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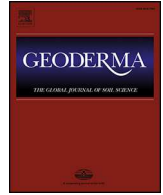
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# Seasonal differences in soil CO<sub>2</sub> efflux and carbon storage in Ntwetwe Pan, Makgadikgadi Basin, Botswana



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## ABSTRACT

The carbon cycle in salt pans is complex and poorly understood. Field-based data are needed to improve regional estimates of C storage and land–atmosphere CO<sub>2</sub> fluxes from dryland environments where pans are prevalent. This paper provides a first estimate of C stores and CO<sub>2</sub> efflux within the salt pan, grassland and woodland of Ntwetwe Pan in the Makgadikgadi Basin, Botswana. C fluxes and stores associated with cyanobacteria–salt crusts are also determined. Total C stores are approximately an order of magnitude greater than on neighbouring Kalahari Sands at 675 ± 41, 760 ± 94 and 274 ± 15 tons ha<sup>-1</sup> to 1 m depth in the woodland, grassland and salt pan respectively. Most of the C is found as carbonate, with organic C comprising 4.6–10% of total C. CO<sub>2</sub> efflux increased with temperature and also increased for a few hours after flooding of the pan surface. Crusts were a small net contributor to CO<sub>2</sub> efflux in the dry season but could be a net CO<sub>2</sub> sink in the wet season. The biogeochemistry of the sediment is likely to facilitate rapid conversion of organic C from aquatic organisms, biological crusts and algal mats into inorganic carbonates. Although further work is required to improve estimates of the spatial and temporal distribution of C, our data have demonstrated the substantial C store with the Makgadikgadi environment and the important role of biological crusts in the C cycle.

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## 1. Introduction

The amount, distribution and form of soil carbon (C) are of considerable importance for climate, agricultural productivity and ecosystem functioning (Lal, 2009; Schmidt et al., 2011). Yet for many sub-Saharan African environments, processes affecting soil C and land–atmosphere C fluxes remain poorly understood (Bombelli et al., 2009; Bond-Lamberty and Thomson, 2010; Ciaies et al., 2011). This is especially true for African salt pans (also known as playas or sabkhas) and their peripheral saline and alkaline habitats where there are very few, if any, data on the form and amount of C in pan sediment or the atmospheric flux of C (Xie et al., 2009). In most natural terrestrial environments, the size of the soil C store is determined by the balance between inputs from primary production and outputs from gases produced during the decomposition of organic matter, with additional losses in groundwater and eroded material. The C store on salt pans is also affected by these processes but their lack of vascular plant cover and unique hydro-geochemistry means that C cycling has additional complexity and few similarities to soil C in mesic environments (Chairi et al., 2010; Day, 1993; Jellison et al., 1996; Mörner and Etiope, 2002).

Salt pans are nutrient-rich and productive systems. When in flood a variety of algae, cyanobacteria and crustaceans proliferate in conditions of high nutrient concentrations, high temperatures and intense light (McCulloch et al., 2008). Upon desiccation, both organic and inorganic C from aquatic organisms are returned to the sediment (Fig. 1) with primary productivity continuing with algae and cyanobacteria in mats, crusts and surface sediment (Lebogang et al., 2009) (Fig. 2). Organic C inputs from biological crusts to soils are known to be regionally and globally significant (Elbert et al., 2012; Thomas, 2012), but there are very few estimates of their contribution to the C store of salt pans (Chairi et al., 2010 is a rare example).

Salt pan sediment typically contains high concentrations of inorganic C. This is commonly in the form of calcium and magnesium carbonate and bicarbonate, derived from parent material (lithogenic), and from dissolution and precipitation of in-situ carbonates (pedogenic). Pedogenic inorganic C is common where there is an abundance of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions and where carbonate can precipitate and accumulate (White and Eckardt, 2006; Wright and Tucker, 1991). Conditions that lead to carbonate accumulation in soils are varied, but simplified chemical reactions (Eq. (1)) for calcium carbonate are illustrative (see Bohn et al., 2001):



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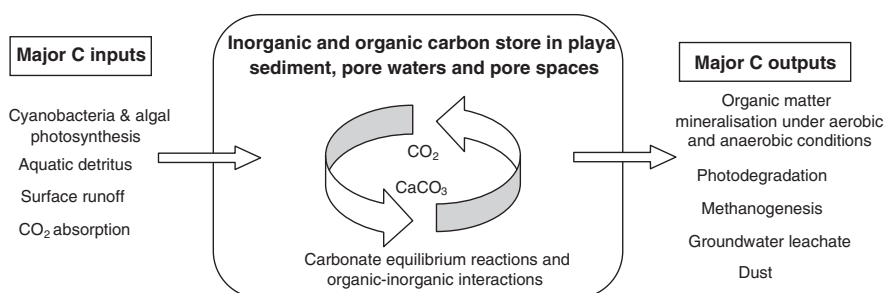
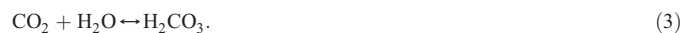


Fig. 1. Simplified schematic of the principal inputs and outputs of carbon on the salt pan. Currently there are too few data to quantify these stores and fluxes.

An increase in partial pressure of  $\text{CO}_2$  can lead to dissociation of  $\text{CaCO}_3$  (Eq. (2)), however in most soils, high  $\text{Ca}^{2+}$  concentration and scarcity of water prevent this from occurring (Bohn et al., 2001).  $\text{HCO}_3^-$  can be formed as  $\text{CO}_2$  dissolves into pore waters, bringing  $\text{Ca}^{2+}$  and/or  $\text{Mg}^{2+}$  ions into solution, and initiating precipitation of carbonate salts (Day, 1993).



