



Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

Geochemical characteristics of soils in Fezzan, Sahara desert: Implications for environment and agriculture

Emohamed Maryol^a, Chuxia Lin^{a,b,*}

^a Australian Centre for Sustainable Catchments, University of Southern Queensland, Toowoomba, QLD 4350, Australia

^b School of Environment and Life Science, University of Salford, Salford, Greater Manchester, M5 4WT, United Kingdom

ARTICLE INFO

Article history:

Received 7 November 2014

Revised 10 May 2015

Accepted 14 July 2015

Available online xxxx

Keywords:

Alkaline soil

Dust

Soil carbon

Hyper-arid

Soil sodicity

Irrigation

ABSTRACT

An investigation was conducted to geochemically characterize the soils in Fezzan of the Sahara desert in order to assess (a) the role of the soils as a carbon store, (b) the potential risk of the fine-grained soil fraction as a dust source, and (c) the potential soil constraints for the development of irrigation agriculture. The results show that, on average, there was about 0.7% of carbon 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 Fe and 252 mg/kg of phosphorus, indicating that the Fezzan area could be an important source of ocean iron and phosphorus. Manganese and strontium were identified as the major chemical pollutants potentially present in the dusts. The soils were generally alkaline and saline. Sodium dominated the soluble basic cations with a mean sodium adsorption ratio > 16. Calcium dominated the exchangeable basic cations with a mean exchangeable sodium percentage of 6.52, suggesting that most of the topsoils were not sodic. However, there was a tendency that sodicity increased with depth for some soils. Different strategies are proposed for reclaiming the soils using the groundwater from the Great Man-made River Project.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Sahara has experienced alternate humid and dry periods at least for the past 7 million years (Schuster et al., 2006). The latest wet/dry cycle commenced about 15,000 years BP with the peak African Humid Period (AHP) lasted from approximately 10,000 to 5000 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 pedogenesis 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 deflation that is dominated in the Sahara desert under current climate conditions.

Detailed information on geochemical characteristics of the Sahara desert soils is useful for a few reasons. First, desert soils are effective sites to hold inorganic carbon. Knowledge of inorganic carbon storage in the Sahara desert soils is important for global inorganic carbon inventory. Second, the Sahara desert is the world's largest source of aeolian soil dusts (Goudie, 2014; Prospero et al., 2002; Swap et al., 1996). These Saharan 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 and Forsberg, 2005; Prospero, 1999). There have been increasing researches conducted to evaluate the transport and deposition of aerosols from the Sahara desert (Barkan et al., 2005; Goudie and Middleton, 2001). Most of these researches have used the concentration of total suspended particles (TSP), PM_{2.5} (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; Rodríguez 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. Third, 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.

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 PM_{2.5} in the dust samples collected in 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 dustfall samples collected from Algeria, Chad, Niger and Western Sahara and found marked

* Corresponding author at: School of Environment and Life Science, University of Salford, Salford, Greater Manchester M5 4WT United Kingdom.
E-mail address: C.Lin@salford.ac.uk (C. Lin).

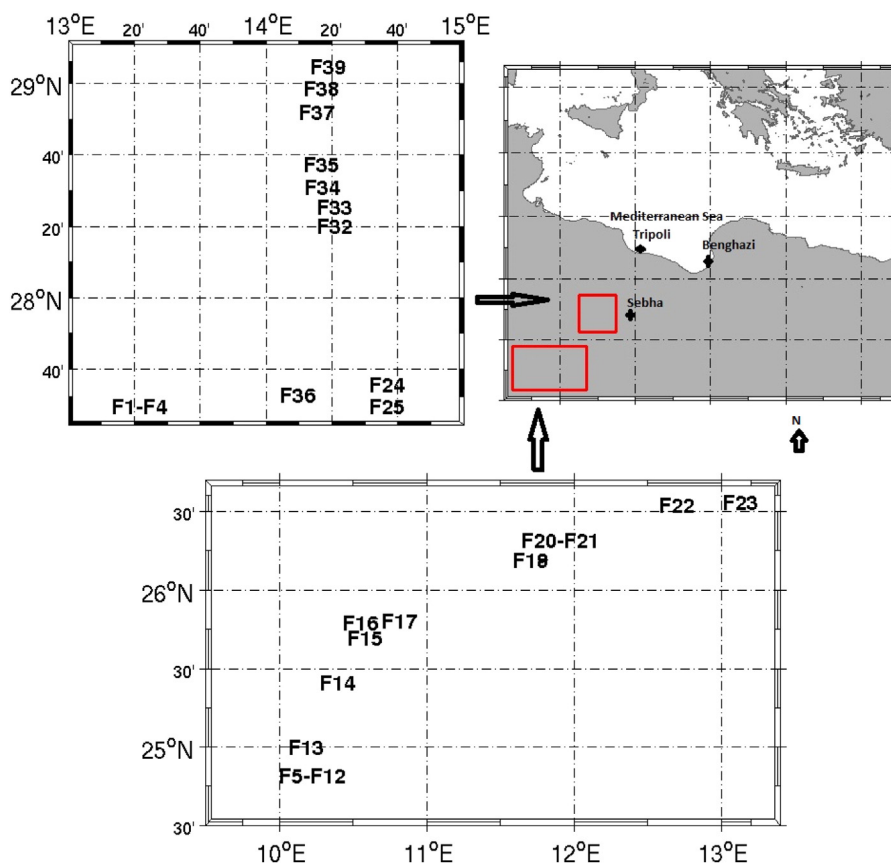


Fig. 1. Map showing the soil sampling locations in the Fezzan region, Libyan Sahara.

