1999). Many studies were recently conducted to evaluate the transport and deposition of aerosols from the Sahara Desert (Barkan et al. 2005; Goudie & Middleton 2001). Most of these studies have used the concentration of total suspended particles (TSP), PM2.5 (particle with a diameter <2.5 µm) and PM10 particle with a diameter <10 µm with limited information on major chemical constituents to characterize the dusts (Alastuey et al. 2005; Rodrıguez et al. 2001). While these physical parameters give indication of dust load and rough elemental signatures of the dusts, it provides no insights into the presence of potentially toxic elements, which is needed for better assessment of environmental risk from the dusts. Second, the development of Desert agriculture using the available irrigation water requires a good understanding of soil chemical properties in order to develop appropriate strategies and methods for soil amendment. Third, Desert soils are effective sites to hold inorganic carbon (Wang et al. 2013). Knowledge of inorganic carbon storage in the Sahara Desert soils is important for global inorganic carbon inventory.

So far there has been only limited work reported on the chemical characterization of the Sahara Desert soils. Alastuey et al. (2005) presented data on mineral and chemical composition of TSP and PM2.5 in the dust samples collected on the Canary Islands during a strong African dust outbreak episode. Borbély-Kiss et al. (2004) investigated some major elements contained in the dusts collected from Hungary during Saharan dust episodes. Moreno et al. (2006) reported the chemical characteristics of a small amount of soil and dust samples collected from Algeria, Chad, Niger and Western Sahara and found marked variation in the geochemical composition of the soils among these different locations of dust source areas. In spite of these efforts, the available information is still far from sufficient for understanding the geochemical characteristics of soils in this vast Desert. Substantial amounts of further work are required to accumulate knowledge that is needed to inform the development of strategies for minimizing the environmental impacts and maximizing the beneficial uses of the Desert soils in Sahara.

The geochemical processes associated with the formation of alkaline soils in different parts of the world will be discussed. In this chapter, the results from the Fezzan basin, south-western Libya will be presented. This part of the Sahara Desert has so far received relatively little attention despite its important role as a dust source (Falkovich et al. 2001). Another reason for selecting this area for the study is its relevance to Desert irrigation agriculture. The construction of the Great Man-made River in Libya has provided the opportunities for agricultural production in its hyper-arid area (Elhassadi 2007; Gijsbers & Loucks 1999). However, detailed soil information covering a large area is lacking though limited number of small-scale soil investigations with varying purposes were conducted at some locations (e.g (El-Ghawi et al. 2005; Salem & Al-ethawi 2013).To develop sustainable agricultural systems in these areas, there is a need to understand the soil properties of the potential agricultural areas.

The aim of this chapter was to understand the major geochemical characteristics of the Desert soils in the Fezzan basin in order to (a) evaluate the role of the Desert soils as a carbon store; (b) assess the potential role of the fine-grained soil fraction as a dust source, and (c) to evaluate the potential soil constraints and provide recommendations for improving the soil conditions to allow sustainable development of irrigation agriculture.

3.2 Material and methods

3.2.1 The study area

Libya is situated between latitude 20° and 33° N and between longitude 10° and 25° E. It is located in North Africa. It has a total area of about 1.76 million Km^2. In the north it borders on the Mediterranean Sea, in the east on Egypt and Sudan, in the west on Tunisia and Algeria, and in the south on the Republic of Chad, the Republic of Niger, and Sudan The country is divided into three main regions: Tripolitania in north-western Libya, Cyrenaica in eastern Libya and Fezzan in south-western part of the country. Libya includes a large part of the Sahara Desert, which extends across North Africa from the Atlantic Ocean to the Red Sea. More than 90% of the country is covered by Desert Figure 3.1.

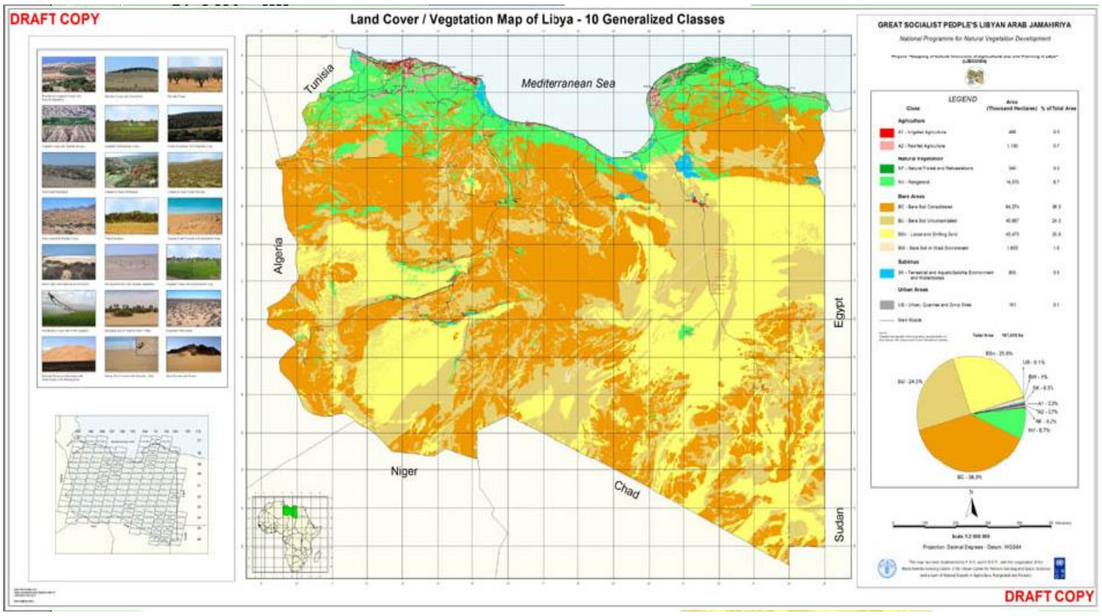


Figure 3.1: Land use geographical position map of Libya http://www.glcn.org/databases/ly_landcover_en.jsp

3.2.1.1 Population

Although the Desert is a relatively uninhabitable area, some people are still living in such a hard environment. People who are living in this environment can be divided into two groups: the first group are the migratory people who mainly live on communal land and the other group are the people who lead settled life around the oases and in some governmental agriculture projects. More than 90% of the population are living along the 1900 km coastal regions of the Mediterranean Sea, where the major cities, Tripoli, Benghazi, Misurata and Zawia are situated. The population growth of Libya has been influenced mainly by the discovery of oil in the country. This has significantly increased the population. The official estimate of Libya's population in 2007 was 6.4 million (Casterline 2011).

3.2.1.2 Water resources

An arid climate can burden the economy and hinder future expansion. Over the last three decades, the increasing demand for ground water has led to many serious problems like water shortages. The ground water is the main source of water for both domestic and agricultural purposes. (See Quantity of available water resources in North Africa (Alsamrai 1990).

Table 3.1: Quantity of available water resources in North Africa (Alsamrai 1990).

Country	**Surface water resources(million metre^3 /year)**	**Ground water resources (million metre^3/year)**	**Total water Resources(million meter^3/year)**
1. Algeria	13000	4200	17200
2. Libya	170	2500	2670
3. Mauritanian	23000	10000	33000
4. Egypt	62000	4500	66500
5. Morocco	5800	1500	7300

As shown in the (Table 3.1), Libya has the lowest ground water source in the region. This has resulted in apparent ground water scarcity. The Libyan major cities mainly affected are Tripoli and Benghazi which are the most inhabited places in the country. The exploitation of ground water sources has led to sea water intrusion into underground water reservoirs (Elhassadi 2008a). To address the water shortage in the northern side of the country by transferring fresh water from the Desert to the coastal line, a Man-made River was constructed.

3.2.1.3 Man-Made River

The Man Made River Project (MMRP) was executed after many years of studies and monitoring of the aquifer's behaviour in response to water pumping for large-scale agricultural development. Hundreds of wells were drilled during the last 20 years for local irrigation in Sarir, Kufra and at many locations in the Murzuk basin. Total production from these and other wells is recorded on an annual basis. However, the (MMRP) has been designed to be implementing in five main phases and stages as shown in (Figure 3.2). This project when completed will therefore be capable of providing 6.1Mm^3/day at a reasonable cost per unit of water. Table 3.2 summarises the total water demand in comparison with the available supply including the MMRP (Gijsbers & Loucks 1999; Salem 1992).

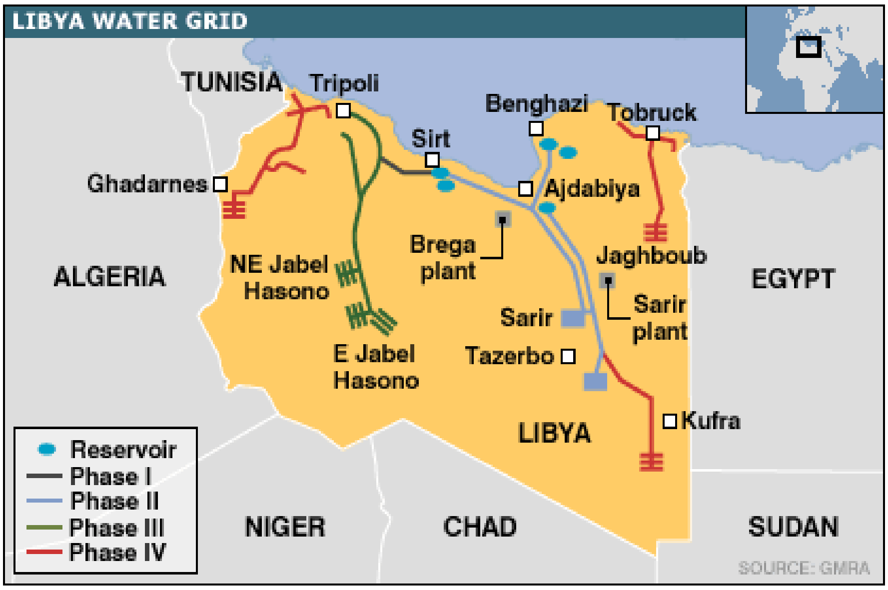
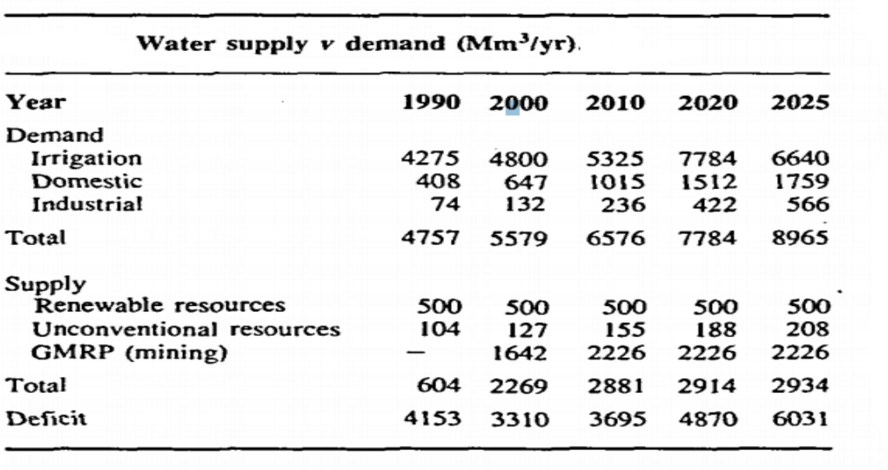


Figure 3.2: GMRP location map source: http://news.bbc.co.uk/2/hi/science/nature/4814988.stm

Table 3.2: Total deficits calculated on 100% food self- sufficiency(Salem 1992)



Water supply *v* demand (Mm^3/yr).

Year	**1990**	**2000**	**2010**	**2020**	**2025**
Demand					
Irrigation	4275	4800	5325	7784	6640
Domestic	408	647	1015	1512	1759
Industrial	74	132	236	422	566
Total	4757	5579	6576	7784	8965
Supply					
Renewable resources	500	500	500	500	500
Unconventional resources	104	127	155	188	208
GMRP (mining)	—	1642	2226	2226	2226
Total	604	2269	2881	2914	2934
Deficit	4153	3310	3695	4870	6031

3.2.1.4 Climate

The North African climate is mainly controlled by two different climate regimes the Mediterranean and the Saharan. The Mediterranean climate in the coastal lowland is controlled mainly by colder temperatures and higher rainfall with westerlies in winter and subtropical heat and dryness in summer. The interior of the country, the Saharan Desert climate leads to extremely dry, hot summers and extreme temperature changes between night and day. The average annual temperature in El-Kufra is 23.3^{o}C and in Sebha 23.4^{o}C and irregular annual rain fall in Al-Kufra is only 2.1mm and in Sebha 9.0mm. Summer temperatures are extremely hot, the mean summer temperature being 30.8 ^{o}C and 30.6 ^{o}C in EL-Kufra and Sebha, respectively. The total annual precipitation under the Desert climate type is generally less than 50mm (Hamad 2012).

3.2.1.5 Geomorphology of Libya

For many decades, most desert geomorphology emanated from short expeditions, the geomorphology of any place is defined as a study of the scenery. Various parts of the landscape are analysed-the mountains, valleys, plains, plateaus, lake basins, river channels and sand dunes, as well as salt pans, and other features that make up the landscape. How did these landscapes develop? Geomorphological research seeks to answer this question and is mainly concerned with the origin and evolution of them. Libya’s land formations are varied and diverse, ranging from low lands to high mountain regions and from sandy Deserts to rocky plateaus (Figure: 3.3). Land forms of the country is divided into six main regions- the first region is the Gefara plain and the foot hills of Nafusa Mountain, the Hamada Al-hamra plateau and the eastern Tripolitania Vals, the coastal region along the Gulf of Sirt from Alkhums to Ajdabia, the northern and southern Cyrenaica and Fezzan regions.

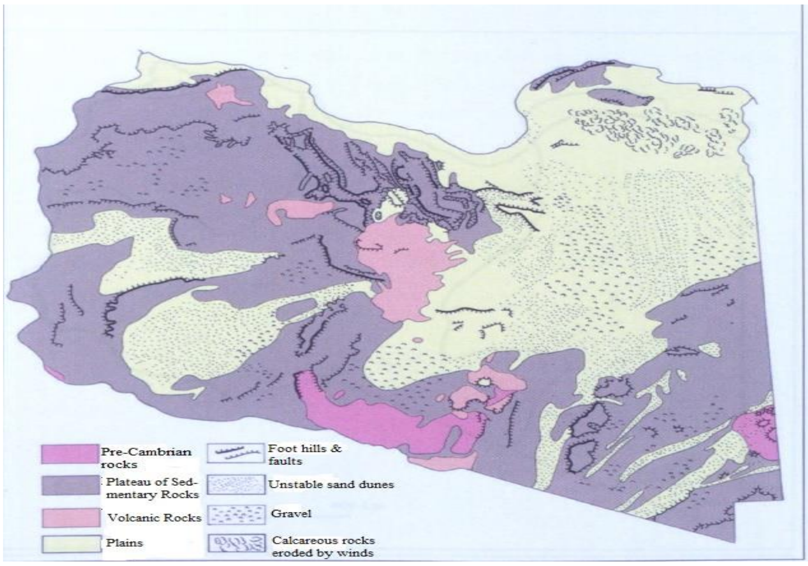


Figure: 3.3 Land form of Libya
<https://www.google.com.au/search?q=geology+map+of+libya&rlz>

3.2.1.6 The southern region

The main areas of Libya, Fezzan region and the southern region of Cyrenaica which are the main regions represent the huge southern land. The Desert is named according to the nature of its surface. Gravel surface is known as Sarir, such as Sarir Tibesti and Desert Pavement are known as Hamadah al Hamra in the southern part of Tripolitania. Sandy regions are referred to as Idhan such as Idhan Murzug and Ubari in the southern part of Fezzan region.

3.2.1.7 Fezzan region geomorphology

In Fezzan, there are many land forms ranging from sand dunes to valleys and mountains. Near to Sebha which is the capital of this region, even a small rock or vegetation can create sand traps above the general level of the sand sea. Another type of spread sand dunes in this area, simple crescentic sand dunes can be occurring in the area where the wind direction and sand supply remain constant. The second major geomorphological natural features in this region are wadis, their width about 2 km and they have a very gentle slope towards a narrow central channel. In this area, where some vegetation can be found preferentially in the north, precipitation is slightly higher (10-20 mm/year). The wadis are rich in salty sands, silt and clay. The playas are cut by present day wadis and locally overlain by colluvial deposits which are small fans near rock exposures, along wadi slopes and across rock plateaus. These deposits contain debris of carbonate rock and are bounded by gypsiferous soils (Fookes & Gahir 1995).

3.2.2 Research methods

A total of 53 soil samples were collected from 33 locations within the Fezzan basin (Figure 3.4). At most of the sampling locations, soil samples were taken from the surface layer (0-30 cm) and the elevation of the sampling areas ranges from 400 to 600m above the sea level. At Sampling Sites F4, F7, F12, F21 and F24, soil samples were also taken from sub-soil layers to a depth that could be practically reached during the field operations. After air-drying in the Libyan laboratory, Sebha University, the soil samples were crushed to pass a 2 mm sieve. Gravel (>2 mm fraction) were then discarded. After homogenization, two subsamples of the <2 mm soil fraction were used to obtain the sample of the <0.2 mm and <0.1 mm fractions by sieving with a 0.2 mm and 0.1 mm sieves, respectively. All the soil samples were stored in air-tight re-sealable laboratory polyethylene bags and shipped to the Australian laboratory for various analyses.

For each soil sample, the <2 mm soil fraction was used to prepare a 1:5 (soil: water) extract using the following procedure: 25 mL of deionized water was added into a centrifuge tube containing 5 g of soil; the tube was shaken in a rotary shaker for 1 h and then centrifuged at 3000 rpm for 5 min; the supernatant was removed and stored in a clean tube for further analysis. The soil residue from the water extraction was then used to prepare 1:5 (soil: 1M NH_4Cl) extract with a procedure that was exactly the same as the water extraction except that 25 mL of 1M NH_4Cl solution was used to replace deionized water as an extracting agent. The pH and EC in the water extracts were measured using a calibrated pH meter and EC meter, respectively. Ca, Mg, K, and Na in water and NH_4Cl extracts were determined using an atomic absorption spectrometer (AAS). A portion of each soil sample (<2 mm fraction) was pulverized for further instrumental and chemical analysis. X-ray fluorescence (XRF) analysis was used to determine the content of Al_2O_3, BaO, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, SrO and TiO_2. Total carbon was determined by a LECO CNS Analyzer. Organic carbon was determined using the Walkley–Black method. For all the soil fractions (<2 mm, <0.2 mm and <0.1 mm), a wide range of elements were extracted by an aqua regia one acid digestion method and measured by inductively coupled plasma mass spectrometry (ICP-MS). The concentration of soluble cations was estimated from the water-extractable cations and the concentration of exchangeable cations was estimated from the NH_4Cl-extractable cations. Sodium adsorption ratio (SAR) of the water extract was calculated using the following formula (equation 3.1):

$$SAR = Na^{+} / (Ca^{2+} + Mg^{2+})^{1/2} \tag{3.1}$$

Where the unit of soluble Na^+, Ca^{2+} and Mg^{2+} is mmol/L. The exchangeable sodium percentage (ESP) was obtained by the following formula:

$$ESP = Na^{+} / (Na^{+} + K^{+} + 2 \times Ca^{2+} + 2 \times Mg^{2+}) \times 100 \tag{3.2}$$

Where the unit of exchangeable Na^+, K^+, Ca^{2+} and Mg^{2+} is in mmol/kg. The inorganic carbon content was calculated by the difference between the total carbon and the organic carbon.

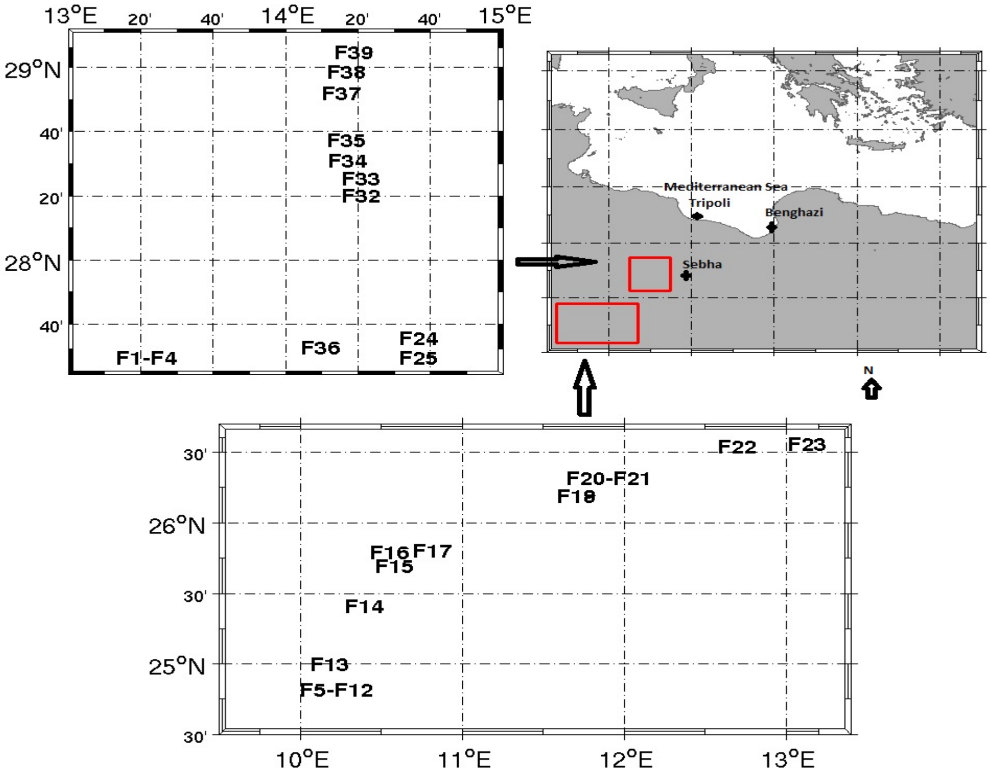


Figure 3.4: Map showing the soil sampling locations in the Fezzan region, Libyan Sahara

3.3 Results and Discussion

3.3.1 Soil pH and EC

For the upper soil layer (0-30 cm), pH ranged from 6.92 to 10.1 with a mean value of 8.80. EC had an average >4 dS/m with a range of 0.145-18.51 dS/m Table 3.3. These data indicate that the soils were generally alkaline and saline in nature although the spatial variation in soil pH and EC was remarkable. Different vertical variation patterns in pH were observed at different locations F4, F21 and F24 showed little change in soil pH along the soil profile; F7 had higher pH in the upper soil layers, relative to the lower soil layers; and F12 exhibited a higher pH at a depth of 20-30cm than the upper soil layer (0-10 cm) and the lower soil layer (70-90 cm). EC value in F4 increased with depth to the sampling base (50 cm depth). F7 also showed an increase in EC value with depth to the 20-30 cm layer; the EC value was maintained at very high level (>6 dS/m) in the soil layers located between 20 and 70 cm of the soil profile but suddenly reduced to 1.550 dS/m in the 70-90 cm layer (sampling base) (Table 3.4). F12 and F21 all had lower EC value in the 20-30 cm layer, relative to the upper soil layer and lower soil layer. But the absolute value of EC was much smaller in F12 (<1 dS/m) than in F21 (>9 dS/m). F24 showed insignificant variation in EC value along the soil profile down to the 2 m depth (sampling base). The above results suggest that either alkalinity or salinity will be a soil constraint for crop growth in most of the investigated soils if irrigation water becomes available in these sites. To effectively develop irrigation agriculture using these soils, reduction of soil alkalinity and salinity is required. This will be further discussed with the problems associated with soil sodicity in Chapter 6.

Table 3.3 : Average range of pH, EC, various carbon fractions, soluble and exchangeable basic cations for the upper layer (0-30cm) of the 33 soils from the Fezzan area, Sahara Desert

Soil Parameter	**Average**	**Minimum**	**Maximum**
pH	8.8	6.92	10.11
EC (dS/m)	4.214	0.145	18.51
Organic C (%)	0.42	0.16	0.67
Inorganic C (%)	0.26	0	2.24
Soluble K (mmol/kg)	1.49	0	11.8
Soluble Na (mmol/kg)	45.7	0.1	300
Soluble Ca (mmol/kg)	3.81	0.01	12.3
Soluble Mg (mmol/kg)	3.77	0.28	12.3
SAR	16.5	0.03	101
Exchangeable K (mmol/kg)	6.97	0.56	21.8
Exchangeable Na (mmol/kg)	11.7	2.18	53.5
Exchangeable Ca (mmol/kg)	90.9	16.1	192
Exchangeable Mg (mmol/kg)	5.86	1.24	10.4
ESP	6.52	0.87	24.9

Table 3.4: Vertical variation in pH, EC, organic C and inorganic C along the 5 selected soil profiles in the Fezzan area, Sahara Desert

Sampling site	Depth (cm)	pH	EC (dS/m)	Organic C (%)	Inorganic C (%)
F4	0-10	9.30	1.347	0.34	0.00
	10-20	9.40	1.228	0.51	0.03
	20-30	9.48	2.904	0.33	0.00
	30-50	9.35	4.550	0.40	0.00
F7	0-10	10.1	0.720	0.44	0.00
	10-20	9.51	3.670	0.49	0.02
	20-30	8.76	12.76	0.62	0.55
	30-50	8.78	9.230	0.51	0.35
	50-70	8.94	6.560	0.36	0.44
	70-90	8.81	1.550	0.38	0.15
F12	0-10	9.07	0.960	0.60	0.14
	20-30	9.50	0.247	0.26	0.13
	70-90	8.95	0.758	0.34	0.00
F21	0-10	8.31	10.22	0.38	0.32
	20-30	8.54	9.500	0.49	0.61
	30-60	8.61	15.90	0.59	0.53
F24	0-50	8.60	2.789	0.16	0.00
	150-160	8.61	2.700	0.27	0.06
	190-200	8.54	2.489	0.31	0.00

3.3.2 Soluble and exchangeable basic cations

From Table 3.3, it can be seen that Na dominated the soluble basic cations with a mean SAR greater than 16. But Ca dominated the exchangeable basic cations with a mean ESP of 6.52, suggesting that most of the upper soil layers were not technically sodic if the threshold value of 15% is used for evaluation (Brady & Weil 1996). ESP 15% adapted in Libyan soils is attributed to the high content of soluble minerals, especially calcium. For soils such as F12 and F24 that were non-sodic in both surface and subsoil layers (Table 3.5 and Table 3.6), leaching of alkali and salts by irrigation water alone may be sufficient for reducing soil alkalinity and salinity to a level that allow the growth of crops. However, for sodic soils (e.g. F7), the presence of excessive amounts of exchangeable Na (Table 3.6) can cause soil dispersion to prevent formation of soil aggregates, which reduces water infiltration and could lead to waterlogging conditions. The resulting poor soil aeration can restrict plant root development and adversely affect crop yields. To improve such soil physical conditions, application of gypsum, coupled with an appropriate drainage system is required to reduce soil ESP and remove excess soluble Na from the soils. Gypsum addition can also be used to decrease soil pH by forming calcium carbonates, which simultaneously sequester atmospheric CO_2, as shown in the following chemical equation (3.3):

$$CaSO_4 \bullet 2H_2O + 2NaOH + CO_2 \rightarrow CaCO_3 + Na_2SO_4 + 3H_2O \tag{3.3}$$

Gypsum is locally available in Fezzan. Therefore, amelioration of sodic soils with gypsum is likely to be cost-effective for the reclamation of sodic soils in the irrigation area. Although most of the investigated soils were not sodic in the surface soil layer, there was a tendency that sodicity increased with depth, as shown in F4 and F21 (Table 3.5 and Table 3.6). While sodic subsoil layers may not affect the growth of shallow-rooted crops if appropriate water management strategies are taken, it limits the uses of such soils for deep-rooted crops. In these areas, irrigation water penetration into soil could be limited due to low hydraulic conductivity in the subsoil layer. This could impede root growth in the subsoil layers. Treatment of subsoil sodicity is likely to be uneconomic in most situations. Therefore, it is more appropriate to use these soils for production of shallow-rooted crops such as vegetables. As a matter of fact, the presence of the sodic subsoil layer with low permeability can act as a barrier to minimize the loss of irrigation water due to infiltration. This is actually beneficial from a water-saving point of view.

Table 3.5: Vertical variation in soluble K, Na, Ca, Mg and SAR along the five selected soil profiles in the Fezzan area, Sahara Desert

Sampling site	Depth (cm)	K (mmol/kg)	Na (mmol/kg)	Ca (mmol/kg)	Mg (mmol/kg)	SAR
F4	0-10	1.61	11.9	0.76	0.91	9.22
	10-20	2.10	16.7	0.76	0.49	14.9
	20-30	3.22	38.9	0.58	0.54	36.7
	30-50	3.64	66.1	0.58	3.60	32.3
F7	0-10	1.61	9.70	0.09	0.43	13.6
	10-20	0.00	64.7	0.16	1.99	44.1
	20-30	0.84	270	2.84	3.82	105
	30-50	0.98	221	5.07	2.65	79.6
	50-70	1.26	183	4.37	1.69	74.3
	70-90	0.91	1.84	4.83	0.99	0.76
F12	0-10	0.49	7.89	2.24	0.28	4.97
	20-30	0.21	2.80	0.43	0.47	2.95
	70-90	0.00	0.31	3.14	0.40	0.16
F21	0-10	1.68	7.99	12.3	6.57	1.84
	20-30	3.08	78.4	5.94	6.36	22.4
	30-60	1.61	144	5.83	7.06	40.0
F24	0-50	0.35	56.0	5.27	1.96	20.8
	150-160	0.35	2.55	5.42	2.02	0.93
	190-200	0.84	3.17	5.29	0.24	1.35

Table 3.6: Vertical variation in exchangeable K, Na, Ca, Mg and ESP along 5 selected soil profiles in the Fezzan area, Sahara Desert

Sampling site	Depth (cm)	K (mmol/kg)	Na (mmol/kg)	Ca (mmol/kg)	Mg (mmol/kg)	ESP
F4	0-10	18.0	10.7	30.0	6.02	10.6
	10-20	19.4	10.5	33.6	7.10	9.41
	20-30	21.8	22.0	28.4	5.68	19.7
	30-50	29.1	25.8	23.3	3.30	23.9
F7	0-10	11.0	40.5	48.8	7.01	24.9
	10-20	11.2	63.3	46.2	6.39	35.2
	20-30	7.74	67.0	47.5	5.03	37.3
	30-50	8.33	46.1	64.9	4.82	23.8
	50-70	9.52	38.4	54.9	2.38	23.6
	70-90	7.39	26.7	55.2	0.81	18.3
F12	0-10	2.31	2.18	28.4	5.54	3.02
	20-30	1.61	2.53	35.2	3.98	3.06
	70-90	1.47	0.88	31.0	2.14	1.28
F21	0-10	3.57	11.4	63.9	5.66	7.42
	20-30	4.83	22.5	60.1	4.70	14.3
	30-60	3.57	41.8	40.0	4.47	31.1
F24	0-50	0.56	3.14	177	1.24	0.87
	150-160	0.98	3.04	112	1.33	1.31
	190-200	1.75	3.38	34.2	1.26	4.44

3.3.3 Organic and inorganic carbon

Organic carbon content in the investigated soils was generally low (<0.5% on average), which is understandable. Virtually, the soils did not support any vegetation except in the areas where irrigation water was available Table 3.3. Therefore, it is likely that the organic carbon in these soils originated from the soil parent materials (lake sediments). This is supported by the fact that soil organic carbon content tended to increase with increasing depth except for F12 that was collected from agricultural land where crop growth allowed ongoing accumulation of organic carbon in the surface soil layer (Table 3.4). Under the current hyper-arid climate conditions, decomposition of organic carbon is slow. Therefore this relict soil organic carbon represents a stable carbon pool in the Sahara Desert that may play a role in affecting the global carbon cycling. The development of irrigation agriculture using these soils will impact on soil organic carbon dynamics. First, the increase in soil moisture content as a result of land irrigation will promote, through enhanced microbial activity, the decomposition of this stored organic carbon. This could make the soil organic C a source of atmospheric CO_2. Second, the production of organic matter from the introduced crops will result in atmospheric CO_2 sequestration. Part of the biomass-C will enter the soils and raise the level of soil organic C over time. The interaction of these two factors will eventually determine that the irrigated Desert soils are a source or sink of atmospheric CO_2.

The average of inorganic C in the upper soil layer was 0.26%, indicating that there was only limited amount of inorganic C stored in the surface soil layer Table 3.3. Two of the five investigated soil profiles (F4 and F24) showed negligible presence of inorganic C to the sampling depths. F4 had a soil pH >9 (Table 3.4) and high levels of soluble Na (Table 3.5), suggesting that the soil contained $NaHCO_3$ and NaOH. However, the lack of soluble Ca Table 3.5 did not favour the formation of calcium carbonates and this explains the maintenance of high pH and the general absence of mineral carbonates in the soil. The high pH and low inorganic C in the upper soil layers (0-10 cm and 10-20 com) of F7 (Table 3.4) can also be explained by the same reason. The elevated inorganic C content in the lower soil layers of F7 corresponded to the drop in pH, reflecting enhanced carbonation due to increased availability of soluble Ca in these layers (Table 3.5):

$$2NaOH + Ca^{2+} + CO_2 \rightarrow CaCO_3 + 2Na^{+} + H_2O \tag{3.4}$$

$$2NaHCO_3 + Ca^{2+} \rightarrow CaCO_3 + 2Na^{+} + CO_2 + H_2O \tag{3.5}$$

As to be discussed in later section, the soluble Ca for soil carbonation was supplied by gypsum present in the soil profiles.