$\text{CO}_2$  uptake can also occur due to  $\text{CO}_2$  absorption by alkaline soil pore waters (Xie et al., 2009), forming carbonic acid and decreasing pH, and is another potential route for long-term C storage (Eq. (3)):



The amount of organic and inorganic C in salt pan sediment is also a function of preservation, and organic C and  $\text{CaCO}_3$  concentrations are

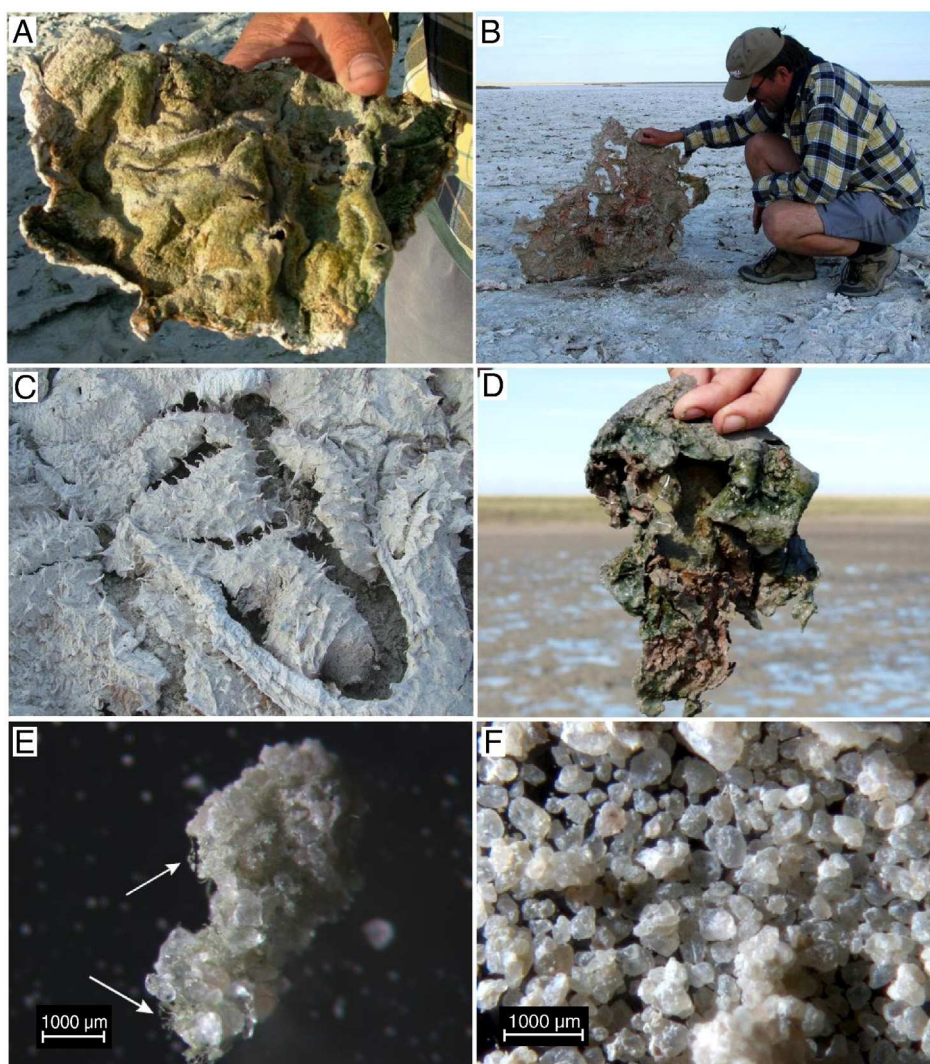


Fig. 2. Crusts, algal mats and salt pan sediments. A) The underside of a salt crust, coloured by chlorophyll produced by autotrophic microorganisms. B) The underside of a salt crust with red-pink colouration of cyanobacteria. C) Surface patterns on a salt crust surface. D) Algal mat after rainfall in April 2011. E) Salt/carbonate aggregate in surface salt pan sediments bound with cyanobacterial filaments (arrowed). F) Carbonate and salt granules from 0.75 to 1 m depth on the salt pan. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

often inversely correlated (Dean, 1999; Jellison et al., 1996). For example, CO<sub>2</sub> produced by decomposition of organic C and production of organic acids in lake sediment from Minnesota lowered the pH of anoxic pore waters enough to dissolve CaCO<sub>3</sub> (Dean, 1999). Conversely, biogenic removal of CO<sub>2</sub> and the accompanying rise in pH increased CaCO<sub>3</sub> production.

Anaerobic microbial processes such as sulphate reduction, acetogenesis, and methanogenesis also play important roles in the cycling and storage of C in salt pan systems (Fig. 1). Anaerobic conditions will be generated in pan sediments when oxygen utilised in microbial respiration cannot be replenished by photosynthesis and diffusion. This state is likely to occur in surface sediments during flood events when respiration rates are very high, and more permanently below the water table where organic C is present. In the absence of oxygen, alternative electron acceptors such as sulphate may be utilised to enable continued microbial respiration of organic C and sulphate-reducing bacteria are likely to be a major component of the C cycle. They are known to be abundant in microbial mats and to be associated with lithification and the precipitation of carbonate (Baumgartner et al., 2006; Dupraz et al., 2004). Acetogenic bacteria can also utilise CO<sub>2</sub> as a terminal electron acceptor and in doing so they generate acetate, a key metabolite of C in anoxic sediments. This generates organic C which can serve as a substrate for other anaerobic organisms including sulphate reducing bacteria and methanogens (Heuer et al., 2009). Methanogenesis has been observed in many hyper-saline environments and methane generation is a potential route for C loss from salt pan systems, but little is known about the methanogenic microbial communities of hyper-saline systems (Smith et al., 2008).

Most of the pathways in Fig. 1 are not well parameterised and the major inputs and outputs of C to salt pans remain poorly quantified (Briere, 2000; Emmerich, 2003). Alkaline soils and sediments are, however, a potentially significant store of global C (e.g. Xie et al., 2009) and new data are needed to improve estimates of C storage and land-atmosphere C fluxes. Only then will there be improvements in regional C flux models and budgets across southern Africa and other dryland environments where salt pans are prevalent.

The aim of this research was to provide the first field-based estimate of the C store and CO<sub>2</sub> efflux from the salt pan, saline grassland and palm woodland of Ntwetwe Pan in the Makgadikgadi Basin, Botswana. The objectives of the fieldwork were to determine: i) how much organic and inorganic C is contained in the soils and sediments; ii) CO<sub>2</sub> efflux from the sediment and how this is affected by temperature and moisture; and iii) the proportion of C and CO<sub>2</sub> efflux originating from salt-cyanobacteria crusts on the pan. These data, together with the conceptual model, can then be used as a basis for testing future hypotheses relating to processes affecting the C cycle in salt pans and their peripheral environments.

## 2. Research design and methods

### 2.1. Study site

The Makgadikgadi Basin comprises a series of shallow ephemeral lakes covering an area of approximately 37,000 km<sup>2</sup> in northern Botswana (Fig. 3). The contemporary pans of Ntwetwe, Sua, and the numerous smaller pans that surround them are relics of paleolakes that once covered much of northern Botswana (Burrough et al., 2009; Ringrose et al., 2005). Average annual rainfall ranges from 359 mm in Rakops to 545 mm in Maitengwe, along a southwest–northeast rainfall gradient. Highest mean monthly rainfall is in January–February, and July–August are the driest months, with average evapotranspiration rates exceeding 2500 mm per year (Department of Environmental Affairs and Centre for Applied Research, 2010).

