Variability in chemistry of surface and soil waters of an evapotranspiration-dominated flood-pulsed wetland: solute processing in the Okavango Delta, Botswana

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ABSTRACT

Water chemistry is important for the maintenance of wetland structure and function. Interpreting ecological patterns in a wetland system therefore requires an in-depth understanding of the water chemistry of that system. We investigated the spatial distribution of chemical solutes both in soil pore water and surface water, along island-floodplain-channel hydrological gradients in seasonally and permanently inundated habitats between major regions in the Okavango Delta, Botswana. Our results show that major cations (Ca, Na, Mg, and K), dissolved silica (DSi), dissolved boron (B), dissolved organic matter (DOC) and electrical conductivity increased significantly, at $p \leq 0.05$, from the inlet of the Delta (the Panhandle) to the distal downstream reaches, suggesting the influence of evapoconcentration. Concentrations of dissolved Fe, Al, Zn, Cu, and Mn significantly decreased, at $p \leq 0.05$, from the inflow of the Delta to the distal reaches. Only Na, Mn, Fe, Al, and DOC showed significant differences, at $p \leq 0.05$, along the local floodplain-channel hydrological gradients, with higher solute concentrations in the floodplains than the channels. Solute concentrations in soil water exhibited similar distribution patterns to those in surface water, but concentrations were higher in soil water. Based on the results, we hypothesise that floodplain emergent vegetation and the channel-fringing vegetation in the Panhandle (a fault-bounded entry trough to the Delta) and the permanently inundated eco-region together influence the cycling of solutes that enter the Delta through uptake.

Keywords: wetland vegetation, water chemistry, pore water, surface water, emergent macrophytes

INTRODUCTION

Processes of solute transport and storage in wetlands are crucial for wetland functions and structure (Mitsch and Gosselink, 2007). The introduction of solutes into wetland systems occurs with the inflow of water as dissolved chemical species, or as a result of the dissolution of riverine or aeolian particulates (Garstang et al., 1998; Krah et al., 2004; Krah et al., 2006; Baker et al., 2009). Once in the system the solutes may undergo a series of transformations due to interactions between hydrological, biological and geochemical processes (Mitsch and Gosselink, 2007). Solute processing has important implications for biogeochemical processes, and thus for water quality functions. Water quality affects the ability of aquatic environments to sustain healthy ecosystems and thereby the provision of ecosystem services (Stark et al., 2000). Therefore, identifying factors that affect solute processing in a wetland system is fundamental for sustainable management of the resources to ensure sustained provision of ecosystem services.

In evapotranspiration-dominated wetland systems, the input and final fate of solutes is of critical ecological importance (Eugster and Jones, 1979; Eugster and Maglione, 1979;

McCarthy and Ellery, 1998; Boettinger and Richardson, 2001). The progressive removal of water by evapotranspiration may ultimately cause solutes to reach saturation, resulting in their removal from solution through precipitation (Barbiero et al., 2002; Barnes et al., 2002; Furquim et al., 2004; Humphries et al., 2010; Humphries et al., 2011). This plays a major role in the chemical evolution of waters in such systems. For example, in the lower floodplain of the Mkuze wetland of South Africa, chemical precipitation under the influence of evapotranspiration was identified as the main factor responsible for the permanent removal of chemical solutes from solution (Humphries et al., 2010). Similar processes have been observed in the Florida Everglades (Wetzel et al., 2005).

In the Okavango Delta (Fig. 1), approximately 98% of the water that enters the system (rainfall and catchment runoff) is lost to the atmosphere due to evapotranspiration throughout the year (Wilson and Dinçer, 1976; Gumbricht and McCarthy, 2003), leaving only about 2% of the mean inflow to be drained at the distal end (Gieske, 1996; Wolski et al., 2006). Despite such evaporative losses, the Delta remains a predominantly freshwater system. This is because solutes are sequestered beneath the islands by a process of unidirectional mass transfer from the floodplains to the numerous islands that are present in the Delta (McCarthy et al., 1993; McCarthy and Ellery, 1995). This process is driven by vegetation-induced local lowering of the water-table beneath the islands, and is thought to maintain
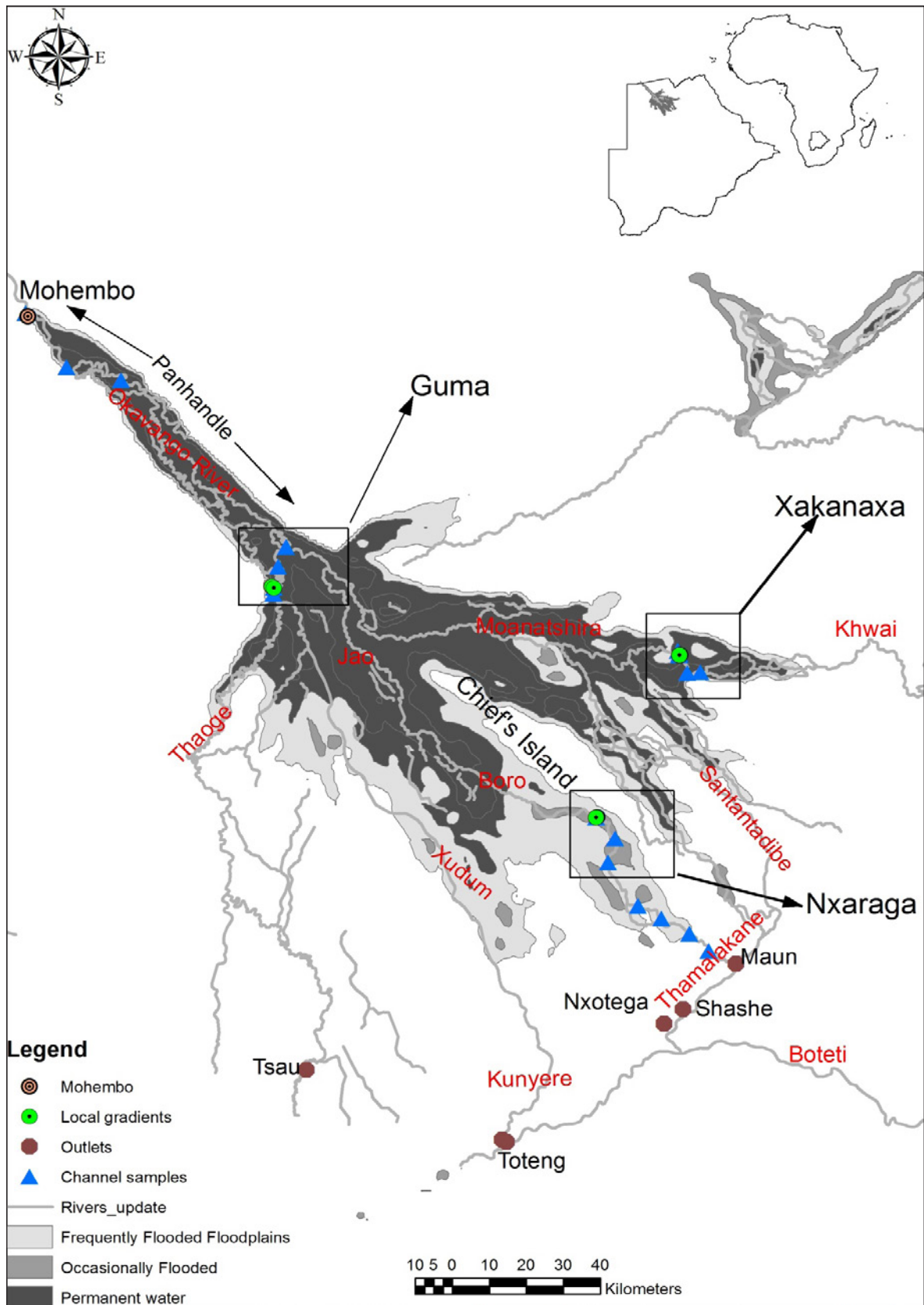
Figure 1
The Okavango Delta, Botswana, showing study localities and major features