3.3.4 XRF results

XRF analysis indicates that the soil chemical composition was highly variable among the soils collected from different locations. The mean content of different chemical constituents in the surface soil layers was in the following decreasing order: SiO_2 $>Al_2O_3$ $>CaO$ $>Fe_2O_3$ $>K_2O$ $>MgO$ $>Na_2O$ $>TiO_2$ $>MnO$ $>P_2O_5$ $>SrO$ $>BaO$ (Table3.7) and (Table A.1). The molar ratio of SiO_2 to Al_2O_3 (SiO_2/Al_2O_3) averaged 18.5%, which was much higher than those reported for lacustrine sediments (Minyuk et al. 2007; Roy et al. 2012). This may partly result from selective removal of Al-rich clay minerals from the topsoils due to wind erosion. For example in F4, there was a clear trend showing the decrease in SiO_2/Al_2O_3 with depth (Table3.8). Fe_2O_3/Al_2O_3 had a mean value of less than 0.3% with a range of 0.15-0.84%. Vertical variation in Fe_2O_3/Al_2O_3 along the soil profile was not significant (Table3.8). The mean of SiO_2/CaO and SiO_2/TiO_2 were 32.5 and 240, respectively (Table3.7). Mixed vertical variation patterns were observed for different soil profiles (Table3.8), probably reflecting the inherent characteristics of the palaeo lacustrine sediment layers. Depending on the degree of wind velocity, the original soil layers developed during the wet period prior to the present hyper-arid conditions might have been largely or even completely removed at some locations, leaving the original lake sediments exposed on the land surface. These newly, about a decade exposed lake sediments have experienced only weak pedogenesis under the current hyper-arid climate and this explains the weak modern pedogenic footprints that can be observed from the soil profiles/regoliths. CaO/Na2O averaged 50, indicating the predominant presence of Ca over Na (Table3.7).

Table3.7: Chemical composition of the upper soil layer (0-30 cm) for the 33 soils from the Fezzan area, Sahara Desert

Parameter	**Average**	**Minimum**	**Maximum**
Al_2O_3 **(%)**	8.32	1.37	25.6
BaO **(%)**	0.03	0.01	0.06
CaO **(%)**	5.55	0.26	28.8
Fe_2O_3 **(%)**	3.64	0.49	10.5
K_2O **(%)**	1.16	0.04	2.65
MgO **(%)**	1.14	0.07	4.95
MnO **(%)**	0.12	0.01	1.36
Na_2O **(%)**	0.70	0.03	2.71
P_2O_5 **(%)**	0.08	0.02	0.43
SiO_2 **(%)**	68.3	20.4	92.1
SrO **(%)**	0.03	0.01	0.30
TiO_2 **(%)**	0.48	0.07	1.30
SiO_2/Al_2O_3	18.5	4.41	52.7
Fe_2O_3/Al_2O_3	0.29	0.15	0.84
SiO_2/CaO	32.5	0.66	184
SiO_2/TiO_2	240	61.3	852
CaO/Na_2O	50.0	0.70	659

Table3.8: Vertical variation in selected elemental ratio along the 5 selected soil profiles in the Fezzan area, Sahara Desert

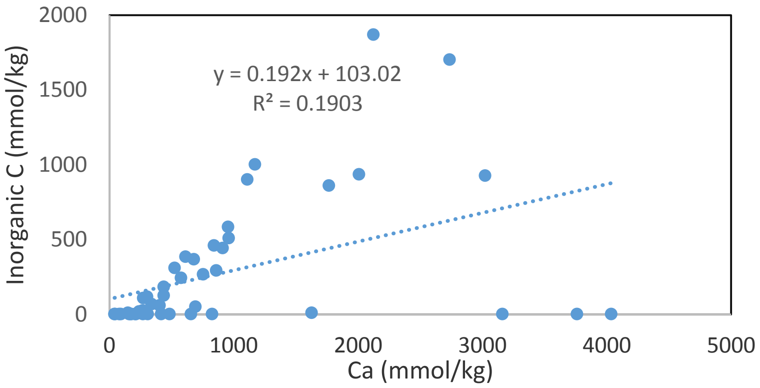
Sampling site	**Depth (cm)**	**SiO_2/ Al_2O_3**	**Fe_2O_3/ Al_2O_3**	**SiO_2/ CaO**	**SiO_2/ TiO_2**	**CaO/ Na_2O**
F4	0-10	17.3	0.5	58	232	5.0
	10-20	17.2	0.6	43	226	7.2
	20-30	8.4	0.3	59	144	2.2
	30-50	3.3	0.2	178	64	0.4
F7	0-10	11.2	0.2	51	170	2.1
	10-20	10.8	0.2	44	165	1.3
	20-30	8.2	0.2	11	130	2.0
	30-50	9.5	0.2	12	157	2.8
	50-70	12.3	0.2	16	198	2.6
	70-90	17.4	0.2	27	271	2.5
F13	0-10	33.4	0.3	42	392	4.6
	20-30	71.2	0.4	55	763	14
	70-90	54.9	0.3	162	584	3.5
F21	0-10	18.7	0.3	16	243	6.0
	20-30	18.9	0.3	13	262	4.8
	30-60	18.9	0.3	13	256	2.3
F24	0-50	47.6	0.2	2	731	659
	150-60	45.5	0.3	21	512	84
	190-200	47.1	0.3	50	595	62

3.3.5 Aqua regia-extractable elements in different soil particle fractions

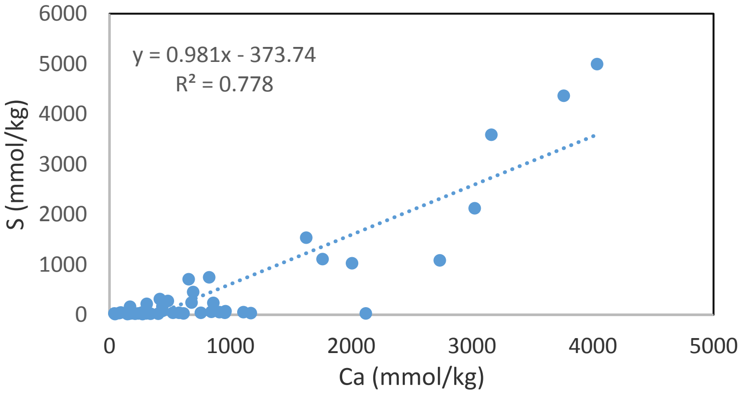
In comparison with the XRD results, Aluminium (Al) extracted by aqua regia was much lower (Table3.7, Table 3.9 & Table A.2).

This suggests that much of the Aluminium was bound to silicate minerals, which are not readily extractable with aqua regia (Niskavaara et al. 1997). Almost all the Calcium (Ca) was extractable with aqua regia, indicating that silicate-bound Ca was negligible. There was no close relationship between Calcium and inorganic carbon (Figure 3.5a). Figure 3.5b shows that Calcium was closely related to S (R2=0.778), suggesting that Calcium was largely bound to gypsum (confirmed by XRD, data not shown). However, a closer relationship (R2=0.978) was observed when Calcium was plotted against the sum of Sulphur (S) and Carbon (C) (Figure 3.5c), suggesting that Calcium was also largely bound to calcium carbonates for some soil samples.

(a)



(b)



(c)

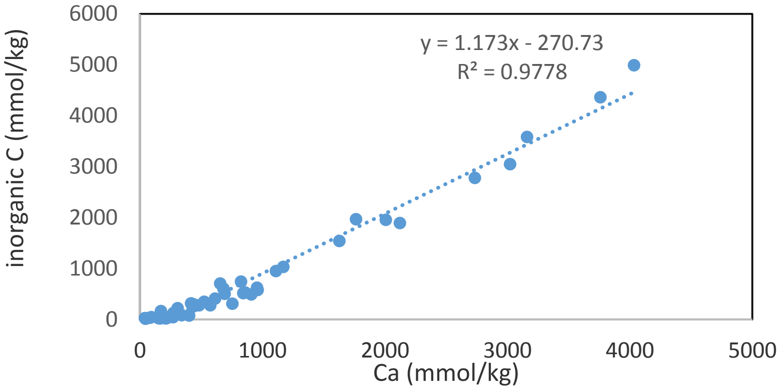


Figure 3.5: Scatter plot showing the relationship between aqua regia-extractable Ca and (a) Inorganic C (b) aqua regia-extractable S, and (c) the sum of inorganic C and aqua regia- extractables

The concentration of various elements was generally consistent between the <0.2mm fraction and the <2 mm fraction except for Sb, which was much lower in the former than in the latter. There was also a high degree of consistency between the <0.1 mm fraction and the <0.2 mm fraction for most of the elements. The major elements showing the difference in the abundance between the <0.1 mm fraction and the <0.2mm fraction included Al, B, Hf, K and Rb that were less abundant in the former than in the latter, and Bi, Co, Hg, Mg, Nb, S, Sn, W and Zr that were more abundant in the former than in the latter.

From a perspective of dust storm-related environmental issues, the <0.1 mm soil fraction is more relevant, as compared to other soil particle fractions. Therefore, data analysis is focussed on this particle fraction for this purpose. The mean concentration of iron and phosphorus in the fine-grained fraction was 2.13% and 252 mg/kg, respectively Table 3.9. The mean concentration of Sr was 231 mg/kg with the maximum concentration as high as 2720 mg/kg. Although Sr is less toxic, exposure to high level of Sr could cause health problems to children (ATSDR 2004).

There was no clear relationship between Mn and the major elements in the fine-grained soil fraction except for Fe, which was closely related to Mn (R^2=0.677) (Figure 3.6).Sr showed certain relationship with Ca (R^2=0.333) but no clear relationship with any of other major elements (Figure 3.7). This suggests that the Fezzan area could be an important source of airborne iron and phosphorus, which may play an important role in controlling nitrogen fixation in oceans (Mills et al., 2004).

There was no clear relationship between P and Al or Ca (Figure 3.5a & b), suggesting that P was not, to any significant extent, bound to these two metals. However, P was somewhat related to Fe (Figure 3.5c and Mn Figure 3.5d), indicating that the soil P had a higher affinity to Fe and Mn than Al and Ca. Sulphur was highly enriched in the fine-grained soil fraction with a mean value of 1.67%, which was much higher than that in the <0.2 mm fraction (1.17%) and <2mm fraction (0.97%).There have been research interests in soil-derived sulfate in atmospheric dust particles from Deserts in other parts of the world (Abuduwaili et al. 2008; Wu et al. 2012). Zhang et al. (2014) determined the Sulphur content in the suspended particles extracted from some Desert soils in China and found that the mean content of soil-derived S ranged from 0.089 to 0.366%, which was much lower, as compared to the soils in the Fezzan Desert. It is therefore likely that Fezzan is an important source to the atmospheric Sulphur loading. Amongst the elements of potential toxicity, the concentration of Mn and Sr was unusually high. Manganese averaged 865 mg/kg with the maximum concentration up to 9230 mg/kg Table 3.9. Inhalation of airborne Mn compounds could pose a significant health risk (Adkins Jr et al. 1980; Wennberg et al. 1991).

Table 3.9: Abundance of various elements in different particle fractions in the 33 soils from the Fezzan area, Sahara Desert

Element	**<0.1 mm fraction**			**<0.02 mm fraction**			**<2mm fraction**		
	Average	**Min.**	**Max.**	**Average**	**Min.**	**Max.**	**Average**	**Min.**	**Max.**
Ag	0.03	0.01	0.10	0.03	0.01	0.09	0.03	0.01	0.06
Al	1.10	0.15	2.36	1.90	0.88	2.89	1.83	1.04	2.98
As	4.59	1.00	12.6	4.15	1.10	9.30	4.38	1.70	9.20
B	10.5	5.00	60.0	15.5	10.0	40.0	13.9	10.0	40.0
Ba	125	10.0	470	138	40.0	320	134	40.0	350
Be	0.90	0.06	2.28	0.90	0.50	1.90	0.88	0.48	2.02
Bi	0.22	0.04	0.89	0.10	0.05	0.22	0.11	0.05	0.24
Ca	3.65	0.17	16.2	3.19	0.26	11.25	3.03	0.28	11.4
Cd	0.07	0.01	0.24	0.06	0.02	0.18	0.06	0.02	0.16
Ce	22.2	1.60	59.5	29.9	12.5	56.1	26.2	7.34	39.4
Co	12.6	0.80	119	8.07	3.50	16.7	7.83	3.50	22.3
Cs	1.49	0.06	5.20	1.57	0.69	3.82	1.54	0.58	4.14
Cu	25.0	5.90	247	15.5	6.3	31.9	27.1	7.50	139
Fe	2.13	0.27	6.26	2.12	1.16	3.99	2.29	1.23	4.27
Ga	4.26	0.63	9.76	6.30	3.04	9.26	5.77	3.34	9.49
Ge	0.06	0.04	0.11	0.08	0.05	0.11	0.07	0.05	0.10
Hf	0.20	0.06	0.38	0.38	0.21	0.59	0.35	0.17	0.64
Hg	0.08	0.01	0.36	0.02	0.01	0.12	0.02	0.01	0.15
In	0.02	0.00	0.06	0.02	0.01	0.05	0.02	0.01	0.05
K	0.26	0.01	0.46	0.39	0.18	0.68	0.37	0.16	0.61
La	9.64	0.60	24.7	13.6	5.80	27.4	11.7	2.90	17.9
Li	17.4	1.20	49.0	21.4	6.40	47.4	21.8	6.80	51.5
Mg	0.48	0.02	2.34	0.55	0.20	1.40	0.52	0.18	1.30
Mn	865	18.0	9230	437	105	2340	468	113	3700
Mo	1.38	0.26	4.63	1.51	0.42	4.87	1.04	0.43	4.04
Na	0.37	0.01	1.70	0.33	0.04	1.87	0.31	0.04	1.70
Nb	0.67	0.13	2.84	0.38	0.09	1.22	0.32	0.07	1.00
Ni	17.6	1.70	48.4	17.81	9.10	30.30	16.9	10.2	31.8
P	252	30.0	1720	238	80.00	710	241	60.0	770
Pb	11.5	0.40	29.2	10.7	3.40	24.9	9.57	2.90	23.4
Rb	14.9	0.70	35.1	20.7	10.1	32.0	19.3	9.20	36.2
Re	0.00	0.00	0.02	0.01	0.00	0.02	0.00	0.00	0.02
S	1.67	0.03	16.0	1.17	0.04	10.55	0.97	0.05	8.52
Sb	0.12	0.04	0.25	0.12	0.08	0.22	4.02	0.95	18.8
Sc	3.49	0.60	8.50	4.03	2.20	6.80	4.02	2.50	7.60
Se	0.79	0.20	6.00	0.88	0.30	5.50	0.70	0.20	5.70
Sn	1.80	0.40	14.0	0.93	0.50	1.40	0.91	0.50	1.90
Sr	231	22.6	2720	249	29.3	3120	241	25.3	3260
Te	0.02	0.01	0.07	0.01	0.01	0.02	0.01	0.01	0.02
Th	4.78	0.30	12.5	6.35	2.90	11.4	5.75	2.50	10.0
Ti	0.02	0.01	0.04	0.03	0.01	0.05	0.03	0.01	0.05
Tl	0.24	0.03	2.02	0.21	0.07	0.60	0.18	0.05	0.47
U	2.03	0.10	13.3	2.07	0.60	12.3	1.94	0.38	12.4
V	33.0	6.00	78.0	37.8	15.0	61.0	36.2	16.0	61.0
W	0.15	0.04	0.52	0.09	0.05	0.25	0.11	0.05	0.43
Y	8.71	0.76	76.7	8.33	4.21	15.2	7.97	4.08	16.0
Zn	42.7	3.00	162	37.1	17.0	96.0	37.4	17.0	105

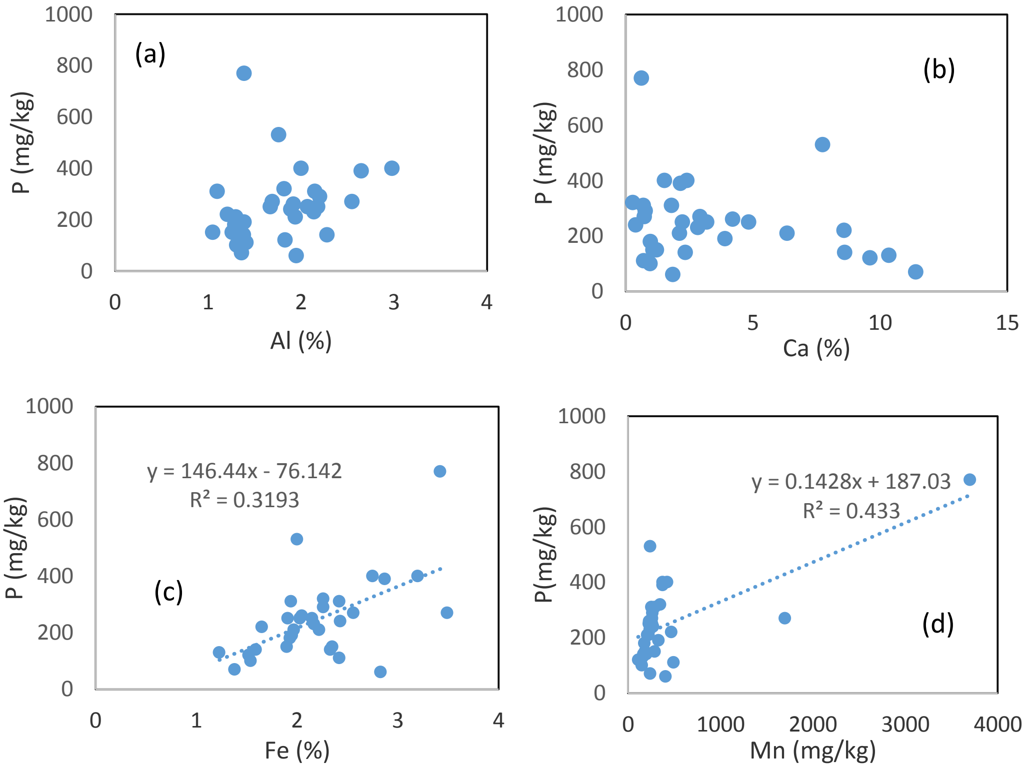


Figure 3.5: Scatter plots showing the relationship between phosphorus and (a) aluminum, (b) calcium, (c) iron, and (d) Mn (All elements were determined in aqua regia extracts)

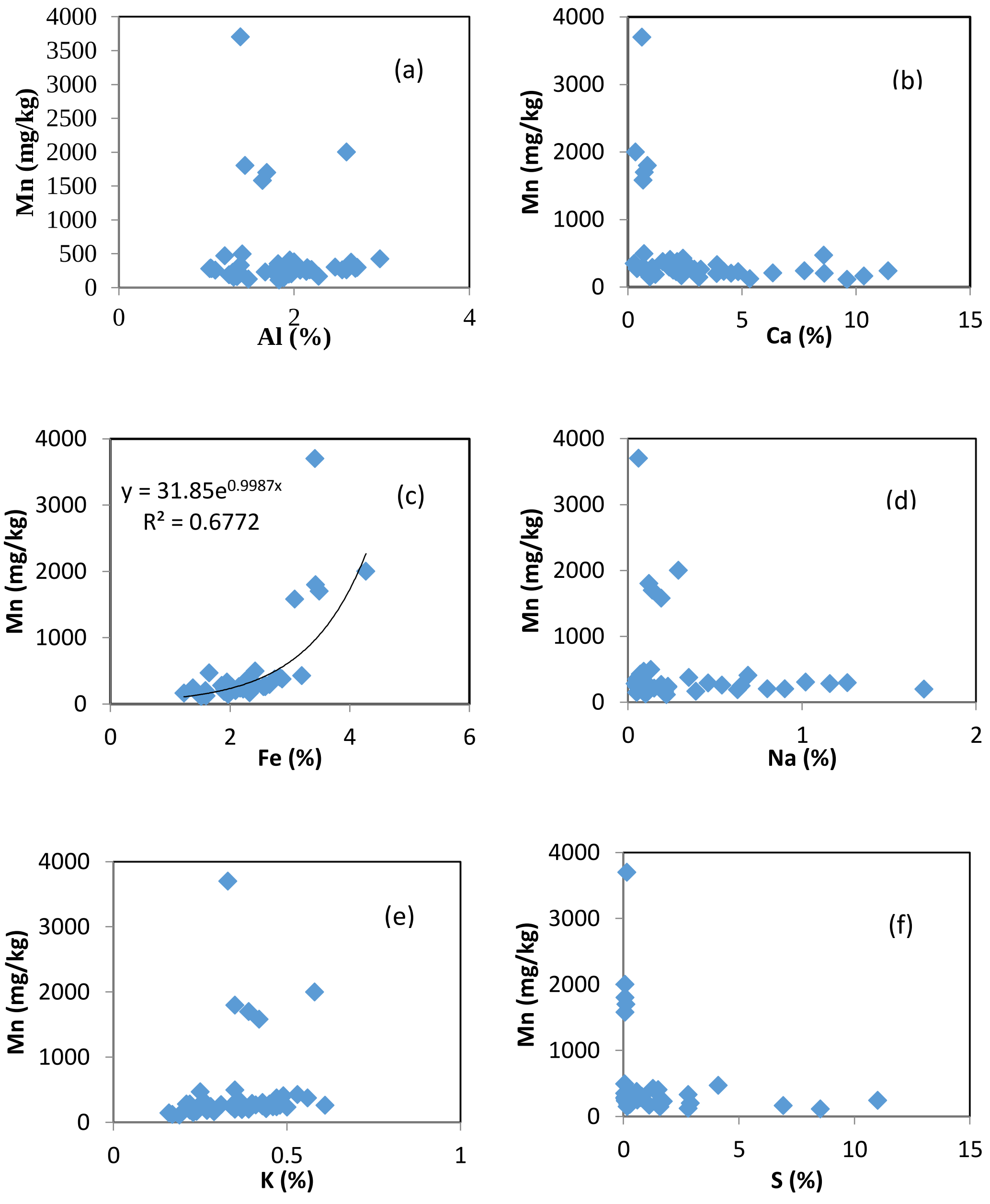


Figure 3.6: Scatter plots showing the relationship between manganese and (a) aluminium, (b) calcium, (c) iron, and (d) sodium,(e) potassium, and (f) Sulphur (All elements were determined in aqua regia extracts)

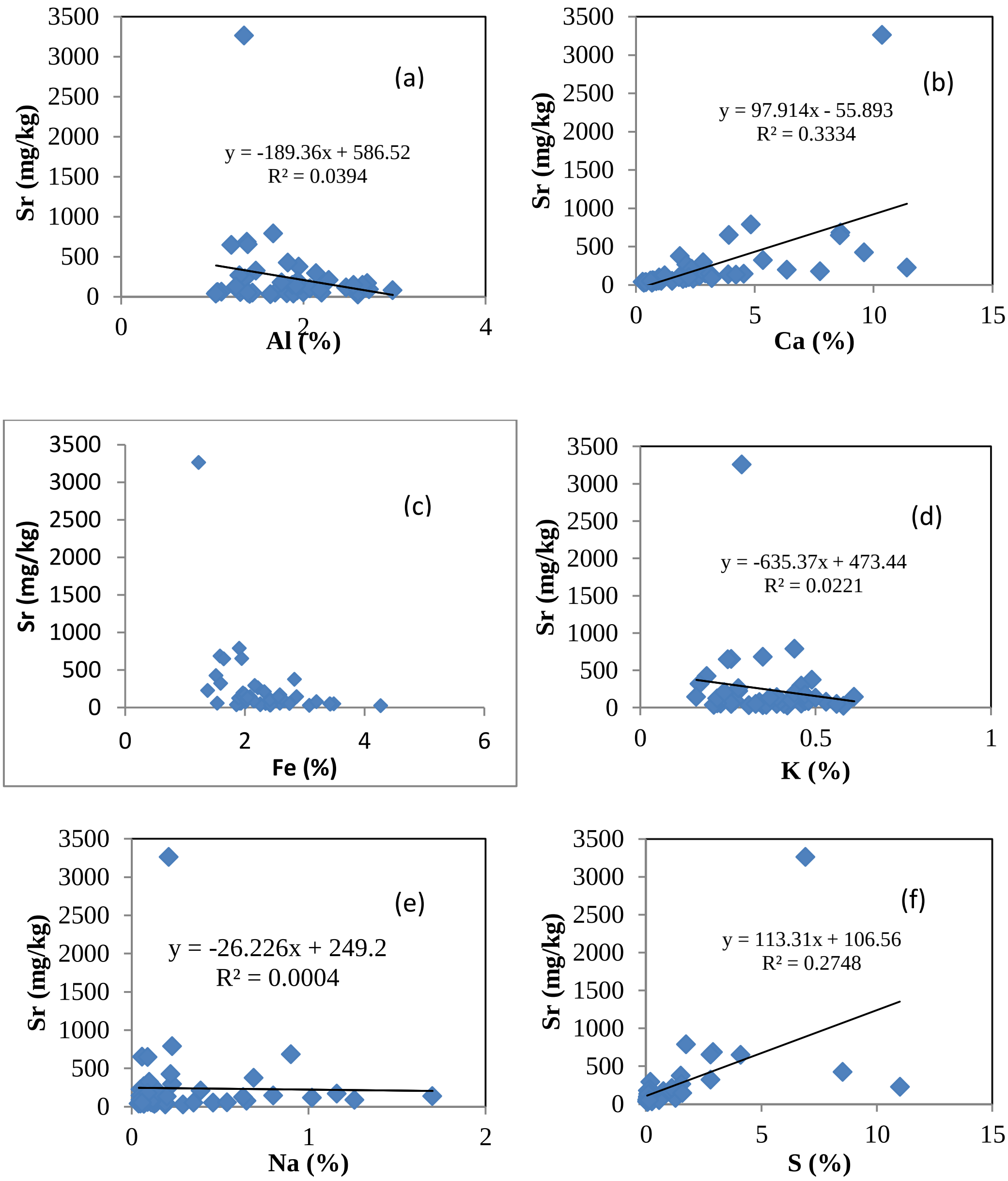


Figure 3.7: Scatters plot showing the relationship between strontium and (a) aluminium, (b) calcium, (c) iron, (d) sodium, (e) potassium, (f) Sulphur (All elements were determined in aqua regia extracts)

3.3.6 Control on vertical variation in pH and inorganic C within the soil profile

F7 is used as an example to illustrate the control on vertical variation in pH and inorganic C along the soil profile. From (Figure 3.8a) and (Figure 3.8b), it can be seen that there was a good correspondence in vertical variation between pH and inorganic C; the pH was higher and inorganic C content was lower in the top 20 cm of the soil profile, as compared to the subsoil layers. The maintenance of high pHs in the topsoil layers was attributable to limited carbonation due to insufficient supply of soluble Ca. It is clearly shown in (Figure 3.8c), that soluble Ca concentration was virtually negligible in the 0-10 cm and 10-20 cm layers. Soluble Ca then sharply increased with depth and this roughly corresponded with the increase in the aqua regia-extractable Ca, which in turn corresponded with the increase in aqua regia-extractable S. This suggests the presence of substantial amounts of gypsum in the subsoil layers (confirmed by XRD, data not shown). The gypsum acted as a major source of soluble Ca for pedogenic carbonate formation while simultaneously reduced soil pH, as shown in Equation 3.1. This reaction produced substantial amounts of soluble Na_2SO_4, which raised the value of EC in the subsoil layers (Figure 3.8f). To ameliorate this type of alkaline soils, deep ploughing to bring gypsum-rich and less alkaline soil materials from the subsoil layers to the soil surface could effectively eliminate highly basic soil conditions in the plant root zone. However, there is a need to reduce the soil salinity by forced leaching using the irrigation water. This practice has the potential to capture atmospheric CO_2 through the combined effect of enhanced pedogenic carbonation and organic carbon accumulation in the soils following cropping. Of course, the economic viability to adopt such a practice needs to be evaluated by reliable cost-benefit analysis.

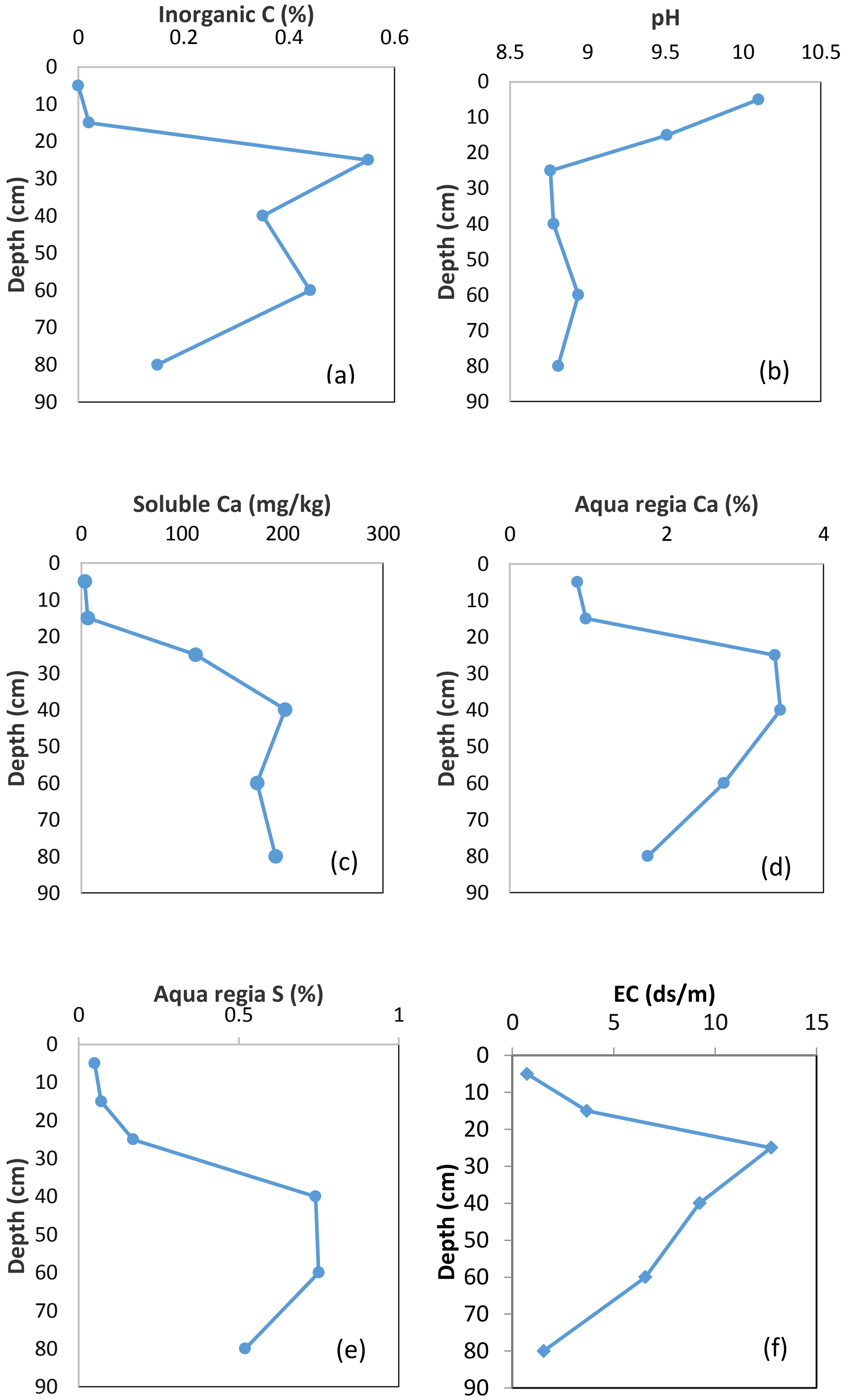


Figure 3.8: Vertical variations in (a) inorganic C, (b) pH, (c) soluble Ca, (d) aqua regia Ca, (e) aqua regia S and (f) EC along soil profile F7

3.4 Conclusions and Implications for Environment and Agriculture

The total carbon storage in the investigated soils was generally low (<1%) with the organic carbon mainly originated from the soil parent materials (lake sediments). However, under the current hyper-arid climate conditions, decomposition of organic carbon is slow. Therefore this relict soil organic carbon represents a stable carbon pool in the Sahara Desert. There was only a limited amount of inorganic C present in the topsoils. However, inorganic C content tended to increase with depth, particularly at locations where substantial amounts of gypsum were present with the soil profiles. Iron, phosphorus and Sulphur were abundant in the fine-grained fraction of the investigated soils. This has important implications for global geochemical cycling of these elements. In particular, the soil-derived iron and phosphorus from the Fezzan Sahara may be an important source of aerosol iron and phosphorus, and consequently contribute to the control on the nitrogen fixation in oceans. Manganese and strontium were the major toxic elements potentially present in the dusts derived from the Fezzan area, which may cause health problems in the affected areas.

The soils were generally alkaline and saline. There was a tendency that sodicity increased with depth for some soils. The Man-made River Project has provided opportunities to use the groundwater resource for developing irrigation agriculture in the Fezzan area. However, the problems associated with soil salinity, alkalinity and sodicity represent major challenges for the farmers. Appropriate strategies need to be developed to allow cost-effective reclamation of the Desert soils and sustainable development of the Desert soil-based irrigation agriculture. In general, a few points are worth mentioning here. First, gypsum is an abundant resource that is locally available in the Fezzan area; this material can be used to reclaim the alkaline/sodic soils in an economic manner. Second, it is more beneficial to take into account the factors such as minimization of dust formation, soil carbon sequestration, and water use efficiency when selecting farming methods and crop types.