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.

As part of a larger project to investigate the geochemical processes associated with the formation of alkaline soils in different parts of the world, we present here the results from the Fezzan basin, southwestern Libya. This part of the Sahara desert has so far received relatively less attention despite that its role as a dust source is significant (Falkovich et al., 2001). Another reason for selecting this area for the

study is its relevance to desert irrigation agriculture. There is a need to enhance agricultural activities in Africa to allow its sustainable development (Valipour, 2014, 2015). 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 and Loucks, 1999). However, detailed soil information covering a large area is lacking though a limited number of small-scale soil investigations with varying purposes were conducted at some locations (e.g. El-Ghawi et al., 2005; Salem and Al-ethawi, 2013). To develop sustainable agricultural

Table 1
Average and range of pH, EC, various carbon fractions, soluble and exchangeable basic cations for the upper layer (0–30 cm) 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	0.00	2.24
Soluble K (mmol/kg)	1.49	0.00	11.8
Soluble Na (mmol/kg)	45.7	0.10	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 2
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
F7	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

Table 3

Vertical variation in soluble K, Na, Ca, Mg and SAR along the 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)	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
F12	70–90	0.91	1.84	4.83	0.99	0.76
	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

systems in these areas, there is a need to understand the soil properties of the potential agricultural lands.

The aim of this work 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 risk 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.

2. Materials and methods

A total of 53 soil samples were collected from 33 locations within the Fezzan basin (Fig. 1). For most of the sampling locations, soil samples were taken from the surface layer (0–30 cm). 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, the soil samples were crushed to pass a 2 mm sieve. Gravels (>2 mm fraction) were then discarded. After homogenization, two subsamples of the <2 mm soil fraction

Table 4

Vertical variation in exchangeable K, Na, Ca, Mg and ESP along the 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
F12	70–90	7.39	26.7	55.2	0.81	18.3
	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

Table 5

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 ₂ O ₃ (%)	8.32	1.37	25.6
BaO (%)	0.03	0.01	0.06
CaO (%)	5.55	0.26	28.8
Fe ₂ O ₃ (%)	3.64	0.49	10.5
K ₂ O (%)	1.16	0.04	2.65
MgO (%)	1.14	0.07	4.95
MnO (%)	0.12	0.01	1.36
Na ₂ O (%)	0.70	0.03	2.71
P ₂ O 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 ₂ O ₃	18.5	4.41	52.7
Fe ₂ O ₃ /Al ₂ O 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 ₂ O	50.0	0.70	659

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 Australian laboratory for various analyses.

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 NH₄Cl) extract with the procedure that was exactly the same as the water extraction except that 25 mL of 1 M NH₄Cl 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 NH₄Cl 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 Al₂O₃, BaO, CaO, Cr₂O₃, Fe₂O₃, K₂O, MgO, MnO, Na₂O, P₂O₅, SiO₂, SrO and TiO₂. Total carbon was determined by a LECO CNS Analyzer. Organic carbon was determined using a Walkley–Black method. For all the soil fractions (<2 mm,

Table 6

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 ₂ O ₃	Fe ₂ O ₃ /Al ₂ O ₃	SiO ₂ /CaO	SiO ₂ /TiO ₂	CaO/Na ₂ O
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
F12	70–90	17.4	0.2	27	271	2.5
	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
	150–160	45.5	0.3	21	512	84
	190–200	47.1	0.3	50	595	62

<0.2 mm and <0.1 mm), 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 NH₄Cl-extractable cations. Sodium adsorption ratio (SAR) of the water extract was calculated using the following formula:

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

where the unit of soluble Na⁺, Ca²⁺ and Mg²⁺ is in mmol/L. The exchangeable sodium percentage (ESP) was obtained by the following formula:

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

where the unit of exchangeable Na⁺, K⁺, Ca²⁺ and Mg²⁺ is in mmol/kg. The inorganic carbon content was estimated by the difference between the total carbon and the organic carbon.

3. Results and discussion

3.1. 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 1). These 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 (Table 2). 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 20–30 cm 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). F12 and F21 all had lower EC value in the 20–30 cm layer, relative to the upper soil

Table 7
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			<2 mm 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
Zr	7.33	2.10	15.2	13.0	7.80	18.8	12.8	5.60	25.8

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 the next section.