the Delta as a freshwater wetland system (Fig. 2) (McCarthy et al., 1986; McCarthy et al., 1993; Bauer, 2004; Bauer et al., 2007; Ramberg and Wolski, 2008). From mass-balance calculations this results in the accumulation of about 360 000 t of dissolved solutes per year in the Okavango Delta (McCarthy and Ellery, 1998). There are indications that differential partitioning of various solute species occurs in the transition between surface water and island groundwater (Mladenov et al., 2014; Struyf et al., 2015; Schoelynck et al. (2015), possibly as a result of pH or redox potential (Eh) changes. The processes dominating

the cycling of solutes in surface- and soil waters of the Delta, before they eventually precipitate or are sequestered in highly saline groundwater beneath island centres, are not fully understood, however.

While there have been studies on water chemistry in the Okavango Delta (Sawula and Martins, 1991; McCarthy and Ellery, 1995; Cronberg et al., 1996a; Cronberg et al., 1996b; Mladenov et al., 2005; Bauer et al., 2007; Mackay et al., 2011; Cawley et al., 2012), the scope was primarily focused on concentrations of solutes in surface water and groundwater;
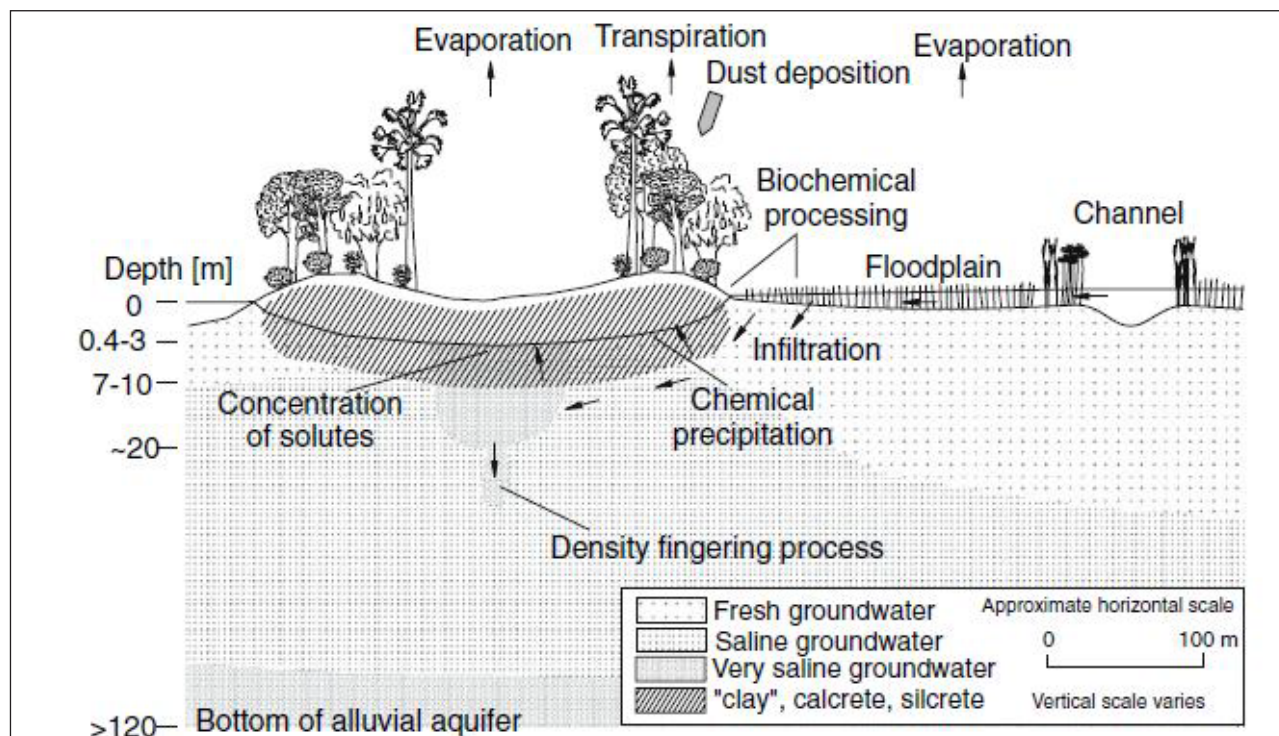

Figure 2
Main biogeochemical processes in water and islands of the Okavango Delta (Source: Ramberg and Wolski, 2008)

Eco-region	Regions	Dominant floodplain emergent and channel fringing vegetation [ab]	Water fluctuation[c]
Table 1 The hydrology (water fluctuation) and dominant vegetation types at the different study regions in the Okavango Delta			
Panhandle	The Panhandle	*Cyperus papyrus Phragmites australis, Miscanthus junceus*	1.5 m or greater
Permanent	Guma	*Cyperus papyrus, Phragmites australis, Vossia cuspidata*	0.7 m
	Xakanaxa	*Miscanthus junceus, Thelypteris interrupta*	0.1-0.3 m
Seasonal	Nxaraga	*Panicum repens, Sorgastrum friesii, Imperata cylindrica*	1.0 m
Occasional	Outlets	Various spp. typical of seasonally flooded systems	1.5 m or greater

[a] *Gumbricht et al. (2004b)*
[b] *Ellery et al. (2003)*
[c] *Okavango Delta Monitoring & Forecasting (2015)*

none of these studies looked at concentrations in pore water. These previous studies, with the exception of those of Mackay et al. (2011) and Mladenov et al. (2005), were either strictly localised or focused mainly along the Jao-Boro channel (Fig. 1). They found a gradient of increasing solute concentration in surface water from the Panhandle to the outlet of the Jao-Boro channel. Pronounced gradients in vegetation standing stock and hydroperiod (both in terms of duration and depth) exist at the landscape scale and at the sub-kilometre scale of the complex mosaic of channels, floodplains and islands that characterises the Delta. We hypothesise that these gradients may both result from, and influence, the distribution and biogeochemical behaviour of solutes.

To understand the early stages of solute cycling in the Delta we studied their spatial distribution and the associated processes in surface water and pore water. This paper provides a comparison of the distribution of chemical species, in soil pore water and surface water, along island-floodplain-channel gradients, in seasonally and permanently inundated habitats, and between major regions (the Panhandle, Guma, Xakanaxa, Nxaraga and outlets) in the Okavango Delta. We hypothesised that in the Panhandle and the permanent floodplains, solute processing is biologically dominated by floodplain emergent vegetation, whereas in the more distal parts of the Delta, it is driven by chemical precipitation through evapotranspiration.