Chapter 4 : Comparison of Soil Geochemical Characteristics and Isotopic Signatures between the Upper and Lower Catchment Zones in the Murray-Darling River Basin, Australia

4.1 Introduction

Catchment processes drive redistribution of surface materials with the upland portion being the erosion-dominated zone and the lowland portion being the deposition-dominated zone (Négrel et al. 2014). It may be possible that some dusts from lower catchment can be deposited in the upper catchment during certain period of time. However, these aeolian sediments should eventually be transported back to lower catchment by surface runoff. Depending on climatic regime, this could, to a varying degree, complicate spatial variability of soil properties, which is part of the important knowledge for informing management of natural resources at catchment-scale level.

In semi-arid regions, soil erosion rate tends to be high due to insufficient protection from vegetation cover, coupled with frequent rainfall regime of high-intensity (despite that rain events are generally of short duration) (Lima et al. 2013; Wei et al. 2007). On the other hand, the sediment yield (*i.e* materials in both particulate and dissolved forms that are discharged to ocean per unit of land surface) of rivers in semi-arid catchments is lower, as compared to river basins in high-rainfall regions. Therefore, it is likely that more erosional products are retained within the catchment. Prominently, the soluble salts that are generated from the erosional zone through carbonic acid-driven chemical weathering can be transported as dissolved loads from the upper catchment area and trapped in the lower catchment area to cause soil salinization. Where sodium silicates dominate parent rocks in the erosional zone, soil alkalinity may also develop, as shown in the following example chemical equations:

$$2NaAlSi_3O_{8(s)} + 2CO_{2\,(g)} + 11H_2O \rightarrow 2NaHCO_{3\,(aq)} + 4H_4SiO_{4\,(aq)} + Al_2Si_2O_5\,(OH)_{4(s)} \qquad (4.1)$$

$$2NaHCO_3\,(aq) \rightarrow NaOH(aq) + CO_2(g) \qquad (\,4.2)$$

The elevated concentration of Na in the soils can further alter soil characteristics, leading to formation of sodic soils, which reduces water infiltration and results in waterlogging conditions during and after rainfall events (Rengasamy & Olsson 1991).

Where calcium- or magnesium-bearing rocks dominates, the carbonic acid-driven chemical weathering (Equations (4.3) and (4.4)) in the erosional zone results in formation of soluble calcium bicarbonates (Schlesinger & Bernhardt 2013), which are then transported from the erosional zone to the lower catchment area where precipitation takes place to form insoluble carbonate minerals (*i.e.* calcium carbonate in Equation (4.5)).

$$CaAl_2Si_2O_{8(s)} + 2CO_{2(g)} + 3H_2O \rightarrow Al_2Si_2O_5(OH)_{4(s)} + Ca(HCO_3)_{2(aq)} \tag{4.3}$$

$$CaCO_{3(s)} + H_2O + CO_{2(g)} \rightarrow Ca(HCO_3)_{2(aq)} \tag{4.4}$$

$$Ca\,(HCO_3)_{2(aq)} \rightarrow CaCO_{3(s)} + H_2O + CO_{2(g)} \tag{4.5}$$

The combination of Equations 4.3 and 4.5 is a process leading to sequestration of atmospheric CO_2 while the combination of Equations 4.4 and 4.5 does not result in fixation of atmospheric CO_2. Understanding the origin and distribution of soil carbonate-C can provide useful information for evaluating soil carbon sequestering capacity at catchment-scale.

Murray Darling Basin (MDB) is one of the largest and driest river systems in the world. Since the European settlement in the mid-19th century, native vegetation was cleared and replaced with crops and pasture, coupled with extensive irrigation systems (Gordon et al. 2000). These agricultural practices have markedly altered the hydrological regimes in the MDB, which is likely to (a) enhance the retention of erosional products due to reduced river flow and (b) intensify soil salinization as a result of rising water-table in the cultivated and grazing areas. The removal of native vegetation also accelerates soil erosion and increase the frequency of dust storms, which may further complicate the re-distribution of the surface soil materials.

Currently, the available catchment-wide soil information in MDB only covers a few soil parameters such as pH, organic carbon, total phosphorus, total nitrogen, thickness, texture, and clay content (Henderson et al. 2005). More detailed soil information is limited to particular locations (Biggs et al. 2012; Creeper et al. 2013).

There is currently a paucity of information on detailed soil geochemical characteristics in MDB. The objective of this chapter was to improve the understanding of geochemical characteristics in the soils within MDB with a focus on identifying the differences in key soil geochemical parameters between the erosional and depositional zones of the catchment.

4.2 Materials and Methods

4.2.1 Regional Settings

The Murray-Darling Basin is the catchment of the combined Murray River-Darling River system. It is situated in the south eastern part of Australian continent and covers a total area of 1,059,000 km^2 (Figure 4.1). MDB is characteristic of extensive plains with the Quaternary sediments overlying the Tertiary rocks, which were in turn underlain by rock formations predominantly of the Paleozoic Age (250-350 million years old). Marine incursions took place during the Tertiary period, resulting in formation of limestone in the southernmost part of the catchment (Kingham 1998). Semi-arid climate dominates the MDB although the eastern uplands are relatively humid with mean annual rainfall exceeding 600 mm (Stern et al. 2000) and the western parts of the catchment tend to be arid or even hyper-arid. However, the average annual discharge is only about 0.89 m^3/sec at the river mouth, indicating that only about 4% of the rainfall falling into the catchment is discharged into the ocean (Qureshi et al. 2009).

4.2.2 Soil Sampling

Soil samples were collected from 93 locations across the catchment (Figure 4.1). A precise geographical location of the soil samples was showed in Table A.1 and B.1. Samples were taken along the highway from Yelarbon crossing Goondiwindi in Queensland. Dubbo, Griffith in New South Wales Mildura in South Australia The physiographic attributes of the basin (geology, topography, land use) are summarised below.

The study area mainly covered three major catchment areas. Maranoa-Balonne Catchment, the Border Rivers Catchment which are under the supervision of

Queensland Murray Darling Committee(QMDC), and the Nebine-Mungallala Catchment (for which QMDC shares responsibilities with South West NRM).

Land use of this area has changed greatly over the last 200 years. Abroginal use of the land is “hnter-gather” land use with widespread use of “fire-stick” farming. These areas were quickly settled in the late 1840s and initially experienced widespread sheep grazing. This later gave way to cattle grazing in the poorer watered areas, due to the ability of cattle to travel further distances for water. Grain production, mainly wheat, did not begin to fully develop throughout these areas until the 1890s. Grain production became more prevalent after the Second World War, as mechanisation allowed greater ease of clearing and cultivation on the heavier clay soils prevalent throughout the QMDC area. However, the current land use is widely varied with majority of the region being used for grazing of native pastures (beef and sheep), with better land used for dryland cropping (wheat, sorghum, chick peas), irrigated cropping (cotton, wheat, lucerne) and irrigated horticulture (apples, lettuce, berries).

Mining and natural gas extraction are increasing in importance in the region. Remnant vegetation is present in various land uses such as forestry (hardwood, softwood), nature conservation areas (national parks, reserves) and some native pasture areas.

Geology, soils and vegetation of the region is primarily comprised of sedimentary rock outcrop and derived colluvia/alluvia, and is part of the Great Artesian Basin. Soils vary from sands to clays, and are generally well related to geology. Cracking clay soils (Vertosols) on plains to undulating rises are very common and heavily exploited for cropping. Coarser grained sandstones such as in the Carnarvon Ranges produce rugged terrain with shallow sandy soils (Biggs et al. 2010).

For most of the sampling locations, soil samples were taken from the surface layer (0-30 cm). At Sampling Sites 10, 33, 34, 35, 36, 37, 45, 46, 47, 50, 52, soil samples were also taken from sub-soil layers to a depth that could be practically reached during the field operations. After air-drying, the soil samples were crushed to pass a 2 mm sieve. Gravels (>2 mm fraction) were then discarded. All the soil samples were stored in air-tight re-sealable polyethylene bags prior to various laboratory analyses.

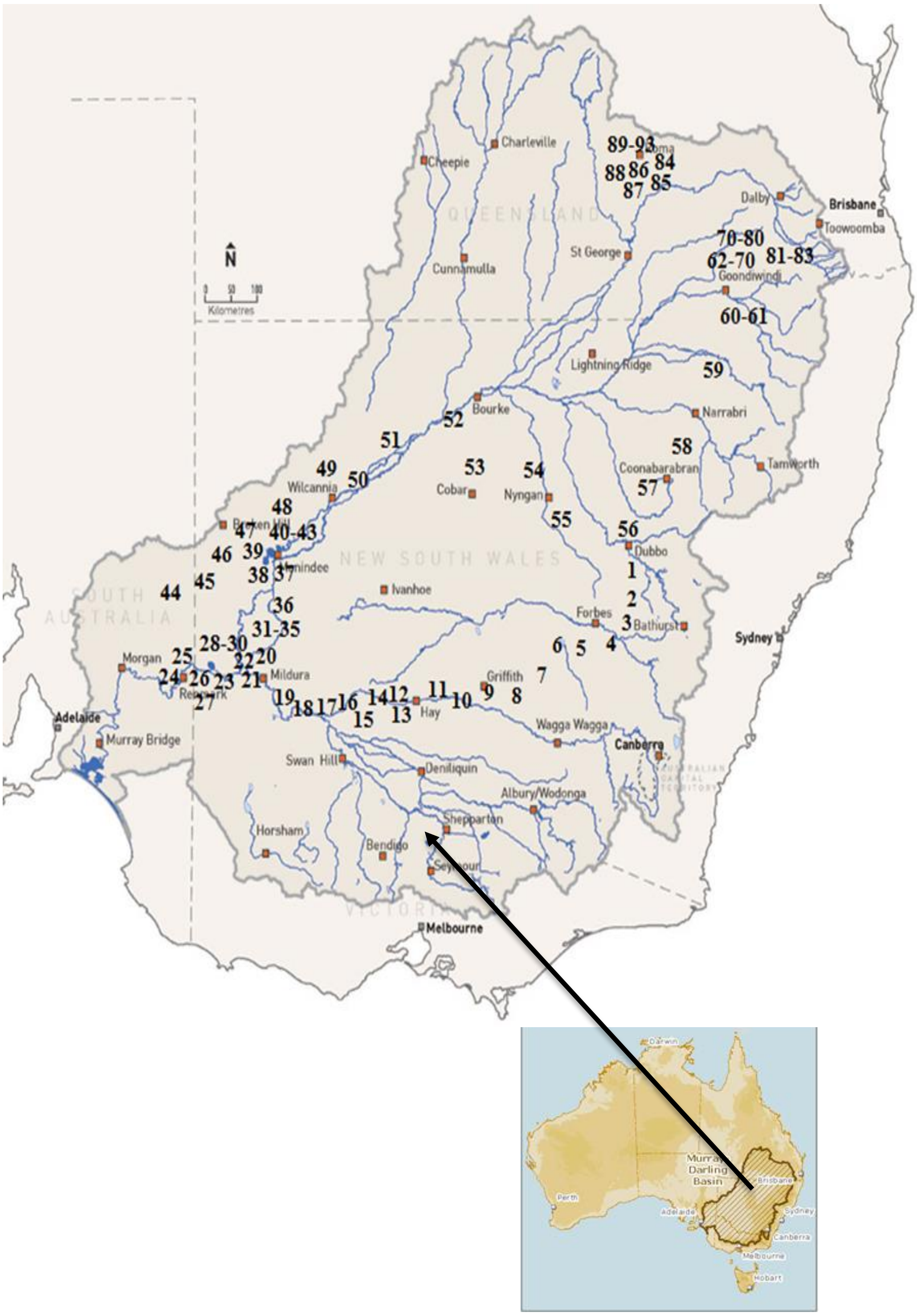


Figure 4.1: Map of Murray Darling Basin showing the sampling locations

4.2.3 Analytical methods

For each soil sample, the <2 mm soil fraction was used to prepare 1:5 (soil: water) extract with the following procedure: 25 mL of deionized water was added into a centrifuge tube containing 5 g of soil; the tube was shaken in a rotary shaker for 1 h and then centrifuged at 3000 rpm for 5 min; the supernatant was removed and stored in a clean tube for further analysis. The soil residue from the water extraction was then used to prepare 1:5 (soil: 1 M NH_4Cl) extract with the procedure that was exactly the same as the water extraction except that 25 mL of 1 M NH_4Cl solution was used to replace deionized water as an extracting agent.

pH and EC in the water extracts were measured using a calibrated pH meter and EC meter, respectively. Ca, Mg, K, and Na in water and NH_4Cl extracts were determined using an atomic absorption spectrometer (AAS).

A portion of each soil sample (<2 mm fraction) was pulverized for further instrumental and chemical analysis. XRF analysis was used to determine the content of Al_2O_3, BaO, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, SrO and TiO_2. Total carbon was determined by a LECO CNS Analyzer. Organic carbon was determined using a Walkley–Black method. A wide range of elements were extracted by an aqua regia digestion method and measured by inductively coupled plasma mass spectrometry (ICP-MS).

The concentration of soluble cations was estimated from the water-extractable cations and the concentration of exchangeable cations was estimated from the NH_4Cl-extractable cations. Sodium adsorption ratio (SAR) of the water extract was calculated using equations 3.1 and 3.2.

The inorganic carbon content was estimated by the difference between the total carbon and the organic carbon. $^{87}Sr/^{86}Sr$ ratio in the labile fraction of a soil sample was determined on a VG Sector 54 thermal ionization mass spectrometer (TIMS) at the University of Queensland. The labile fraction was extracted by leaching the soil samples with a 1 M acetic acid solution. A modified procedure (Deniel & Pin 2001; Mikova & Denkova 2007; Pin & Zalduegui 1997) was used to separate Sr from the matrix using Sr-Spec resin. The purified solution was then loaded into a pre-degassed tungsten filament, and Sr isotope ratios were measured with a three-cycle dynamic protocol. The results obtained from 149 analyses of SRM-987 with samples since 2012 yielded a mean $^{87}Sr/^{86}Sr$ value of 0.710222 ± 20 (2σ standard deviation), which is used for normalization to previous laboratory long-term average by static analysis (0.710249 ± 28).

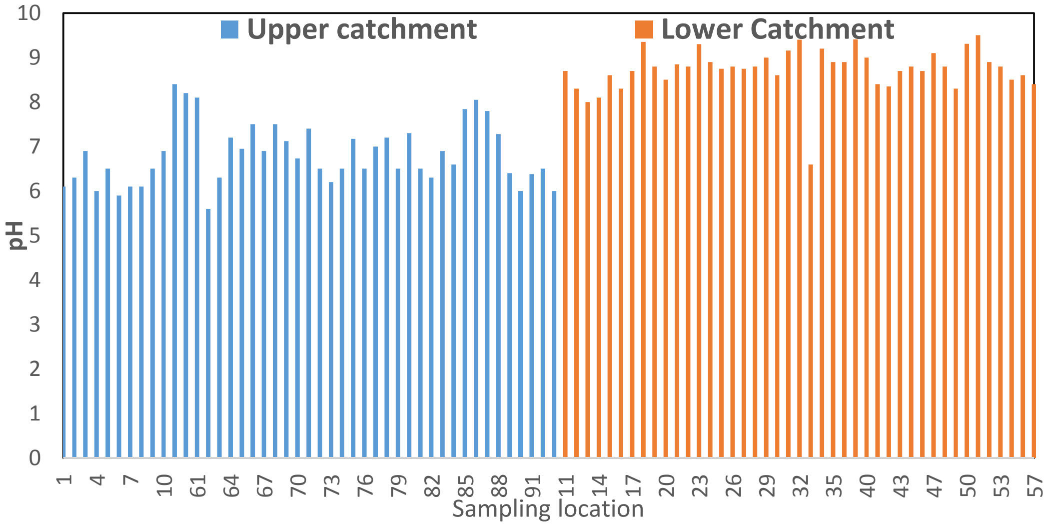
4.3 Results

4.3.1 pH and Electrical Conductivity (EC)

Soil pH was much lower in the upper catchment than in the lower catchment. The mean pH in the upper catchment soils was 6.81 with a range of 5.6-8.4 while the mean pH in the lower catchment soils was 8.73 with a range of 6.6-9.5 (Figure 4.2a).

Electrical conductivity (EC) was also lower in the upper catchment than in the lower catchment. EC in the upper catchment soils averaged at 0.151 dS/m with a range of 0.023-0.989 dS/m, as compared to 0.314 dS/m with a range of 0.026-1.940 dS/m (Figure 4.2b).

(a)



(b)

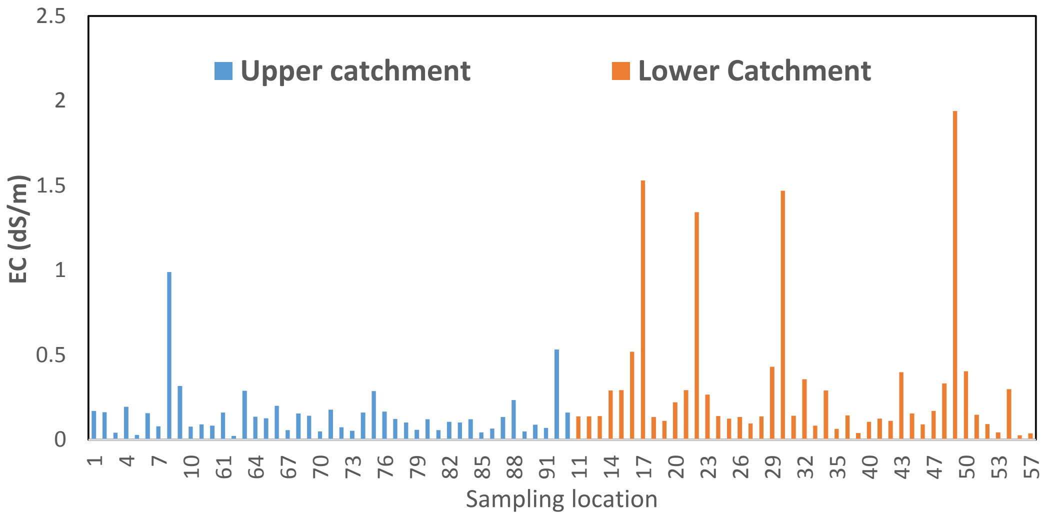


Figure 4.2: Comparison of (a) pH and (b) electrical conductivity (EC) in the soils between the upper catchment and the lower catchment of MDB

4.3.2 Organic and Inorganic carbon

The organic carbon content in the surface layer (0-30 cm) of the soils collected from the 93 locations within the MDB is shown in (Figure 4.3a). The soils in the upper catchment had a mean value of 0.879% with a range of 0.3-2.0%. In the lower catchment, the organic carbon content ranged from 0.13 to 1.84% with a mean value of 0.631%, which was only slightly lower than that in the upper catchment. In contrast, the inorganic carbon content in the soils was much lower in the upper catchment than in the lower catchment. The mean content of inorganic carbon in the upper catchment soils was 0.179% with a range of 0-0.94%, as compared to 0.807% with a range of 0-2.9% in the lower catchment soils (Figure 4.3b).

4.3.3 SAR and ESP

Sodium adsorption ratio (SAR) tended to be greater in the upper catchment soils than in the lower catchment soils. SAR averaged at 16.8 with a range of 1.2-74.3 in the upper catchment, as compared to 6.91 with a range of 1.0-19.2 in the lower catchment (Figure 4.4a). This was consistent with the ESP results, which had a mean

of 9.62 with a range of 1.13-39.7% in the upper catchment soils, as compared to 4.69 with a range of 1.59-17.2 % in the lower catchment soils (Figure 4.4b).

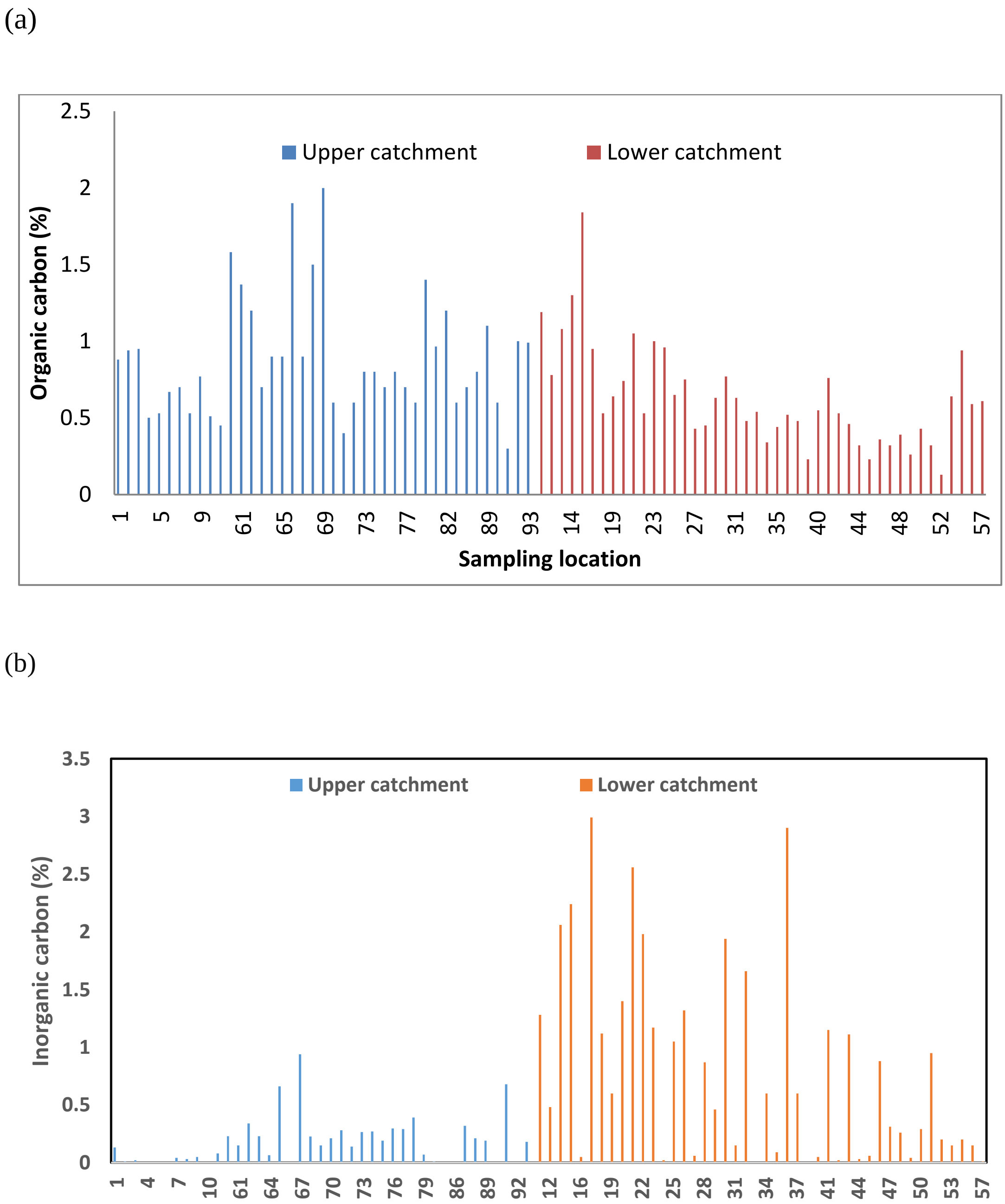
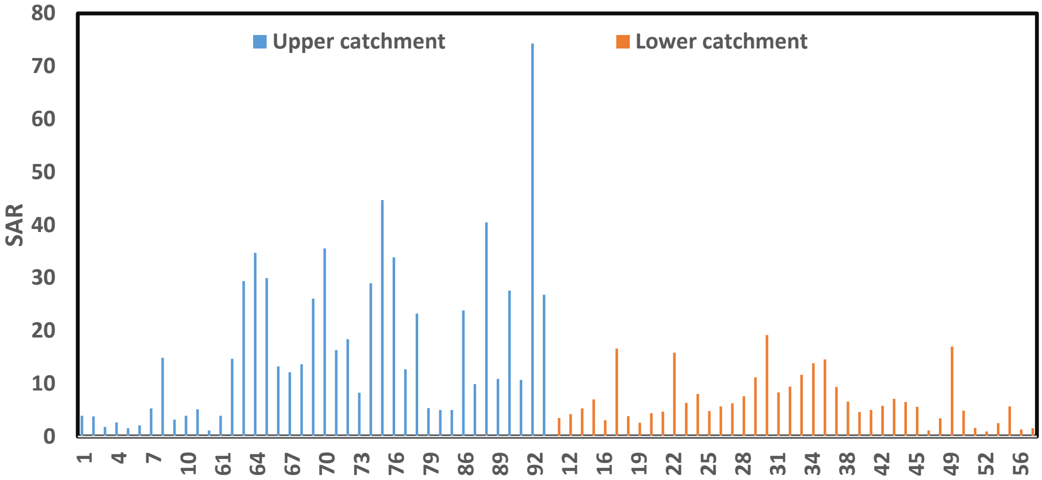


Figure 4.3: Comparison of (a) organic carbon and (b) inorganic carbon in the soils between the upper catchment and the lower catchment of MDB

(a)



(b)

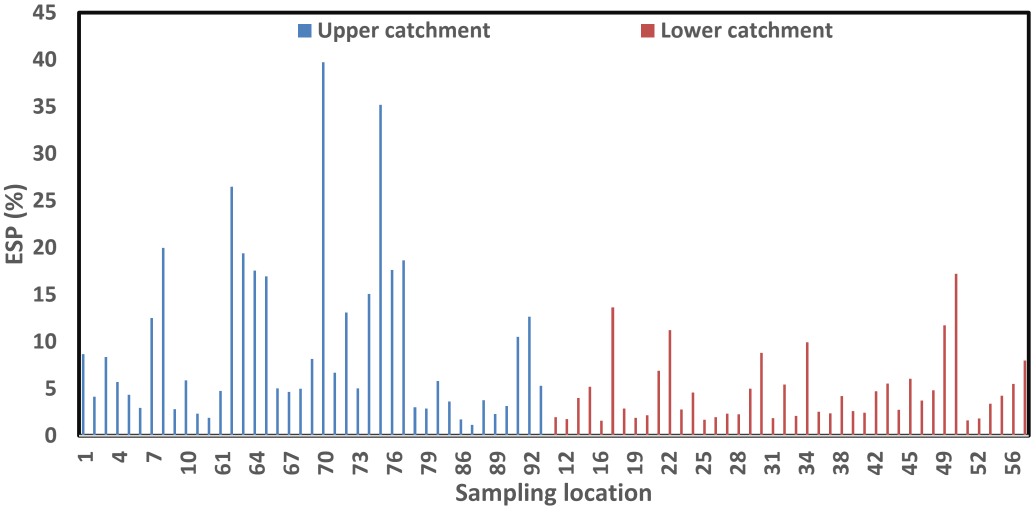


Figure 4.4: Comparison of (a) SAR (b) ESP in the soils between the upper catchment and the lower catchment of MDB

4.3.4 Molar Ratios of Major Chemical Constitutes

There was only slight difference in SiO_2/Al_2O_3 in the soils between the upper catchment and the lower catchment. SiO_2/Al_2O_3 averaged at 16.2 with a range of 4.99-50.7 in the upper catchment soils, as compared to 17.9 with a range of 5.12-39.9 in the lower catchment soils (Figure 4.5a). However, SiO_2/CaO was much greater in the upper catchment soils than in the lower catchment soils; the former had a mean SiO_2/CaO of 311 with a range of 17.2-1406 while the latter only had a mean ratio of 81.7 with a range of 3.29-755 (Figure 4.5b). The average of Al_2O_3/Fe_2O_3 was slightly higher in the upper catchment soils than in the lower catchment soils. The former had the mean Al_2O_3/Fe_2O_3 of 4.53 with a range of 1.65-7.43, as compared to 3.72 with a range of 2.03-4.46 in the latter (Figure 4.5c).

There was no marked difference in the mean K_2O/Na_2O between the upper catchment soils and the lower catchment soils. The K_2O/Na_2O in the upper catchment soils averaged at 2.17 with a range of 0.51-6.97, as compared to 2.79 with a range of 0.29-9.17 in the lower catchment soils (Figure: 4.6a). In contrast, CaO/Na2O was much smaller in the upper catchment soils than in the lower catchments soils. The upper catchment soils had a mean CaO/Na2O of 1.86 with a range of 0.16-11.5, as compared to 14.5 with a range of 0.23-57.4 in the lower catchment soils (Figure: 4.6b). CaO/MgO showed the similar trend to CaO/Na_2O but the mean value was smaller in the former than in the latter for either the upper catchment soils or the lower catchment soils (Figure: 4.6c).

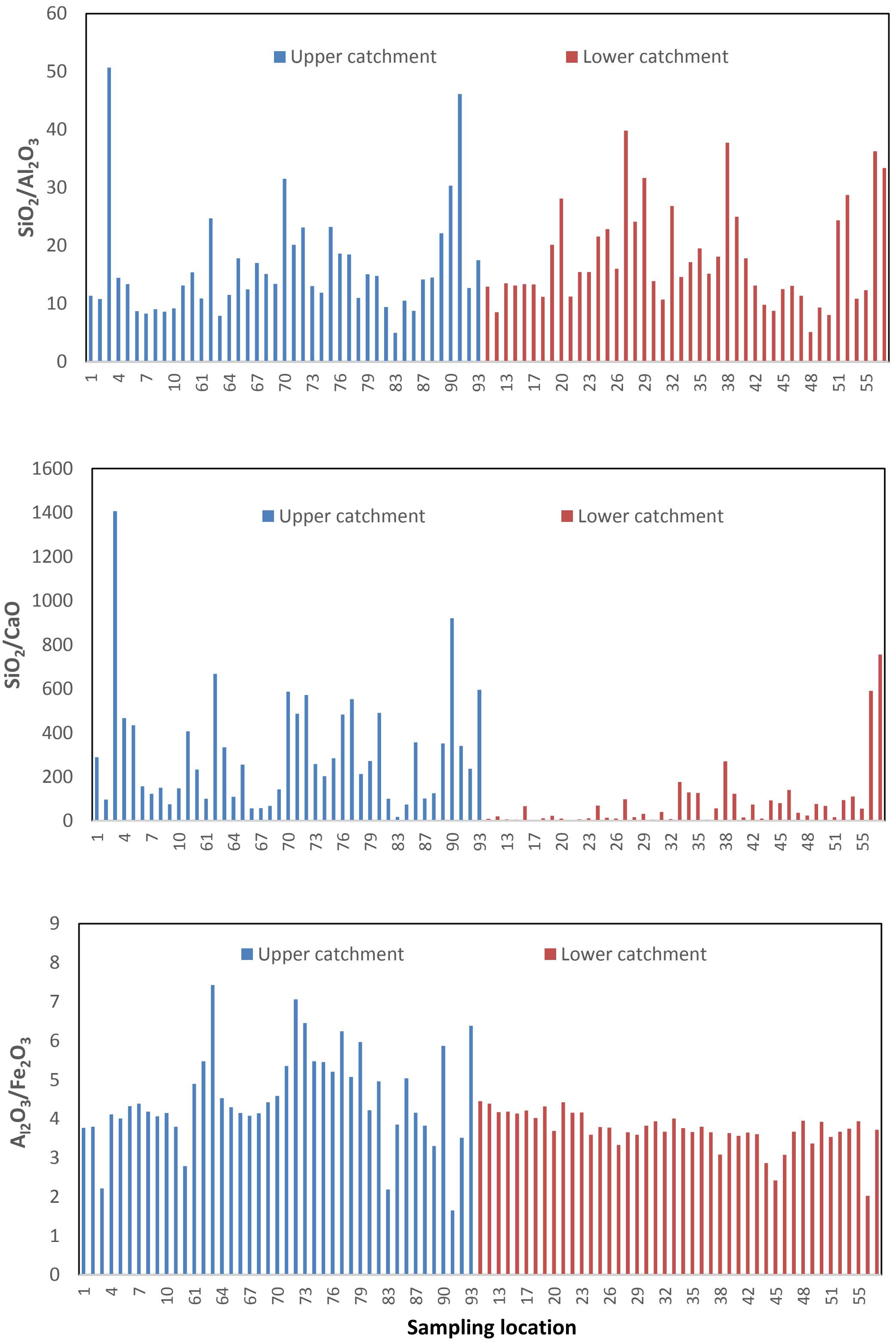


Figure 4.5: Comparison of (a) SiO_2/Al_2O_3, (b) SiO_2/CaO and (c) Al_2O_3/Fe_2O_3 in the soils between the upper catchment and the lower catchment of MDB

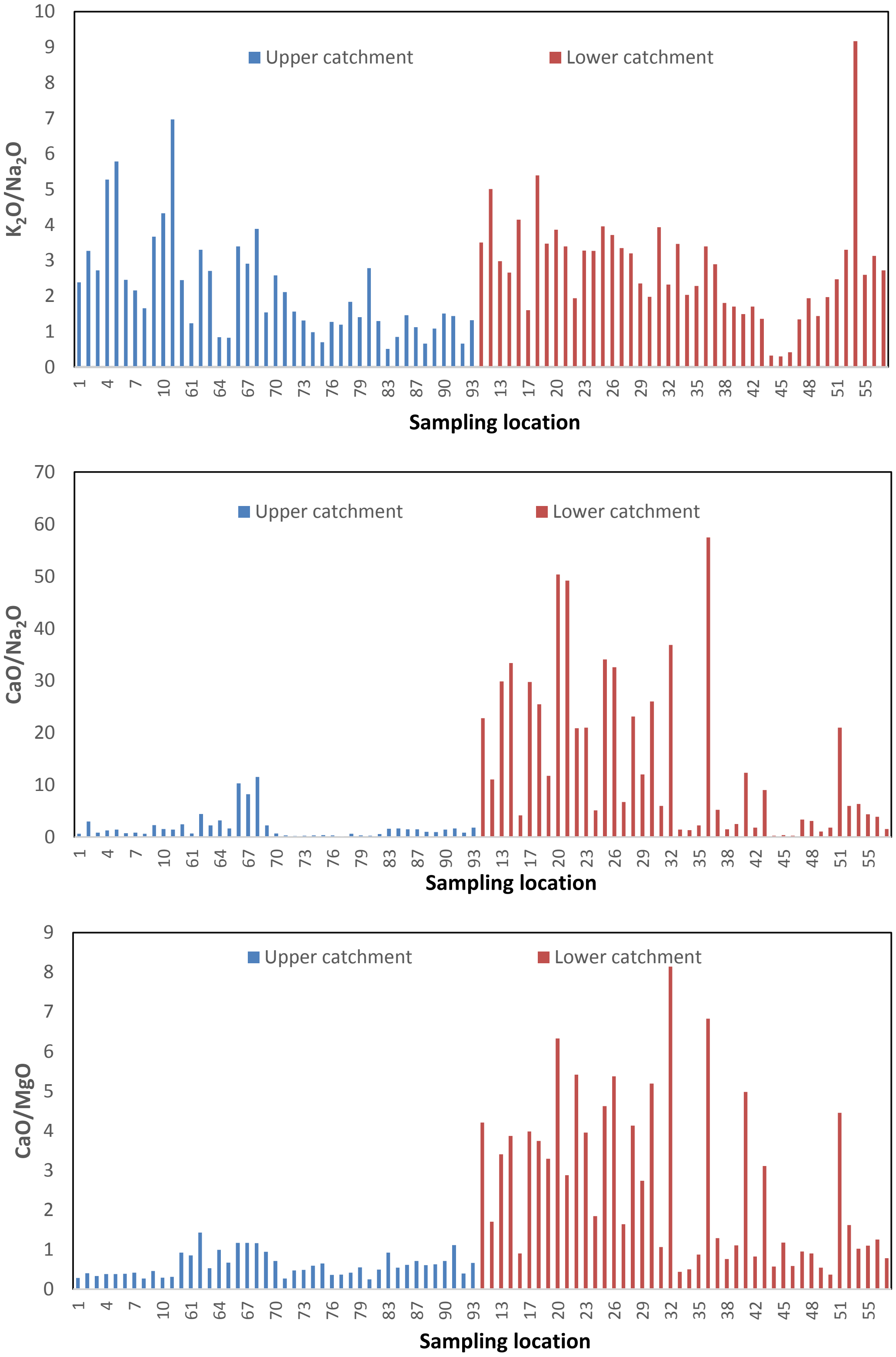


Figure: 4.6: Comparison of (a) K_2O/Na_2O, (b) CaO/Na_2O and (c) CaO/MgO in the soils between the upper catchment and the lower catchment of MDB

4.3.5 Elemental composition

The elemental composition of both the upper catchment and the lower catchment soils, as determined by the aqua regia digestion method, is shown in (Table 4.1). The mean concentration of various elements in both zones was very similar except for calcium, potassium, lithium, magnesium, manganese, sodium, strontium and tungsten. Manganese was higher in the upper catchment soils than in the lower catchment soils while the rest of the above-listed elements showed the opposite.