3.2. Soluble and exchangeable basic cations

From Table 1, it can be seen that the concentration of soluble Na, K, Ca and Mg was highly variable among the surface soils collected from different locations within the Fezzan area. This is likely to be related to soil parent materials and geomorphic positions of various sampling sites. Where the soils have been developed from saline lake sediments or are located in the low-lying areas, the concentration of soluble salts tend to be much higher, as compared to the soils developed from non-saline soil parent materials. In general, 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 only 6.52, suggesting that most of the upper soil layers were not technically sodic if the threshold value of 15% (Brady and Weil, 1996) is used for evaluation. For soils such as F12 and F24 that were non-sodic in both surface and subsoil layers (Tables 3 and 4), 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 4) can cause soil dispersion to prevent formation of soil aggregates, which reduces water infiltration and could lead to waterlogging conditions. The poor soil aeration caused by destruction of soil structure can restrict plant root development and adversely affect crop yields, especially in fine-textured soils. To improve such soil physical conditions, application of gypsum, coupled with appropriate drainage system is required to reduce soil ESP and remove excess soluble Na from the soils. Gypsum addition can also decrease soil pH by forming calcium carbonates, which simultaneously sequesters atmospheric CO₂, as shown in the following chemical equation:



Gypsum is locally available in Fezzan. Therefore, amelioration of sodic soils with gypsum is likely to be cost-effective for 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 (Tables 3 and 4). 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 probably 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.

3.3. Organic and inorganic carbon

Organic carbon content in the investigated soils (Table 1) 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. 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 (Table 2) that was collected from agricultural land where crop growth allowed ongoing accumulation of organic carbon in the surface soil layer. 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 have impacts on soil organic carbon dynamics. First, the increase in soil moisture content as a result of land irrigation is likely to promote, through enhanced microbial activities, the decomposition of this stored organic carbon. This could make the soil organic C a source of atmospheric CO₂. Second, the production of organic matter from the introduced crops will result in atmospheric CO₂ 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 CO₂.

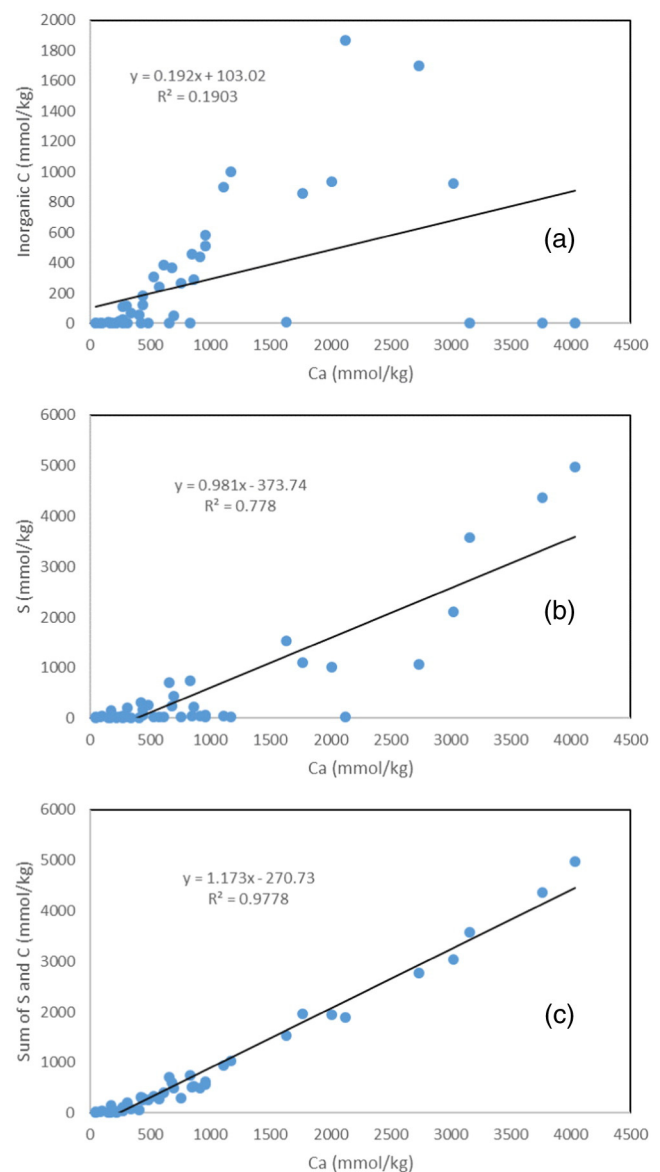


Fig. 2. Scatter plot showing the relationship between aqua regia-extractable Ca and (a) inorganic C, (b) aqua regia-extractable S, and (c) the sum of inorganic C and aqua regia-extractable S.