MATERIALS AND METHODS

Study area and site description

The Okavango Delta (Fig. 1), ~19˚ to 20˚ S and 22˚ to 24˚ E, is geomorphologically the terminal alluvial fan of the Okavango River in north-western Botswana. It experiences annual flood-pulsing by Okavango River flows from seasonal rainfall in the Angolan highlands, 1 000 km to the north-west. Mean annual discharge into the Delta is approximately 9×10^9 m^3 while local summer rainfall contributes an additional 42% (about 6×10^9 m^3 per year) to the mean flow (McCarthy et al., 2004; Gumbricht et al., 2004a; Gumbricht et al., 2004b; Ramberg and Wolski, 2008). The annual flood pulse that inundates the Delta causes fluctuations in the size of the inundated area, from 3 500 to 6 000 km^2 during low-flow seasons to ≤ 9 000–13 000 km^2 during high-flow seasons (Gieske 1997; McCarthy et al., 2004). Consequently, the Delta has been categorised into different eco-regions. These include the Panhandle (~800 km^2), permanent swamp (~2 500 km^2), seasonal floodplains (~3 300 km^2) and occasional floodplain (~7 100 km^2) (Gumbricht et al., 2004b).

Four study regions, namely, the Panhandle, Guma, Xakanaxa and Nxaraga (hereafter referred to as the system-scale longitudinal gradient), were selected for sampling (Fig. 1). These regions were chosen in order to cover different habitat types with different hydrological and vegetation gradients (Table 1). The Panhandle, Guma and Xakanaxa are generally characterised by permanently flooded habitats but with different ranges of water fluctuation, while Nxaraga is characterised by seasonally inundated floodplains. South-east of the lower Panhandle the main channel (Okavango River) splits into three distributaries, the Thaoge to the west, the Jao-Boro flowing south-east and the Nqoga flowing eastwards. Guma is located within the Thaoge distributary system. Xakanaxa is part of the main distributary (Nqoga) just east of Chief's Island (the Delta's largest island). Nxaraga makes up part of the Jao-Boro secondary distributary system, on the south-east tip of Chief's Island. In all the regions except the Panhandle, transects spanning local gradients

in hydrology and vegetation, from island centres across the floodplain and into the channel (hereafter referred to as local gradients), were established. A total of 10–11 sample points along each transect (1 transect per region, a total of 3 transects (n = 3)) were selected purposively to capture the variation apparent in the vegetation cover.

Sample collection

In September 2011, a total of 52 channel and floodplain surface water samples were collected from the Okavango River at Mohembo, Thaoge River at Guma, Moanatshira River at Xakanaxa and along the Boro River from Nxaraga to Maun (Fig. 1). Additional surface water samples were collected from river outlets near bridges at Maun, Shashe, Nxotega, Toteng, and Tsau (Fig. 1). All surface water samples were collected from 10 cm below the surface, avoiding any surface debris, and filtered through 0.45 µm nitrocellulose Chromafil syringe filters (A-45/25) into clean acid-washed polyethylene bottles. Water samples for metal analyses were acidified to pH < 2 with 1 N nitric acid. All samples were stored at < 4˚C, both in the field (using a portable car freezer) and in the environmental laboratory at the Okavango Research Institute (ORI), before transport for analysis at the University of Antwerp, Belgium.

At each sampling point, surface water temperature (˚C) and electrical conductivity (EC, µS·cm^{-1}) were measured in situ using a Cond 3110/SET conductivity meter. Dissolved oxygen (DO, mg·L^{-1}) was measured using an Oxi 3203/SET oxygen meter and pH was measured using a pH 3110/SET meter, all by Wissenschaftlich-Technische Werkstätten (WTW), Germany. All field equipment was calibrated before each set of data collection.

Soil water samples were obtained from surface soil (5 cm) samples collected along island-floodplain transects at Guma, Nxaraga and Xakanaxa (Fig. 1). A total of 3 surface soil samples (which were later pooled together) were collected from 0.25 m^2 plots at each sampling point along the three island-floodplain transects using Kopecky rings (5.1 cm height, 5 cm diameter, 100 cm^3 volume), following the method described by Javaux and Vanclooster (2006). All soil samples were stored at < 4˚C during sampling (using a portable car freezer) and frozen until further processing in the environmental laboratory at ORI. Soil water was extracted from the pooled soil samples by centrifuging thawed samples at 3 000 r·min^{-1} for 10 min. To minimise changes in redox potential (Eh), every attempt was made to limit air exposure during the handling and centrifugation of sediment samples. Soil samples were stored in sealed polyethylene bags to prevent water loss and limit air exposure. After centrifuging, the displaced water was acidified and stored in air-tight scintillation bottles. All water samples were transported in a controlled environment at < 4˚C from Botswana to Belgium for analyses.

Sample analysis

All water samples were analysed colorimetrically for dissolved organic carbon (DOC), chloride (Cl), ammonium (NH$_4$), nitrate (NO$_3$), and nitrite (NO$_2$), and soluble reactive phosphorus (PO$_4$) using a SKALAR SA 5100 Segmented Flow Analyzer at the University of Antwerp, Belgium. For DOC determination, water samples were acidified with H$_2$SO$_4$ and flushed with pure nitrogen gas to remove background CO$_2$ concentration before analysis with the SKALAR (phenolphthalein, detection at 550 nm).

All water samples were analysed for dissolved silica (Si), potassium (K), sodium (Na), magnesium (Mg), calcium

(Ca), iron (Fe), aluminium (Al), manganese (Mn), copper (Cu) and zinc (Zn) using an ICP-AES (inductively coupled plasma-atomic emission spectroscopy, iCAP 6300 Duo SERIES Thermo Fisher Scientific, Waltham, USA) at the University of Antwerp, Belgium.

Statistical analyses

All variables were subjected to normality tests using histograms, the Shapiro-Wilk normality test, and quantile-quantile (Q-Q) plots in the freeware package R version 2.15.0 (R Development Core Team, 2012), before analysis. The Levene test was employed to test the data for the assumption of homogeneity of variance. All of this was done to ensure that appropriate tests were used. Analysis of variance (ANOVA), at $p \leq 0.05$, was used in the present study to test for significant differences of solute concentrations between regions and between channels and floodplains. The Tukey HSD post-hoc test was further used to determine the source of the significant differences by comparing pairs of regions and pairs along local gradients.

RESULTS

Surface water physicochemical parameters

A summary of in-situ physicochemical measurements for surface waters across the Delta (from the inlet to outlets) is given in Table 2. Generally, the surface waters in the sampled floodplains and channels in the Delta were slightly acidic to neutral (pH 6.2 to 6.8). The pH levels in floodplains and channels were generally similar at each study site (varying by a maximum pH of 0.2). In contrast, in the outlets the pH varied from around neutral to slightly alkaline. EC in the floodplains was lower at Guma than at Xakanaxa and Nxaraga (Table 2). EC in the channels increased from Mohembo (inlet) (45 ± 15 µS·cm⁻¹) to the outlets (112 ± 36 µS·cm⁻¹) (Table 2).

Concentrations of dissolved inorganic nitrogen (NO_3, NO_2 and NH_4), orthophosphate (PO_4), sulphate (SO_4) and chloride (Cl) in surface waters across the Delta were all below the detection limits (0.08 mg·L⁻¹ for NH_4, 0.02 mg·L⁻¹ for PO_4, 0.04 mg·L⁻¹ for SO_4, and 0.03 mg·L⁻¹ for Cl) for the analytical method used. Soil water SO_4 was also undetectable. All solute concentrations in surface waters were below and/or within the threshold guidelines for natural riverine surface waters (Carr and Neary 2006) (Table 3).