4.3.6 Strontium Isotope Signature

There was a marked difference in $^{87}Sr/^{86}Sr$ in the labile fraction of the soils between the upper catchment and the lower catchment; $^{87}Sr/^{86}Sr$ in the upper catchment soils averaged at 0.707968 with a range of 0.706766-0.709335 while the lower catchment soils had a mean of 0.711275 with a range of 0.710289-0.712799. It is also interesting to note that the $^{87}Sr/^{86}Sr$ showed little vertical variation along the soil profiles in the lower catchment soils (Table 4.2).

Table 4.1: Elemental composition of the soils in the upper and lower catchment zones

Element	Upper catchment			Lower catchment		
	Mean	Min	Max	Mean	Min	Max
Ag (ppm)	0.05	udl	0.18	0.04	0.01	0.11
Al (%)	1.68	0.27	3.77	2.09	0.73	4.18
As(ppm)	3.06	0.50	8.10	4.00	0.90	38.8
Ba(ppm)	130	20.0	490	102	30.0	240
Be(ppm)	0.77	0.06	2.16	0.82	0.30	1.80
Bi(ppm)	0.15	0.01	0.34	0.12	0.05	0.28
Ca (%)	2500	100	9000	25300	700	103000
Cd(ppm)	0.02	udl	0.14	0.06	0.00	0.37
Ce(ppm)	39.1	3.70	75.8	39.7	9.04	103
Co(ppm)	9.60	0.60	32.2	8.07	3.80	18.0
Cs(ppm)	1.52	0.19	4.44	1.66	0.32	3.72
Cu(ppm)	12.6	2.30	31.6	17.4	4.30	39.5
Fe(%)	18100	3500	59100	19800	10800	39900
Ga(ppm)	5.30	0.94	11.2	6.16	3.01	12.9
Ge(ppm)	0.10	udl	0.23	0.11	0.05	0.20
Hf(ppm)	0.13	udl	0.43	0.14	0.02	0.45
Hg(ppm)	0.02	0.01	0.05	0.02	udl	0.05
In(ppm)	0.02	0.01	0.05	0.02	0.01	0.05
K(%)	2100	200	8600	4700	400	9000
La(ppm)	16.8	2.10	33.6	18.1	4.60	46.5
Li(ppm)	7.62	0.40	23.0	13.2	1.90	27.1
Mg (%)	2300	200	9400	4600	300	15000
Mn(ppm)	685	10.0	2380	335	74.0	1070
Mo(ppm)	0.50	0.09	1.64	0.50	0.20	1.09
Na (%)	400	100	2700	700	100	2600
Nb(ppm)	0.28	0.06	1.85	0.33	0.12	0.65
Ni(ppm)	13.7	0.90	64.1	16.9	6.00	31.9
P(ppm)	216	10.0	2070	202	70.0	590
Pb(ppm)	11.0	1.00	21.4	10.6	3.70	31.9
Rb(ppm)	23.6	2.60	58.6	29.3	4.60	65.9
S (%)	0.02	0.01	0.04	0.02	0.01	0.05
Sb(ppm)	0.15	udl	0.42	0.20	0.08	1.11
Sc(ppm)	4.29	1.10	11.7	4.48	1.70	10.2
Se(ppm)	0.78	0.20	2.00	0.57	0.20	1.40
Sn(ppm)	0.92	0.20	1.90	0.96	0.40	1.70
Sr(ppm)	41.5	3.60	157	149	8.60	1090
Th(ppm)	4.26	1.10	10.3	4.86	1.90	11.1
Ti(ppm)	0.02	0.01	0.25	0.02	0.01	0.07
Ti(%)	0.13	udl	0.31	0.15	0.02	0.31
U(ppm)	0.49	0.08	1.70	0.48	0.17	1.18
V(ppm)	41.0	10.0	107	38.1	17.0	82.0
W(ppm)	0.33	udl	6.48	1.52	0.05	9.18
Y(ppm)	12.3	0.66	50.7	11.3	2.56	32.9
Zn(ppm)	32.2	2.00	148	43.9	7.00	219
Zr(ppm)	4.74	0.60	23.3	5.11	0.90	15.2

udl: under detection limit

Table 4.2: $^{87}Sr/^{86}Sr$ ratio of the soils in the upper and lower catchment zones

	Sampling location	Depth (cm)	$^{87}Sr/^{86}Sr$	±2σ
Upper catchment	62	0-30	0.706766	0.000010
	63	0-30	0.707687	0.000006
	63	0-30	0.707721	0.000010
	65	0-30	0.708587	0.000007
	66	0-30	0.708139	0.000008
	67	0-30	0.708513	0.000010
	68	0-30	0.708171	0.000007
	69	0-30	0.709335	0.000007
	84	0-30	0.707909	0.000008
	86	0-30	0.706897	0.000008
	89	0-30	0.707920	0.000007
Lower catchment	13	0-30	0.712359	0.000014
	14	0-30	0.712433	0.000013
	17	0-30	0.711970	0.000010
	18	0-30	0.712285	0.000009
	22	0-30	0.711469	0.000009
	29	0-30	0.710373	0.000009
	30	0-30	0.710519	0.000007
	32	0-30	0.710561	0.000009
	33	0-10	0.710676	0.000010
	33	20-40	0.710783	0.000009
	33	40-60	0.710770	0.000009
	33	60-80	0.710773	0.000009
	34	0-10	0.710692	0.000009
	34	20-40	0.710289	0.000009
	34	50-60	0.710293	0.000011
	37	0-10	0.710747	0.000009
	37	20-30	0.710682	0.000009
	37	40-50	0.710649	0.000009
	46	0-10	0.712062	0.000010
	46	20-30	0.712789	0.000009
	46	40-50	0.712799	0.000007
	50	0-10	0.711853	0.000009
	50	20-30	0.711875	0.000010
	50	40-50	0.711862	0.000009
	52	0-10	0.710972	0.000007
	52	20-30	0.710939	0.000009
	52	40-50	0.710939	0.000009

4.4 Discussion

The high degree of similarity in SiO_2/Al_2O_3 and most elements in the soils between the upper catchment and the lower catchment appears to suggest that the surface soil materials in the lower catchment tended to be of upper catchment origin. The lower mean concentration of Ca, Na, K, and Mg in the soils of the upper catchment was likely to be caused by the relocation of these elements from the upper catchment to the lower catchment. As illustrated in Equations 5.1,5.2, 5.3 and 5.5, the carbonic acid-driven weathering of silicate minerals results in the formation of basic metal bicarbonates, which are soluble and therefore subject to transport through either surface and sub-surface runoff from the upper catchment zone to the lower catchment zone. In the lower catchment zones, $NaHCO_3$ can release CO_2 to produce NaOH, giving rise to increase in soil pH. This explains the higher mean pH in the lower catchment soils, as compared to the soils in the upper catchment zone. The accumulation of soluble salts also caused the increase in EC in the lower catchment soils. It is interesting to note that both SAR and ESP had higher mean value in the upper catchment soils than in the lower catchment soils.

However, close examination found that, within the upper catchment zone, there was marked difference in SAR between the wetter NSW upland area (Sampling locations 1-10 and 58-61) and the drier Queensland upland area (Sampling Locations 62-93); the former had the SAR frequently less than 5 while the latter had the SARfrequently greater than 10. The higher SAR in the Queensland upland area can be attributed to weak leaching, resulting in more sodium being retained in the surface layer. The lower SAR and ESP in the surface soils of the lower catchment zone might be caused by stronger downward movement of sodium, relative to calcium and magnesium that are partially retained in the surface soil layer due to formation of calcium and magnesium carbonates and adsorption by soil colloids and vegetation.

The lower mean organic carbon content in the lower catchment soils, relative to that in the upper catchment soils, probably reflects the smaller organic matter input from the plants due to generally alkaline soil conditions, which are less favourable for plant growth and due to poor agricultural practices. The higher inorganic carbon content in the lower catchment soils, as compared to the upper catchment soils, indicates that strong carbonation only took place in the low-lying floodplains. The plot of inorganic carbon vs total calcium gives a R^2 of 0.9767 and a slope of 1.0033, suggesting that the inorganic carbon was predominantly combined with calcium and almost all the calcium in the soils was in carbonate-bound forms (Figure 4.7).

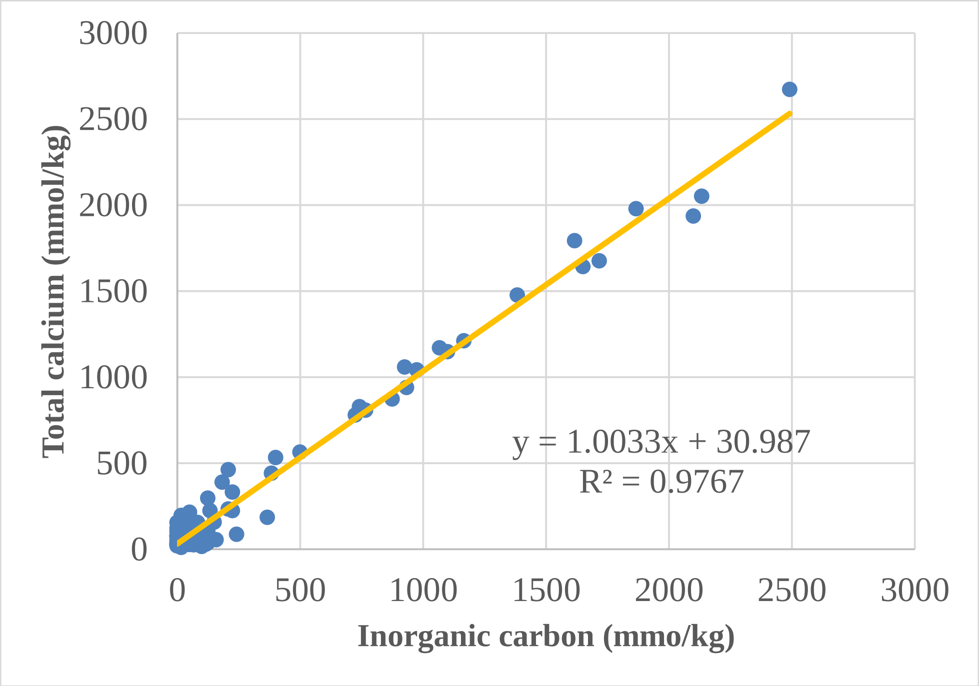


Figure 4.7: Relationship between inorganic carbon and total calcium in the lower catchment soils

The marked difference in $^{87}Sr/^{86}Sr$ ratio of the acetic acid-extractable fraction between the upper catchment soils and the lower catchment soils suggests that the labile pool of strontium in these two different topographic zones had different origins. It has been generally believed that soil strontium with an $^{87}Sr/^{86}Sr$ similar to that in seawater indicates a marine origin. Available data have suggested that ocean-originated carbonates had the $^{87}Sr/^{86}Sr$ ratio ranged from 0.706 to 0.709 throughout the Phanerozoic time (Burke et al. 1982; Thomas et al. 2004). The $^{87}Sr/^{86}Sr$ in the upper catchment soils ranged from 0.706766 to 0.709335 with a mean value of 0.707968. However, carbonate rocks are not common in the upper MDB, which appears not to suggest that the soil Sr was mainly derived from this source. Volcanic rocks usually have a lower $^{87}Sr/^{86}Sr$ ratio. For example, McNutt et al. (1975) found that the mid-Cretaceous to Quaternary volcanic rocks had a $^{87}Sr/^{86}Sr$ ratio ranging from 0.7022 to 0.7077 in the Central Andes between latitudes 26° and 29° south.

Volcanic rocks are present in the Great Dividing Range and this is likely to be a source of strontium with low ^{87}Sr/^{86}Sr ratio for the upper catchment soils. Therefore, the strontium signatures in the upper catchment soils may indicate the mixing of strontium from the weathering of both volcanic rocks and other silicate rocks. Contribution from the rainwater-borne strontium was also possible because the rainwater had a ^{87}Sr/^{86}Sr ratio of 0.707697, as determined from a rainwater sample collected from Toowoomba on March, 2014. The remarkably higher ^{87}Sr/^{86}Sr ratio in the lower catchment soils, relative to those for carbonate rocks, volcanic rocks and rainwater, suggests a significant contribution of silicate rock-originated Sr towards the composition of soil strontium in these soils. ^{87}Sr/^{86}Sr ratio can be used as a tracer for Ca sources in (Capo & Chadwick 1999; Van der Hoven & Quade 2002).

Based on this assumption, then it is suggestable that the calcium being incorporated into the calcium carbonates in the lower catchment soils was, to a significant degree, derived from the weathering of the silicate minerals. Consequently, these carbonates represent a sink of atmospheric CO_2 according to Equations (4.3) and (4.5).

4.5 Conclusion

In the Murray Darling Basin, the SiO_2/Al_2O_3 and most elements in the soils between the upper catchment and the lower catchment were very similar, suggesting that the surface soil materials in the lower catchment tended to be of upper catchment origin. However, there were marked differences in pH, electrical conductivity, sodium adsorption ratio, exchangeable sodium percentage, inorganic carbon, and ^{87}Sr/^{86}Sr ratio of the acetic acid-extractable fraction between the upper catchment soils and the lower catchment soils. This is attributable to the catchment processes, which drive the re-distribution of readily movable bicarbonates of basic metals within the catchment. The elevated pH in the lower catchment zone inhibits the growth of plants, resulting in lower soil organic carbon content, as compared to the upper catchment zone. Given the relatively low outward discharge rate, large amounts of carbonates were deposited within the lower catchment zone. The strontium isotopic signatures obtained from this study suggests a significant contribution of silicate rock-originated Sr towards the composition of soil strontium in these soils, inferring that silicate rock-originated Ca might play an important role in the formation of carbonate minerals in the lower catchment zone, and consequently contribute significantly to CO_2 sequestration.

Chapter 5 : Limitation of Strontium Isotopic Signatures for Inferring Calcium Sources to Form Pedogenetic Carbonates in Highly Alkaline Soils

5.1 Introduction

Pedogenetic carbonates represent an important terrestrial carbon pool (Lal 2008; Schlesinger 1985). However, it was thought that pedogenetic carbonation played an insignificant or no role in atmospheric CO_2 sequestration (Capo & Chadwick 1999; Dart et al. 2007) because pedogenetic carbonate formation was only the result of dissolution (Equation 5.1) and re-precipitation Equation 5.2 of the primary carbonate minerals present in the soil parent materials or entering into soils by atmospheric deposition (Dart et al., 2007):

$$CaCO_3(s) + H_2O + CO_2\,(g) \rightarrow Ca2+\,(aq) + 2HCO^{3-}\,(aq) \qquad 5.1$$

$$Ca^{2+}\,(aq) + 2HCO^{3-}\,(aq) \rightarrow CaCO_3(s) + H_2O + CO_2\,(g) \qquad 5.2$$

While there is no doubt that this is a pathway for the formation of pedogenetic carbonates, it does not explain the presence of pedogenetic carbonates in highly alkaline soils that are widely distributed in arid and semi-arid regions (Bertrand et al. 2003; de Caritat et al. 2011). If the pedogenetic carbonates were formed through the reworking of calcareous parent rocks or dust-derived carbonates (Dart et al. 2007), the soil pH should not exceed 8.5 that can possibly be raised by dissolution of the primary calcium carbonates (Etherington 1981; Leytem & Mikkelsen 2005; Panigrahy & Raymahashay 2005; Rowe & Johnson 1988; Turner & Clark 1956; Yaalon 1957). The generation of high alkalinity (rise in pH to greater than 8.5) can only result from the weathering of alkali metal silicates (Rhoades et al. 1968).

For example:

$$2NaAlSi_3O_{8(s)} + 2CO_{2(g)} + 11H_2O \rightarrow 2NaHCO_{3(aq)} + 4H_4SiO_{4(aq)} + Al_2Si_2O_5(OH)_{4(s)} \qquad 5.3$$

$$2NaHCO_{3\,(aq)} \rightarrow NaOH_{(aq)} + CO_{2(g)} \qquad 5.4$$

Therefore, the presence of highly alkaline soils indicates the occurrence of silicate weathering although this may not necessarily reflect in-situ weathering within a soil profile. From a catchment-scale perspective, silicate weathering products ($NaHCO_3$

and NaOH) present in the soil at a given location can derive from runoff (Chen, 2002). It is also likely that in-situ weathering of alkali-generating silicates took place during past wet episodes in the present Desert areas(Chadwick et al. 1995).

Although Ca-bearing silicates are slightly less weatherable, as compared to their Na or/and K counterparts, there is no reasons to exclude the possibility of simultaneous weathering of these silicate mineral types in environments where Na or/and K silicates experience decomposition to a degree that causes generation of substantial alkalinity. Weathering of alkaline earth metal silicates does not result in production of soluble OH^-, but leads to formation of carbonates, as shown in the following example reactions:

$$CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_{4(s)} + Ca(HCO_3)_2 \quad 5.5$$

$$Ca(HCO_3)_2 \rightarrow CaCO_{3(s)} + H_2O + CO_{2(g)} \quad 5.6$$

Therefore, pedogenetic carbonates in soils with pH <8.5 are also likely to be of silicate weathering origin according to Equations 5.5 and 5.6.

Strontium isotopic signatures have been used as primary evidence to support the hypothesis that Ca of atmospheric sources controls the pedogenetic carbonation in arid and semi-arid regions (Capo & Chadwick 1999; Chiquet et al. 1999; Dart et al. 2007; Hamidi et al. 2001). The utilization of $^{87}Sr/^{86}Sr$ as a tracer for Ca sources in ecosystems is based on the following theoretical assumptions (Van der Hoven & Quade 2002): (a) There is no significant fractionation between the strontium isotopic species as Sr passes through various phase transformations, such as precipitation or dissolution; (b) Because Sr and Ca have similar ionic radii, their chemical behaviors in the environments are also similar to each other and consequently, Sr can be used as a chemical proxy for Ca. Nevertheless, there have so far been no serious efforts made to test the validity of these hypotheses in alkaline soil environments.

The objective of this chapter was to test the validity of the second theoretical assumption mentioned above by investigating $^{87}Sr/^{86}Sr$ ratio, chemical behaviours of Sr, Ca, Mg and other relevant elements in highly alkaline soils, as well as Sr, Ca and other major chemical constituents in rainwater samples collected in the region where the highly alkaline soils were selected for investigation.

5.2 Materials and Methods

5.2.1 The investigated soils

Soil samples were obtained from Yelarbon, southern Queensland, Australia where previous investigations revealed the presence of highly alkaline soils with pH >10 (Biggs et al., 2010). Three soil profiles were selected and examined in details: (a) Soil Profile YP1 (0-80 cm), (b) Soil Profile YP2 (0-50 cm), and (c) Soil/Regolith Profile QMDSC (0-610 cm). Figure 5.1 shows the exact geographical locations of these three soil profiles.

Figure 5.1: Location map showing the soil sampling sites

The three sampling points are located less than 6 km apart from each other. Soil Profile YP2 was located within a pasture-cropped paddock that was subject to influences by agricultural practices, including application of gypsum. Soil Profile YP1 was situated at the north margin of an extensive area of barren land. Selected soil samples from Soil/Regolith Profile QMDSC were provided by the Queensland Department of Environment and Resource Management, Toowoomba. The location of this soil/regolith profile is less than two km apart from Soil Profile YP2. It was used in this study to obtain supplementary data on regolith materials occurring below the soil profile.

The sampling area is part of the alluvial plain along the north bank of the Macintyre Brook. The development of sodicity and alkalinity in the soils has been attributed to upward leakage of Great Artesian Basin groundwater along parts of a major fault (Fensham et al. 2007). The area is also affected by flood inundation during wet seasons.

5.2.2 Soil characterization

The soil samples were air-dried and then crushed to pass a 2 mm sieve. The gravel particles that did not pass the sieve were discarded. One to five (1:5) water extracts were prepared for determination of pH and water-extractable Sr, Ca, Mg, Na and K. A portion of each soil sample was pulverized for further chemical and instrumental analysis. The labile fraction of Sr, Ca, Mg, Na and K was extracted with 1 M acetic acid (CH_3COOH) and measured using an atomic absorption spectrometer (AAS). A wider range of elements (51 elements including Al, Ca, Fe, K, Mg, Na, Rb, S and Sr) were extracted by an aqua regia digestion method and measured by inductively coupled plasma mass spectrometry (ICP-MS). X-ray fluorescence (XRF) analysis was used to determine the total content of Al_2O_3, BaO, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, SrO and TiO_2. Total carbon was determined by a Skalar Primacs^{SNC} carbon and nitrogen analyzer. Organic carbon was determined using a Walkley–Black method (Maryol & Lin 2015; Nelson & Sommers 1982). The concentration of an element bound to silicate minerals was estimated by the difference between the total concentration (obtained from XRF analysis) and the labile fraction (acetic acid-extractable). The inorganic carbon content was estimated by the difference between the total carbon and the organic carbon.

$^{87}Sr/^{86}Sr$ ratio in the labile fraction and residual fraction of a soil sample was determined on a VG Sector 54 thermal ionization mass spectrometer (TIMS) at the University of Queensland. The labile fraction was extracted by leaching the soil samples with a 1 M acetic acid solution, and the residual fraction was extracted by digestion with HF and HNO_3. A modified procedure (Deniel & Pin 2001; Mikova & Denkova 2007; Pin & Zalduegui 1997) was used to separate Sr from the matrix using Sr-Spec resin. The purified solution was then loaded into a pre-degassed tungsten filament, and Sr isotope ratios were measured with a three-cycle dynamic protocol. The results obtained from 149 analyses of SRM-987 with samples since 2012 yielded a mean $^{87}Sr/^{86}Sr$ value of 0.710222 ± 20 (2σ standard deviation), which is used for normalization to previous laboratory long-term average by static analysis (0.710249 ± 28).

5.2.3 Rainwater sample collection and analysis

Nine rainwater samples were collected at a location (27° $35^{'}$ $28.7^{''}$S; 151° $46^{'}$ $08.98^{''}$) in Toowoomba, southern Queensland during March 2013. A pre-cleaned glass container was placed on a wooden stool (height: approximately 60 cm) in the open space. The rainwater samples were stored at $4^{o}C$ prior to chemical analysis. pH in the rainwater was measured using a calibrated pH meter. The concentrations of Sr, Ca, Mg, Na and K were determined by ASS. The concentrations of Cl and SO_4 were measured by ion chromatography (IC).

5.3 Results

5.3.1 Soil pH and inorganic carbon

The pH of Soil Profile YP2 ranged from 8.56 to 9.49 and showed a trend to increase with increasing depth. In contrast, Soil Profile YP1 had higher pH, as compared to Soil Profile YP2. There was no clear trend of vertical variation in pH for YP1. The inorganic carbon content tended to be higher in YP2 than in YP1 except for the surface soil layer (0-10 cm). It can be seen from Soil/Regolith Profile QMDSC that high pH extended at least to a depth of 6.1 m. The soil/regolith layer at a depth of 120-130 cm contained extremely high inorganic carbon (>5%). At a depth of 600-

610 cm, inorganic carbon was hardly detectable (Table 5.1).

5.3.2 ^{87}Sr/^{86}Sr ratio

The 87Sr/86Sr ratio of the labile fraction had a mean of 0.708109 with a range of 0.707654-0.708923, which was smaller than that of the residual fraction (mean: 0.711678; range: 0.708895-0.713828). There was no clear variation trend in 87Sr/86Sr ratio for the labile fraction along the soil/regolith profiles. However, 87Sr/86Sr ratio in the residual fraction tended to be greater in the surface soil layer (0-20 cm) than in the subsoil layer. There was a marked difference in the residual ^{87}Sr/^{86}Sr ratio between YP1 and YP2; the former had much higher values (Table 5.1).

Table 5.1: pH, inorganic carbon content and ^{87}Sr/^{86}Sr ratios of the three investigated soil profiles

Soil Profile	**Depth (cm)**	**pH**	**Inorganic C (%)**	**^{87}Sr/^{86}Sr (labile)**	**^{87}Sr/^{86}Sr (residue)**
YP1 **Longitude: 150° 45' 2.52"E** **Latitude: 28° 34' 49.65"S** **Altitude 250 m**	0-10	10.09	0.13	0.708792	0.713229
	10-20	10.19	0.15	0.708456	0.713828
	20-30	10.23	0.06	0.708210	0.712790
YP2 **Longitude:150.51.548** **Latitude: 28.31.6205**	30-40	10.16	0.1	0.707970	0.712553
	40-50	10.18	0.09	0.707813	0.712385
	50-60	10.17	0.1	0.707802	0.712860
	60-70	10.11	0.12	0.707950	0.712966
	70-80	10.2	0.06	0.707654	0.712540
	0-10	8.56	0.06	0.707865	0.709992
	10.2	9.19	0.3	0.707815	0.709160
	20-30	9.21	0.023	0.707841	0.708895
	30-40	9.46	0.78	-	-
	40-50	9.49	0.38	0.707839	0.708934
QMDSC **Latitude: 28.31.6205** **Longitude:150.51.548**	30-40	8.82	-	0.707829	-
	90-100	-	-	0.708148	-
	120-130	9.86	5.2	0.708923	-
	390-400	-	-	0.708615	-
	600-610	9.55	0.02	0.708326	-

Table 5.2: Chemical composition of the two contrasting soil profiles(YP1 and YP2)

Soil Profile	**Depth (cm)**	**Al_2O_3**	**BaO**	**CaO**	**Fe_2O_3**	**K_2O**	**MgO**	**Na_2O**	**SiO_2**	**SrO**
YP1	0-10	9.220	0.060	0.580	2.610	1.820	0.480	2.270	79.600	0.020
	10-20	11.300	0.060	0.410	3.470	1.970	0.620	1.860	76.500	0.020
	20-30	11.150	0.060	0.400	3.410	1.960	0.600	1.860	76.700	0.020
	30-40	11.300	0.070	0.350	3.420	2.000	0.590	1.780	76.700	0.020
	40-50	11.750	0.070	0.360	3.600	2.000	0.610	1.790	75.700	0.020
	50-60	10.800	0.070	0.370	3.220	1.960	0.520	1.740	77.600	0.020
	60-70	10.800	0.070	0.390	3.180	1.950	0.530	1.820	77.300	0.020
	70-80	10.900	0.070	0.320	3.220	1.980	0.520	1.740	77.500	0.020
YP2	0-10	6.470	0.030	0.490	2.490	0.370	0.590	0.530	83.000	0.010
	10.2	7.410	0.050	2.570	2.850	0.350	1.010	0.850	76.900	0.030
	20-30	6.960	0.080	4.840	2.620	0.330	1.120	0.900	73.800	0.060
	30-40	6.810	0.120	6.100	2.580	0.320	1.400	0.990	71.700	0.090
	40-50	7.060	0.110	4.460	2.680	0.330	1.200	1.000	74.700	0.070

5.3.3 XRF analysis results

There was a marked difference in the abundance of the major elements between Soil Profiles YP1 and YP2. YP1 tended to contain more Al, Fe, K, Na and Si and less Ca, Mg, Sr and Ba except for Ba, Ca, Si and Sr in the surface layer (0-10 cm)(Table 5.2).

5.3.4 Sr/Ca ratio in various soil fractions

The molar ratio of Sr to Ca (Sr/Ca) was highly variable among the soil samples for any of the three investigated fractions. The mean value of Sr/Ca was 176 (with a range of 0.2-463), 0.072 (with a range of 0.004-0.858) and 0.13526 (with a range of 0.0002-0.9296) for the water-extractable, acetic acid-extractable and residual fractions, respectively. The molar ratios of the water-extractable Sr to acetic acid-extractable Sr (Sr_w/Sr_{ace}) and the water-extractable Ca to acetic acid-extractable Ca (Ca_w/Ca_{ace}) were also highly variable among the samples. Sr_w/Sr_{ace} ranged from 1.669 x 10^{-3} to 4.435 x 10-1 (mean: 0.1638) and Caw/Caace ranged from 7.9 x 10-7 to 3.85 x 10-3 (mean: 0.0005) (Table 5.3).

5.3.5 Distribution of aqua regia-extractable elements along the soil profiles

There was marked difference in the abundance and vertical distribution of the aqua regia-extractable Al, Ca, Fe, K, Mg, Na, Rb, Sr and S between YP1 and YP2. YP1 tended to contain more Al, Fe, K, Na and Rb and less Ca, Mg, Sr and S than did YP2 (Figure 5.2). This was consistent with the XRF analysis results (not include Rb and S, which were under the detection limits of the XRF method). Ca, Mg, Sr and S had a high degree of similarity in the variation pattern along the soil profiles; YP1 showed little downward change while YP2 exhibited a marked increase from the surface to the depth of 30-40 cm and then a decrease to the sampling base (40-50 cm). This trend was more or less consistent with the vertical variation in inorganic carbon (Table 5.1).

5.3.6 Chemical composition of rainwater samples

The chemical composition of the rainwater samples is shown in (Table 5.4) Na, Mg and K were closely related to Cl and SO_4.In particular, there was a very close relationship between Na and Cl (R^2 = 0.9785) and the mean Na/Cl ratio was 0.698, which is close to that of seawater (0.86) (Thimonier et al. 2008) (Table 5.4). Sr was also related to Cl (R^2=0.6756) and SO_4 (R^2 = 0.7612). In contrast, Ca was only slightly related to Cl (R^2 = 0.2193) and SO_4 (R^2 = 0.4201). It is interesting to note that Sr was not related to Ca (R^2 = 0.0928) but fairly well related to Mg, Na and K (Table 5.5). The molar ratio of Sr to Ca ranged from 0.001039-0.042769, which depart markedly from that (varying from 0.008487 to 0.008612 across the oceans) of the temporary seawater (de Villiers 1999). The mean Sr/Ca molar ratio of the rainwater was 0.017513, which doubled that of the seawater.