Pan soils are solonchaks, with shallow leptosols, regosols and arenosols in fringing areas (De Wit and Nachtergaele, 1990; Wang et al., 2007) which can become calcified in areas immediately

surrounding the pans (Mees and Van Ranst, 2011; Ringrose et al., 2005; White and Eckardt, 2006). Pan sediment is clay-rich and mixed with salts derived from shallow near-surface water, as well as deeper brines dominated by NaCl and Na<sub>2</sub>CO<sub>3</sub> (Department of Environmental Affairs and Centre for Applied Research, 2010; Gould, 1986). The proximity of shallow ground water and the fine-grained sediment means that heavy or prolonged precipitation frequently leads to flooding. The pan surface is also covered with a brittle crust, comprised of salt and cyanobacteria (Lebogang et al., 2009) (Fig. 2).

Salinity is the dominant factor in determining vegetation cover. On the pan where salinity is highest, there is no vascular plant cover. Extensive saline grasslands surround the pans where wind-blown sand forms a rooting zone for *Odyssea paucinervis* (Stapf) and *Sporobolus* species (Department of Environmental Affairs and Centre for Applied Research, 2010). With increasing sand depth and decreasing salinity, the grassland becomes more species rich with mixed *Acacia* spp. and *Colophospermum mopane* (Benth.) stands (Bekker and De Wit, 1991). Elevated areas above the grasslands are commonly covered in Mokolowane palm trees (*Hyphaene petersiana*).

### 2.2. Field sampling

Field experiments were undertaken on the salt pan, saline grassland and palm woodland (Fig. 3) on Ntwetwe Pan (20° 29' 35" S; 25° 07' 08" E) in the dry season in July 2010 and the wet season in April 2011. The effect of flooding on CO<sub>2</sub> efflux from the pan sediments was assessed during a 20 mm rainfall event which inundated the salt pan in April. In both seasons, samples of soils and sediment were taken at regular 5 cm depth intervals in triplicate 1 m deep pits, and used to determine geochemical depth profiles and to estimate C storage. Samples were analysed for their total-C, organic C, carbonate, total N, pH and bulk density. Total-C and -N contents were determined using a Leco TruSpec® CN element analyser and organic C using the Walkley–Black titration method (Rowell, 1994). Carbonate-C was determined gravimetrically by digestion with HCl (Loeppert and Suarez, 1996). H<sup>+</sup> ion activity was measured using a pH meter within a 1:5 soil–water concentration after shaking for 1 h. Cation (Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>+</sup>, Ca<sup>2+</sup>) and anion (Cl<sup>-</sup>, SO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>) concentrations in the soils and sediment were determined in distilled water extracts (also shaken for 1 h) using a Dionex ion chromatograph after the solutions were centrifuged and passed through a 0.2 µm filter.

Samples were collected from the upper 7 mm of the surface in order to obtain measurements of C and N in the surface crust. The chlorophyll *a* content of the samples was determined after grinding, heating to 60 °C in the dark in HPLC-grade 100% methanol for 20 min, and pressure filtering. Concentrations in the extract were determined with an Ocean Optics HR4000 spectrometer from the absorbance values at 652 nm, 665.2 nm and 750 nm using the equations of Porra (1990).

In-situ soil and sediment moisture was determined using a Delta-T ML2x theta probe (Delta-T Devices, Cambridge, UK).

### 2.3. CO<sub>2</sub> efflux

Soil/sediment CO<sub>2</sub> efflux was determined using static respiration chambers (based on a design described in Hoon et al., 2009 with modifications outlined in Thomas, 2012). Chambers and the methodology were designed to minimise the likelihood of errors in efflux estimation associated with the use of closed chambers (Davidson et al., 2002; Pumpanen et al., 2004), particularly changes in the surface environment, pressure, and the soil–gas diffusion gradient (further details can be found in Thomas et al., 2011). Three replicate chambers were located approximately 4 m apart on each surface and inserted to a depth of c. 35 mm. Chamber volume was 510 ml, enclosing 106 cm<sup>2</sup> of soil. Chamber lids with a borosilicate glass window were used at all sites to allow sunlight to reach the surface (except on subsoils where opaque