Table 2
Summary of surface water physicochemical parameters (x̄ ± 1SD) in the study regions and outlets of the Okavango Delta

Sites	pH	Electrical conductivity (µS·cm⁻¹)	Temperature (°C)
Panhandle (n = 4)	6.4 ± 0.1	45 ± 15	23.1 ± 0.7
Guma channel (n = 3)	6.4 ± 0.1	54 ± 4	23.3 ± 1.1
Guma floodplain (n = 4)	6.2 ± 0.2	47 ± 5	25.4 ± 1.0
Xakanaxa channel (n = 6)	6.8 ± 0.2	70 ± 4	21.5 ± 0.7
Xakanaxa floodplain (n = 4)	6.7 ± 0.2	73 ± 5	22.3 ± 2.42
Nxaraga channel (n = 8)	6.1 ± 0.1	74 ± 6	23.9 ± 0.9
Nxaraga floodplain (n = 5)	6.3 ± 0.2	81 ± 13	22.9 ± 0.6
Outlets (n = 6)	7.7 ± 0.4	112 ± 36	24.4 ± 1.2

Table 3
Comparison of surface hydro-chemical data between the study regions in the Okavango Delta and the threshold guidelines for natural riverine surface waters by WHO (2003). Mean (±SD) values are given for each of the 4 regions and outlets

S olute	Units	WHO[a]	UPH n = 4	Gum n = 3	Xak n = 6	Nxa n = 8	Out n = 6
K	mg·L⁻¹	82	1.45 ± 0.19	1.12 ± 0.19	2.13 ± 0.67	2.30 ± 0.01	3.84 ± 0.56
Na	mg·L⁻¹	200	1.82 ± 0.08	1.86 ± 0.41	3.84 ± 0.87	4.73 ± 0.04	7.09 ± 1.22
Mg	mg·L⁻¹	300	0.98 ± 0.13	1.21 ± 0.25	1.48 ± 0.08	1.81 ± 0.01	2.66 ± 0.27
Ca	mg·L⁻¹	300	4.20 ± 0.73	4.75 ± 0.87	5.52 ± 0.38	6.51 ± 0.01	9.54 ± 0.98
Fe	µg·L⁻¹	300	12.48 ± 4.44	14.50 ± 2.43	11.17 ± 1.79	5.35 ± 1.56	28.27 ± 9.51
Al	µg·L⁻¹	200	1.43 ± 1.28	0.23 ± 0.21	1.90 ± 1.03	0.46 ± 0.35	25.42 ± 21.5
B	µg·L⁻¹	300	0.75 ± 0.1	0.33 ± 0.21	1.63 ± 0.31	2.11 ± 0.07	5.55 ± 2.30
Mn	µg·L⁻¹	500	34.50 ± 5.86	5.50 ± 0.87	3.40 ± 1.72	1.90 ± 0.07	1.25 ± 0.40
Cu	µg·L⁻¹	2 000	0.48 ± 0.25	0.10 ± 0.10	1.13 ± 0.95	0.54 ± 0.14	0.43 ± 0.31
Zn	µg·L⁻¹	3000	0.88 ± 0.53	1.07 ± 0.75	3.70 ± 1.52	0.80 ± 0.70	0.97 ± 0.45
Si	mg·L⁻¹	NP	4.98 ± 0.94	2.97 ± 0.80	6.84 ± 0.86	6.11 ± 0.19	13.79 ± 5.72

a (Carr and Neary, 2006)
NP - not provided

Local gradients

Concentrations of chemical solutes (Na, Mn, Fe, Al, and DOC) in surface water showed pair-wise significant differences, at $p \leq 0.05$, between channel and floodplain of the same region (i.e., along the local gradients), with higher concentrations in the floodplains than channels (Fig. 3). Na showed a significant channel-floodplain difference only in Guma (Fig. 3), with mean concentrations of 1.86 ± 0.41 and 2.36 ± 0.33 mg·L^{-1} in Guma channel and Guma floodplains, respectively. Fe and Al showed significant channel-floodplain lateral heterogeneity in surface water at Nxaraga only (Fig. 3). Fe concentrations in the floodplains ranged between 7.40 and 10.70 µg·L^{-1} while in the channel the range was between 2.40 and 9.50 µg·L^{-1}. The variation of Al concentrations in the floodplains was six-fold, whereas in the channels concentrations of Al ranged between 0.20 and 0.70 µg·L^{-1}. Significant differences between channel and floodplain at Xakanaxa were evident for Mn, at 3.62 ± 1.72 and 25.95 ± 15.32 µg·L^{-1}, respectively, and DOC, at 3.88 ± 0.56 and 6.02 ± 2.84 mg·L^{-1}, respectively. From Fig. 3, it can be seen that Xakanaxa and Nxaraga regions, in most cases, had higher concentrations of dissolved solutes than the Guma region. Fe and Mn were the only two chemical solutes that showed higher concentrations in the Guma region than in the Xakanaxa and Nxaraga regions.
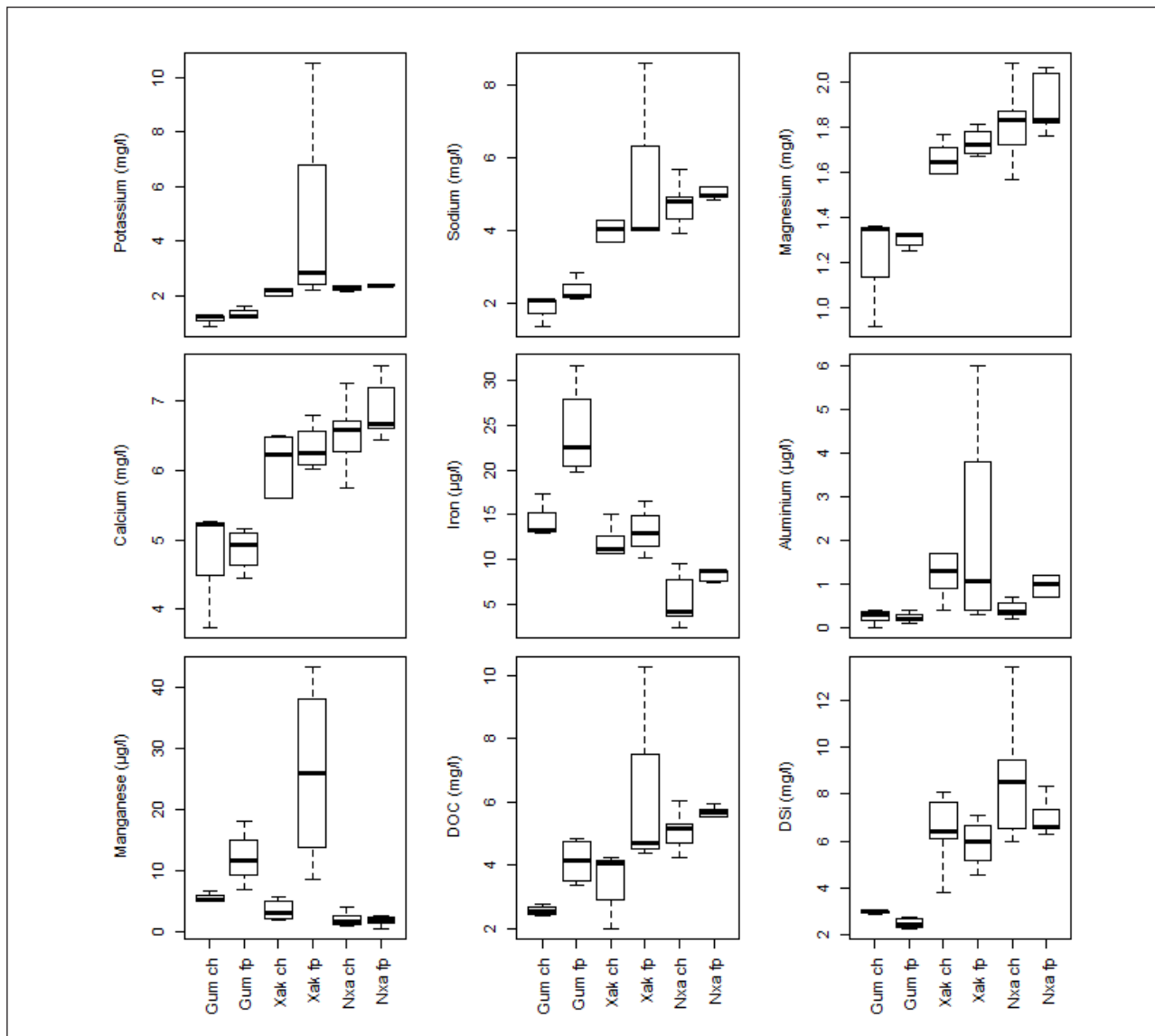