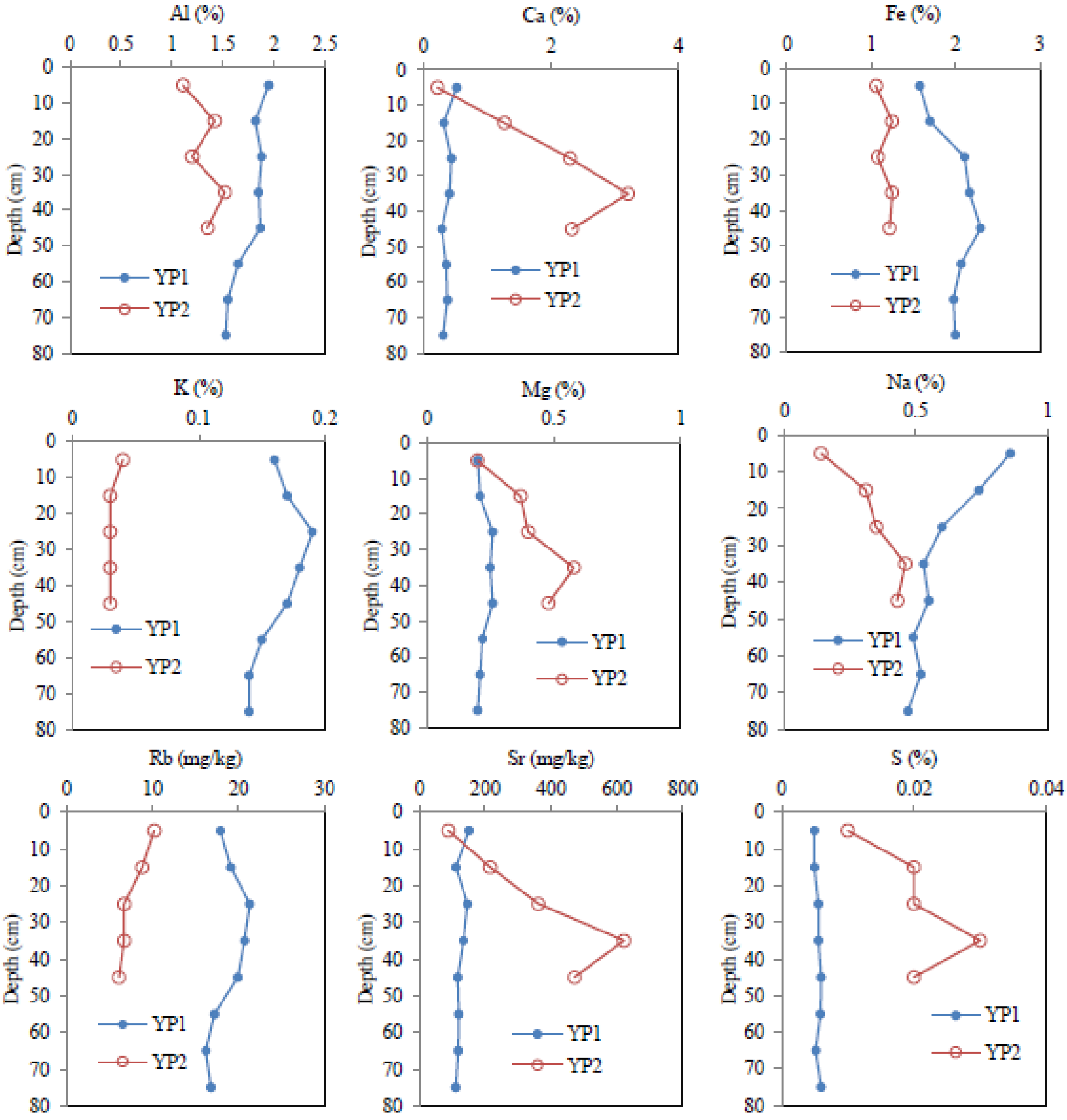


Figure 5.2: Vertical variation in a range of elements along the two selected soil profiles

Table 5.3: Strontium, calcium and their ration in various soil fractions for the three investigated soil/regolith profiles

Sample ID	**Depth (cm)**	**Water-extractable(mmol/kg)**			**Acetic Acid-extractable(mmol/kg)**			**Residual fraction (mmol/kg)**		
		Sr	**Ca**	**Sr/Ca**	**Sr**	**Ca**	**Sr/Ca**	**Sr**	**Ca**	**Sr/Ca**
YP1	0-10	0.091	0.001	121	1.424	33.75	0.042	0.506	1.000	0.5060
	Oct-20	0.262	0.001	349	1.225	42.72	0.029	0.706	30.49	0.0232
	20-30	0.248	0.001	331	1.812	45.41	0.040	0.118	26.02	0.0045
	30-40	0.255	0.001	340	0.575	25.63	0.022	1.355	36.87	0.0368
	40-50	0.016	0.001	20.8	0.702	22.5	0.031	1.229	41.79	0.0294
	50-60	0.0347	0.001	49.5	0.598	56.86	0.011	1.333	9.209	0.1447
	60-70	0.173	0.001	230	1.001	75.06	0.013	0.930	1.000	0.9300
	70-80	0.347	0.001	463	1.175	40.19	0.029	0.756	16.96	0.0446
YP2	0-10	0.502	0.012	41.8	1.248	35.39	0.035	0.010	52.11	0.0002
	10.2	0.44	1.04	0.42	1.125	269.6	0.004	1.7710	189.4	0.0094
	20-30	0.291	1.48	0.2	4.117	648.3	0.006	1.6750	215.9	0.0078
	30-40	0.258	0.762	0.34	3.39	668.2	0.005	5.2970	421.1	0.0126
	40-50	0.244	0.287	0.85	4.466	547	0.008	2.2900	249.5	0.0092
QMDSC	30-40	0.275	0.004	76.5	1.391	234.4	0.006	-	-	-
	90-100	-	-	-	-	-	-	-	-	-
	120-130	0.03	0.001	48.5	17.97	1261	0.014	-	-	-
	390-400	-	-	-	-	-	-	-	-	-
	600-610	0.36	0.001	256	21.5	25.07	0.858	-	-	-

Table 5.4: The concentration (mg/L) of selected ions in the rainwater samples collected during March 2013

	Sr	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO_4**
Sample 1	0.055	0.621	1.45	3.432	2.207	11.446	6.739
Sample 2	0.014	1.155	1.185	2.443	0.09	5.097	6.287
Sample 3	0.009	0.433	0.621	2.971	1.45	7.241	6.086
Sample 4	0.001	0.448	0.787	2.198	0.363	3.809	6.075
Sample 5	0.001	0.351	0.722	2.032	0.339	3.277	5.994
Sample 6	0.018	0.707	1.591	3.358	1.321	9.894	6.398
Sample 7	0.023	0.767	1.042	2.935	0.646	6.809	6.275
Sample 8	0.037	0.565	1.428	3.376	2.176	11.1	6.555
Sample 9	0.032	0.348	0.77	2.007	0.365	3.293	5.981

Table 5.5: Correlation matrix of the major chemical constituents in the rain water sample (n=9) in the southern Queensland region, Australia

	Sr	Ca	Mg	Na	K	Cl	SO_4
Sr	1.000						
Ca	0.0928	1.0000					
Mg	0.5994	0.5257	1.0000				
Na	0.5791	0.2742	0.7547*	1.0000			
K	0.6720*	-0.1192	0.5696	0.8736**	1.0000		
Cl	0.6756*	0.2193	0.8031**	0.9785**	0.9248**	1.0000	
SO_4	0.7612	0.4201	0.8809**	0.8517**	0.7774*	0.9095**	1.00

*Correlation is significant at the 0.05 level (2-tailed)
**Correlation is significant at the 0.01 level (2-tailed)

5.4 Discussion

Under highly alkaline conditions, it is unlikely that soil carbonates of atmospheric sources undergo dissolution (Equation 5.1) since any carbonic acid formed from the reaction between CO_2 and H_2O tends to be removed from the soil solutions by NaOH:

$$2NaOH + H_2CO_3 \rightarrow Na_2CO_3 + 2H_2O \qquad (5.7)$$

Therefore, any dust-derived carbonates received by the soils tend to be retained in the surface soil layer because H_2CO_3 that is required for dissolving the primary carbonates is not readily available (Equation 5.1), which prevents downward movement of carbonate-Ca from occurring. Clearly, the enrichment of pedogenetic calcium carbonates in the subsoil layers of YP2 and QMDSC cannot be convincingly explained by the reworking of the dust-derived carbonates. Furthermore, YP1 and YP2 are located less than 6 km apart from each other. Therefore it is likely that they received a similar level of atmospheric deposition inputs. However, YP1 only contained limited amounts of carbonates within the sampled profile (Table 5.1).

These observations suggest that there were more important factors that controlled the pedogenetic carbonation in the study area. Gypsum has been applied to the soils where YP2 is located (personal communication with the land owner). The good correspondence between Sulphur and Ca/inorganic carbon for YP2 appears to suggest that gypsum application played an important role in supplying soluble Ca for the pedogenetic carbonation if we use soil Sulphur as a tracer for gypsum.

It is also interesting to note that there was a good relationship between the silicate-Ca fraction and labile Ca fraction for the investigated soils (Figure 5.3a), suggesting a possible link between the Ca released from in-situ silicate weathering and the Ca incorporated into pedogenetic carbonates. There was also a good relationship between silicate-Mg fraction and labile Mg fraction (Figure 5.3b). However, the relationship between silicate-Sr and labile Sr was poor (Figure 5.3c), suggesting that Sr might actually behaved differently from Ca during the weathering of the silicate minerals. The concentration of Rb was much greater in YP1 than in YP2, which can be attributed to the K silicate-enriched nature of YP1 since Rb tends to substitute for K in silicate minerals (Salminen et al. 2005). The higher 87Sr/86Sr of the residual fraction in YP1 than in YP2 probably reflects the greater input of 87Sr from the decay of 87Rb in the former than in the latter. It is worthwhile to note that a large proportion of the labile Sr pool was in water-extractable form (>16%) while the water-extractable Ca fraction only accounted for about 0.05% of the labile Ca pool (Table 5.3). This indicates that the water-soluble Ca tended to be preferentially immobilized, as compared to the water-soluble Sr. Our results are consistent with what was observed by (Khaleghpanah et al. 2010), suggesting that the soluble Sr is less competitive than the soluble Ca for occupying the binding sites in the soils.

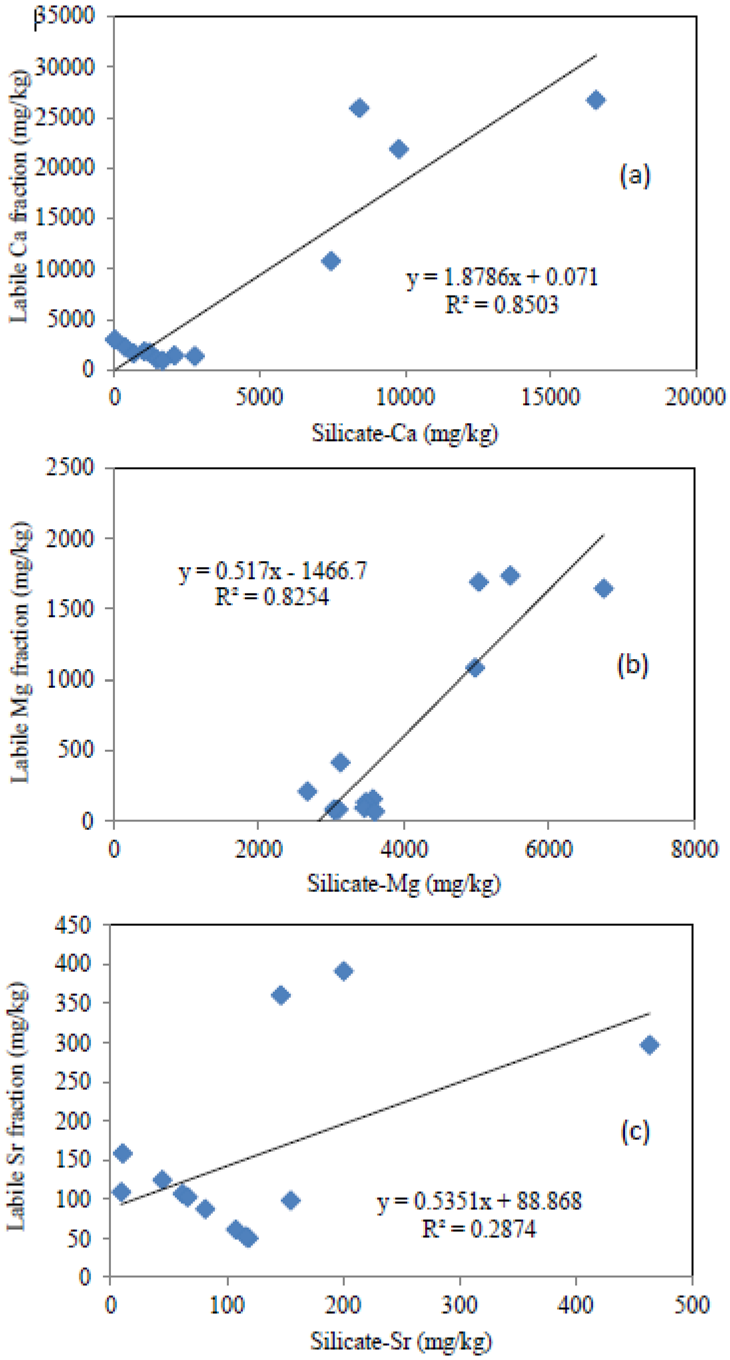


Figure 5.3: Relationship between (a) labile Ca fraction and silicate-Ca fraction, (b) labile Mg fraction and silicate-Mg fraction, and (c) labile Sr fraction and silicate-Sr fraction in the investigated alkaline soils

The extremely low level of soluble Ca in the soils may be attributable to the strong capacity of the highly alkaline materials to scavenge Ca, as expressed by the following equations:

$$Ca^{2+} + 2NaOH \rightarrow Ca\,(OH)_2 + 2Na^+ \qquad (5.8)$$

or

$$Ca^{2+} + 2NaOH + H_2O + CO_2 \rightarrow CaCO_3 + 2H_2O + 2Na^+ \qquad (5.9)$$

Equation 5.9 has implications for sequestration of atmospheric CO_2 and simultaneous reduction of soil sodicity and alkalinity for improving plant growth conditions, as in the case of gypsum applications.

The extremely variable Sr/Ca ratio in both the water-extractable and labile fractions Table 5.3 suggests that Ca and Sr had very different chemical behaviors in the investigated soils. Wiegand et al. (2005) investigated Ca cycling and isotopic fluxes in forested ecosystems in Hawaii and found that there were considerable differences in the biogeochemical behaviour of Ca and Sr that led to divergent pathways of the two elements in the plant-soil system.

The $^{87}Sr/^{86}Sr$ ratio of the labile fraction in the investigated soils fell within a range that was similar to the contemporary seawater (Burke et al. 1982; Jones & Jenkyns 2001) which may suggest that the labile Sr fraction in the soils under investigation was predominantly of marine source. This appears reasonable because the study area is in close proximity to the ocean and received rainwater (directly or indirectly from surface runoff) formed by condensation of atmospheric water vapour that was predominantly supplied by evaporation from the ocean surface (Hendon et al. 2007). However, the poor relationship between Sr and Ca in the rainwater indicates that these two elements behaved differently during the course of transport from the ocean surface to the land surface. The marked fractionation between Sr and Ca in the water-extractable and labile fractions strongly suggests that Sr was not a reliable surrogate for Ca in the investigated soil systems. Therefore, despite that the data on $^{87}Sr/^{86}Sr$ ratio of both labile and residual fractions were comparable with those reported by the previous authors (Chiquet et al. 1999; Dart et al. 2007; Hamidi et al. 2001; Van der Hoven & Quade 2002), they do not make reliable inference about the actual source of Ca for pedogenetic carbonation in these soils.

5.5 Conclusion

Calcium and strontium are behaved differently in the investigated highly alkaline soil system. There was also a marked difference in geochemical behaviour between the two elements during the course of atmospheric transport from the ocean surface to the land surface. Therefore, $^{87}Sr/^{86}Sr$ provided no reliable indication of the Ca source to form pedogenetic carbonates in the investigated alkaline soils. This raises concerns over the suitability of strontium isotopic signatures in tracing Ca source for pedogenetic carbonation in alkaline soils.

Chapter 6 : Evaluation of Atmospheric CO_2 Sequestration by Alkaline Soils through Simultaneous Enhanced Carbonation and Biomass Production

6.1 Introduction

Alkaline soils are referred to as the soils with a high pH (Van Beek & Van Breemen 1973). These soils have the potential to sequester CO_2 according to the following chemical equation:

$$M^{2+} + 2OH^{-} + CO_2 \rightarrow MCO_3 + H_2O \qquad (6.1)$$

M^{2+} in the above equation represents a divalent metal that can combine with CO_3^{2-} to form stable metal carbonates. In the Earth's surface environments, Mg and Ca are two such binding major cations that are present at substantial amounts under oxic conditions. Other binding metals are practically less important in terms of mineral carbonation for CO_2 sequestration. Under alkaline conditions, the available soluble Ca^{2+} and Mg^{2+} tend to be removed from the soil solution to form solid carbonate minerals (Equation 6.1) therefore, the proportion of soluble Na^+ in the soils increases, which may lead to soil sodification and the formation of alkaline sodic soils (Pessarakli 1991; Singh et al. 2013). The maintenance of high pH in alkaline soils indicates that the supply of binding divalent metals is limited. Therefore, addition of substances containing soluble divalent metals into alkaline soils is likely to facilitate sequestration of atmospheric CO_2.

Application of gypsum and other calcium-containing materials is a common agricultural practice to ameliorate sodic soils by reducing the exchangeable sodium percentage (ESP) (Chawla & Abrol 1982; Hanay et al. 2004; Mace et al. 1999). Substantial amounts of research have been conducted to examine the effects of gypsum application on correcting soil sodicity and consequently enhancing crop growth (Abdel-Fattah 2012; Hamza & Anderson 2003; Rasouli et al. 2013). However, there has so far been no work reported with a focus on atmospheric CO_2 sequestration associated with these agricultural practices. The application of gypsum or other Ca and Mg-bearing materials to alkaline soils could result in fixation of atmospheric CO_2 by both carbonate formation and organic matter production, which has implications for mitigating climate change. The potential carbon credit benefit from the amendment of alkaline soils may become a factor for consideration when developing plans for alkaline sodic soil reclamation. This is particularly relevant to situations where irrigation water becomes available from groundwater exploitation(Gijsbers & Loucks 1999) or where there is a need for groundwater disposal due to e.g. coal seam gas extraction operations (Hamawand et al. 2013). Evaluation of carbon credit from the uses of improved alkaline soils for biomass production will provide useful information that can be used to assist in performing cost-benefit analysis for alkaline soil reclamation projects.

This chapter aims to (a) examine the effects of gypsum application rate on carbon dynamics and alkalinity reduction in the test alkaline soil; (b) compare the effects of various Ca- and Mg-bearing materials on pedogenic carbonation, and (c) compare the effects of gypsum application-derived reduction in the alkalinity on the biomass production, and consequently carbon sequestration among different plant species.

6.2 Materials and methods

6.2.1 Study area description

The alkaline soil material used for various experiments was collected from Yelarbon, southern Queensland- Australia. Yelarbon area was initially settled in the 1840s. It is located on (28° 34' 20.3" S, 150° 45' 10.1" E). It was a part of a large essentially unfenced pastoral field (Breazeale 1927). It covers an approximate area of 34.4 km^2 and it is locally called “Desert”. Despite its local name, the climate is sub humid, receiving a mean annual rainfall of 595mm, most of this falls during summer months. The nearby town of Goondiwindi has mean monthly minimum temperatures between 4.9°C and 20.1°C and mean monthly maximum temperatures between 18.1°C and 33.4°C. The area has low relief and lies to the north of the junction of Macintyre Brook and the Dumaresq River, the latter forming the Queensland-New South Wales state border .

6.2.2 The experimental materials

Approximately 190 kg of the soil material was taken from the upper 30 cm of the soil profile. In the laboratory, the soil material was air-dried and crushed to pass a 2 mm sieve. Gravel particles greater than 2 mm were discarded. The <2mm soil fraction was thoroughly mixed. The soil sample had a pH of 10.2 and a value of electrical conductivity (EC) of 1.366 dS/m (1:5, soil: water extract). The soil contained no detectable soluble Ca. Soluble concentration of Na, K and Mg was 1190, 107 and 19 mg/kg, respectively. Agricultural gypsum ($CaSO_4 \bullet H_2O$) and powdered talc ($Mg_3Si_4O_{10}(OH)_2$) used for the incubation experiments were purchased from commercial sources. The gypsum product had a purity of 67%. Aquasol soluble fertilizer used for the growth experiment contained 23% of nitrogen, 3.95% of phosphorus,14% of potassium,6.6% sulphur,0.15% of magnesium, 0.13% of manganese, 0.06% of copper (Cu), 0.06 of iron, 0.04% of zinc,0.01% boron, and 0.001 of molybdenum. Calcium chloride and magnesium chloride used in the experiments were of analytical reagent grade.

Ultrapure water (18.2 MΩ/cm) was used throughout the entire course of the laboratory incubation experiments. For the greenhouse plant growth experiment, five grass species were used in the experiment (Table 6.1). Seeds of the grass species were purchased from commercial source.

Table 6.1: Five grass species and their sowing rates used in the experiment

Common name	**Scientific name**	**Sowing rate(Kg/ha)**	**C4/C3 plants**	**Gypsum (Kg)**	**Sodic/alkaline soil weight(kg)**
Gatton panic	*Panicum- maximum*	2-4kg/ha	C4	1.725	30.81
Bambatsi panic	*Panicum- coloratum*	2-4kg/ha	C4	1.725	30.81
Digit grass	*Digitaria- eriantha*	1-2kg/ha	C4	1.725	30.81
Rhodes grass	*Chloris- gayana*	2-4kg/ha	C4	1.725	30.81
Blue grass	*Bothriochloa- insculpta*	1-2kg/ha	C3	1.725	30.81

6.2.2. Experiment 1: Effect of gypsum dosage on CO_2 sequestration

The alkaline soil material was amended with gypsum at varying application rates. Six treatments were set with 500 g of the soil material being mixed with the gypsum at the following rate: 0.5, 1.5, 2.5, 4.5, 7, 9 and 11.5%. The amended soil of each treatment was placed in a plastic container with dimensions of 19.5 cm (length) x 12 cm (width) x 6 cm (height). The soil material with no added gypsum was used to serve as the control of the experiment. At the beginning of the experiment, the soils were saturated with deionized water and then exposed to ambient air. An appropriate amount of deionized water was added to the soil in each incubation chamber to compensate soil water loss due to evaporation at times when the surface soil layer dried out. Pre-experiment test showed that soil pH tended to become stable after initial drop within 25 days for all the treatments. Therefore, the duration of the incubation experiment was set at 30 days to ensure that the equilibrium for the reaction (Equation 1) was approached. The experiment was run in triplicate. At the end of the experiment, the soil in each incubation chamber was air-dried, crushed and homogenized. A sample from each incubation chamber was used to determine pH, organic carbon, total carbon, and water-extractable and exchangeable basic cations (Ca, Na, Mg and K).

6.2.2. Experiment 2: Comparison among different Ca- or Mg-containing materials

This experiment was to examine the effects of four different treatments on CO_2 sequestration by the alkaline soil material: (a) Treatment 1 (T1) addition of powdered talc, (b) addition of gypsum, (c) addition of $MgCl_2$, and (d) addition of $CaCl_2$. Two hundred mL plastic beakers were used as incubation chambers. In each of the incubation chamber, 20 g of soil was thoroughly mixed with an appropriate amount of a relevant additive to achieve an application rate of divalent cation (Ca^{2+} or Mg^{2+}) at 230mmol/kg. The amended soil was then placed in the incubation chamber, followed by saturation with deionized water. The soils were exposed to ambient air for three weeks before being harvested for various chemical analyses. During the period of the experiment, an appropriate amount of water was added into the soil to compensate water loss due to evaporation. A “soil only” treatment served as the control and the experiment was in triplicate.

6.2.2. Experiment 3: Effect of gypsum on plant biomass production

A one-year microcosm experiment was conducted from January to December 2013. Plastic buckets with dimensions of 79cm (length) x 39 cm (width) x 35.5 cm (height) were used as growth chambers for the five test grass species. In each bucket, a growth medium was formulated by thoroughly mixing 1.725 kg of gypsum with

30.81 kg of soil. Appropriate amounts of seeds were sown following the supplier's instruction (refer to Table 6.1).

Each of the test plants was grown in a separate growth chamber and all the plant species were subject to the same watering and fertilizing schedule during the entire period of the experiment. An un-vegetated bucket containing the soil with no added gypsum was used as the control. The growth chambers were randomly placed in a greenhouse during the entire period of the experiment.

The above-ground portion of the plants was harvested on the 66th and 190th day of the experiment to determine the biomass of each plant species, as well as Ca, Na, Mg and K in the plant tissues. On the same days, soil samples were also collected to determine major soil parameters, including pH, EC, total carbon, and various basic metals. In each growth chamber, nine subsamples were taken from different spots to form a composite sample. Each subsample was collected using a plastic pile, which was inserted into soil from the top to the bottom. On the 336th day of the experiment, the whole plant of each bucket was harvested to determine the biomass of both above-ground and below-ground portions. The carbon content in the plant tissues was also determined. The soil in each bucket was completely mixed and then 1 kg of the soil sample was taken for analysis.

6.2.3 Analytical methods

Both 1:5 (soil: water) and 1:5(soil: 1 M NH4Cl) extracts were prepared. The pH and EC in the water extracts were determined using a calibrated pH and EC meter, respectively. Cations in the water and NH_4Cl extracts were determined by atomic absorption spectrometry. Soluble K, Na, Ca and Mg were estimated from water-extractable K, Na, Ca and Mg, respectively. Exchangeable K, Na, Ca and Mg were obtained by the difference between water-extractable K, Na, Ca and Mg and NH_4Cl-extractable K, Na, Ca and Mg, respectively. Soil organic carbon was determined by a Walkley-Black method (Nelson & Sommers 1982). Total carbon in the soil was measured by a PrimacsSNC carbon and nitrogen analyser. Carbon content in the plant dry biomass was measured by a LECO CNS analyzer. Na, K, Ca and Mg in the plant tissue samples were measured following the method described in (Faithfull 2002).

6.2.2.1 Preparation of plant sample solution by dry combustion

A 0.5 g dried grass sample was transferred, grounded to 1 mm, and placed into a silica basin; then placed in a cool muffle furnace, and the temperature was increased to 500°C, which was maintained overnight (Faithfull 2002). The resulting ash should be whitish-grey. Ten ml of approximately 6 M HCl, was added. The basin was placed on a water-bath and the solution evaporated to dryness. When dry, heating was continued for 1 hr either on top of the water bath or in it. The residues were moistened with 2 ml of hydrochloric acid approximately 36% m/m and gently boiled for 2 min. Approximately 10 ml of water were added and the solution again boiled. Remove the watch glass and rinse into the basin. Content of the basin was transferred into a 50-ml volumetric flask and diluted to the mark with water and mixed. The solution was then filtered through a 90-mm Whatman No. 541 filter paper, the first few millilitres were rejected, and the remainder retained for analysis in a polythene sample tube. A blank extraction was performed. Suitable determinations include Ca, K, Mg, Mn, P and Na.

6.3 Results and Discussion

6.3.Experiment 1: Effect of gypsum dosage on CO_2 sequestration

As expected, the addition of gypsum into the soils caused a drop in soil pH (Figure 6.1a). With a gypsum dose of >1.5%, the soil pH decreased to around 8.5, which is characteristic of the soils containing calcium carbonates (Leytem & Mikkelsen 2005; Panigrahy & Raymahashay 2005). In this incubation experiment, a gypsum dose of 0.5% only resulted in a decrease in soil pH from 10.2 to 9.6, which is still inhibits the growth of most plants (Miller & Donahue 1990).

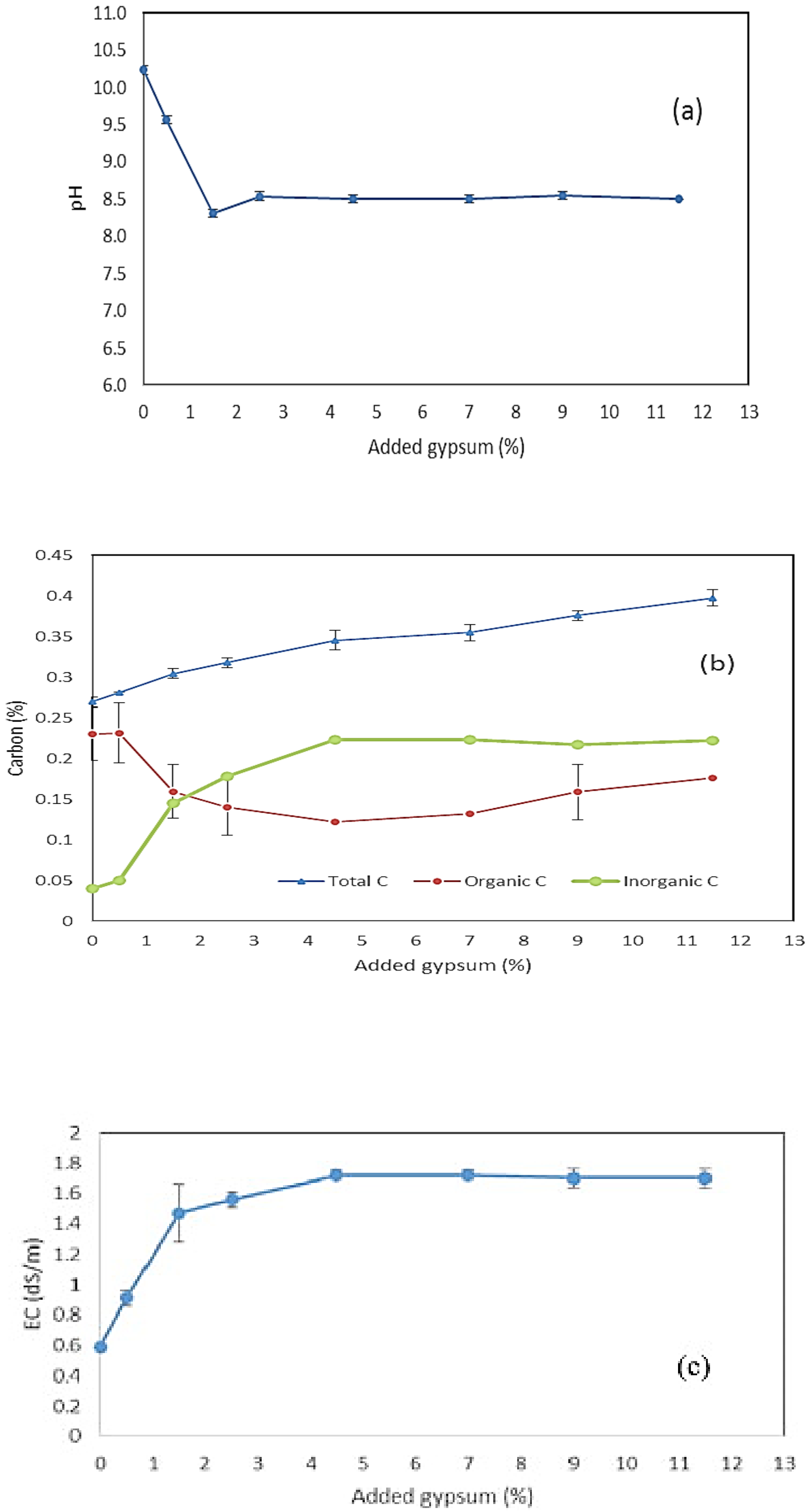


Figure 6.1: Gypsum application rate versus (a) soil pH and (b) total carbon, organic carbon and inorganic carbon, electrical conductivity EC in the soils

There was a clear trend showing the increase in total soil carbon with increasing dosage level of gypsum (Figure 6.1b). However, this cannot be completely attributable to the formation of carbonates since increase in inorganic carbon content with increasing dose of gypsum only held up to a rate of 4.5%. After this point, the variation curve reached a plateau (Figure 6.1b), suggesting that further increases in the gypsum dose had no effects on CO_2 sequestration.

It is interesting to note that soil organic carbon content was greater in the control than in all the treatments except for the lowest-dose treatment (0.5%) (Figure 6.1b). This suggests that addition of gypsum enhanced the decomposition of organic matter present in the soil, possibly through increased microbial activities as a result of improved pH conditions (DeLaune et al. 1981). The rate of organic matter decomposition increased from the 0.5% treatment to the 4.5% treatment and then decreased to the highest-dose treatment (11.5%). This suggests that while the reduction in soil alkalinity favoured microbially mediated degradation of organic matter the addition of excessive amounts of gypsum disfavoured organic matter decomposition. This may be due to the increase of soil salinity associated with the release of exchangeable sodium, which inhibited microbial activities (Table 6.2) (Batra & Manna 1997; Elgharably & Marschner 2011; Rietz & Haynes 2003). However, EC value did not show a trend to increase with increasing gypsum dose after the 4.5% point (Figure 6.1c). This appears to suggest that other factors may play a more important role in inhibiting microbially mediated decomposition of organic matter.