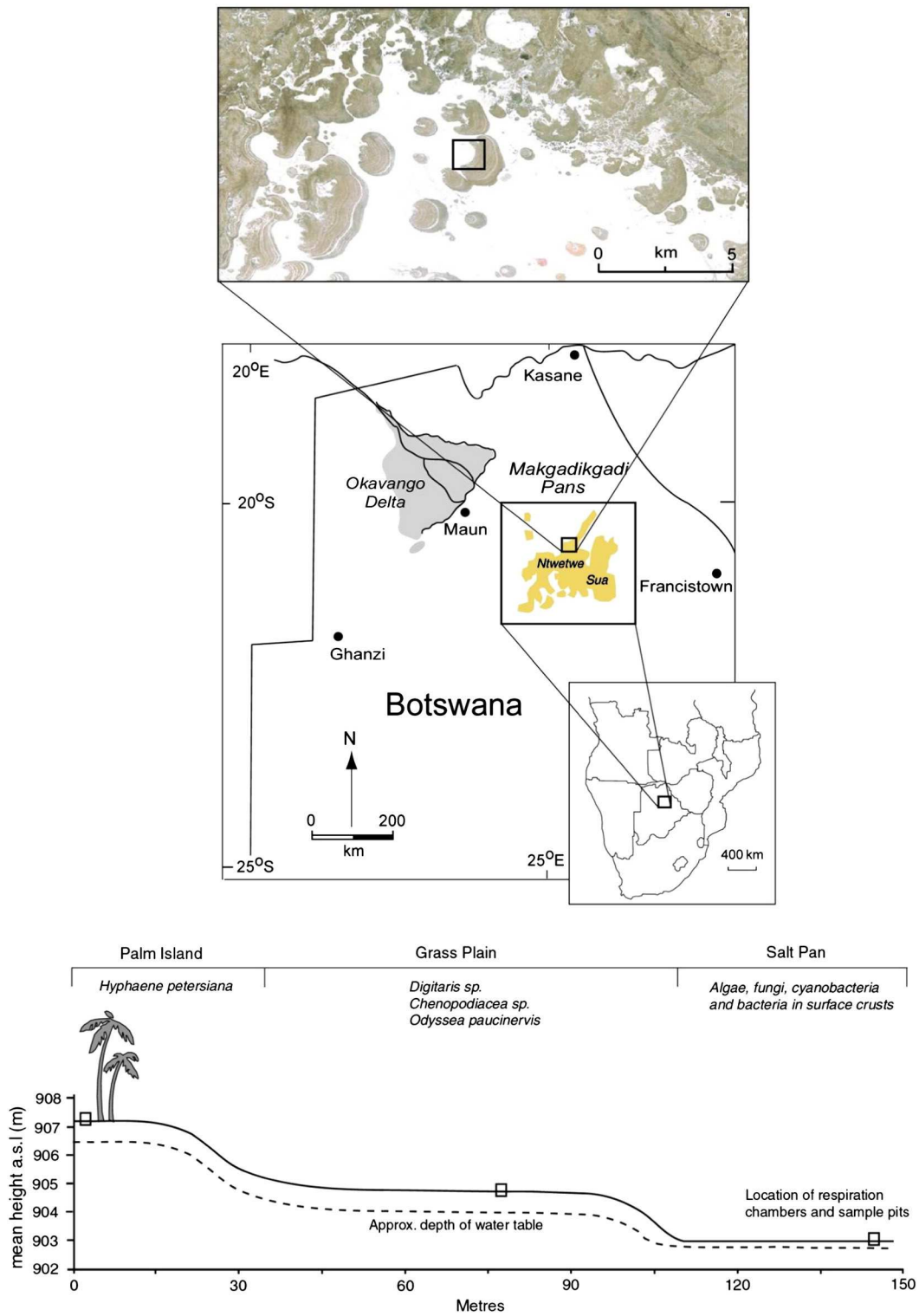


Fig. 3. Location of study site and cross-section of palm woodland, grassland and salt pan sites.

lids were used). Chamber air temperature and relative humidity were recorded at 10 minute intervals using USB502 loggers (Adept Science, UK).

CO<sub>2</sub> efflux in all chambers was determined every 2 h between 07:00 and 18:00 (local time) over 5 days in the dry season of July 2010 and then in the wet season of April 2011. Prior to sampling, air inside the chamber was mixed by gently pumping with the syringe. Within each measurement cycle, two 10 ml air samples were extracted from the

chambers using a gas syringe at 15 minute intervals and injected into 6 ml pre-evacuated glass vials. Samples were thus stored in a slightly over-pressurised state to minimise the risk of vial contamination before CO<sub>2</sub> concentrations were determined using an Agilent gas chromatograph (GC 3000).

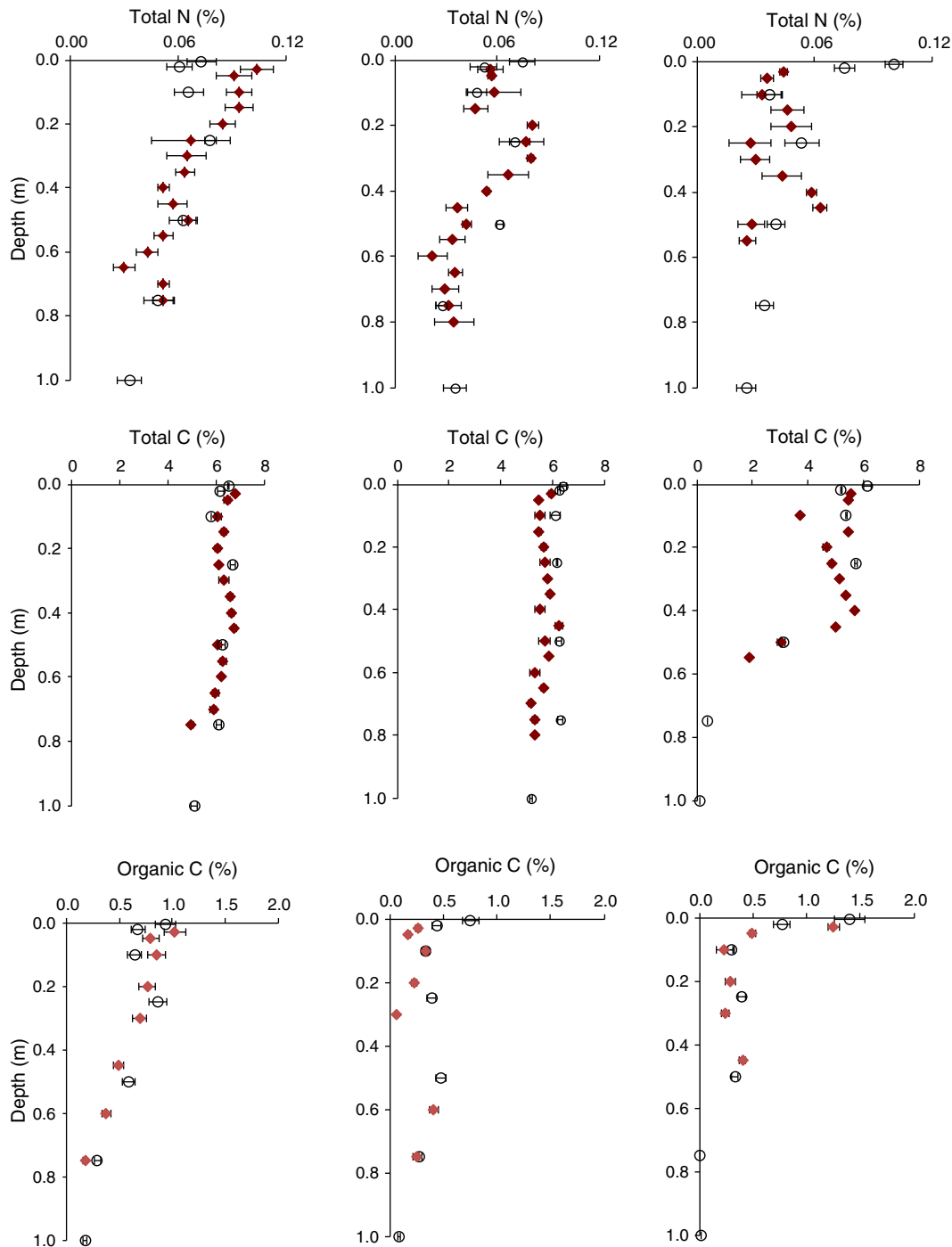
On the salt pan, two different methods were used to determine the proportion of CO<sub>2</sub> efflux originating from the crust and subsurface sediment. To isolate crust CO<sub>2</sub> efflux from the underlying sediment,

triplicate samples of intact crusts were carefully removed from the pan surface and placed on sterilised subsurface sediment within shallow trays. A fourth tray of sterilised sand without a crust acted as a control. Trays were used to prevent mixing of CO<sub>2</sub> originating from the subsurface with that from the crusts. The trays were dug into the pan with the lip of the tray level with the surface. Respiration chambers were placed over the trays and CO<sub>2</sub> efflux determined 4 times a day. Crust CO<sub>2</sub> efflux was calculated from the difference between the

**Table 1**Total and organic C stores (tons ha<sup>-1</sup> to 1 m depth) on woodland, grassland and salt pan.

Tons ha <sup>-1</sup> to 1 m	Palm woodland	Grassland	Salt pan
Total C	675 ± 41	760 ± 94	274 ± 15
Organic C	54.4 ± 0.4	34.7 ± 7.7	27.3 ± 5.8

Means (with standard error) derived from pit samples taken in July 2010 and April 2011 (n = 42).