Inorganic C in the upper soil layer ranged from non-detectable to more than 2% with a mean value of only 0.26% (Table 1). This suggests that, in general, there was only limited amount of inorganic C stored in the surface soil layer in the Fezzan area despite that inorganic C-rich soils can be found in isolated area. For the five investigated soil profiles, two of them (F4 and F24) showed negligible presence of inorganic C to the sampling depths (Table 2). F4 had soil pH > 9 (Table 2) and high levels of soluble Na (Table 3), suggesting that the soil contained NaHCO₃ and NaOH. However, the lack of soluble Ca (Table 3) did not favor 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 cm) of F7 (Table 2) 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):



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

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: SiO₂ > Al₂O₃ > CaO > Fe₂O₃ > K₂O > MgO > Na₂O > TiO₂ > MnO > P₂O₅ > SrO > BaO (Table 5). The molar ratio of SiO₂ to Al₂O₃ (SiO₂/Al₂O₃) 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 SiO₂/Al₂O₃ with depth (Table 6). Fe₂O₃/Al₂O₃ had a mean value < 0.3 with a range of 0.15–0.84. Vertical variation in Fe₂O₃/Al₂O₃ along the soil profile was not remarkable (Table 6). The mean of SiO₂/CaO and SiO₂/TiO₂ were 32.5 and 240, respectively (Table 5). Mixed vertical variation patterns were observed for different soil profiles (Table 6), probably reflecting the inherent characteristics of the palaeo lacustrine sediment layers. Depending on the degree of wind deflation, 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 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 (Table 5), indicating the predominant presence of Ca over Na.

3.5. Aqua regia-extractable elements in different soil particle fractions

In comparison with the XRD results, Al extracted by aqua regia was much lower (Tables 5 and 7). This suggests that much of the Al was bound to silicate minerals, which are not readily extractable with aqua regia (Niskavaara et al., 1997). Almost all the Ca was extractable with aqua regia, indicating that silicate-bound Ca was negligible. There was no close relationship between Ca and inorganic C (Fig. 2a). Fig. 2b shows that Ca was closely related to S (R² = 0.778), suggesting that Ca was largely bound to gypsum (confirmed by XRD, data not shown). However, a closer relationship (R² = 0.978) was observed when Ca is plotted against the sum of S and C (Fig. 2c), suggesting that Ca was also largely bound to calcium carbonates for some soil samples.

The concentration of various elements was generally consistent between the <0.2 mm 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

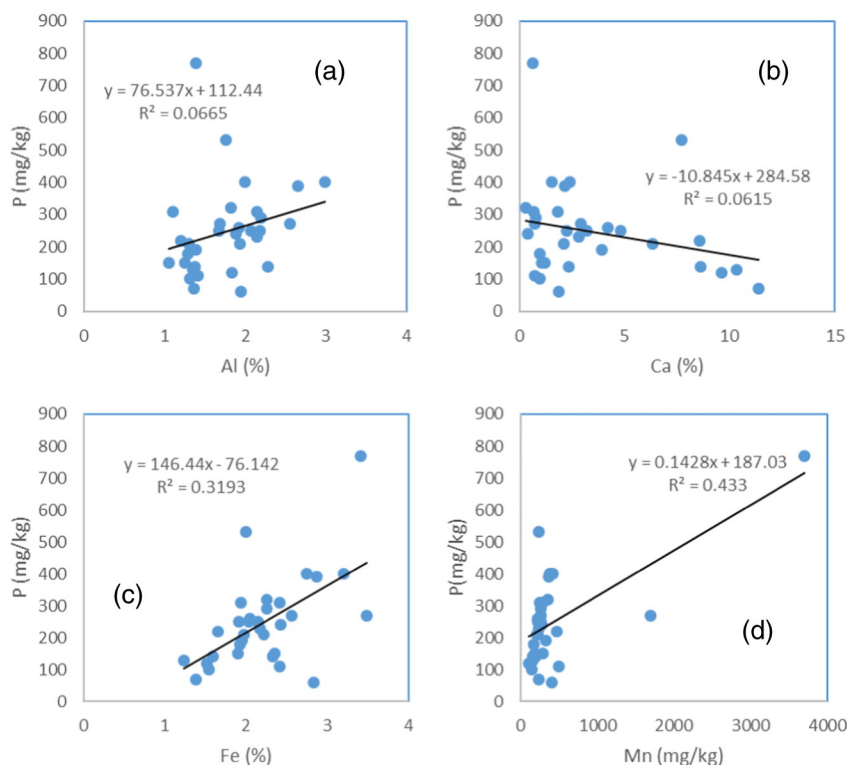


Fig. 3. Scatter plot showing the relationship between phosphorus and (a) aluminium, (b) calcium, (c) iron, and (d) Mn (all elements were determined in aqua regia extracts).

showing the difference in the abundance between the <0.1 mm fraction and the <0.2 mm 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 (IUPAC, 1990), 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 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 (Fig. 3a and b), suggesting that P was not, to any significant extent, bound to these two metals. However, P was somewhat related to Fe (Fig. 3c) and Mn (Fig. 3d), indicating that the soil P had a higher affinity to Fe and Mn than Al and Ca.