The addition of gypsum led to increase in both soluble and exchangeable Ca; there was a clear trend that exchangeable Ca increased with increasing dosage of gypsum (Figure 6.2a). In contrast, exchangeable Na showed a general trend to decrease with increasing gypsum dose, which was accompanied with a sharp increase in soluble Na up to the point of 2.5% treatment (Figure 6.2b). This reflects the release of Na from the surfaces of negatively charged colloids due to cation exchange reactions involving displacement of exchangeable Na by dissolved Ca from the added gypsum. The sudden increase in soluble Na was responsible for the elevated soil salinity, which could adversely affect soil microbial activities and plant growth (Luan, Sheng et al. 2009).

Gypsum addition also caused increase in soluble and exchangeable Mg (Figure 6.2c). This may be due to displaced of Mg by Ca and introduction of Mg from application of gypsum, which only had a purity of 67%. Addition of gypsum tended to reduce the level of soluble K and increase the level of exchangeable K (Figure 6.2d). The reason for this is not known.

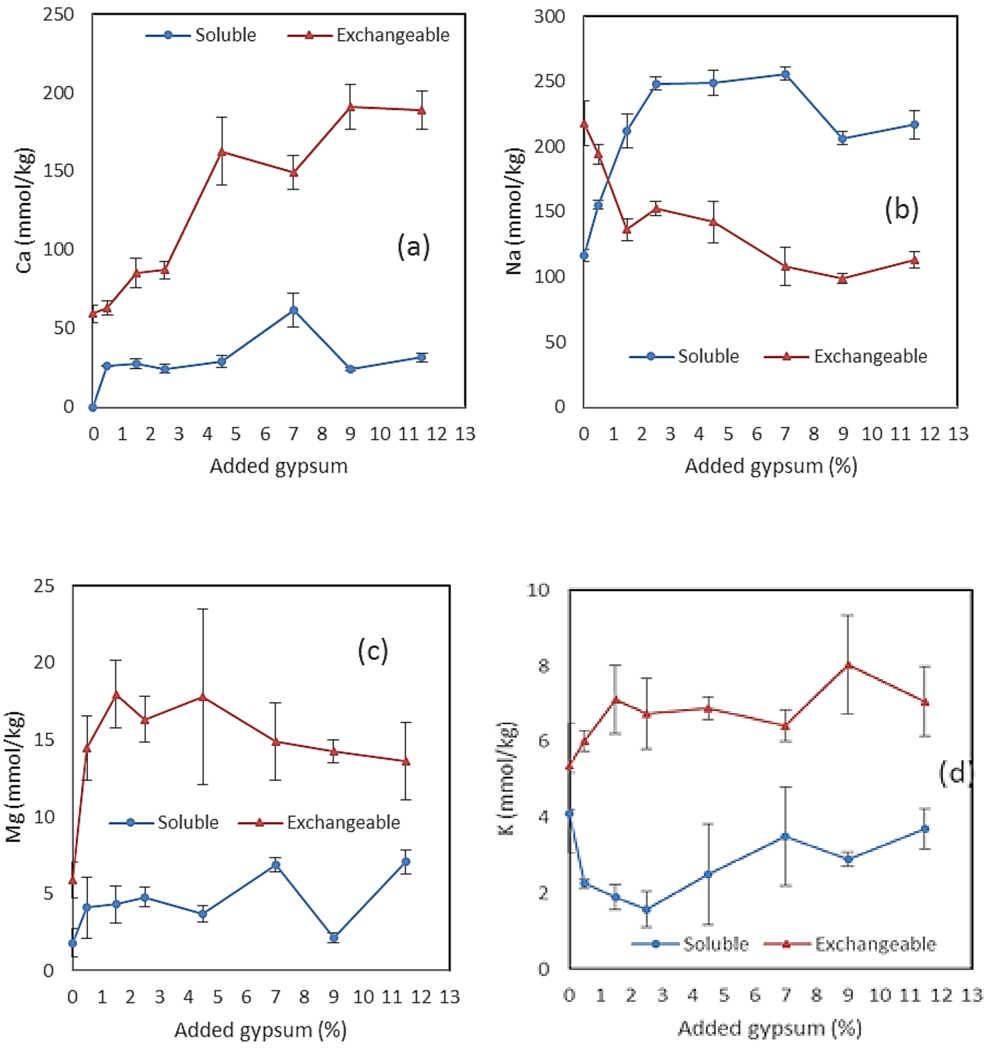


Figure 6.2: Gypsum application rate versus (a) soluble and exchangeable Ca, (b) soluble and exchangeable Na, soluble and exchangeable Mg, and (d) soluble and exchangeable K in the soils

6.3. Experiment 2: Effects of different Ca- or Mg-containing materials on atmospheric CO_2 sequestration

There was no significant ($P > 0.05$) difference in the total carbon between the control and the talc-amended soil (Figure 6.3), indicating that addition of talc had no significant effect on atmospheric CO_2 capturing. This suggests that under the experimental conditions set in this study, the talc powders were not sufficiently reactive in terms of sequestering CO_2. Addition of gypsum, $MgCl_2$ and $CaCl_2$ into the soils all significantly ($P < 0.05$) increased the total soil carbon content. Although the total carbon in the soil showed the following decreasing order: $CaCl_2$-treated > gypsum-treated > $MgCl_2$-treated, there was no statistically significant ($P > 0.05$) difference in total carbon among these three treatments (Figure 6.3a). This suggests that the uses of base-neutralizing agents that are more soluble than gypsum are not necessary in order to achieve a similar carbon sequestration effect.

The application of $MgCl_2$ and $CaCl_2$ resulted in a dramatic increase in EC value (Table 6.3b), indicating a marked increase in soil salinity. This could cause problems with plant growth. Consequently, gypsum is superior to the more soluble $MgCl_2$ and $CaCl_2$ in terms of alkaline sodic soil reclamation. For this reason, $MgCl_2$ and $CaCl_2$ were not further used for the plant growth experiment.

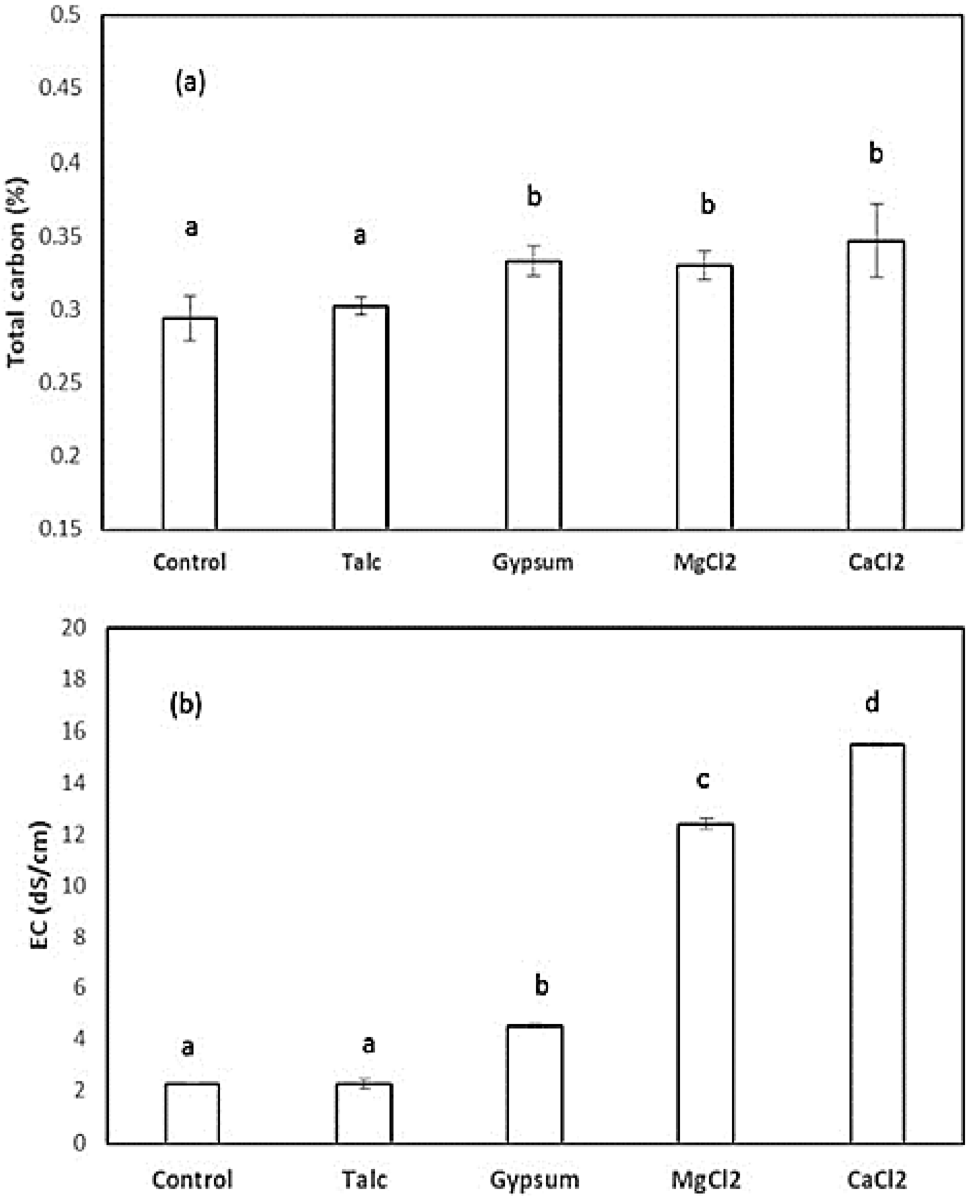


Figure 6.3: Comparison of (a) the total soil carbon and (b) electrical conductivity between the control and the treatments with different Ca/Mg-containing materials after incubation for three weeks. Means with different letters above the bars indicate that there was a statically significant difference ($P < 0.05$) between the two treatments.

6.3. Experiment 3: Effect of gypsum on plant biomass production

In general agreement with the results obtained from the soil incubation experiment (Experiment 1), the addition of gypsum resulted in a decrease in pH and an increase in soil salinity, as indicated by EC in the plant growth experiment (Table 6.2). However, the soil pH in the growth experiment was almost one unit lower than that in the “no plant” soil incubation experiment (refer to Figure 6.1a). This can be attributed to the acidifying effects of organic acid exudates from the plant roots (Dakora & Phillips 2002). In addition, the enhanced microbial activities in the vegetated soils might result in the generation of organic acids as a result of enhanced biodegradation of organic matter.

Table 6.2: pH and EC in the soils measured at various harvest events in the control and different treatments

Parameter	Treatment	1st harvest	2nd harvest	3rd harvest
pH	Control	10.23±0.06	9.88±0.47	9.85±0.50
	Gatton panic	7.63±0.04	7.22±0.03	7.54±0.08
	Bambatsi panic	7.47±0.04	7.26±0.02	7.57±0.04
	Digit grass	7.39±0.01	7.06±0.08	7.64±0.06
	Rhodes grass	7.45±0.07	7.41±0.09	7.31±0.02
	Blue grass	7.27±0.04	7.55±0.07	7.31±0.02
EC (dS/m)	Control	1.27±0.01	1.44±.020	1.69±0.05
	Gatton panic	3.48±0.04	4.13±0.02	4.58±0.04
	Bambatsi panic	3.85±0.07	4.19±0.3	3.93±0.06
	Digit grass	3.14±0.03	2.76±0.06	3.46±0.06
	Rhodes grass	3.95±0.07	4.08±0.12	4.16±0.05
	Blue grass	3.91±0.02	3.46±0.06	4.48±0.06

The dry biomass of the five different grass species grown in the amended soils varied markedly with Digit grass having the highest productivity in all the three harvest events (Figure 6.4). As shown in Experiment 1, addition of gypsum resulted in desorption of exchangeable Na. In spite of improved pH conditions, the elevated concentration of soluble Na in the gypsum-amended soils could be toxic to the plants and therefore become a constraint to the growth of plants(Luan, S. et al. 2009). This explains the observed poor growth performance for all the test plant species except for Digit grass, which was well adapted to the soluble Na-rich conditions.

The Na concentration in the shoots was much lower in the Digit grass than other grass species (Figure 6.5), indicating that the Digit grass was able to limit the transport of Na to the shoots and consequently reduce Na toxicity to the plant leaves.

Comparison among the control and various treatments revealed that amendment of the alkaline soil for plant growth tended to increase total soil carbon content.

This is particularly evident for the treatment with the highest-yielding Digit grass, which showed a trend to increase total soil carbon content over time, and at the end of the experiment, it had the highest total soil carbon content among the treatments. However, mixed temporal variation patterns were observed for different grass species (Figure 6.6). This indicates the high complexity of carbon dynamics in the amended soils. The carbon status was likely to be shaped by interaction of various processes, including carbonation by gypsum application, dissolution of carbonates by organic acids secreted from plant roots (Qadir et al. 2007), microbial decomposition of organic matter due to improvement of soil conditions and organic inputs from the growing plants.

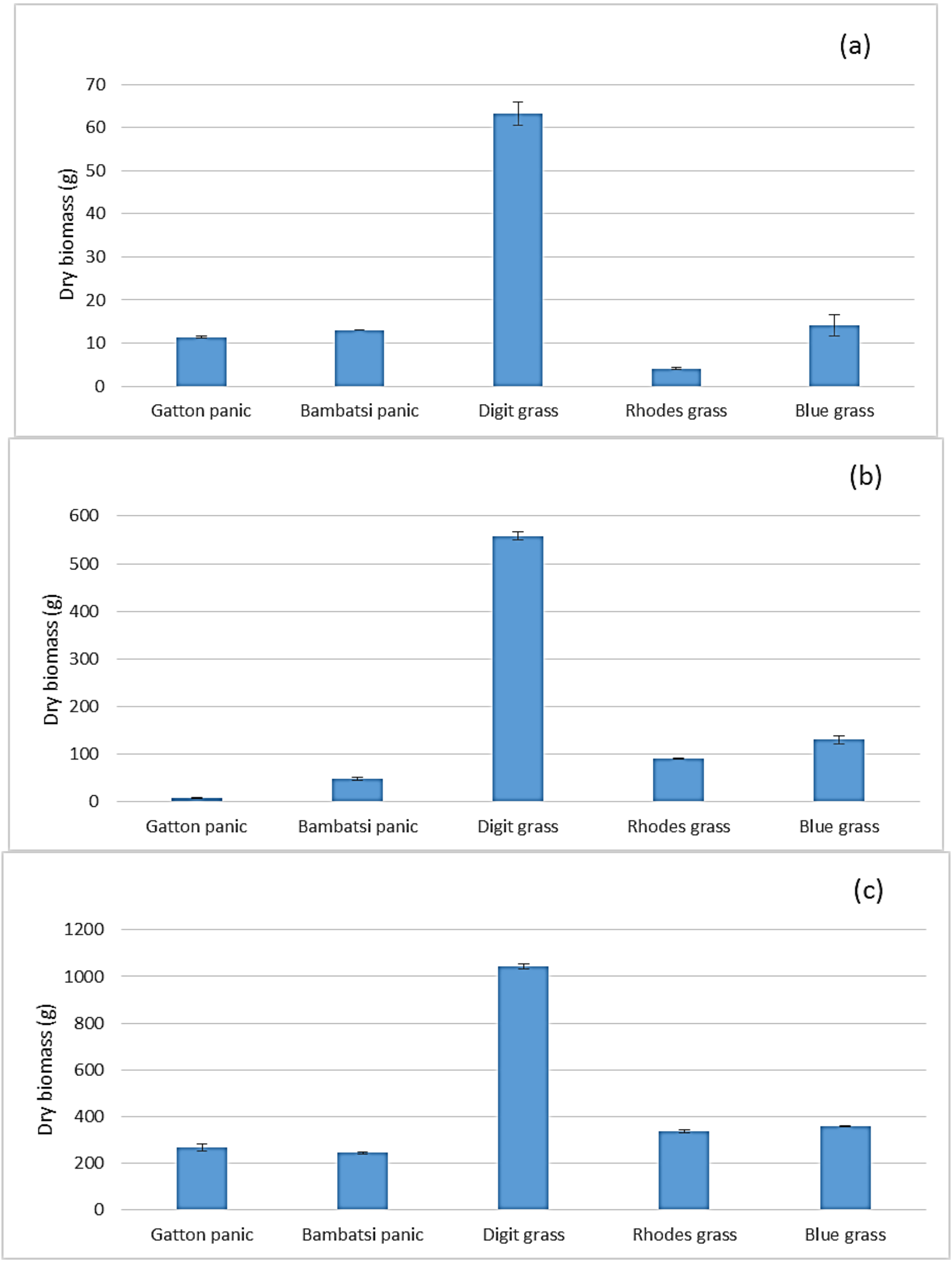


Figure 6.4: Comparison of dry biomass among the five test grass species at (a) the 1st harvest, (b) 2nd harvest, and (c) 3rd harvest events

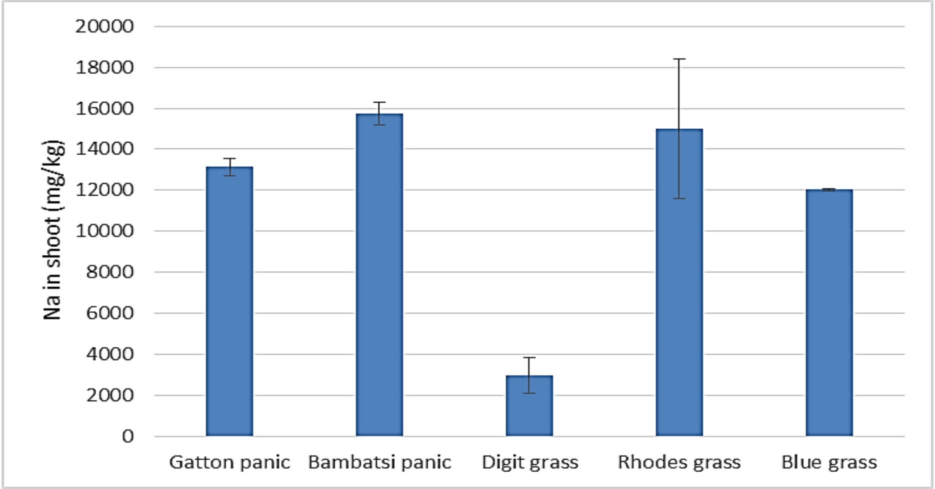


Figure 6.5: Comparison of Na concentration in the shoot (on a dry weight basis) among the five test grass species

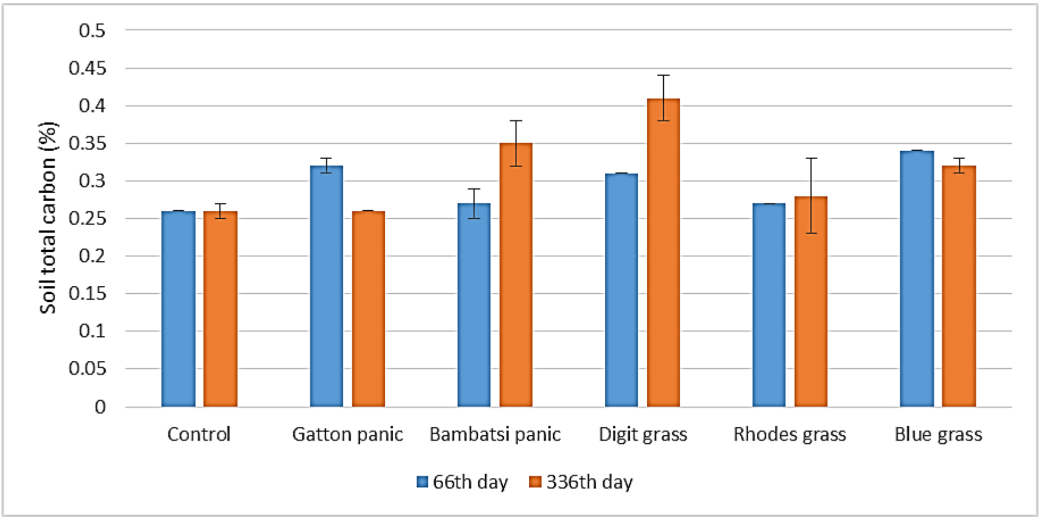


Figure 6.6: Soil total carbon measured on the 66th and 336th day of the experiment in the control and the five plant growth treatments.

6.3.4 Evaluation of atmospheric CO_2 sequestration potential

The estimated carbon stock in the biomass produced during the one-year greenhouse experiment for the five different plant growth treatments is shown in (Table 6.3). It ranged from 120 to 721g per growth chamber. In contrast, the soil carbon gain for these five different plant growth treatments (in the range of 0-43 g) at the end of the growth experiment was much smaller, as compared to total biomass carbon gain. The cultivation area of the growth chamber was approximately 0.3 m^2, which gives a calculated atmospheric CO_2 sequestration gain of 15, 23, 93, 28 and 28 metric tonnes per hectare for the treatments with growing Gatton panic, Bambatsi panic, Digit grass, Rhodes grass and Blue grass, respectively. Highly alkaline soils such as the soil used in this experiment do not support plant growth under unamended conditions. Therefore, the sequestration of CO_2 as a result of soil improvement for plant growth can be viewed as a carbon credit that adds value to an alkaline soil reclamation project as long as the annual above-ground biomass productivity can be maintained. The ratio of shoot to root (shoot: root) at the 3rd harvest was 2.59, 2.49, 4.56, 2.51 and 2.71 for Gatton panic, Bambatsi panic, Digit grass, Rhodes grass and Blue grass, respectively. This is comparable to the shoot: root ratios in the first year for perennial grasses observed by other authors (Bolinder et al. 2002; Pietola & Alakukku 2005). Long-term field experiments revealed that shoot: root tends to decrease over time as a result of continuous root development (Bolinder et al. 2002; Kätterer et al. 2011). Therefore, it is expected that root biomass will continue to increase over time.

In this experiment, the above-ground portion of plants was removed from the system and thus contributed insignificantly to the accumulation of soil organic carbon. This simulates the hay production scenarios. If the land is used for grazing, a large proportion of the shoot biomass may eventually contribute to the annual input of soil organic matter(Baldock 2008).Franzluebbers (2005) reported an annual increase in soil organic carbon at a rate greater than one metric tonne per hectare in the pasture land.

Table 6.3: Various parameters used to calculate the total carbon gain for the treatments with five plant species

Plant species	Gatton panic	Bambatsi panic	Digit grass	Rhodes grass	Blue grass
Shoot biomass*[1] (g)	288	306	1664	432	503
Root biomass*[2] (g)	103	98	229	134	132
Total biomass*[3] (g)	391	404	1893	566	635
Carbon content*[4] (%)	31	41	38	39	33
Biomass carbon*[5] (g)	120	165	721	223	210
Soil carbon gain*[6] (g)	0	25	43	5	17
Total carbon gain*[7] (g)	120	190	764	228	227

*[1]Sum of shoot dry biomass obtained from the three harvest events
*[2]Root dry biomass measured at the 3rd harvest
*[3]Sum of shoot and root biomass
*[4]Carbon content in the shoot tissue measured at the 3rd harvest
*[5]= carbon content x total biomass
*[6]= (soil carbon in treatment – soil carbon in the control) x 300
*[7]Sum of biomass carbon and soil carbon gain

6.4 Conclusions

Under the experimental conditions set for this study, application of gypsum to the highly alkaline soil caused an increase in inorganic carbon and a decrease in organic carbon. Mg-containing talc did not have a significant effect on soil carbonate formation while soluble $CaCl_2$ and $MgCl_2$ were similar to gypsum in terms of facilitating pedogenic carbonation. Plant growth tended to complicate pedogenic carbonation; the organic acids secreted from plant roots were likely to cause dissolution of soil carbonates. Biomass production played a much more important role in atmospheric CO_2 sequestration, as compared to soil carbonation. However, the biomass carbon gain varied markedly among the five different grass species. Plant species adapted to the soluble Na-dominated soil conditions tends to produce much more biomass carbon and enhance the accumulation of soil organic carbon. The Digit grass used in the plant growth experiment has demonstrated an estimated CO_2 sequestering capacity of 93 t/ha. The research findings obtained from this study have implications for cost-benefit analysis of alkaline soil reclamation projects.

Chapter 7 : Conclusions and Recommendations

7.1 Conclusions

The research outcomes generated from various themes investigated in this study allow the following general conclusions being drawn.

I. Some conclusions regarding the geochemistry of alkaline soils in the Fezzan region, Sahara Desert, Libya are:
    - The total carbon storage in the investigated soils was generally low (<1%) with the organic carbon mainly originated from the soil parent materials (lake sediments).
    - There was only a limited amount of inorganic C present in the topsoils. However, inorganic C content tended to increase with depth, particularly at locations where substantial amounts of gypsum were present with the soil profiles.
    - The soil-borne iron and phosphorus from the Fezzan Sahara may be an important source of aerosol iron and phosphorus, and consequently contribute to the control on the nitrogen fixation in oceans.
    - Manganese and strontium were the major toxic elements potentially present in the dusts derived from the Fezzan area, which may cause human health problems in the affected areas.
    - Gypsum is locally available in the Fezzan area; this material can be used to reclaim the alkaline/sodic soils for development of desert agriculture in an economic manner.
    - It is more beneficial to take into account factors such as minimization of dust formation, soil carbon sequestration, and water use efficiency when selecting farming methods and crop types.

II. Conclusions regarding to comparison of Soil geochemical characteristics and isotopic signatures between the upper and lower catchment zones in the Murray-Darling River Basin, Australia:

- In the Murray Darling Basin, the SiO_2/Al_2O_3 and most elements in the soils between the upper catchment and the lower catchment were very similar, suggesting that the surface soil materials in the lower catchment tended to be of upper catchment origin.
- However, there were marked differences in pH, electrical conductivity, sodium adsorption ratio, exchangeable sodium percentage, inorganic carbon, and $^{87}Sr/^{86}Sr$ ratio of the acetic acid-extractable fraction between the upper catchment soils and the lower catchment soils.
- The elevated pH in the sampling area of the lower catchment zone inhibits the growth of plants, resulting in lower soil organic carbon content, as compared to the upper catchment zone.
- The strontium isotopic signatures obtained from this study suggests a significant contribution of silicate rock-originated Sr towards the composition of soil strontium in these soils, inferring that silicate rock-originated Ca might play an important role in the formation of carbonate minerals in the lower catchment zone, and consequently contribute significantly to CO_2 sequestration.

III. Some conclusions regarding the validity of using the $^{87}Sr/^{86}Sr$ ratio to trace Ca source for pedogenetic carbonation in alkaline soils are:

- Investigations on alkaline soils and rain water suggest that Sr and Ca behaved differently.
- $^{87}Sr/^{86}Sr$ May not provided reliable indications of the Ca sources to form pedogenetic carbonates in the investigated highly alkaline soils.

IV. With regard to the ability of various Ca- and Mg-bearing materials and different plant species on soil carbon sequestration are:

- Under the experimental conditions set for this study, application of gypsum to the highly alkaline soil caused an increase in inorganic carbon and a decrease in organic carbon however talc powders were not sufficiently reactive in terms of sequestering CO_2.
- Plant species adapted to the soluble Na-dominated soil conditions tends to produce much more biomass carbon and enhance the

accumulation of soil organic carbon. The Digit grass used in the plant growth experiment has demonstrated an estimated CO_2 sequestering capacity of 93 t/ha.

7.2 Further research directions and recommendations

This study highlights many important issues concerning some environmental and agricultural characteristics of alkaline soils.

- Fezzan Basin, the problems associated with soil salinity, alkalinity and sodicity represent major challenges facing the farmers. Appropriate strategies need to be developed to allow cost-effective reclamation of the desert soils and sustainable development of the Desert soil-based irrigation agriculture. In general, a few points are worth mentioning here.
  - Gypsum is an abundant resource that is locally available in the Fezzan area; this material can be used to reclaim the alkaline/sodic soils in an economic manner.
  - It is more beneficial to take into account the factors such as minimization of dust formation, soil carbon sequestration, and water use efficiency when selecting farming methods and crop types.
- The study has demonstrated that plant species adapted to the soluble Na-dominated soil conditions tend to produce much more biomass carbon and enhance the accumulation of soil organic carbon. Future work is required to investigate more local Na- tolerable grasses and crops.
- Substantial amounts of pedogenetic carbonates have been formed and stored in the lower catchment zone, suggesting that this area is an important carbon sink. Currently, soil carbon accounting in Australia has focussed on organic carbon with insufficient attention being paid to the role of soil inorganic carbon in soil carbon sequestration. Further work is therefore required to quantify the soil inorganic carbon stock in Australia's semi-arid areas.

References

Abdel-Fattah, MK 2012, 'Role of gypsum and compost in reclaiming saline-sodic soils', *Journal of Agricultural and Veterinary Sciences*, vol. 1, pp. 30-8.

Abrol, I, Yadav, Pal, JS & Massoud, F 1988, *Salt-affected soils and their management*, Food & Agriculture Org., United Nations, Rome, FAO Soils Bulletin. 39.

Abuduwaili, J, Gabchenko, M & Junrong, X 2008, 'Eolian transport of salts—a case study in the area of Lake Ebinur (Xinjiang, Northwest China)', *Journal of Arid Environments*, vol. 72, no. 10, pp. 1843-52.

Adcock, D, McNeill, AM, McDonald, GK & Armstrong, RD 2007, 'Subsoil constraints to crop production on neutral and alkaline soils in south-eastern Australia: a review of current knowledge and management strategies', *Animal Production Science*, vol. 47, no. 11, pp. 1245-61.

Adkins Jr, B, Luginbuhl, GH, Miller, FJ & Gardner, DE 1980, 'Increased pulmonary susceptibility to streptococcal infection following inhalation of manganese oxide', *Environmental research*, vol. 23, no. 1, pp. 110-20.

Alastuey, A, Querol, X, Castillo, S, Escudero, M, Avila, A, Cuevas, E, Torres, C, Romero, P-M, Exposito, F & García, O 2005, 'Characterisation of TSP and PM2. 5 at Izana and Sta. Cruz de Tenerife (Canary Islands, Spain) during a Saharan Dust Episode (July 2002)', *Atmospheric Environment*, vol. 39, no. 26, pp. 4715-28.

Alsamrai, HA 1990, *Economies of natural resources*, Alany, Bagdad.

Anderson-Teira, K, Davis, SC, Masters, MD & Delucia, EH 2009, 'Changes in soil organic carbon under biofuel crops', *Global Change Biology Bioenergy*, vol. 1, no. 1, pp. 75-96.

Ardahanlioglu, O, Oztas, T, Evren, S, Yilmaz, H & Yildirim, ZN 2003, 'Spatial variability of exchangeable sodium, electrical conductivity, soil pH and boron content in salt-and sodium-affected areas of the Igdir plain (Turkey)', *Journal of Arid Environments*, vol. 54, no. 3, pp. 495-503.

ATSDR 2004, *Public Health Statment-Strontiumr (CAS#: 7440-24-6).*

Baker, JM, Ochsner, TE, Venterea, RT & Griffis, TJ 2007, 'Tillage and soil carbon sequestration—What do we really know?', *Agriculture, Ecosystems & Environment*, vol. 118, no. 1, pp. 1-5.

Baldock, J 2008, 'The low down on soil carbon', Proceedings of the *New Zealand Grassland Association* Bleneim, New Zeland, pp. 101-6.

Banner, JL 1995, 'Application of the trace element and isotope geochemistry of strontium to studies of carbonate diagenesis', *Sedimentology*, vol. 42, no. 5, pp. 805-24.

Barkan, J, Alpert, P, Kutiel, H & Kishcha, P 2005, 'Synoptics of dust transportation days from Africa toward Italy and central Europe', *Journal of Geophysical Research.*, vol. 110, pp. 2156-202.

Batra, L & Manna, M 1997, 'Dehydrogenase activity and microbial biomass carbon in salt‐affected soils of semiarid and arid regions', *Arid Land Research and Management*, vol. 11, no. 3, pp. 295-303.

Battle, M, Bender, M, Tans, PP, White, J, Ellis, J, Conway, T & Francey, R 2000, 'Global carbon sinks and their variability inferred from atmospheric O_2 and δ13C', *science*, vol. 287, pp. 2467-70.

Beek, C & Breemen, NV 1973, 'The alkalinity of alkali soils', *Journal of soil science*, vol. 24, no. 1, pp. 129-36.

Berner, RA 1964, 'Distribution and diagenesis of sulfur in some sediments from the Gulf of California', *Marine Geology*, vol. 1, no. 2, pp. 117-40.

Berner, RA, Lasaga, AC & Garrels, RM 1983, 'The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years', *American Journal of Science*, vol. 283, no. 7, pp. 641-83.

Bertrand, I, Holloway, RE, Armstrong, RD & McLaughlin, MJ 2003, 'Chemical characteristics of phosphorus in alkaline soils from southern Australia', *Soil Research*, vol. 41, no. 1, pp. 61-76.

Bettenay, E, Blackmore, A & Hingston, F 1964, 'Aspects of the hydrologic cycle and related salinity in the Belka Valley, Western Australia', *Soil Research*, vol. 2, no. 2, pp. 187-210.

Bickle, M, Harris, N, Bunbury, J, Chapman, H, Fairchild, I & Ahmad, T 2001, 'Controls on the 87Sr/86Sr ratio of carbonates in the Garhwal Himalaya, headwaters of the Ganges', *The Journal of Geology*, vol. 109, no. 6, pp. 737-53.