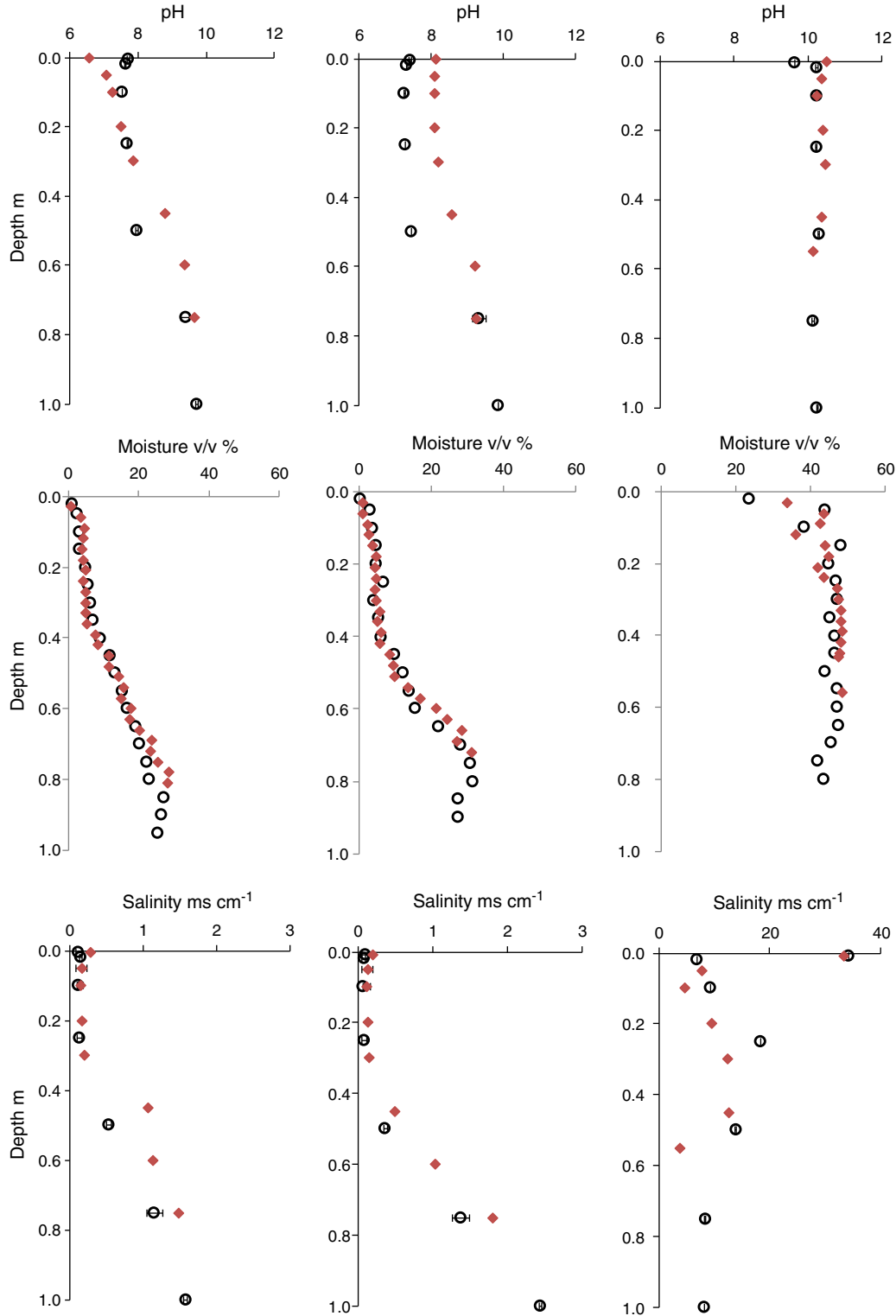


**Fig. 4.** Total N, total C and organic C (%) with depth on woodland (left), grassland (middle) and salt pan (right) in July 2010 (red diamonds) and April 2011 (open circles). Bars represent the standard error (not always visible on some data points) and n = 3 in all cases. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

trays with crusts and the one without. Subsurface  $\text{CO}_2$  efflux was quantified using three chambers located in the centre of a broad trench where the uppermost 10 cm had been removed. Crust  $\text{CO}_2$  efflux was then determined by the difference between the subsurface and surface values.

#### 2.4. Analysis of $\text{CO}_2$ efflux data

Equations described in Kutzbach et al. (2007) were used to determine mass C flux in  $\text{mg m}^{-2} \text{h}^{-1}$  from the diffusion corrected changes in  $\text{CO}_2$  concentration in the chambers. To ensure that soil  $\text{CO}_2$  efflux was



**Fig. 5.** pH, moisture and salinity with depth on woodland (left), grassland (middle) and salt pan (right) soils and sediment in July 2010 (red diamonds) and April 2011 (open circles). Bars (where visible) represent the standard error.  $n = 3$  in all cases. Note scale change on salt pan salinity graph. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

representative of the full range of temperature conditions, data from each chamber were integrated over the measurement period, and the resulting cumulative change in C flux used to determine mean efflux rates. A Van't Hoff/Arrhenius equation (Eq. (4)) was used to derive estimates of the temperature sensitivity of respired CO<sub>2</sub>, where  $R_s$  is the total soil CO<sub>2</sub> efflux at temperature  $T$  and  $R_{s0}$  the efflux at 0 °C. To ensure unbiased fitting of the data,  $T_0$  was set at 0 °C for all treatments and  $Q_{10}$  and  $R_0$  changed to generate the best fit within the measured temperature range. This was determined by optimisation of the correlation coefficient and root mean squared error (RMSE).

$$R_s(T) = R_{s0} Q_{10}^{(T-T_0)/10} \quad (4)$$

Univariate analysis of variance was undertaken (ANOVA) using SPSS (IBM, v. 20) to test the significance of any differences in mean soil CO<sub>2</sub> efflux in each season and on each land cover type.