Figure 3

Concentrations of solutes in surface waters of floodplains and nearby channels, and of either permanently- or seasonally-flooded habitats in the Delta. The central line represents the median value, the top and bottom of the box represents the 75th and 25th percentiles. Gum = Guma, Xak = Xakanaxa, and Nxa = Nxaraga. Ch = channel and Fp = floodplain.

System-scale longitudinal gradient

In Fig. 4, box plots are shown only for concentrations of solutes in surface water that exhibit significant differences, at $p \leq 0.05$, between the selected regions and outlets. Ca, K, Mg and Na exhibited similar patterns throughout the Delta for surface waters. Their concentrations increased from the Panhandle to the outlets, with approximately a threefold increase in mean concentrations. The concentration of Fe generally decreased from the Panhandle to the downstream reaches, with a twofold increase at the outlets. Al followed the same pattern but concentrations at the outlets were an order of magnitude higher than elsewhere in the Delta. Mn decreased strongly from the Panhandle to Nxaraga, with almost undetectable concentrations in the outlets at 1.25 ± 0.40 μg·L^{-1}. DOC showed an increase in concentration with distance along the axis of the Delta, with a significant fivefold increase in the outlets. DSi concentrations decreased from the upper Panhandle to Guma, and then gradually increased from Guma to the downstream reaches, with highest concentrations at the outlets.

The relationship between conductivity (μS·cm^{-1}) and dissolved cation concentration (Ca, Na Mg, and K, mg L^{-1}) show that Ca and Na have steeper slopes (0.08 as opposes to 0.02 and 0.04, respectively) (Fig. 5). The higher slopes for Ca and Na indicate that they remain in solution to a greater extent than Mg and K over the entire conductivity range (Barnes et al., 2002).
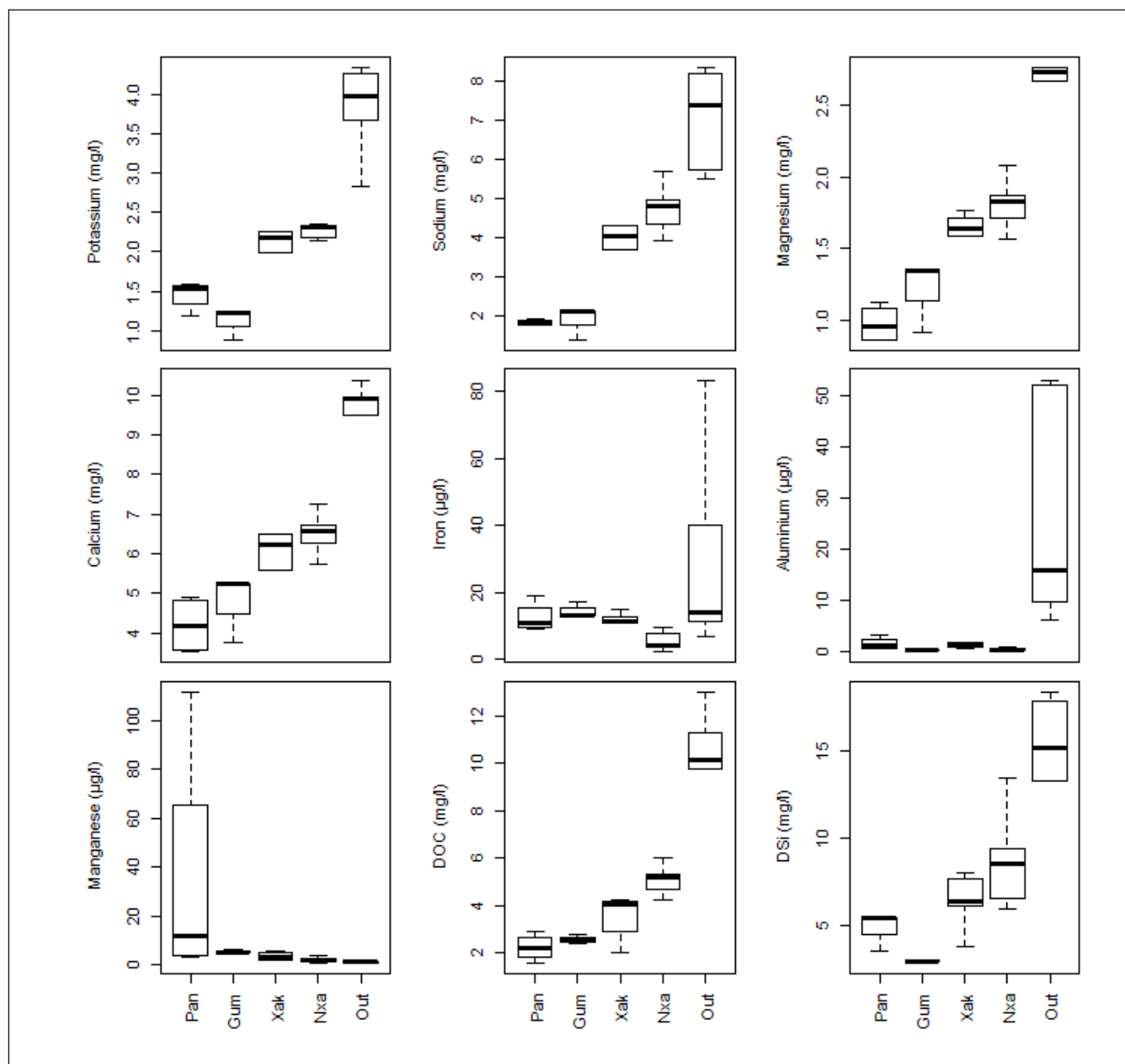