Biggs, A, Watling, K, Cupples, N & Minehan, K 2010, 'Salinity risk assessment for the Queensland Murray-Darling region', *Queensland Department of Environment and Resource Management, Toowoomba*,

Biggs, A, Witheyman, S, Williams, K, Cupples N, , de Voil CA, Power, R & Stone, B 2012, *Assessing the salinity impacts of coal seam gas water on landscapes and surface streams*, Final report of Activity 3 of the Healthy Head Waters Coal Seam Gas Water Feasibility Study, Department of Natural Resources and Mines, Toowoomba, Australia.

Bolinder, M, Angers, D, Bélanger, G, Michaud, R & Laverdière, M 2002, 'Root biomass and shoot to root ratios of perennial forage crops in eastern Canada', *Canadian Journal of Plant Science*, vol. 82, no. 4, pp. 731-7.

Borbély-Kiss, I, Kiss, A, Koltay, E, Szabó, G & Bozó, L 2004, 'Saharan dust episodes in Hungarian aerosol: elemental signatures and transport trajectories', *Journal of Aerosol Science*, vol. 35, no. 10, pp. 1205-24.

Brady, NC & Weil, RR 1996, *The nature and properties of soils*, Prentice-Hall Inc.

Breazeale, JF 1927, 'A Study of Toxicity of Salines that Occur in Black Alkali Soils', *Technical Bulletin*, vol. 14, pp. 338-57.

Bresler, E, McNeal, BL & Carter, DL 1982, *Saline and sodic soils. Principles-dynamics-modeling*, Springer-Verlag.

Brinkman, R 1988, *Saline and sodic soils. In: International Instutute for Land Reclamation and Improvment. land Reclamation and Water Management*, land Reclamation and Water Management., Netherlands:Wageningen.

Brock, AL & Buck, BJ 2009, 'Polygenetic development of the Mormon Mesa, NV petrocalcic horizons: Geomorphic and paleoenvironmental interpretations', *Catena*, vol. 77, no. 1, pp. 65-75.

Bronick, CJ & Lal, R 2005, 'Soil structure and management: a review', *Geoderma*, vol. 124, no. 1–2, pp. 3-22.

Brunekreef, B & Forsberg, B 2005, 'Epidemiological evidence of effects of coarse airborne particles on health', *European Respiratory Journal*, vol. 26, no. 2, pp. 309-18.

Burke, W, Denison, R, Hetherington, E, Koepnick, R, Nelson, H & Otto, J 1982, 'Variation of seawater 87Sr/86Sr throughout Phanerozoic time', *Geology*, vol. 10, no. 10, pp. 516-9.

Campbell, S & Nishio, J 2000, 'Iron deficiency studies of sugar beet using an improved sodium bicarbonate-buffered hydroponic growth system', *Journal of Plant Nutrition*, vol. 23, no. 6, pp. 741-57.

Capo, RC & Chadwick, OA 1999, 'Sources of strontium and calcium in desert soil and calcrete', *Earth and Planetary Science Letters*, vol. 170, no. 1–2, pp. 61-72.

Capo, RC, Stewart, BW & Chadwick, OA 1998, 'Strontium isotopes as tracers of ecosystem processes: theory and methods', *Geoderma*, vol. 82, no. 1-3, pp. 197-225.

Casterline, JB 2011, *Fertility Prospects in the Arab Region*, United Nations, Department of Economic and Social Affairs, Population Division.

Chadwick, OA, Nettleton, WD & Staidl, GJ 1995, 'Soil polygenesis as a function of Quaternary climate change, northern Great Basin, USA', *Geoderma*, vol. 68, no. 1, pp. 1-26.

Chan, K, Chan, K, Dexter, A, Dexter, A, McKenzie, D & McKenzie, D 1999, 'Categories of soil structure based on mechanical behaviour and their evaluation using additions of lime and gypsum on a sodic Vertisol', *Soil Research*, vol. 37, no. 5, pp. 903-12.

Chartres, C 1993, 'Sodic soils - an introduction to their formation and distribution in Australia', *Soil Research*, vol. 31, no. 6, pp. 751-60.

Chawla, K & Abrol, I 1982, 'Effect of gypsum fineness on the reclamation of sodic soils', *Agricultural Water Management*, vol. 5, no. 1, pp. 41-50.

Chen, E 1962, 'Origin and accumulation of salinity and sodicity in Qianguo irrigated area Jilin province', *Acta Pedofil Sinica*, vol. 10, pp. 201-14.

Chiquet, A, Michard, A, Nahon, D & Hamelin, B 1999, 'Atmospheric input vs in situ weathering in the genesis of calcretes: An Sr isotope study at Galvez (Central Spain)', *Geochimica et Cosmochimica Acta*, vol. 63, no. 3, pp. 311-23.

Choobari, OA, Zawar-Reza, P & Sturman, A 2014, 'The global distribution of mineral dust and its impacts on the climate system: A review', *Atmospheric Research*, vol. 138, pp. 152-65.

Cochrane, H, Scholz, G & Vanvreswyk, A 1994, 'Sodic soils in Western Australia', *Soil Research*, vol. 32, no. 3, pp. 359-88.

Creeper, N, Fitzpatrick, R & Shand, P 2013, 'The occurrence of inland acid sulphate soils in the floodplain wetlands of the Murray–Darling Basin, Australia, identified using a simplified incubation method', *Soil Use and Management*, vol. 29, no. 1, pp. 130-9.

Crocker, RL 1946, *Post-Miocene climatic and geologic history and its significance in relation to the genesis of the major soil types of South Australia*, Council for Scientific and Industrial Research.

Dakora, FD & Phillips, DA 2002, 'Root exudates as mediators of mineral acquisition in low-nutrient environments', *Plant and Soil*, vol. 245, no. 1, pp. 35-47.

Dart, RC, Barovich, KM & Chittleborough, D 2005, 'Pedogenic carbonates, strontium isotopes and their relationship with Australian dust processes', Proceedings of the *Regolith*, Adelaide, Australia, pp. 64-6.

Dart, RC, Barovich, KM, Chittleborough, DJ & Hill, SM 2007, 'Calcium in regolith carbonates of central and southern Australia: Its source and implications for the global carbon cycle', *Palaeogeography, Palaeoclimatology,Palaeoecology*, vol. 249, no. 3, pp. 322-34.

David, R & Dimitrios, P 2002, 'Diffusion and cation exchange during the reclamation of saline-structured soils', *Geoderma*, vol. 107, no. 3–4, pp. 271-9.

Davidson, E & Ackerman, I 1993, 'Changes in soil carbon inventories following cultivation of previously untilled soils', *Biogeochemistry*, vol. 20, no. 3, pp. 161-93.

de Caritat, P, Cooper, M & Wilford, J 2011, 'The pH of Australian soils: field results from a national survey', *Soil Research*, vol. 49, no. 2, pp. 173-82.

de Villiers, S 1999, 'Seawater strontium and Sr/Ca variability in the Atlantic and Pacific oceans', *Earth and Planetary Science Letters*, vol. 171, no. 4, pp. 623-34.

DeLaune, R, Reddy, C & Patrick Jr, W 1981, 'Organic matter decomposition in soil as influenced by pH and redox conditions', *Soil Biology and Biochemistry*, vol. 13, no. 6, pp. 533-4.

Demenocal, P, Ortiz, J, Guilderson, T, Adkins, J, Sarnthein, M, Baker, L & Yarusinsky, M 2000, 'Abrupt onset and termination of the African Humid Period: rapid climate responses to gradual insolation forcing', *Quaternary Science Reviews*, vol. 19, no. 1, pp. 347-61.

Deniel, C & Pin, C 2001, 'Single-stage method for the simultaneous isolation of lead and strontium from silicate samples for isotopic measurements', *Analytica Chimica Acta*, vol. 426, no. 1, pp. 95-103.

Dexter, AR 2004, 'Soil physical quality: Part I. Theory, effects of soil texture, density, and organic matter, and effects on root growth', *Geoderma*, vol. 120, no. 3–4, pp. 201-14.

Dimmock, G, Bettenay, E & Mulcahy, M 1974, 'Salt content of lateritic profiles in the Darling Range, Western Australia', *Soil Research*, vol. 12, no. 2, pp. 63-9.

Doyle, R & Habraken, F 1993, 'The distribution of sodic soils in Tasmania', *Soil Research*, vol. 31, no. 6, pp. 931-47.

Drake, N, El-Hawat, A, Turner, P, Armitage, S, Salem, M, White, K & McLaren, S 2008, 'Palaeohydrology of the Fazzan Basin and surrounding regions: the last 7 million years', *Palaeogeography, Palaeoclimatology, Palaeoecology*, vol. 263, no. 3, pp. 131-45.

El-Ghawi, U, Bejey, M, Al-Fakhri, S, Al-Sadeq, A & Doubali, K 2005, 'Analysis of Libyan arable soils by means of thermal and epithermal NAA', *Arabian Journal forl Science and Engineering*, vol. 30, no. 1A, pp. 147-53.

Elgharably, A & Marschner, P 2011, 'Microbial activity and biomass and N and P availability in a saline sandy loam amended with inorganic N and lupin residues', *European Journal of Soil Biology*, vol. 47, no. 5, pp. 310-5.

Elhassadi, A 2007, 'Libyan National plan to resolve water shortage problem Part Ia: Great Man-Made River (GMMR) project—capital costs as sunk value', *Desalination*, vol. 203, no. 1, pp. 47-55.

Elhassadi, A 2008a, 'Sea water intrusion in Derna located in the Green Mountain region, Libya — a threatening recurrent phenomenon calling for desalination', *Desalination*, vol. 220, no. 1–3, pp. 189-93.

Elhassadi, A 2008b, 'Views on Libyan national plan (LNP) to resolve water shortage problem (WSP). Part Ib: Great Man-Made River (GMMR) project—capital cost with interest rates', *Desalination*, vol. 220, no. 1, pp. 184-8.

Emery, D, Dickson, JAD & Smalley, PC 1987, 'The strontium isotopic composition and origin of burial cements in the Lincolnshire Limestone (Bajocian) of central Lincolnshire, England', *Sedimentology*, vol. 34, no. 5, pp. 795-806.

Essington, ME 2004, *Soil and water chemistry: An integrative approach*, CRC press.

Etherington, J 1981, 'Limestone heaths in south-west Britain: their soils and the maintenance of their calcicole-calcifuge mixtures', *The Journal of Ecology*, vol. 69, no. 1, pp. 277-94.

Eugster, HP & Jones, BF 1979, 'Behavior of major solutes during closed-basin brine evolution', *American Journal of Science*, vol. 279, no. 6, pp. 609-31.

Faithfull, NT 2002, *Methods in agricultural chemical analysis: a practical handbook*, CABI.

Falkovich, AH, Ganor, E, Levin, Z, Formenti, P & Rudich, Y 2001, 'Chemical and mineralogical analysis of individual mineral dust particles', *Journal of Geophysical Research: Atmospheres (1984–2012)*, vol. 106, no. D16, pp. 18029-36.

Fensham, R, Silcock, J & Biggs, A 2007, 'Vegetation-soil relations in a highly sodic landscape, Yelarbon, southern Queensland', *Cunninghamia*, vol. 10, no. 2, pp. 273-84.

Fitzpatrick, RW, Fritsch, E & Self, P 1996, 'Interpretation of soil features produced by ancient and modern processes in degraded landscapes: V. Development of saline sulfidic features in non-tidal seepage areas', *Geoderma*, vol. 69, no. 1, pp. 1-29.

Fookes, PG & Gahir, JS 1995, 'Engineering performance of some coarse-grained arid soils in the Libyan Fezzan', *Quarterly Journal of Engineering Geology and Hydrogeology*, vol. 28, no. 2, pp. 105-30.

Franzluebbers, AJ 2005, 'Soil organic carbon sequestration and agricultural greenhouse gas emissions in the southeastern USA', *Soil and Tillage Research*, vol. 83, no. 1, pp. 120-47.

Gijsbers, P & Loucks, D 1999, 'Libya's choices: Desalination or the Great Man-made River Project', *Physics and Chemistry of the Earth, Part B: Hydrology, Oceans and Atmosphere*, vol. 24, no. 4, pp. 385-9.

Gordon, S, Kemp, A & Mues, C 2000, *Irrigation in the Murray Darling Basin and the impact of water policy reforms*, ABARE report to the Natural Heritage Trust, Canberra.

Goudie, A & Middleton, N 2001, 'Saharan dust storms: nature and consequences', *Earth-Science Reviews*, vol. 56, no. 1, pp. 179-204.

Goudie, AS 2014, 'Desert dust and human health disorders', *Environment International*, vol. 63, pp. 101-13.

Gunn, R & Richardson, D 1979, 'The nature and possible origins of soluble salts in deeply weathered landscapes of eastern Australia', *Soil Research*, vol. 17, no. 2, pp. 197-215.

Hamad, SM 2012, 'Status of Groundwater Resources of Al Jabal Al Akhdar Region, North East Libya', *International journal of environment and water*, pp. 68-78.

Hamawand, I, Yusaf, T & Hamawand, SG 2013, 'Coal seam gas and associated water: A review paper', *Renewable and Sustainable Energy Reviews*, vol. 22, pp. 550-60.

Hamidi, EM, Colin, F, Michard, A, Boulangé, B & Nahon, D 2001, 'Isotopic tracers of the origin of Ca in a carbonate crust from the Middle Atlas, Morocco', *Chemical Geology*, vol. 176, no. 1, pp. 93-104.

Hamza, M & Anderson, W 2003, 'Responses of soil properties and grain yields to deep ripping and gypsum application in a compacted loamy sand soil contrasted with a sandy clay loam soil in Western Australia', *Crop and Pasture Science*, vol. 54, no. 3, pp. 273-82.

Hanay, A, Büyüksönmez, F, Kiziloglu, FM & Canbolat, MY 2004, 'Reclamation of saline-sodic soils with gypsum and MSW compost', *Compost science & utilization*, vol. 12, no. 2, pp. 175-9.

Hayward, H & Wadleigh, C 1949, 'Plant growth on saline and alkali soils', *Adv. Agron*, vol. 1, pp. 1-38.

Hazelton, PA & Murphy, BW 2007, *Interpreting soil test results: what do all the numbers mean?*, CSIRO publishing, Melbourne, Australia.

Henderson, BL, Bui, EN, Moran, CJ & Simon, D 2005, 'Australia-wide predictions of soil properties using decision trees', *Geoderma*, vol. 124, no. 3, pp. 383-98.

Hendon, HH, Thompson, DW & Wheeler, MC 2007, 'Australian rainfall and surface temperature variations associated with the Southern Hemisphere annular mode', *Journal of Climate*, vol. 20, no. 11, pp. 2452-67.

Hess, PC 1989, *Origins of igneous rocks*, Harvard University Press Cambridge.

Hesse, PP & McTainsh, GH 2003, 'Australian dust deposits: modern processes and the Quaternary record', *Quaternary Science Reviews*, vol. 22, no. 18–19, pp. 2007-35.

Hinsinger, P 1998, 'How do plant roots acquire mineral nutrients? Chemical processes involved in the rhizosphere', *Advances in agronomy*, vol. 64, pp. 225-65.

Hinsinger, P, Plassard, C, Tang, C & Jaillard, B 2003, 'Origins of root-mediated pH changes in the rhizosphere and their responses to environmental constraints: A review', *Plant and Soil*, vol. 248, no. 1-2, pp. 43-59.

Holloway, RE, Bertrand, I, Frischke, AJ, Brace, DM, McLaughlin, MJ & Shepperd, W 2001, 'Improving fertiliser efficiency on calcareous and alkaline soils with fluid sources of P, N and Zn', *Plant and Soil*, vol. 236, no. 2, pp. 209-19.

Houghton, RA 1995, 'Land‐use change and the carbon cycle', *Global Change Biology*, vol. 1, no. 4, pp. 275-87.

Huang, J, Zhang, W, Zuo, J, Bi, J, Shi, J, Wang, X, Chang, Z, Huang, Z, Yang, S & Zhang, B 2008, 'An overview of the semi-arid climate and environment research observatory over the Loess Plateau', *Advances in atmospheric sciences*, vol. 25, pp. 906-21.

Ilyas, M, Qureshi, RH & Qadir, MA 1997, 'Chemical changes in a saline-sodic soil after gypsum application and cropping', *Soil Technology*, vol. 10, no. 3, pp. 247-60.

IUPAC 1990, 'Glossary of atmospheric chemistry terms', *Pure and Applied Chemistry*, vol. 62, no. 11, pp. 2167-219.

Jacobson, AD 2004, 'Has the atmospheric supply of dissolved calcite dust to seawater influenced the evolution of marine 87Sr/86Sr ratios over the past 2.5 million years?', *Geochemistry, Geophysics, Geosystems*, vol. 5, no. 12, p. Q12002.

Jiménez, E, Linares, C, Martínez, D & Díaz, J 2010, 'Role of Saharan dust in the relationship between particulate matter and short-term daily mortality among the elderly in Madrid (Spain)', *Science of the Total Environment*, vol. 408, no. 23, pp. 5729-36.

Jobbágy, EG & Jackson, RB 2000, 'The vertical distribution of soil organic carbon and its relation to climate and vegetation', *Ecological applications*, vol. 10, no. 2, pp. 423-36.

Jones, CE & Jenkyns, HC 2001, 'Seawater strontium isotopes, oceanic anoxic events, and seafloor hydrothermal activity in the Jurassic and Cretaceous', *American Journal of Science*, vol. 301, no. 2, pp. 112-49.

Kätterer, T, Bolinder, MA, Berglund, K & Kirchmann, H 2012, 'Strategies for carbon sequestration in agricultural soils in northern Europe', *Acta Agriculturae Scandinavica: Section A, Animal Science*, vol. 62, no. 4, pp. 181-98.

Kätterer, T, Bolinder, MA, Andrén, O, Kirchmann, H & Menichetti, L 2011, 'Roots contribute more to refractory soil organic matter than above-ground crop residues, as revealed by a long-term field experiment', *Agriculture, Ecosystems & Environment*, vol. 141, no. 1, pp. 184-92.

Kelley, W 1934, 'The formation, evolution, reclamation and the absorbed bases of alkali soils', *Journal of Agriculture Science*, vol. 24, pp. 72-92.

Kelley, WP & Brown, SM 1939, 'An Unusual Alkali Soil1', *Agronomy Journal*, vol. 31, no. 1, pp. 41-3.

Keren, R & Shainberg, I 1981, 'Effect of dissolution rate on the efficiency of industrial and mined gypsum in improving infiltration of a sodic soil', *Soil Science Society of America Journal*, vol. 45, no. 1, pp. 103-7.

Khaleghpanah, N, Roozitalab, MH, Majdabadi, A & Mirkhani, R 2010, 'The adsorption of Strontium on soils developed in arid region as influenced by clay content and soluble cations', Proceedings of the *19th World Congress of Soil Science, Soil Solutions for a Changing World*, Brisbane, Australia.

Kingham, R 1998, *Geology of the Murray-Darling Basin: Simplified Lithostratigraphic Groupings*, Australian Geological Survey Organisation, Department of Primary Industries & Energy.

Kirschbaum, MU 1995, 'The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage', *Soil Biology and Biochemistry*, vol. 27, no. 6, pp. 753-60.

Kovda, V & Samoilova, E 1969, 'Some problems of soda salinity', *Agrokémia és Talajtan*, vol. 18, pp. 21-36.

Kraimer, RA, Monger, HC & Steiner, RL 2005, 'Mineralogical distinctions of carbonates in desert soils', *Soil Science Society of America Journal*, vol. 69, no. 6, pp. 1773-81.

Krueger, BJ, Grassian, VH, Cowin, JP & Laskin, A 2004, 'Heterogeneous chemistry of individual mineral dust particles from different dust source regions: the importance of particle mineralogy', *Atmospheric Environment*, vol. 38, no. 36, pp. 6253-61.

Kump, LR, Brantley, SL & Arthur, MA 2000, 'Chemical weathering, atmospheric $CO_{2,}$ and climate', *Annual Review of Earth and Planetary Sciences*, vol. 28, no. 1, pp. 611-67.

Lai, L, Li, Y, Tian, Y, Jiang, L, Zhao, X, Zhu, L, Chen, X, Gao, Y, Wang, S, Zheng, Y & Rimmington, GM 2013, 'Effects of Added Organic Matter and Water on Soil Carbon Sequestration in an Arid Region', *PLoS ONE*, vol. 8, no. 7, pp. 1-9.

Lal, R 2004, 'Soil carbon sequestration impacts on global climate change and food security', *science*, vol. 304, no. 5677, pp. 1623-7.

Lal, R 2008, 'Sequestration of atmospheric CO 2 in global carbon pools', *Energy & Environmental Science*, vol. 1, no. 1, pp. 86-100.

Lal, R & Kimble, J 1997, 'Conservation tillage for carbon sequestration', *Nutrient Cycling inAgroecosystems*, vol. 49, no. 1-3, pp. 243-53.

Leytem, A & Mikkelsen, R 2005, 'The nature of phosphorus in calcareous soils', *Better Crops*, vol. 89, no. 2, pp. 11-3.

Lima, CAd, Palácio, HAdQ, Andrade, EMd, dos Santos, JC & Brasil, PP 2013, 'Characteristics of rainfall and erosion under natural conditions of land use in semiarid regions', *Revista Brasileira de Engenharia Agrícola e Ambiental*, vol. 17, no. 11, pp. 1222-9.

Luan, S, Lan, W & Chul Lee, S 2009, 'Potassium nutrition, sodium toxicity, and calcium signaling: connections through the CBL–CIPK network', *Current opinion in plant biology*, vol. 12, no. 3, pp. 339-46.

Luan, S, Lan, W & Chul Lee, S 2009, 'Potassium nutrition, sodium toxicity, and calcium signaling: connections through the CBL-CIPK network', *Current opinion in plant biology*, vol. 12, no. 3, pp. 339-46.

Mace, J, Amrhein, C & Oster, J 1999, 'Comparison of gypsum and sulfuric acid for sodic soil reclamation', *Arid Soil Research and Rehabilitation*, vol. 13, no. 2, pp. 171-88.

Mahmoodabadi, M, Yazdanpanah, N, Sinobas, LR, Pazira, E & Neshat, A 2013, 'Reclamation of calcareous saline sodic soil with different amendments (I): Redistribution of soluble cations within the soil profile', *Agricultural Water Management*, vol. 120, pp. 30-8.

Mahowald, NM, Baker, AR, Bergametti, G, Brooks, N, Duce, RA, Jickells, TD, Kubilay, N, Prospero, JM & Tegen, I 2005, 'Atmospheric global dust cycle and iron inputs to the ocean', *Global Biogeochemical Cycles*, vol. 19, no. 4, p. GB4025.

Mahowald, NM, Kloster, S, Engelstaedter, S, Moore, JK, Mukhopadhyay, S, McConnell, JR, Albani, S, Doney, SC, Bhattacharya, A & Curran, M 2010, 'Observed 20th century desert dust variability: impact on climate and biogeochemistry', *Atmospheric Chemistry and Physics*, vol. 10, no. 22, pp. 10875-93.

Mann, L 1986, 'Changes in soil carbon storage after cultivation', *Soil Sciences*, vol. 142, no. 5, pp. 279-88.

Marlet, S, Barbiero, L & Valles, V 1998, 'Soil alkalinization and irrigation in the sahelian zone of Niger II: agronomic consequences of alkalinity and sodicity', *Arid Land Research and Management*, vol. 12, no. 2, pp. 139-52.

Maryol, E & Lin, C 2015, 'Evaluation of atmospheric CO 2 sequestration by alkaline soils through simultaneous enhanced carbonation and biomass production', *Geoderma*, vol. 241, pp. 24-31.

McCarl, B, Metting, FB & Rice, C 2007, 'Soil carbon sequestration', *Climatic Change*, vol. 80, no. 1-2, pp. 1-3.

McNutt, RH, Crocket, JH, Clark, AH, Caelles, JC, Farrar, E, Haynes, SJ & Zentilli, M 1975, 'Initial $^{87}Sr/^{86}Sr$ ratios of plutonic and volcanic rocks of the Central Andes between latitudes 26 and 29 south', *Earth and Planetary Science Letters*, vol. 27, no. 2, pp. 305-13.

Merino-Martín, L, Field, JP, Villegas, JC, Whicker, JJ, Breshears, DD, Law, DJ & Urgeghe, AM 2014, 'Aeolian sediment and dust fluxes during predominant “background” wind conditions for unburned and burned semiarid grassland: Interplay between particle size and temporal scale', *Aeolian Research*, vol. 14, pp. 97-103.

Mikhailova, EA, Goddard, MA, Post, CJ, Schlautman, MA & Galbraith, JM 2013, 'Potential Contribution of Combined Atmospheric Ca^{2+} and Mg^{2+} Wet Deposition Within the Continental US to Soil Inorganic Carbon Sequestration', *Pedosphere (Beijing)*, vol. 23, no. 6, pp. 808-14.

Mikova, J & Denkova, P 2007, 'Modified chromatographic separation scheme for Sr and Nd isotope analysis in geological silicate samples', *Journal of Geosciences*, vol. 52, no. 3-4, pp. 221-6.

Millar, A, Rathjen, A & Cooper, D 2007, 'Genetic variation for subsoil toxicities in high pH soils', in HT Buck, et al. (eds), *Wheat Production in Stressed Environments: Proceedings of the 7th International Wheat Conference, 27 November –2 December 2005*, Springer, Berlin, Mar del Plata, Argentina. Developments in Plant Breeding no 12, pp. 395-402.

Miller, RL, Tegen, I & Perlwitz, J 2004, 'Surface radiative forcing by soil dust aerosols and the hydrologic cycle', *Journal of Geophysical Research: Atmospheres,* vol. 109, no. D4, p. D04203.

Miller, RW & Donahue, RL 1990, *Soils: an introduction to soils and plant growth*, Prentice-Hall International Inc.

Minasny, B, Sulaeman, Y & McBratney, AB 2011, 'Is soil carbon disappearing? The dynamics of soil organic carbon in Java', *Global Change Biology,* vol. 17, no. 5, pp. 1917-24.

Minyuk, PS, Brigham-Grette, J, Melles, M, Borkhodoev, VY & Glushkova, OY 2007, 'Inorganic geochemistry of El’gygytgyn Lake sediments (northeastern Russia) as an indicator of paleoclimatic change for the last 250 kyr', *Journal of Paleolimnology*, vol. 37, no. 1, pp. 123-33.

Mishra, A, Sharma, S & Pandey, R 2004, 'Amelioration of degraded sodic soil by afforestation', *Arid Land Research and Management*, vol. 18, no. 1, pp. 13-23.

Moreno, T, Querol, X, Castillo, S, Alastuey, A, Cuevas, E, Herrmann, L, Mounkaila, M, Elvira, J & Gibbons, W 2006, 'Geochemical variations in aeolian mineral particles from the Sahara–Sahel Dust Corridor', *Chemosphere*, vol. 65, no. 2, pp. 261-70.

Mullins, C, MacLeod, D, Northcote, K, Tisdall, J & Young, I 1990, 'Hardsetting soils: Behavior, occurrence, and management', in R Lal & B Stewart (eds), *Soil Degradation*, pp. 37-99.

Mzezewa, J, Gotosa, J & Nyamwanza, B 2003, 'Characterisation of a sodic soil catena for reclamation and improvement strategies', *Geoderma*, vol. 113, no. 1–2, pp. 161-75.

Négrel, P, Merly, C, Gourcy, L, Cerdan, O, Petelet-Giraud, E, Kralik, M, Klaver, G, van Wirdum, G & Vegter, J 2014, 'Soil–sediment–river connections: catchment processes delivering pressures to river catchments', in B J, et al. (eds), *Risk-Informed Management of European River Basins*, Springer, Heidelberg, pp. 21-52.

Nelson, DW & Sommers, LE 1982, 'Total carbon, organic carbon, and organic matter', in AL Page (ed.), *Methods of Soil Analysis. Part 2*, American Society of Agronomy Madison, Wisconsin, USA, pp. 539-80.

Niskavaara, H, Reimann, C, Chekushin, V & Kashulina, G 1997, 'Seasonal variability of total and easily leachable element contents in topsoils (0–5 cm) from eight catchments in the European Arctic (Finland, Norway and Russia)', *Environmental Pollution*, vol. 96, no. 2, pp. 261-74.

Northcote, KH & Srene, J 1972, *Australian soils with saline and sodic properties*, Commonwealth Scientific and Industrial Research Organisation (CSIRO), Soil Publication no. 27, Australia.

Oster, J, Shainberg, I & Abrol, I 1996, 'Reclamation of salt-affected soil', in A M (ed.), *Soil Erosion, Conservation and Rehabilitation*, Marcel Dekker, New York, pp. 315-51.

Pal, DK, Srivastava, P, Durge, SL & Bhattacharyya, T 2003, 'Role of microtopography in the formation of sodic soils in the semi-arid part of the Indo-Gangetic Plains, India', *Catena*, vol. 51, no. 1, pp. 3-31.

Palandri, JL, Rosenbauer, RJ & Kharaka, YK 2005, 'Ferric iron in sediments as a novel CO_2 mineral trap: CO_2–SO_2 reaction with hematite', *Applied Geochemistry*, vol. 20, no. 11, pp. 2038-48.

Pan, G, Li, L, Wu, L & Zhang, X 2004, 'Storage and sequestration potential of topsoil organic carbon in China's paddy soils', *Global Change Biology*, vol. 10, no. 1, pp. 79-92.

Panigrahy, B & Raymahashay, B 2005, 'River water quality in weathered limestone: A case study in upper Mahanadi basin, India', *Journal of Earth SystemScience*, vol. 114, no. 5, pp. 533-43.

Pessarakli, M 1991, 'Formation of saline and sodic soils and their reclamation', *Journal of Environmental Science & Health Part A*, vol. 26, no. 7, pp. 1303-20.

Pietola, L & Alakukku, L 2005, 'Root growth dynamics and biomass input by Nordic annual field crops', *Agriculture, Ecosystems & Environment*, vol. 108, no. 2, pp. 135-44.

Pin, C & Zalduegui, JFS 1997, 'Sequential separation of light rare-earth elements, thorium and uranium by miniaturized extraction chromatography: Application to isotopic analyses of silicate rocks', *Analytica Chimica Acta*, vol. 339, no. 1-2, pp. 79-89.

Post, WM & Kwon, KC 2000, 'Soil carbon sequestration and land‐use change: processes and potential', *GlobalChange Biology*, vol. 6, no. 3, pp. 317-27.

Prospero, JM 1999, 'Long‐term measurements of the transport of African mineral dust to the southeastern United States: Implications for regional air quality', *Journal of Geophysical Research: Atmospheres (1984–2012)*, vol. 104, no. D13, pp. 15917-27.

Prospero, JM, Ginoux, P, Torres, O, Nicholson, SE & Gill, TE 2002, 'Environmental characterization of global sources of atmospheric soil dust identified with the Nimbus 7 Total Ozone Mapping Spectrometer (TOMS) absorbing aerosol product', *Reviews ofGeophysics*, vol. 40, no. 1, pp. 1-3.

Qadir, M & Oster, J 2002, 'Vegetative bioremediation of calcareous sodic soils: history, mechanisms, and evaluation', *Irrigation Science*, vol. 21, no. 3, pp. 91-101.

Qadir, M & Schubert, S 2002, 'Degradation processes and nutrient constraints in sodic soils', *Land Degradation & Development*, vol. 13, no. 4, pp. 275-94.

Qadir, M & Oster, J 2004, 'Crop and irrigation management strategies for saline-sodic soils and waters aimed at environmentally sustainable agriculture', *Science of the Total Environment*, vol. 323, no. 1, pp. 1-19.

Qadir, M, Qureshi, R & Ahmad, N 1996, 'Reclamation of a saline-sodic soil by gypsum and Leptochloa fusca', *Geoderma*, vol. 74, no. 3, pp. 207-17.

Qadir, M, Qureshi, RH & Ahmad, N 1996, 'Reclamation of a saline-sodic soil by gypsum and Leptochloa fusca', *Geoderma*, vol. 74, no. 3–4, pp. 207-17.

Qadir, M, Ghafoor, A & Murtaza, G 2001, 'Use of saline–sodic waters through phytoremediation of calcareous saline–sodic soils', *Agricultural Water Management*, vol. 50, no. 3, pp. 197-210.

Qadir, M, Schubert, S, Ghafoor, A & Murtaza, G 2001, 'Amelioration strategies for sodic soils: A review', *Land Degradation & Development*, vol. 12, no. 4, pp. 357-86.

Qadir, M, Steffens, D, Yan, F & Schubert, S 2003, 'Proton release by N2-fixing plant roots: A possible contribution to phytoremediation of calcareous sodic soils', *Journal of Plant Nutrition and Soil Science*, vol. 166, no. 1, pp. 14-22.

Qadir, M, Oster, JD, Schubert, S, Noble, AD & Sahrawat, KL 2007, 'Phytoremediation of Sodic and Saline ‐ Sodic Soils', in LS Donald (ed.), *Advances in agronomy*, Academic Press, vol. 96, pp. 197-247.

Qiguo, Z, Zhong, L & Yingfei, X 1997, 'Organic carbon storage in soils of southeast China', *Nutrient Cycling inAgroecosystems*, vol. 49, no. 1-3, pp. 229-34.

Quade, J, Chivas, A & McCulloch, M 1995, 'Strontium and carbon isotope tracers and the origins of soil carbonate in South Australia and Victoria', *Palaeogeography, Palaeoclimatology,Palaeoecology*, vol. 113, no. 1, pp. 103-17.