### 3. Results

#### 3.1. Soil and sediment chemistry

Total and organic C concentrations were 4–7% and 0.2–1.1% w/w respectively in the woodland and grassland soils and were similar in the wet and dry seasons (Fig. 4). On the salt pan, total C concentrations were similar to the woodland and grassland in the upper 0.4 m but declined rapidly with depth to <0.5% w/w at 0.75 m. Organic C concentrations were also highest at the surface and declined with depth on the salt pan (Fig. 4). Total C stores were highest in the woodland and grassland sites and lowest on the salt pan (Table 1). Organic C formed between 4.6% and 10% of the total C store, ranging from  $27.3 \pm 5.8$  to  $54.4 \pm 0.4$  tons ha<sup>-1</sup>.

Total N concentrations were  $\leq 0.12\%$  w/w at all sites in both the wet and dry seasons (Fig. 4). On the woodland and grassland soils, total N was concentrated at the surface, reflecting organic inputs from vascular plants. On the salt pan, the distribution of total N with sediment depth

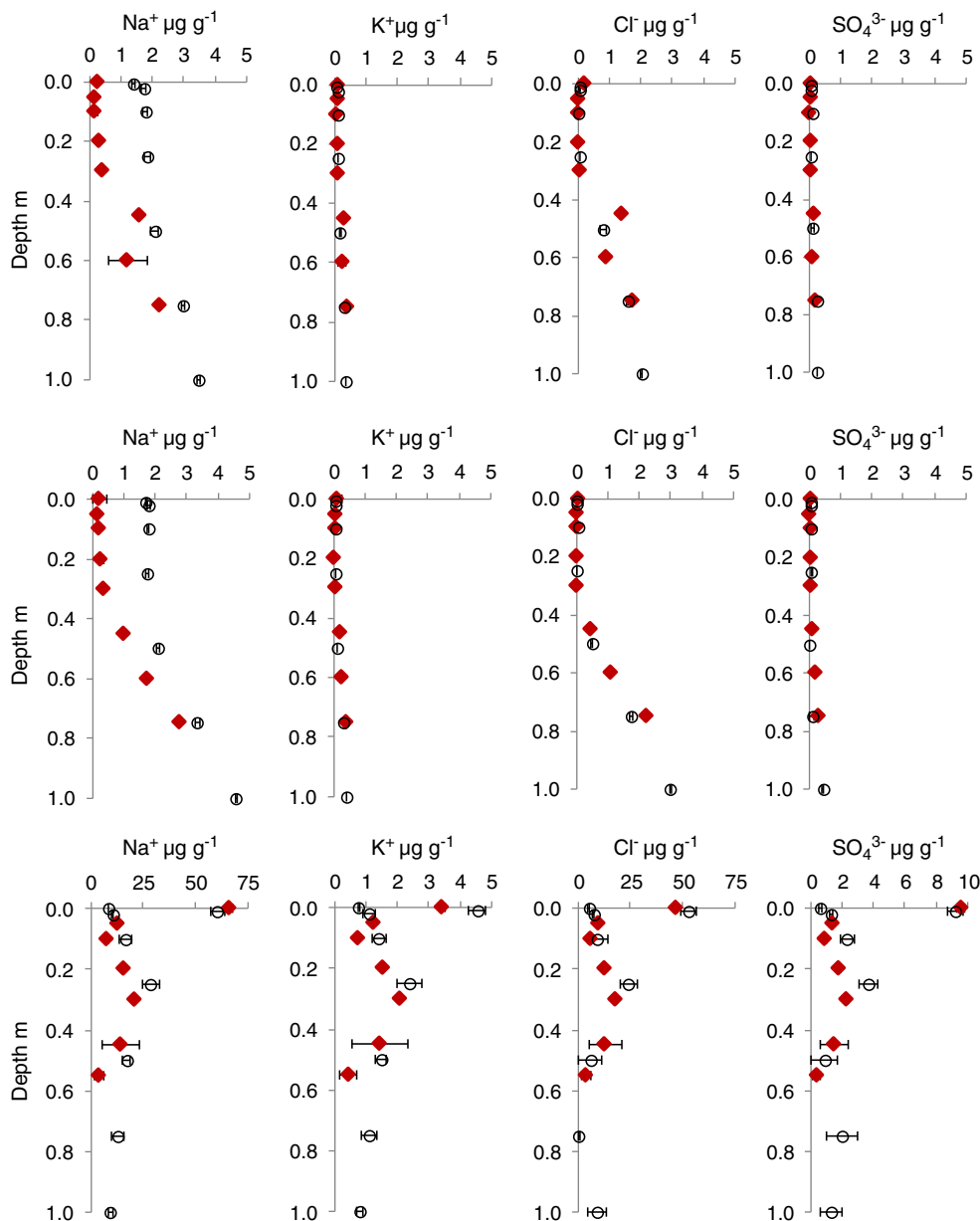


Fig. 6. Mean major cation and anion concentrations with depth in woodland soil (top), grassland soil (middle) and salt pan sediment (bottom) in July 2010 (open circles) and April 2011 (filled diamonds). Standard error bars are given with each mean (but are not always possible to see)  $n = 3$ .



was more uniform, except for the higher concentrations at the surface in April 2011, and a slight declining with depth.

The surface of the woodland soils was slightly acidic but became increasingly alkaline with depth, reaching a pH of close to 10 at 1 m (Fig. 5). The pH of the grassland soils was also increasingly alkaline with depth, whereas the salt pan sediment was uniformly highly alkaline (pH > 10.0) up to a depth of 0.5 m in July and up to a depth of 1.0 m in April (Fig. 5). Soils were slightly less alkaline on the grassland soils in the wet season than in the dry season.

The salinity of the soil surface is low in the woodland and grassland but increased with depth (Fig. 5). Unsurprisingly, salinity on the pan was very high (note change of scale on the horizontal axis in Fig. 5). Salinity was highest in the salt crust then declined rapidly to a depth of c. 0.1 m before increasing. The moisture profile of the woodland and grassland soils was very similar in both seasons (Fig. 5). Moisture increased with depth to approximately 30% v/v at 1 m. On the salt pan moisture content was higher and rapidly increased with depth to c. 40% v/v.

Ca<sup>+</sup> and Mg<sup>+</sup> concentrations were negligible in all soils and only Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>-</sup> were found in measurable concentrations (Fig. 6). On both grassland and woodland soils, Na<sup>+</sup> and Cl<sup>-</sup> ions increased with depth and proximity to the water table. On the salt pan, concentrations of all ions were greater than on the other soils and were strongly concentrated at the surface (Fig. 6).