Sulfur 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 <2 mm fraction (0.97%). There have been research interests in soil-derived sulfate in atmospheric dust particles from deserts in other parts of the world (Abuduwaii et al., 2008; Wu et al., 2012). Zhang et al. (2014) determined the sulfur 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 were much

lower, as compared to the soils in the Fezzan desert. It is therefore likely that Fezzan is an important source to the atmospheric sulfur loading.

Among the elements of potential toxicity, the concentration of Mn and Sr was unusually high (Table 7). Manganese averaged 865 mg/kg with the maximum concentration up to 9230 mg/kg. Inhalation of airborne Mn compounds could pose a significant health risk (Adkins et al., 1980; Wennberg et al., 1991). The mean concentration of Sr was 231 mg/kg with the maximum concentration as high as 2720 mg/kg. Although Sr is relatively 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 ($R^2 = 0.677$) (Fig. 4). Sr showed certain relationship with Ca ($R^2 = 0.333$) but no clear relationship with any of other major elements (Fig. 5).

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 Fig. 6a and b, it can be seen that there was a good correspondence in vertical variation between pH and inorganic C; 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 Fig. 6c that soluble Ca concentration was virtually

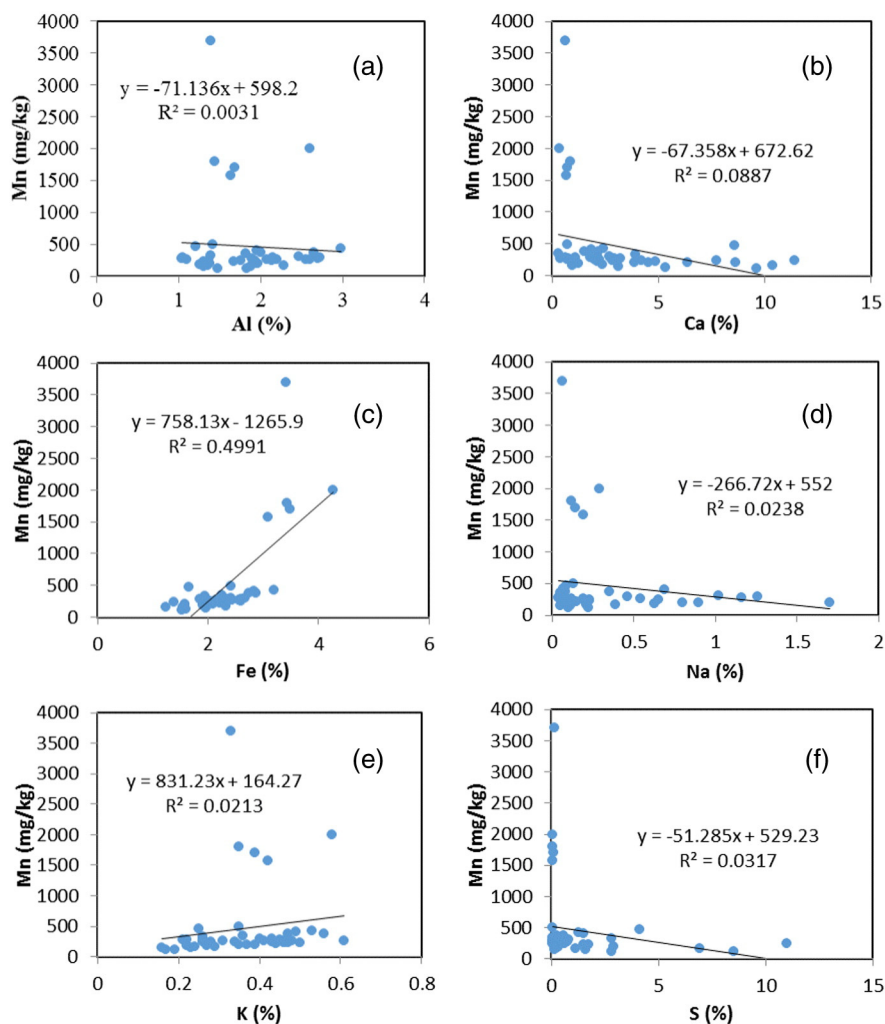


Fig. 4. Scatter plot showing the relationship between manganese and (a) aluminium, (b) calcium, (c) iron, and (d) sodium, (e) potassium, and (f) sulfur (all elements were determined in aqua regia extracts).