Figure 4

Concentrations of solutes in channel surface waters between selected Delta study regions and outlets. The central line represents the median value, the top and bottom of the box represents the 75th and 25th percentiles. Pan = upper Panhandle, Gum = Guma, Xak = Xakanaxa, Nxa = Nxaraga and out = outlets. Ch = channel and Fp = floodplain.
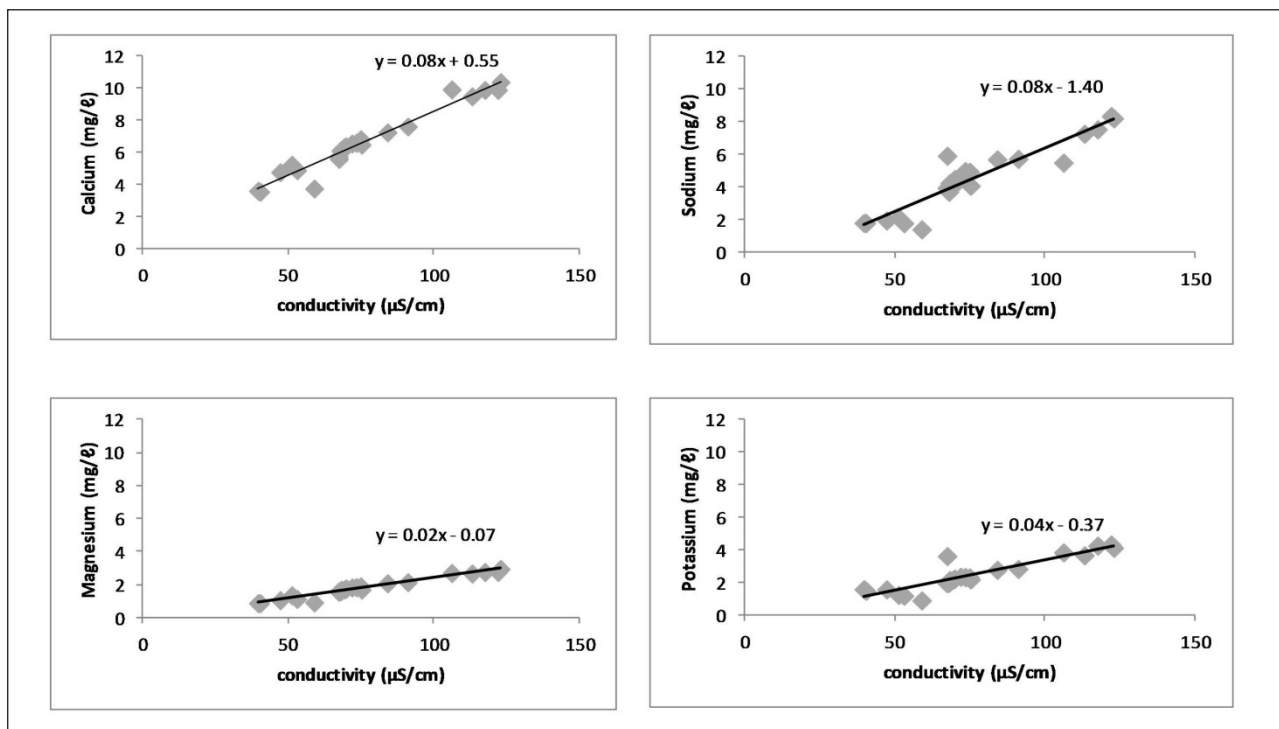
Figure 5
The relationship between cation concentration and conductivity of surface water in the Okavango Delta

Soil water chemistry

Figure 6 presents chemical solutes in water extracted from sediment samples from floodplains at Guma, Nxaraga and Xakanaxa study sites. The extraction of any usable volumes of soil pore water was impossible from the mainly dry island soil samples. In general, Guma had significantly lower solute concentrations than Nxaraga and Xakanaxa. Pairwise comparison of NOx, NH_4, Cl, K, Mg, Na, and Zn only showed significant differences, at $p \leq 0.05$, between Guma and Nxaraga, and Guma and Xakanaxa. On the other hand, the concentrations of Mn differed significantly between all the regions but were highest in Xakanaka. The concentrations of PO_4 and Ca only differed significantly between Guma and Nxaraga. Results for NOx, NH_4^+ and PO_4 revealed that Guma had the lowest concentrations for all of the three parameters for soil water measurements. The highest concentration for NH_4 was registered at Xakanaxa, and increased on average tenfold from Guma to downstream reaches. Nxaraga registered the highest concentration of PO_4. Concentrations of DSi did not vary significantly between the study sites but appeared to increase from Guma to the downstream reaches of the Delta.

DISCUSSION

Local gradients

The results of this study indicate that the concentrations of solute in surface water were noticeably higher in floodplain surface waters than in channel waters. Similar findings have previously been reported by Cronberg et al. (1996b), who attributed the higher solute concentrations in floodplain surface waters to re-dissolution and mobilisation of these ions previously concentrated in the floodplain soils during flood

recession and sediment desiccation. It can thus be suggested that floodplains constitute short-term storages of solutes. Significantly higher DOC in the Xakanaxa floodplain surface waters than in the channel suggest that the Xakanaxa floodplain may be a source of plant-derived DOC from floodplain soils and plant litter (Cronberg et al., 1996a; Mladenov et al., 2005), which was remobilised with the arrival of the annual flood. This is consistent with the results of Mladenov et al., (2005) and Gondwe and Masamba (2014), who found greater DOC concentrations in floodplains of the seasonal swamps than in nearby channels. Despite the observed higher concentrations in the floodplain waters than channel waters, most solute concentrations were not significantly different along the three channel-floodplain gradients studied. This suggests that lateral exchange is more important than vertical exchange, resulting in fast mixing of surface waters between channels and floodplains. This is consistent with the prevalent mode of surface water–groundwater interaction in the Okavango, where unidirectional infiltration of floodplain water into soil is present throughout the flooding season (Wolski and Savenije, 2006). This implies that mobilisation of chemicals from floodplains takes place through dissolution and diffusion, and perhaps by advective transport induced by micro-gradients within superficial soil layers rather than by advection from deeper layers of the soil.