### 3.2. CO<sub>2</sub> efflux

Mean hourly soil CO<sub>2</sub> efflux ranged from nearly 50 mg C m<sup>-2</sup> h<sup>-1</sup> in the wet season on the woodland soils to 0.5 mg C m<sup>-2</sup> h<sup>-1</sup> on the salt pan in the dry season. Soil CO<sub>2</sub> efflux was significantly higher from the woodland and grassland soils compared to the salt pan ( $p < 0.01$  in both cases) (Table 2), reflecting the relative size of the organic C store (Table 1). Fluxes were significantly higher at all sites in the wet season compared to the dry season ( $p < 0.01$  on woodland and grassland soil and  $p = 0.04$  on the salt pan) (Table 2). CO<sub>2</sub> efflux increased at all sites immediately after the 20 mm rainfall event that led to widespread flooding of the pan surface, but the increase was short-lived and there were no significant differences between mean daily efflux before and after the flooding event ( $p > 0.05$ ). CO<sub>2</sub> efflux at all sites increased with chamber air temperature (Fig. 7). The  $Q_{10}$  of CO<sub>2</sub> efflux was 1.45 ( $r^2$  0.54, RMSE 13.5), 1.30 ( $r^2$  0.45, RMSE 9.14), and 1.15 ( $r^2$  0.34, RMSE 7.3) on the palm woodland, grassland and salt pan respectively. The temperature sensitivity of CO<sub>2</sub> ( $Q_{10}$ ) efflux was linearly positively correlated ( $r^2 = 0.94$ ) to the organic C content of the soil.

**Table 2**

Soil CO<sub>2</sub> efflux from palm woodland, grassland and salt pan surfaces. Salt pan efflux is partitioned into total, crust and subsurface efflux (mg C m<sup>-2</sup> h<sup>-1</sup>). Means ± standard error.

	Palm woodland	Grassland	Salt pan			
			Pan	Crust <sup>1</sup>	Crust <sup>2</sup>	Subsurface
July 2010 Dry season	19.8 ± 1.3 <sup>ac</sup> n = 43	17.1 ± 0.8 <sup>bd</sup> n = 42	0.59 ± 1.6 <sup>ab</sup> n = 41	2.2 ± 1.7 <sup>e</sup> n = 54	2.8 n = 54	7.8 ± 0.5 n = 54
April 2011 Wet season	49.4 ± 2.1 <sup>ac</sup> n = 54	25.7 ± 3.9 <sup>bd</sup> n = 51	2.1 ± 2.4 <sup>ab</sup> n = 49	0.4 ± 2.9 <sup>e</sup> n = 54	-4.8* n = 54	6.0 ± 0.5 n = 54
April 2011 Post flood	59.4 ± 12.8 n = 9	31.5 ± 4.3 n = 9	4.1 ± 6.3 n = 9	No data	No data	No data

Statistically significant differences:

Effects of land cover

<sup>a</sup>Soil CO<sub>2</sub> efflux from the woodland was significantly >pan in July ( $p < 0.01$ ,  $f = 154$ ,  $df = 1$ ) and April ( $p < 0.01$ ,  $f = 886$ ,  $df = 1$ ).

<sup>b</sup>Soil CO<sub>2</sub> efflux from the grassland was significantly >pan in July ( $p < 0.01$ ,  $f = 116$ ,  $df = 1$ ) and April ( $p < 0.01$ ,  $f = 223$ ,  $df = 1$ ).

Effects of season

<sup>c</sup>Soil CO<sub>2</sub> efflux from the woodland soil was significantly different in July and April ( $p < 0.01$ ,  $f = 79$ ,  $df = 1$ ).

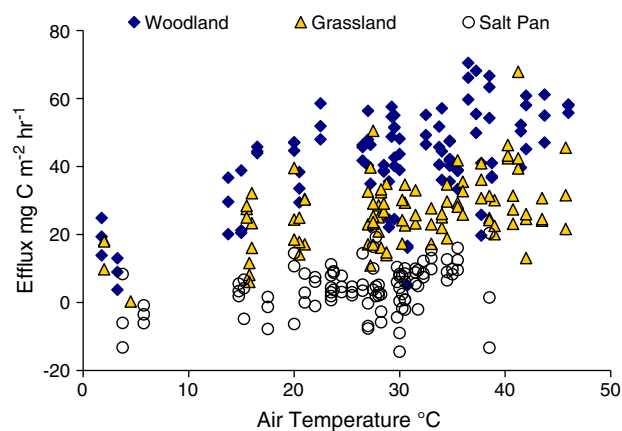
<sup>d</sup>Soil CO<sub>2</sub> efflux from the grassland soil was significantly different in July and April ( $p = 0.01$ ,  $f = 7.6$ ,  $df = 1$ ).

<sup>e</sup>Soil CO<sub>2</sub> efflux from the pan crust was significantly different in July and April but on at the 95% confidence level ( $p = 0.04$ ,  $f = 4.3$ ,  $df = 1$ ).

<sup>1</sup> CO<sub>2</sub> efflux from surface crusts determined by direct measurement of crust only efflux.

<sup>2</sup> CO<sub>2</sub> efflux from surface crust determined by the difference between total and subsurface efflux.

\* The negative value implies a net uptake of CO<sub>2</sub> to the crust.



**Fig. 7.** Soil CO<sub>2</sub> efflux (mg C m<sup>-2</sup> h<sup>-1</sup>) and respiration chamber air temperature (°C) on woodland (blue diamonds), grassland (yellow triangles) and salt pan (open circles) soil and sediment. Data from July 2010 and April 2011 and are on soils prior to the rainfall event in April 2011. For woodland, grassland and pan soils,  $n = 98$ , 96 and 97 respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

### 3.3. CO<sub>2</sub> efflux, C, N and chlorophyll *a* in surface crusts

Estimates of CO<sub>2</sub> efflux originating from the salt pan crust suggest that in the dry season they were a small net C source (Table 2). Wet season estimates vary according to the method used to isolate crust fluxes. Direct measurement estimates of crust efflux in April were  $0.4 \pm 2.9$  mg C m<sup>-2</sup> h<sup>-1</sup> whilst indirect measurement (derived from the difference between total and sub-surface CO<sub>2</sub> efflux) were  $-4.8$  mg C m<sup>-2</sup> h<sup>-1</sup> (Table 2). Irrespective of the measurement method there were periods when net C uptake to the crust was occurring in the wet season.