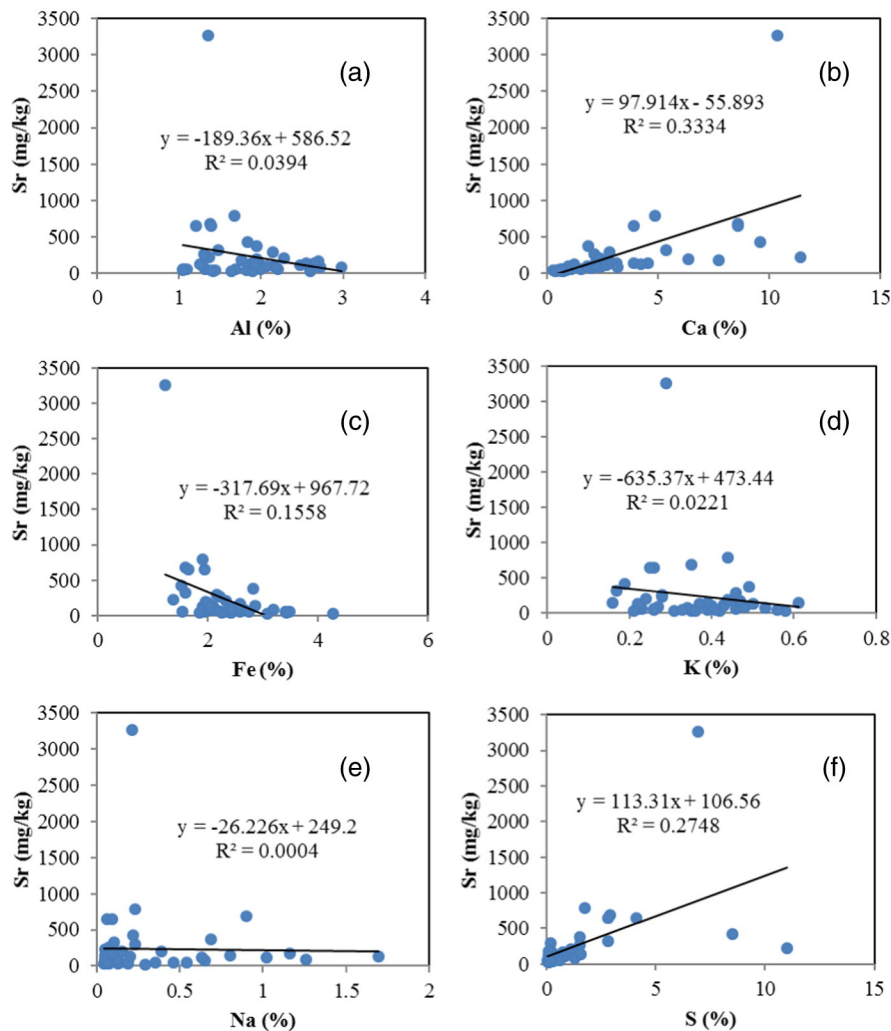


Fig. 5. Scatter plot showing the relationship between strontium and (a) aluminium, (b) calcium, (c) iron, and (d) sodium, (e) potassium, and (f) sulfur (all elements were determined in aqua regia extracts).

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 Eq. (1). This reaction produced substantial amounts of soluble Na_2SO_4 , which raised the value of EC in the subsoil layers (Fig. 6f).

To ameliorate this type of alkaline soils, soil ripping 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.

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 sulfur 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 Great 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 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. 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.