System-scale longitudinal gradient

Concentrations of solutes in surface water would be expected to increase identically along the axis of the Delta as a result of the process of evapotranspiration, which dominates the water balance of this wetland. However, concentrations of various ions increase differently along the axis of the Delta. This implies that there must be some differentiation in the processes affecting individual ions.
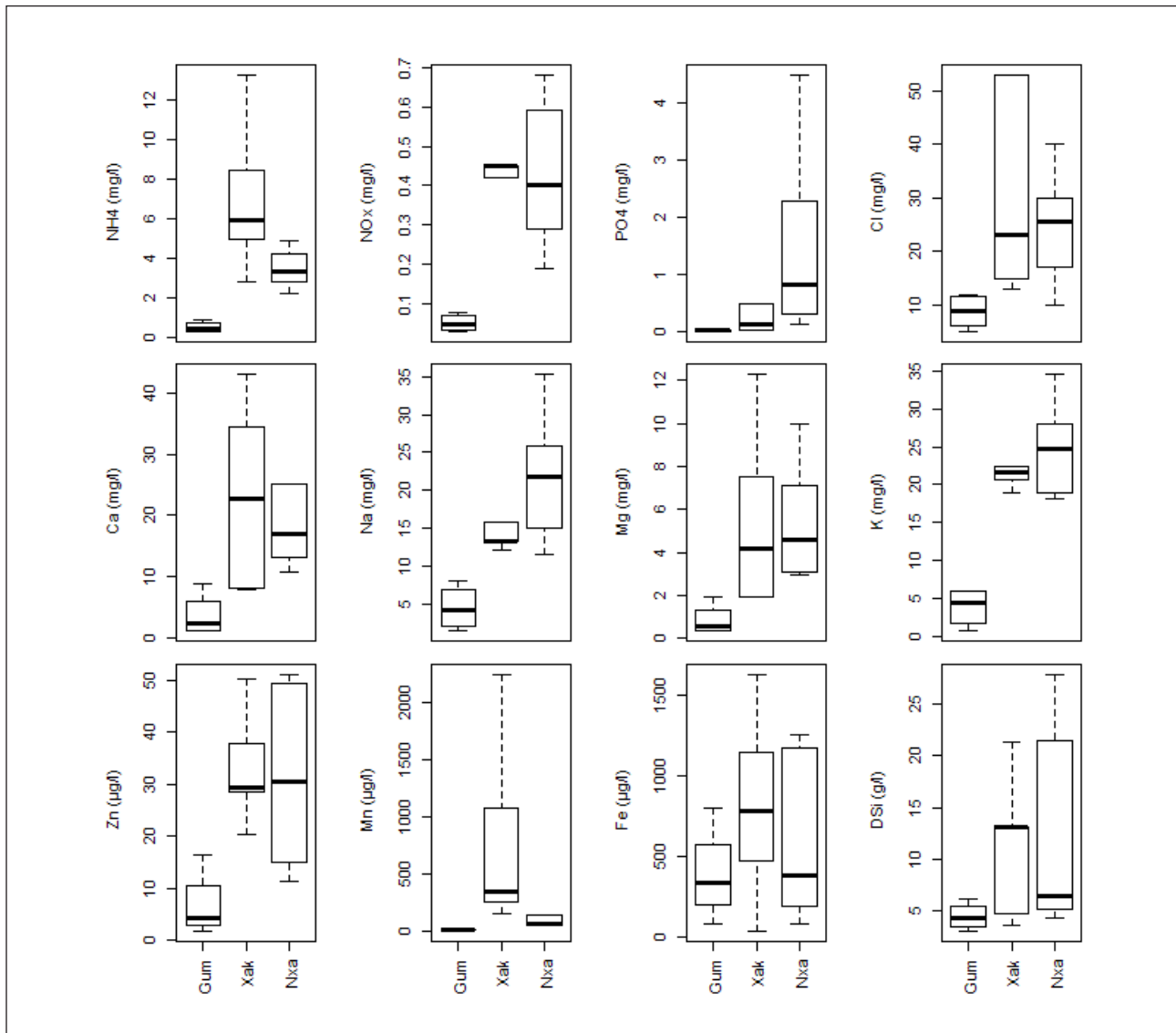
Figure 6
Concentrations of solutes in floodplain soil waters between Guma, Xakanaxa and Nxaraga, and either permanently- or seasonally-flooded habitats.
Gum = Guma (lower Panhandle), Xak = Xakanaxa, and Nxa = Nxaraga.

The concentrations of major cations (Ca, K, Mg and Na) increased generally throughout the Delta for surface waters, similar to the trends reported by Sawula and Martins (1991) and Mackay et al. (2011). This correlates well with a general increase in conductivity along the Delta distributaries. Although the EC of the water increases progressively, the net proportion of each ion species contribution to EC changes along the gradient. In groundwater, these cations are usually associated with the reactions of the carbonate systems and also form compounds with silica (McCarthy and Ellery 1994). Here, evapoconcentration initially results in saturation with respect to calcium carbonate (calcite), while magnesium and silica are removed at a later stage of concentration by precipitation of sepiolite ($Mg_2Si_3O_8 \cdot H_2O$) (McCarthy et al., 1986). Some of these cations, for example Ca, are essential for the growth and development of prokaryotes, fungi, and plants, and these organisms may sequester them in biomass. The order of solutes in concentration was Ca > Na > K > Mg, consistent with the findings of Sawula and Martins (1991) and Masamba and Muzila

(2005). This was, however, contradictory to results of Mackay et al., (2011) who found a greater concentration of potassium than sodium. There has been little or no systematic change in water chemistry (major ions) over the years, with calcium the dominant cation in the Delta (Sawula and Martins, 1991; Mackay et al., 2011).

Surface water concentrations of DSi and K decreased between the Panhandle and Guma. These declines are likely due to the assimilation of solutes by emergent vegetation on the floodplains of the Panhandle and permanent swamps, and are an important process in the retention of nutrients (Struyf et al., 2015). The vegetation in the perennial swamps (Panhandle and Guma) is dominated by extensive stands of the giant sedge *Cyperus papyrus*, the reed *Phragmites australis* and the grass *Miscanthus junceus* (Gumbricht et al., 2004b). Previous studies on Si cycling in aquatic vegetation worldwide have noted the importance of emergent species (amongst which are sedges and grasses) and submerged species as a sink for Si accumulating up to 27 mg·g⁻¹ (Struyf et al., 2015). Struyf et al., (2015) has also

shown that floodplain vegetation in Guma contained between 20 and 80 g·m^{-2} of Si in the biomass.

The concentrations of some surface water solutes (Fe, Al, Zn, Cu, and Mn) decreased from the Panhandle to downstream reaches of the Delta. These solutes (Fe, Zn and Mn) are all important nutrients for plants (especially Fe) and are generally redox sensitive, and hence are usually present only in small quantities in the waters of the Delta. They are thus at a premium and will be scavenged by emergent macrophytes from passing water. Furthermore, there may be additional removal of these ions by precipitation as insoluble metal oxide and/or by sorption onto organic matter or clays. Most of the stability fields of these solutes are highly sensitive to changes in pH (Reddy and Delaune 2008). In this case, however, there was insignificant variation in pH in the Delta surface waters between the regions. In the outlets, the slightly alkaline surface water pH might be expected to favour a degree of immobilisation of Fe, Zn, Mn, and Al, whose solubility increases with decreasing pH (Osman, 2014). Similar patterns were observed for Fe and Mn by Masamba and Muzila (2005) in the Delta. In contrast to our findings, they also found increasing Zn concentrations with increasing distance from the Panhandle, suggesting that dissolution effects were more dominant than deposition effects. The concentration peak observed in the outlets for Fe and Al suggests local introduction of these ions, possibly from natural origins, such as oxidised organic matter.

Solute distribution patterns in pore water were similar to those in surface water, but the concentrations were generally higher in the pore water. However, several biogeochemical processes affect the various solutes differently. For instance, the detection of nutrients (NH_4, NO_x, and PO_4) in pore waters, despite being below detectable levels in surface waters for the analytic method used, may be a result of processes of remobilisation and remineralisation of accumulated biological material in the near-surface sediments (Cohen 2003). In addition, higher concentrations of major cations (Na, Ca, Mg, and K) were observed in pore waters than in the overlying surface water, which may reflect the effects of evapoconcentration of these solutes, given that evapotranspiration is the major water loss pathway in the Okavango Delta (e.g. Humphries et al., 2011). During this study, floodplains were inundated and saturated with floodwaters, suggesting that the soils were likely reduced. This may consequently affect Fe and Mn concentrations in pore water; for example, under reducing conditions DOC has an important role in Fe dissolution and mobilisation (Mladenov et al., 2005). It should be emphasised that the lack of data on sediment or pore water physicochemical parameters, for example, pH and redox conditions, limited the determination of the most likely processes that affect pore water solute concentrations. Therefore, future studies on pore water biogeochemistry should incorporate sediment and pore water physiochemical parameters.