Qureshi, ME, Shi, T, Qureshi, SE & Proctor, W 2009, 'Removing barriers to facilitate efficient water markets in the Murray-Darling Basin of Australia', *Agricultural Water Management*, vol. 96, no. 11, pp. 1641-51.

Radford, B, Silburn, D & Forster, B 2009, 'Soil chloride and deep drainage responses to land clearing for cropping at seven sites in central Queensland, northern Australia', *Journal of hydrology*, vol. 379, no. 1, pp. 20-9.

Rashid, A & Ryan, J 2004, 'Micronutrient constraints to crop production in soils with Mediterranean-type characteristics: a review', *Journal of Plant Nutrition*, vol. 27, no. 6, pp. 959-75.

Rasouli, F, Kiani Pouya, A & Karimian, N 2013, 'Wheat yield and physico-chemical properties of a sodic soil from semi-arid area of Iran as affected by applied gypsum', *Geoderma*, vol. 193, pp. 246-55.

Ravi, S, D'Odorico, P, Breshears, DD, Field, JP, Goudie, AS, Huxman, TE, Li, J, Okin, GS, Swap, RJ, Thomas, AD, Van Pelt, S, Whicker, JJ & Zobeck, TM 2011, 'Aeolian processes and the biosphere', *Reviews of Geophysics,*, vol. 49, no. 3, p. RG3001.

Rech, JA, Currie, BS, Michalski, G & Cowan, AM 2006, 'Neogene climate change and uplift in the Atacama Desert, Chile', *Geology*, vol. 34, no. 9, pp. 761-4.

Rengasamy, P 2006, 'World salinization with emphasis on Australia', *Journal of Experimental Botany*, vol. 57, no. 5, pp. 1017-23.

Rengasamy, P & Olsson, KA 1991, 'Sodicity and soil structure', *Soil Research*, vol. 29, no. 6, pp. 935-52.

Rhoades, J, Krueger, D & Reed, M 1968, 'The effect of soil-mineral weathering on the sodium hazard of irrigation waters', *Soil Science Society of America Journal*, vol. 32, no. 5, pp. 643-7.

Richards, L 1954, *Diagnosis and improvement of saline and alkali soils*, Agriculture Handbook No. 60, United States Department of Agriculture, Washington.

Ridgwell, A & Kohfeld, KE 2007, 'Dust in the Earth system: The biogeochemical linking of land, air, and sea', in PR Sammonds & JMT Thompson (eds), *Advances in Earth Science: From Earthquakes to Global Warming* Imperial Coll. Press, London, vol. 2, pp. 51-68.

Rietz, DN & Haynes, RJ 2003, 'Effects of irrigation-induced salinity and sodicity on soil microbial activity', *Soil Biology and Biochemistry*, vol. 35, no. 6, pp. 845-54.

Rodrıguez, S, Querol, X, Alastuey, A, Kallos, G & Kakaliagou, O 2001, 'Saharan dust contributions to PM10 and TSP levels in Southern and Eastern Spain', *Atmospheric Environment*, vol. 35, no. 14, pp. 2433-47.

Rowe, B & Johnson, D 1988, 'Residual effects of limestone on pasture yields, soil pH and soil aluminium in a krasnozem in north-western Tasmania', *Animal Production Science*, vol. 28, no. 5, pp. 571-6.

Roy, PD, Arce, JL, Lozano, R, Jonathan, M, Centeno, E & Lozano, S 2012, 'Geochemistry of late Quaternary tephra-sediment sequence from north-eastern Basin of Mexico (Mexico): implications to tephrochronology, chemical weathering and provenance', *Revista Mexicana de Ciencias Geológicas*, vol. 29, no. 1, pp. 24-38.

Ruprecht, J & Schofield, N 1991, 'Effects of partial deforestation on hydrology and salinity in high salt storage landscapes. II. Strip, soils and parkland clearing', *Journal of hydrology*, vol. 129, no. 1, pp. 39-55.

Salameh, D, Detournay, A, Pey, J, Pérez, N, Liguori, F, Saraga, D, Bove, MC, Brotto, P, Cassola, F, Massabò, D, Latella, A, Pillon, S, Formenton, G, Patti, S, Armengaud, A, Piga, D, Jaffrezo, JL, Bartzis, J, Tolis, E, Prati, P, Querol, X, Wortham, H & Marchand, N 2015, 'PM2.5 chemical composition in five European Mediterranean cities: A 1-year study', *Atmospheric Research*, vol. 155, pp. 102-17.

Salem, MA & Al-ethawi, LH 2013, 'Evaluation of Salinity in Some Soils of Irrigated Brack–Ashkada Agriculture Project, Fezzan, Libya', *Journal of Agriculture andVeterinary Science*, vol. 2, no. 1, pp. 5-9.

Salem, OM 1992, 'The great manmade river project: A partial solution to Libya's future water supply', *International Journal of Water Resources Development*, vol. 8, no. 4, pp. 270-8.

Salminen, R, Plant, J & Reeder, S 2005, *Geochemical atlas of Europe. Part 1, Background information, methodology and maps*, EuroGeoSurveys, Espoo, Finland.

Schlesinger, WH 1985, 'The formation of caliche in soils of the Mojave Desert, California', *Geochimica et Cosmochimica Acta*, vol. 49, no. 1, pp. 57-66.

Schlesinger, WH & Bernhardt, ES 2013, *Biogeochemistry: an analysis of global change*, Academic press.

Schuster, M, Duringer, P, Ghienne, J-F, Vignaud, P, Mackaye, HT, Likius, A & Brunet, M 2006, 'The age of the Sahara desert', *science*, vol. 311, no. 5762, pp. 821-.

Shaw, R, Brebber, L, Ahern, C & Weinand, M 1994, 'A review of sodicity and sodic soil behavior in Queensland', *Soil Research*, vol. 32, no. 2, pp. 143-72.

Sheoran, AS, Sheoran, V & Choudhary, RP 2010, 'Bioremediation of acid-rock drainage by sulphate-reducing prokaryotes: A review', *Minerals Engineering*, vol. 23, no. 14, pp. 1073-100.

Shivakumar, M, Seenappa, D, Venkatappa, KM & Swamy, AV 2013, 'Saline/alkaline soils-new resources for aquaculture', *Environment and Ecology*, vol. 31, no. 1, pp. 135-8.

Silva, CC, Guido, ML, Ceballos, JM, Marsch, R & Dendooven, L 2008, 'Production of carbon dioxide and nitrous oxide in alkaline saline soil of Texcoco at different water contents amended with urea: A laboratory study', *Soil Biology and Biochemistry*, vol. 40, no. 7, pp. 1813-22.

Singh, K, Singh, B & Tuli, R 2013, 'Sodic soil reclamation potential of Jatropha curcas: A long-term study', *Ecological Engineering*, vol. 58, pp. 434-40.

Smith, A, Chen, D & Chalk, P 2009, 'N2 fixation by faba bean (Vicia faba L.) in a gypsum-amended sodic soil', *Biology and Fertility of Soils*, vol. 45, no. 3, pp. 329-33.

Smith, P 2004, 'Soils as carbon sinks: the global context', *Soil Use and Management*, vol. 20, no. 2, pp. 212-8.

So, H & Aylmore, L 1993, 'How do sodic soils behave - the effects of sodicity on soil physical behavior', *Soil Research*, vol. 31, no. 6, pp. 761-77.

Steel, KM, Alizadehhesari, K, Balucan, RD & Bašić, B 2013, 'Conversion of CO_2 into mineral carbonates using a regenerable buffer to control solution pH', *Fuel*, vol. 111, pp. 40-7.

Stern, H, De Hoedt, G & Ernst, J 2000, 'Objective classification of Australian climates', *Australian Meteorological Magazine*, vol. 49, no. 2, pp. 87-96.

Swap, R, Ulanski, S, Cobbett, M & Garstang, M 1996, 'Temporal and spatial characteristics of Saharan dust outbreaks', *Journal of Geophysical Research: Atmospheres (1984–2012)*, vol. 101, no. D2, pp. 4205-20.

Szabolcs, I 1989, *Salt-affected soils*, CRC Press, Inc.

Szabolcs, I & Darab, K 1958, 'Accumulation and dynamism of silicic acid in irrigated alkali (“szik”) soils', *Acta Agronomy, Academy of Sciences, Hungary*, vol. 8, pp. 213-35.

Tanaka, TY & Chiba, M 2006, 'A numerical study of the contributions of dust source regions to the global dust budget', *Global and Planetary Change*, vol. 52, no. 1–4, pp. 88-104.

Tao, Y, An, X, Sun, Z, Hou, Q & Wang, Y 2012, 'Association between dust weather and number of admissions for patients with respiratory diseases in spring in Lanzhou', *Science of the Total Environment*, vol. 423, pp. 8-11.

Thimonier, A, Schmitt, M, Waldner, P & Schleppi, P 2008, 'Seasonality of the Na/Cl ratio in precipitation and implications of canopy leaching in validating chemical analyses of throughfall samples', *Atmospheric Environment*, vol. 42, no. 40, pp. 9106-17.

Thomas, C, Graham, C, Ellam, R & Fallick, A 2004, '87Sr/86Sr chemostratigraphy of Neoproterozoic Dalradian limestones of Scotland and Ireland: constraints on depositional ages and time scales', *Journal of the Geological Society*, vol. 161, no. 2, pp. 229-42.

Turner, R & Clark, J 1956, 'The pH of calcareous soils', *Soil Science*, vol. 82, no. 4, pp. 337-42.

Van Beek, CGEM & Van Breemen, N 1973, 'THE alkalinity of alkalisoils', *Journal of soil science*, vol. 24, no. 1, pp. 129-36.

Van der Hoven, SJ & Quade, J 2002, 'Tracing spatial and temporal variations in the sources of calcium in pedogenic carbonates in a semiarid environment', *Geoderma*, vol. 108, no. 3, pp. 259-76.

Van Rooyen, PC & Weber, HW 1977, 'Long-term effects of five ameliorants on a saline-sodic soil of South Africa', *Geoderma*, vol. 19, no. 3, pp. 213-25.

Velbel, MA 1993, 'Temperature dependence of silicate weathering in nature: How strong a negative feedback on long-term accumulation of atmospheric CO_2 and global greenhouse warming?', *Geology*, vol. 21, no. 12, pp. 1059-62.

Vorob’eva, LA & Pankova, EI 2008, 'Saline-alkali soils of Russia', *Eurasian Soil Science*, vol. 41, no. 5, pp. 457-70.

Walker, P & Coventry, R 1976, 'Soil profile development in some alluvial deposits of eastern New South Wales', *Soil Research*, vol. 14, no. 3, pp. 305-17.

Wang, Y, Wang, Z & Li, Y 2013, 'Storage/Turnover rate of inorganic carbon and its dissolvable part in the profile of saline/alkaline soils', *PLoS ONE*, vol. 8, no. 11, p. e82029.

Watson, RT 2000, *Land use, land-use change, and forestry: a special report of the intergovernmental panel on climate change*, Cambridge University Press.

Wei, W, Chen, L, Fu, B, Huang, Z, Wu, D & Gui, L 2007, 'The effect of land uses and rainfall regimes on runoff and soil erosion in the semi-arid loess hilly area, China', *Journal of hydrology*, vol. 335, no. 3, pp. 247-58.

Wennberg, A, Iregren, A, Struwe, G, Cizinsky, G, Hagman, M & Johansson, L 1991, 'Manganese exposure in steel smelters a health hazard to the nervous system', *Scandinavian Journal of Work, Environment &Health*, vol. 17, pp. 255-62.

Wiegand, B, Chadwick, O, Vitousek, P & Wooden, J 2005, 'Ca cycling and isotopic fluxes in forested ecosystems in Hawaii', *Geophysical Research Letters*, vol. 32, no. 11, pp. 1-4.

Wiesmeier, M, Hübner, R, Spörlein, P, Geuß, U, Hangen, E, Reischl, A, Schilling, B, Lützow, M & Kögel-Knabner, I 2014, 'Carbon sequestration potential of soils in southeast Germany derived from stable soil organic carbon saturation', *Global Change Biology*, vol. 20, no. 2, pp. 653-65.

Wu, F, Zhang, D, Cao, J, Xu, H & An, Z 2012, 'Soil‐derived sulfate in atmospheric dust particles at Taklimakan desert', *Geophysical Research Letters*, vol. 39, no. 24, p. L24803.

Wu, H, Guo, Z & Peng, C 2003, 'Land use induced changes of organic carbon storage in soils of China', *Global Change Biology*, vol. 9, no. 3, pp. 305-15.

Yaalon, DH 1957, 'Problems of soil testing on calcareous soils', *Plant and Soil*, vol. 8, no. 3, pp. 275-88.

Yang, F, Zhang, G, Yin, X & Liu, Z 2011, 'Field-scale spatial variation of saline-sodic soil and its relation with environmental factors in western songnen plain of china', *International Journal of Environmental Research and Public Health*, vol. 8, no. 2, pp. 374-87.

Yang, X, Römheld, V & Marschner, H 1994, 'Effect of bicarbonate on root growth and accumulation of organic acids in Zn-inefficient and Zn-efficient rice cultivars (Oryza sativa L.)', *Plant and Soil*, vol. 164, no. 1, pp. 1-7.

Yau, SK & Ryan, J 2008, 'Boron toxicity tolerance in crops: a viable alternative to soil amelioration', *Crop Science*, vol. 48, no. 3, pp. 854-65.

Zhang, C, Bian, M, Yu, H, Liu, Q & Yang, Z 2011, 'Identification of alkaline stress-responsive genes of CBL family in sweet sorghum (Sorghum bicolor L.)', *Plant Physiology and Biochemistry*, vol. 49, no. 11, pp. 1306-12.

Zhang, L, Fan, J, Meng, Q, Niu, Y & Niu, W 2013, 'Caragana fabr promotes revegtation and soil rehabilition in saline-alkaliwastland', *International Journal of Phytoremediation*, vol. 15, no. 1, pp. 38-50.

Zhang, R, Cao, J, Tang, Y, Arimoto, R, Shen, Z, Wu, F, Han, Y, Wang, G, Zhang, J & Li, G 2014, 'Elemental profiles and signatures of fugitive dusts from Chinese deserts', *Science of the Total Environment*, vol. 472, pp. 1121-9.

Appendix A. Results of Fezzan's soil samples

Table A.1 Geographical locations and elevation (m) of the Fezzan (F), Libya investigated soil profiles

ID	Latitude	Longitude	elevation
F1	27.496	13.36	525
F2	27.496	13.36	525
F3	27.484	13.295	525
F4	27.516	13.402	525
F5	24.826	10.22	425
F6	24.784	10.216	--
F7	24.786	10.173	--
F8	24.835	10.203	--
F9	24.897	10.185	690
F10	24.905	10.189	679
F11	24.908	10.195	678
F12	24.908	10.195	678
F13	25.006	10.181	680
F14	25.416	10.394	637
F15	25.787	10.579	644
F16	25.801	10.605	633
F17	25.814	10.814	623
F18	26.199	11.706	602
F19	26.199	11.706	602
F20	26.323	11.907	542
F21	26.339	11.931	540
F22	26.545	12.701	483
F23	26.564	13.133	--
F24	27.597	14.613	477
F25	31.783	20.214	390
F32	28.338	14.347	567
F33	28.429	14.347	574
F34	28.582	14.287	584
F35	28.628	14.283	560
F36	27.547	14.163	534
F37	28.87	14.257	364m
F38	28.98	14.282	523
F39	29.085	14.315	500

AppendixA.1 XRF analysis results

Table A.2: Chemical composition and total carbon of the Fezzan region soil samples results in %

Sample describtion	Al_2O_3%	Fe_2O_3%	CaO%	Na_2O%	K_2O%	MgO %	MnO%	SrO%	P_2O_5%	SiO_2%	BaO%	TiO_2 %	Cr_2O_3%	C%
F1 0-30cm	12.0	6.68	0.98	0.42	1.66	1.36	0.18	0.01	0.07	69.1	0.03	0.91	0.04	0.37
F2 0-30cm	15.65	8.92	0.89	0.39	2	1.46	0.26	0.02	0.07	62.1	0.04	1.18	0.03	0.41
F-3 0-30cm	13.95	5.72	3.86	1.3	1.66	0.59	0.08	0.04	0.05	59.8	0.02	1.3	0.03	0.05
F4 0-10cm	7.5	6.04	1.23	0.27	1.02	1.26	0.72	0.01	0.09	76.5	0.05	0.44	0.06	0.29
F4 10-20cm	7.36	6.61	1.62	0.25	1.04	1.38	0.89	0.01	0.1	74.6	0.06	0.44	0.06	0.54
F4 20-30cm	13.6	6.82	1.06	0.53	1.54	0.89	0.55	0.01	0.09	67.2	0.04	0.62	0.03	0.25
F4 30-50cm	25.6	8.81	0.26	0.74	2.54	0.78	0.41	0.02	0.11	49.7	0.04	1.04	0.03	0.09
F5 0-30cm	4.0	1.28	28.8	0.07	0.7	0.36	0.01	0.03	0.03	20.4	0.02	0.23	0.03	0.06
F6 0-30cm	20.4	7.11	2.65	0.52	2.65	2.12	0.07	0.02	0.18	52.9	0.06	1.02	0.02	0.87
F7 0-10cm	11.3	3.78	1.36	0.73	1.66	1.19	0.04	0.02	0.1	74.2	0.04	0.58	0.03	0.37
F7 10-20cm	11.3	4.13	1.53	1.33	1.63	1.16	0.04	0.01	0.12	71.9	0.04	0.58	0.03	0.51
F7 20-30cm	12.55	4.73	4.95	2.71	1.7	1.34	0.06	0.02	0.11	60.5	0.06	0.62	0.02	1.17
F7 30-50cm	11.4	4.21	5.09	1.98	1.61	1.28	0.05	0.03	0.09	63.5	0.04	0.54	0.01	0.86
F7 50-70cm	9.64	3.43	4.02	1.73	1.44	1.08	0.04	0.02	0.08	69.9	0.04	0.47	0.03	0.8
F7 70-90cm	7.58	2.61	2.63	1.16	1.19	0.81	0.03	0.02	0.07	77.4	0.03	0.38	0.04	0.53
F8 0-30cm	6.65	1.55	2.94	0.4	1.16	0.47	0.01	0.01	0.03	81.3	0.03	0.37	0.04	0.71
F9 0-30cm	6.58	2.29	11.75	0.73	1.35	2.24	0.03	0.11	0.06	57.7	0.03	0.42	0.04	1.58
F10 0-30cm	5.23	1.9	15.6	2.12	1.12	1.8	0.03	0.08	0.04	51.2	0.03	0.34	0.03	2.45
F11 0-30cm	6.32	2.47	0.52	0.15	1.1	0.5	0.01	0.01	0.04	84.8	0.03	0.41	0.04	0.14
F12 0-10cm	4.35	1.86	1.88	0.45	0.95	0.56	0.03	0.01	0.07	85.4	0.03	0.29	0.05	0.74
F12 20-30cm	2.19	1.37	1.56	0.12	0.4	0.27	0.02	0.01	0.03	91.7	0.01	0.16	0.07	0.39
F12 70-90cm	2.85	1.46	0.53	0.17	0.54	0.23	0.02	0.01	0.03	92.1	0.02	0.21	0.06	0.15
F13 0-30cm	7.66	2.94	0.42	0.36	1.22	0.68	0.04	0.01	0.09	82.9	0.03	0.39	0.04	0.05
F14 0-30cm	20.5	5.78	1	0.28	2.46	1.22	0.05	0.01	0.12	57.8	0.05	0.93	0.02	0.15
F15 0-30cm	7.27	4.53	2.8	0.88	1.41	1.55	0.06	0.01	0.11	74	0.03	0.45	0.03	0.26
F16 0-30cm	7.13	3.97	4.86	0.21	1.68	0.98	0.03	0.04	0.07	70.8	0.04	0.62	0.04	0.15
F17 0-30cm	5.78	2.38	10.35	0.55	1.17	1.4	0.04	0.09	0.06	60.9	0.03	0.4	0.04	0.38
F18 0-30cm	16.25	5.54	3.45	0.53	1.8	1.88	0.06	0.03	0.13	60.1	0.05	0.82	0.02	0.86

F-19 0-30cm	8.57	3.22	2.49	0.51	1.26	1.03	0.03	0.02	0.07	76.7	0.04	0.5	0.04	0.55
F-20 0-30cm	8.19	3.33	5.53	0.23	1.18	1.41	0.03	0.02	0.07	71	0.04	0.48	0.03	1.15
F-21 0-20	6.79	2.77	4.33	0.8	0.94	1.42	0.03	0.04	0.05	74.8	0.03	0.41	0.03	0.7
F-21 20-30cm	6.54	2.66	5.42	1.26	0.78	1.16	0.02	0.02	0.05	72.9	0.03	0.37	0.04	1.1
F-21 30-60cm	6.4	2.62	5.14	2.45	0.76	1.1	0.02	0.02	0.04	71.1	0.04	0.37	0.04	1.12
F-22 0-30cm	3.81	2.11	1.54	2.43	0.51	0.42	0.02	0.02	0.04	83.1	0.02	0.31	0.04	0.14
F-23 0-30cm	5.97	2.31	2.33	0.47	0.28	0.38	0.01	0.02	0.03	81.3	0.01	0.35	0.05	0.22
F-24 40-50cm	1.37	0.49	23.8	0.04	0.04	0.07	<0.01	0.04	0.02	38.4	<0.01	0.07	0.03	0.04
F-24 1.5m	3.16	1.34	3.8	0.05	0.18	0.26	0.01	0.02	0.03	84.6	0.01	0.22	0.05	0.33
F-24 2.0m	3.22	1.37	1.68	0.03	0.13	0.24	0.01	0.01	0.02	89.3	0.01	0.2	0.06	0.13
F-25	4.61	74.84	1.38	0.04	0.02	0.36	0.45	0.08	1.86	4.97	0.02	0.36	0.01	9.02
F-32	8.14	2.53	3.49	0.21	0.95	1.21	0.03	0.02	0.08	76.2	0.02	0.36	0.03	0.87
F-33 0-30cm	2.89	1.36	1.84	0.05	0.35	0.44	0.01	0.01	0.03	89.6	0.01	0.14	<0.01	0.5
F-34 0-30cm	3.91	1.6	6.38	0.21	0.58	1.12	0.02	0.02	0.04	78.1	0.01	0.24	0.04	1.47
F-35 0-30cm	5.06	2.7	11.85	0.19	0.92	2.6	0.03	0.02	0.12	62.5	0.02	0.35	0.01	2.91
F-36 0-30cm	5.77	2.5	6.75	0.45	1.04	1.54	0.03	0.02	0.06	72.5	0.02	0.37	0.03	1.52
F-37	8.04	10.54	20.1	0.72	0.66	0.27	1.36	0.03	0.43	22.1	0.01	0.37	0.01	0.11
F-38	4.15	2.18	18.7	0.24	0.71	1.88	0.05	0.12	0.05	45.7	0.01	0.37	0.03	1.55
F-39	7.98	2.77	11.6	0.67	1.73	4.95	0.01	0.3	0.04	50	0.03	0.57	0.01	1.49

AppendixA.2 Aqua regia- extractable elements of the Fezzan region soil samples

Table A.3: Distribution of aqua regia- extractable elements of the Fezzan region soil samples

Sample description	Al	Fe	Ca	Na	K	Mg	Mn(ppm)	Sr	P	S	Ba(ppm)	Pb(ppm)	Cr(ppm)
F1 0-30cm	0.97	4.03	0.65	0.21	0.3	0.61	1260	39.9	140	0.04	70	13.7	146
F2 0-30cm	1.07	5.36	0.61	0.21	0.31	0.61	1920	45.9	140	0.03	60	11.6	93
F-3 0-30cm	0.75	3.29	2.63	0.88	0.35	0.16	536	315	50	2.24	20	8.6	89
F4 0-10cm	1.09	3.84	0.84	0.14	0.32	0.62	5420	46.7	330	0.06	380	22.9	243
F4 10-20cm	1.03	4.21	1.08	0.12	0.33	0.69	6790	65.4	350	0.06	470	27	211
F4 20-30cm	0.96	4.23	0.72	0.34	0.37	0.35	4040	32.4	250	0.07	230	22.2	145
F4 30-50cm	0.95	5	0.17	0.48	0.44	0.15	3080	26.5	210	0.06	80	26	68
F5 0-30cm	0.38	0.65	16.15	0.02	0.11	0.11	75	221	40	15.95	50	3.6	31
F6 0-30cm	2.36	3.85	1.76	0.05	0.46	0.85	501	86.1	580	0.22	190	19.1	51
F7 0-10cm	1.89	2.12	0.86	0.26	0.36	0.5	236	55.8	340	0.05	210	28.8	127
F7 10-20cm	1.93	2.4	0.97	0.71	0.35	0.49	240	52.5	360	0.07	190	29.2	130
F7 20-30cm	2.22	2.75	3.38	1.7	0.39	0.57	407	97.1	380	0.17	300	26.5	124
F7 30-50cm	1.95	2.46	3.45	1.21	0.34	0.55	317	180.5	310	0.74	220	18.3	28
F7 50-70cm	1.6	1.99	2.73	1.04	0.28	0.46	281	95.1	250	0.75	140	15.2	164
F7 70-90cm	1.31	1.52	1.76	0.62	0.23	0.35	192	68.4	200	0.52	100	12	190
F8 0-30cm	0.87	0.91	2.11	0.04	0.14	0.19	90	73.2	80	0.1	110	28.2	233
F9 0-30cm	1.12	1.35	8.04	0.28	0.33	1.18	178	942	230	3.26	110	10	155
F10 0-30cm	0.89	1.17	10.95	1.34	0.27	0.95	169	740	130	3.44	70	6.4	143
F11 0-30cm	0.91	1.48	0.38	0.07	0.19	0.2	57	59.4	100	0.13	70	14.1	221
F12 0-10cm	0.6	1.13	1.22	0.04	0.15	0.26	178	55.9	290	0.07	80	13.2	288
F12 20-30cm	0.34	0.86	1.1	0.01	0.07	0.13	155	56.8	90	0.03	60	8.5	360
F12 70-90cm	0.38	0.92	0.33	0.01	0.08	0.09	142	22.6	70	0.08	40	7.5	324
F13 0-30cm	1.27	1.7	0.19	0.03	0.26	0.27	301	30.6	300	0.03	100	11.8	193
F14 0-30cm	1.66	3.15	0.69	0.12	0.31	0.41	324	48.7	380	0.5	100	14.4	98
F15 0-30cm	1.33	2.76	1.94	0.49	0.42	0.72	392	52.7	410	0.86	110	8.7	145
F16 0-30cm	0.96	2.37	3.31	0.04	0.21	0.43	221	271	250	2.36	90	10.7	183
F17 0-30cm	0.9	1.43	6.52	0.03	0.17	0.69	275	745	200	4.89	60	5.4	166

Sample description	Al	Fe	Ca	Na	K	Mg	Mn(ppm)	Sr	P	S	Ba(ppm)	Pb(ppm)	Cr(ppm)
F18 0-30cm	2.19	3.04	2.31	0.05	0.41	0.82	393	123	460	0.1	160	11.9	101
F19 0-30cm	1.2	1.81	1.62	0.03	0.27	0.44	215	74.1	260	0.04	110	5.9	156
F20 0-30cm	1.45	1.87	3.83	0.07	0.44	0.48	189	158	260	0.11	280	6.4	164
F21 20-30cm	1.1	1.58	3.85	0.82	0.25	0.41	155	105	150	0.2	180	7.6	181
F21 30-60cm	1.07	1.5	3.65	1.66	0.24	0.39	127	104	140	0.14	220	8.5	200
F22 0-30cm	0.5	1.25	1.09	1.62	0.13	0.18	112	134.5	120	0.12	60	3.4	224
F23 0-30cm	0.64	1.33	1.68	0.3	0.09	0.14	76	131	70	0.99	60	2.5	258
F24 40-50cm	0.15	0.27	15.05	0.03	0.01	0.02	18	313	30	13.95	10	0.4	106
F24 1.5m	0.42	0.79	2.78	0.02	0.06	0.09	50	182	100	1.43	60	2.3	288
F24 2.0m	0.38	0.81	1.24	0.01	0.05	0.08	53	41.2	60	0.68	90	2.2	329
F25 Ashkda	0.92	34.4	0.85	0.02	0.01	0.13	2600	256	5610	0.06	160	23.5	52
F32 Elshati-	1.32	1.44	2.46	0.09	0.35	0.5	206	91.6	230	0.06	70	7	151
F33 0-30cm	0.53	0.83	1.37	0.01	0.13	0.18	103	31.6	100	0.04	30	3.9	12
F34 0-30cm	0.75	0.92	4.45	0.11	0.19	0.42	102	120.5	130	0.15	70	4.3	164
F35 0-30cm	1.12	1.6	8.5	0.06	0.33	1.18	224	149	550	0.07	140	5.8	23
F36 0-30cm	1.16	1.42	4.69	0.22	0.34	0.59	176	117.5	220	0.08	80	5.4	139
F37 AGAR	0.83	6.26	12.65	0.45	0.21	0.09	9230	136	1720	11.45	40	7.3	34
F38 Albartma	0.89	1.15	12.1	0.08	0.19	0.64	298	1055	200	6.77	70	3.6	101
F39 //	1.96	1.48	7.07	0.4	0.4	2.34	91	2720	140	3.53	170	6.6	50

Appendix B. Geographical position and elevation of MDB’s soil samples

Table B.1 Geographical locations and elevation (m) of the upland and lowland investigated soil profiles

Sample ID	Latitude	Longitude	elevation
1	33° 20' 31.1994"	148° 2' 38.4"	86
2	33° 28' 19.2"	147° 51' 39.59"	229
3	33° 54' 32.3994"	147° 17' 27.59"	240
4	34° 18' 39.5994"	146° 44' 52.79"	193
5	34° 15' 0"	146° 26' 20.39"	140
6	34° 31' 19.1994"	145° 41' 41.99"	115
7	34° 29' 41.9994"	145° 4' 58.79"	92
8	34° 29' 41.9994"	144° 29' 38.39"	113
9	34° 44' 13.2"	143° 42' 50.39"	72
10	34° 36' 39.5994"	143° 18' 21.6"	68
11	34° 36' 21.6"	143° 17' 16.8"	63
12	34° 36' 21.6"	143° 17' 16.8"	71
13	34° 36' 10.8"	143° 17' 16.8"	71
14	34° 35' 34.8"	143° 13' 19.2"	51
15	34° 33' 43.1994"	143° 5' 31.2"	55
17	34° 32' 23.9994"	142° 59' 27.6"	63
18	34° 31' 44.4"	142° 56' 6"	59
20	34° 30' 3.5994"	142° 34' 1.2"	56
21	34° 26' 20.4"	142° 27' 57.6"	56
22	34° 22' 37.2"	142° 27' 57.6"	47
23	34° 19' 15.5994"	142° 21' 43.19"	62
24	34° 17' 9.6"	142° 16' 26.4"	70
25	34° 16' 29.9994"	141° 18' 57.6"	51
26	34° 16' 33.6"	141° 23' 31.19"	62
27	34° 16' 33.6"	141° 23' 31.19"	51
28	34° 16' 33.6"	141° 34' 55.19"	51
29	34° 16' 33.6"	141° 42' 18"	58
30	34° 15' 57.5994"	141° 48' 28.79"	59
31	34° 15' 10.8"	141° 54' 28.79"	52
32	34° 13' 26.3994"	142° 4' 44.4"	58
33	34° 7' 11.9994"	142° 8' 31.19"	64
34	34° 1' 4.8"	141° 50' 49.2"	49
35	33° 40' 1.2"	141° 47' 49.19"	49
36	33° 38' 20.4"	141° 47' 13.2"	36
37	33° 24' 14.4"	141° 41' 6"	66
38	33° 1' 51.5994"	141° 39' 14.39"	55
40	32° 52' 26.4"	141° 37' 8.39"	49
41	32° 48' 46.8"	141° 37' 19.2"	49
42	32° 30' 3.5994"	141° 34' 48"	113
43	32° 17' 52.8"	141° 26' 16.79"	167
44	32° 13' 11.9994"	140° 27' 14.4"	262

45	32° 11' 9.5994"	140° 34' 48"	209
46	32° 7' 48"	140° 44' 38.39"	189
S47	32° 4' 58.7994"	140° 57' 54"	202
S48	32° 2' 16.7994"	140° 12' 43.19"	317
S49	31° 54' 25.2"	141° 33' 46.79"	229
S50	31° 44' 2.4"	142° 29' 16.79"	144
S51	31° 40' 19.2"	143° 26' 20.39"	82
S52	31° 31' 1.1994"	144° 28' 58.8"	101
S54	31° 32' 56.3994"	146° 41' 56.4"	233
S55	31° 41' 31.2"	147° 26' 34.8"	191
S56	32° 8' 2.4"	148° 46' 1.19"	351
S57	31° 13' 30"	149° 19' 19.2"	571
S58	30° 1' 51.5994"	149° 47' 16.8"	236
S61	28° 27' 53.9994"	150° 17' 34.8"	193
(Yelarbon)62-70	28°.525'-28°.584'	150°.7736'-150°.74"	266-243
70-80	28°.525'-28°.584'	150°.7736'-150°.747"	286-299
81-83	28°.07'.17.20"	150°.02'.14.77"	256-321
(Roma) 84-93	26°.571'.26°.595'	148°.854'-149°.268'	356