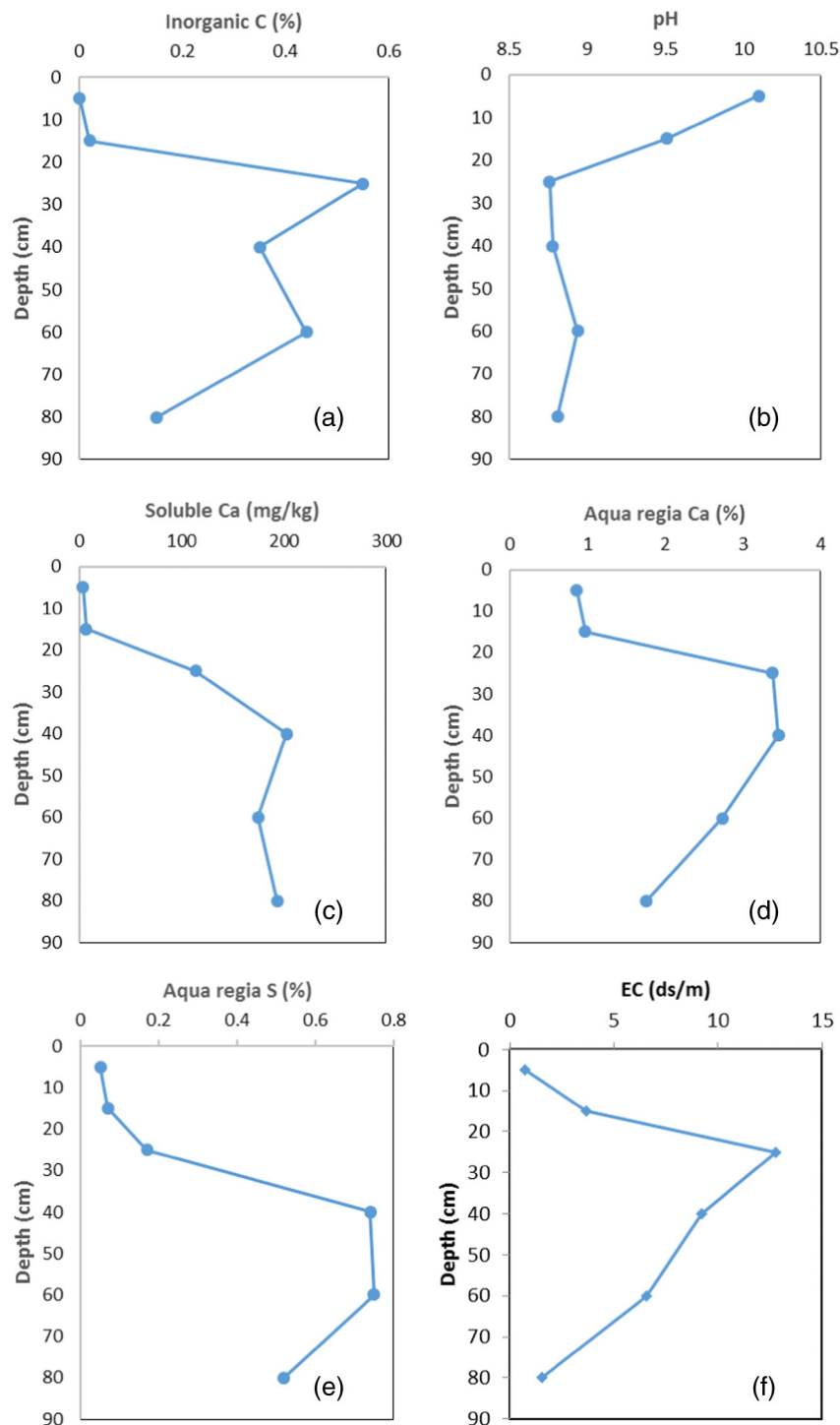


Fig. 6. Vertical variation in (a) inorganic C, (b) pH, (c) soluble Ca, (d) aqua regia Ca, (e) aqua regia S and (f) EC along Soil Profile F7.

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.

Conformation of authorship

Professor Chuxia Lin and Mr. Emohamed Maryol (PhD student) jointly designed the research plan. Emohamed Maryol carried out the field and laboratory investigations under supervision of Chuxia Lin. Chuxia Lin prepared the manuscript.

Acknowledgements

Emohamed Maryol would like to thank the Libyan Government for providing him with a PhD scholarship to enable him to study in Australia.

References

- Abuduwaili, J., Gabchenko, M.V., Xu, J.R., 2008. Eolian transport of salts – A case study in the area of Lake Ebinur (Xinjiang, northwest China). *J. Arid Environ.* 72 (10), 1843–1852. <http://dx.doi.org/10.1016/j.jaridenv.2008.05.006>.