Chlorophyll *a*, total C and N in the upper 7 mm of the soils in the wet and dry seasons are shown in Table 3. Wet season concentrations of all parameters were higher on the salt pan than during the dry season (Table 3). There were no seasonal differences in surface concentrations of total N, total C and chlorophyll *a* on the grassland and woodland soils.

## 4. Discussion and conclusions

This study has provided the first indication of the considerable C storage in soils and sediments on Ntsetse Pan in the Makgadikgadi Basin, Botswana. The mass of total and organic C contained in the

**Table 3**

Mean ( $\pm$  std. error) of total N, total C and chlorophyll *a* content of surface soils and sediments (upper 7 mm) in July 2010 and April 2011.  $n = 5$ .

	Total N (%)	Total C (%)	Chlorophyll <i>a</i> ( $\mu\text{g g}^{-1}$ )
<i>July 2010</i>			
Dry season			
Salt pan	0.02 $\pm$ 0.01	5.80 $\pm$ 0.07	0.22 $\pm$ 0.01
Grassland	0.08 $\pm$ 0.01	5.66 $\pm$ 0.02	0.28 $\pm$ 0.01
Palm woodland	0.10 $\pm$ 0.01	6.55 $\pm$ 0.07	0.55 $\pm$ 0.03
<i>April 2011</i>			
Wet season			
Salt pan	0.87 $\pm$ 0.01	17.64 $\pm$ 0.26	36.81 $\pm$ 11.03
Grassland	0.07 $\pm$ 0.01	6.07 $\pm$ 0.18	1.40 $\pm$ 0.05
Palm woodland	0.04 $\pm$ 0.01	5.74 $\pm$ 0.08	0.80 $\pm$ 0.08

palm woodland, saline grasslands and salt pan sediments (Table 1) is considerably more than the estimated 6–10 tons organic C ha<sup>-1</sup> for the surrounding Kalahari Sand soils and 39 tons C ha<sup>-1</sup> for calcrete pans (Thomas, 2012).

The major inputs, outputs and biogeochemical processes occurring in the pan environment remain poorly understood. This study has not assessed the temporal and spatial variabilities of C stores and fluxes, however these are likely to be high (see for example Chairi et al., 2010) for this system. 90–95% of the C store is inorganic and in carbonate form, but the extent to which this has been generated by organic C inputs from cyanobacteria crusts, algal mats and aquatic detritus remains unknown. Cyanobacteria are known to dominate the phytoplankton of inland salt waters of southern Africa, including the Makgadikgadi (Seaman et al., 1991). It has been established that cyanobacteria actively and passively influence carbonate cycling, facilitating the construction and breakdown of carbonates (see Schneider and le Campion-Alsumard, 1999). Similarly, Ringrose et al. (1999) found evidence that a diplococcus-type bacterium may have provided a focus for CaCO<sub>3</sub> precipitation in sediments from the western Makgadikgadi.

Concentrations of total N, total C and chlorophyll *a* in the surface sediment of the salt pan were greater in the wet season than in the dry season (Table 3). This is likely to reflect the seasonality of biological productivity and C inputs. When flooded, aquatic organisms flourish and will add a large pulse of organic C to the sediment upon desiccation. The presence of water will also facilitate photosynthesis in surface algae and cyanobacteria, continuing the input of C after flood waters have subsided.

The rapid decline in total C concentrations at 0.4 m on the salt pan (Fig. 4) is unrelated to changes in pH and salinity (Fig. 5) but coincides with reductions in the major anions and cations (Fig. 6). This may represent temporal change associated with an increase in the clastic component of sediment. Chairi et al. (2010) also found that C concentrations did not change with sediment depth in the Moknine sabkhas, eastern Tunisia. There were, however, substantial differences in the composition of the n-alkanes, reflecting changes in the different types of C sources (bacteria, cyanobacteria, algae and higher plants) and the extent of bacterial degradation.

Similarities between the moisture and C content of the soils and sediment in the wet and dry seasons (Figs. 4 and 5) suggest that differences in CO<sub>2</sub> efflux are due to temperature. The sensitivity of CO<sub>2</sub> efflux to temperature increases with the organic C content of the substrate. Flooding of the pan in April 2011 led to a brief increase in CO<sub>2</sub> efflux, most likely due to displacement of CO<sub>2</sub>-enriched air in pore spaces. The multiple biotic and abiotic processes that affect CO<sub>2</sub> uptake and release make it challenging to interpret the efflux data. The physical separation of CO<sub>2</sub> efflux measurement on the salt pan into total, subsurface and crust efflux provides an indication of some of the complexity (Table 2) but there are still discrepancies in the estimates of crust contribution to efflux. In the dry season data suggest that crusts are a small net contributor to total CO<sub>2</sub> efflux from the pan but in the wet season there is evidence that they may be a net sink (Table 2). It is likely

that periods of net negative CO<sub>2</sub> efflux are due to photosynthesis of crust organisms (Fig. 7), exceeding CO<sub>2</sub> generated from below the surface. The very low CO<sub>2</sub> efflux rates on the salt pan do not necessarily imply a lack of microbial activity, because the CO<sub>2</sub> generated by respiration can be utilised in carbonate production and photosynthesis.

Interaction between inorganic and organic components of the C cycle is likely to have a significant effect on the C store of the salt pan environment. Respiration of C will generate high CO<sub>2</sub> partial pressures in the sediment pore spaces, which is likely to drive precipitation of carbonates when suitable cations are present (Eq. (1)). This process would explain the negligible concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup> found in the pan sediments, as plentiful CO<sub>2</sub> will eventually exhaust cation supply. Alkaline conditions also favour the production of carbonates and inhibition of CO<sub>2</sub> efflux, by consumption of H<sup>+</sup> ions which will drive the equilibrium of Eq. (1) towards the right (Bohn et al., 2001).

Whilst experiments were undertaken and samples collected from a small area and only during relatively short periods in two seasons, our field-based findings from a dry and a wet season provide important new evidence demonstrating the potential importance of C sequestration in salt pan systems and alkaline soils in drylands. The study shows the significantly greater C storage in playa systems compared to the neighbouring Kalahari sandveld soils. The future size and stability of the C store on the Makgadikgadi will be dependent on numerous climatological, hydrological, chemical and microbial factors and their subtle interactions. The challenge for future research is to determine the relative roles and significance of the biochemical processes affecting the C cycle, in order to identify the controls on CO<sub>2</sub> efflux and C storage in salt pan systems, and ultimately to establish whether the world's salt pans are acting as a source or sink for CO<sub>2</sub>.

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