- Adkins, B., Luginbuhl, G.H., Miller, F.J., Gardner, D.E., 1980. Increased pulmonary susceptibility to streptococcal infection following inhalation of manganese oxide. *Environ. Res.* 23, 110–120.
- Alastuey, A., Querol, X., Castillo, S., Escudero, M., Avila, A., Cuevas, E., Torres, C., Romero, P., Exposito, F., García, O., Diaz, J.P., Van Dingenen, R., Putaud, J.P., 2005. Characterisation of TSP and PM_{2.5} at Izaña and Sta. Cruz de Tenerife (Canary Islands, Spain) during a Saharan dust episode. *Atmos. Environ.* 39, 4715–4728.
- ATSDR, 2004. Public Health Statement — Strontium (CAS#: 7440-24-6).
- Barkan, J., Alpert, P., Kutiel, H., Kishcha, P., 2005. Synoptics of dust transportation days from Africa toward Italy and central Europe. *J. Geophys. Res.* 110, 2156–2202.
- Borbély-Kiss, I., Kiss, Á.Z., Koltay, E., Szabó, Gy., Bozó, L., 2004. Saharan dust episodes in Hungarian aerosol: Elemental signatures and transport trajectories. *J. Aerosol Sci.* 35 (10), 1205–1224.
- Brady, N.C., Weil, R.R., 1996. *The Nature and Properties of Soils*. Eleventh ed. Prentice Hall, Upper Saddle River, New Jersey (740 pp.).
- Brunekreef, B., Forsberg, B., 2005. Epidemiological evidence of effects of coarse airborne particles on health. *Eur. Respir. J.* 26, 309–318.
- 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. *Quat. Sci. Rev.* 19 (1–5), 347–361.
- Drake, N.A., El-Hawat, A.S., Turner, P., Armitage, S.J., Salem, M.J., White, K.H., McLaren, S., 2008. Palaeohydrology of the Fazzan Basin and surrounding regions: The last 7 million years. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 263 (3–4), 131–145.
- El-Ghawi, U.M., Bejey, M.M., Al-Fakhri, S.M., Al-Sadeq, A.A., Doubali, K.K., 2005. Analysis of Libyan arable soils by means of thermal and epithermal NAA. *Arab. J. Sci. Eng.* 30 (1A), 147–153.
- 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* 203 (1–3), 47–55.
- Falkovich, A.H., Ganor, E., Levin, Z., Formenti, P., Rudich, Y., 2001. Chemical and mineralogical analysis of individual mineral dust particles. *J. Geophys. Res.* 106 (D16), 18029–18036.
- Gijssbers, P.J.A., Loucks, D.P., 1999. Libya's choices: Desalination or the Great Man-made River Project. *Phys. Chem. Earth B* 24 (4), 385–389.
- Goudie, A.S., 2014. Desert dust and human health disorders. *Environ. Int.* 63, 101–113.
- Goudie, A.S., Middleton, N.J., 2001. Saharan dust storms: Nature and consequences. *Earth Sci. Rev.* 56 (1–4), 179–204.
- IUPAC, 1990. Glossary of atmospheric chemistry terms. International Union of Pure and Applied Chemistry, Applied Chemistry Division, Commission on Atmospheric Chemistry. *Pure Appl. Chem.* 62 (11), 2167–2219.
- Mahowald, N.M., Kloster, S., Engelstaedter, S., Moore, J.K., Mukhopadhyay, S., McConnell, J.R., Albani, S., Doney, S.C., Bhattacharya, A., Curran, M.A.J., Flanner, M.G., Hoffman, F.M., Lawrence, D.M., Lindsay, K., Mayewski, P.A., Neff, J., Rothenberg, D., Thomas, E., Thornton, P.E., Zender, C.S., 2010. Observed 20th century desert dust variability: Impact on climate and biogeochemistry. *Atmos. Chem. Phys.* 10, 10875–10893. <http://dx.doi.org/10.5194/acp-10-10875-2010>.
- Mills, M.M., Ridame, C., Davey, M., La Roche, J., Geider, R.J., 2004. Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic. *Nature* 429, 292–294.
- Minyuk, P.S., Brigham-Grette, J., Melles, M., Borkhodoev, V.Ya., Glushkova, Yu.O., 2007. Inorganic geochemistry of El'gygytgyn Lake sediments (northeastern Russia) as an indicator of paleoclimatic change for the last 250 kyr. *J. Paleolimnol.* 37, 123–133.
- 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* 65 (2), 261–270.
- 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). *Environ. Pollut.* 96, 261–274.
- Prospero, J.M., 1999. Long-term measurements of the transport of African mineral dust to the southeastern United States: Implications for regional air quality. *J. Geophys. Res.* 104, 15917–15927.
- Prospero, J.M., Ginoux, P., Torres, O., Nicholson, S.E., Gill, T.E., 2002. Environmental characterization of global sources of atmospheric soil dust identified with the nimbus 7 total ozone mapping spectrometer (TOMS) absorbing aerosol product. *Rev. Geophys.* 40 (1), 1–31.
- Rodríguez, S., Querol, X., Alastuey, A., Kallos, G., Kakaliagou, O., 2001. Saharan dust contributions to PM₁₀ and TSP levels in southern and eastern Spain. *Atmos. Environ.* 35 (14), 2433–2447.
- Roy, P.D., Arce, J.L., Lozano, R., Jonathan, M.P., Centeno, E., Lozano, S., 2012. Geochemistry of late Quaternary tephra-sediment sequence from northeastern basin of Mexico (Mexico): Implications to tephrochronology, chemical weathering and provenance. *Rev. Mex. Cienc. Geol.* 29 (1), 24–38.
- Salem, M.A., Al-ethawi, L.H., 2013. Evaluation of salinity in some soils of irrigated Brack-Ashkada agriculture project, Fezzan, Libya. *IOSR J. Agric. Vet. Sci.* 2 (1), 5–9.
- Schuster, M., Düringer, P., Ghienne, J., Vignaud, P., Mackaye, H.T., Likius, A., Brunet, M., 2006. The age of the Sahara desert. *Science* 311 (5762), 821.
- Swap, R., Ulanski, S., Cobbett, M., Garstang, M., 1996. Temporal and spatial characteristics of Saharan dust outbreaks. *J. Geophys. Res.* 101 (D2), 4205–4220.
- Valipour, M., 2014. Land use policy and agricultural water management of the previous half of century in Africa. *Appl. Water Sci.* <http://dx.doi.org/10.1007/s13201-014-0199-1>.
- Valipour, M., 2015. Future of agricultural water management in Africa. *Arch. Agron. Soil Sci.* 61 (7), 907–927.
- 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. *Scand. J. Work Environ. Health* 17, 255–262.
- Wu, F., Zhang, D., Cao, J., Xu, H., An, Z., 2012. Soil-derived sulfate in atmospheric dust particles at Taklimakan desert. *Geophys. Res. Lett.* 39 (24), L24803. <http://dx.doi.org/10.1029/2012GL054406>.
- 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. *Sci. Total Environ.* 472, 1121–1129.