Processing of solutes in the Delta

Previous studies have shown that solutes are chemically precipitated or sequestered beneath the islands by a process of unidirectional mass transfer from the floodplains to the abundant islands that are present in the Delta vegetation (McCarthy et al., 1986; McCarthy et al., 1993; McCarthy and Ellery, 1995; Bauer, 2004; Bauer et al., 2007; Ramberg and Wolski, 2008), a process driven partially by evapotranspiration by riparian woodland. This process is the mechanism responsible

for the counter-intuitive small difference between influent and effluent concentrations of total dissolved solids.

In this study, however, the changes observed in the composition of the total solute load show that evapoconcentration in both floodplains and islands is not the sole process affecting surface water concentrations. For instance, while the surface water conductivity between the Panhandle and Guma increased by 83%, the concentration of K decreased by 77%. Similar patterns were observed for DSi. Given the low nutrient status of inflowing water (Cronberg et al., 1996a; West et al., 2015), and the extensive and dense stands of *Cyperus papyrus* and *Phragmites australis* vegetation in the Panhandle and permanent swamps (Ellery et al., 1995; Ellery et al., 2003), which are the first to make contact with the inflowing water, the question arises: could emergent vegetation in these areas preferentially remove K, and possibly other solutes, from solution? This study suggests that major nutrients (such as P, N, K, Fe, and DSi) brought in solution by surface water may be scavenged by macrophytes in the Panhandle and the permanent swamps, and cycled multiple times before being transported downstream to seasonal floodplains. This is supported by the results of Struyf et al. (2015), who showed that DSi trapping by floodplain vegetation results in a large temporary store of biogenic silica. Downstream of Guma (as the hydroperiod becomes more seasonal), the concentrations of all major cations, DSi, and DOC increased proportional to increasing conductivity, suggesting that processes operating on solutes were dominated by evapoconcentration and bulk sequestration in island soils and groundwater. Our study thus indicates that solute processing in the Panhandle and permanent swamp may be more biologically driven, while that in the seasonal eco-regions is more chemically driven. Trends of solutes in pore waters were similar to those of solutes in surface water but the concentrations were generally higher in the former, indicating that evapoconcentration is already taking place in the floodplains.

CONCLUSIONS

This study indicates that differential uptake of certain solutes needs to be added to the list of processes controlling the ionic concentration and composition of Delta water. The most likely driver for this differential uptake is the nutritional requirements of the extensive and highly productive stands of emergent macrophytes in the perennially flooded part of the Delta. In the more seasonally flooded lower and distal reaches, solute concentrations followed trajectories more typical of the overall solute load, which appear to be simply driven by the physical processes of evapotranspirative concentration, infiltration and sequestration in deep groundwater.

Further work should focus on the dynamics of relationships between chemical constituents of macrophytes of the perennially flooded parts of the Delta, and the composition of the water. This will elucidate the effect of biological processing, and also improve our understanding of potential responses of this vegetation to externally driven changes in nutrient load of influent water.

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REFERENCES

BAKER C, THOMPSON RJ and SIMPSON M (2009) Hydrological dynamics 1: Surface water, flood and sediment dynamics. In: Maltby E and Barker T (eds.) *The Wetlands Handbook.* Blackwell Publishing, Oxford. 120–168. https://doi.org/10.1002/9781444315813.ch6

BARBIERO L, DE QUEIROZ NETO JP, CIORNEI G, SAKAMOTO AY, CAPELLARI B, FERNANDES E and VALLES V (2002) Geochemistry of water and ground water in the Nhecolândia, Pantanal of Mato Grosso, Brazil: Variability and associated processes. *Wetlands* **22** 84–91. https://doi.org/10.1672/0277-5212(2002)022[0528:GOWAGW]2.0.CO;2

BARNES KB, ELLERY WN and KINDNESS A (2002) A preliminary analysis of water chemistry of the Mkuze wetland system, Kwazulu-Natal: A mass balance approach. *Water SA* **28** (1) 1–12. https://doi.org/10.4314/wsa.v28i1.4861

BAUER P (2004) Flooding and salt transport in the Okavango Delta, Botswana: Key issues for sustainable wetland management. PhD thesis, ETH Zurich, Zurich.

BAUER P, LANGER T, PROMMER H, WOLSKI P and KINZELBACH W (2007) Okavango Delta islands: Interaction between density-driven flow and geochemical reactions under evapo-concentration. *J. Hydrol.* **335** (3–4) 389–405. https://doi.org/10.1016/j.jhydrol.2006.12.010

BOETTINGER JL and RICHARDSON JL (2001) Saline and wet soils of wetlands in dry climates. In: Richardson JL and Vepraskas MJ (eds.) *Wetland Soils: Genesis, Hydrology, Landscapes and Classification.* Lewis Publishers, Boca Raton. 383–390.

CARR GM and NEARY JP (2006) *Water Quality for Ecosystem and Human Health.* United Nations Environment Programme Global Environment Monitoring System/Water Programme, Burlington, Ontario, Canada.

CAWLEY K, WOLSKI P, MLADENOV N and JAFFE R (2012) Transformations of dissolved organic matter (DOM) and water chemistry along a transect of the Okavango Delta, Botswana. *Wetlands* **32** (3) 475–486. https://doi.org/10.1007/s13157-012-0281-0

COHEN A (2003) *Paleolimnology: The History and Evolution of Lake Systems.* Oxford University Press, UK.

CRONBERG G, GIESKE A, MARTINS E, PRINCE-NENGU J and STENSTROM I (1996b) Major ion chemistry, plankton, and bacterial assemblages of the Jao/Boro River, Okavango Delta, Botswana: The swamps and flood plains. *Archiv Hydrobiol. Suppl. Monogr. Beitrüge* **3** (107) 335–407.

CRONBERG G, GIESKE A, MARTINS E and STENSTROM I (1996a) Hydrobiological studies of the Okavango Delta and Kwando - Linyanti - Chobe River, Botswana. Surface water quality analysis. *Botsw. Notes Rec.* **27** 151–226.

ELLERY WN, ELLERY K, ROGERS KH and MCCARTHY TS (1995) The role of *Cyperus papyrus* in channel blockage and abandonment in the northeastern Okavango Delta, Botswana. *Afr. J. Ecol.* **33** (1) 25–49. https://doi.org/10.1111/j.1365-2028.1995.tb00779.x

ELLERY WN, MCCARTHY TS and SMITH ND (2003) Vegetation, hydrology, and sedimentation patterns on the major distributary

system of the Okavango fan, Botswana. *Wetlands* **23** (2) 357–375. https://doi.org/10.1672/11-20

EUGSTER HP and JONES BF (1979) Behaviour of major solutes during closed-basin brine evolution. *Am. J. Sci.* **279** (1) 609–631. https://doi.org/10.2475/ajs.279.6.609

EUGSTER HP and MAGLIONE G (1979) Brines and evaporates of the Lake Chad basin, Africa. *Geochim. Cosmochim. Acta* **43** (1) 973–981. https://doi.org/10.1016/0016-7037(79)90087-5

FURQUIM SC, QUEIROZ NETO JP, FURIAN S, BARBIERO L and GRAHAM RC (2004) Mg-mica formation in alkaline environment of the Nhecolândia, south Mato Grosso, Brazil. In: Pecchio, Dias De Andrade FR, Zanchetta Agostino L, Kahn H, Santagostino LM and Tassinari MMML (eds.) *Applied Mineralogy: Developments in Science and Technology.* ICAM-BR, Sao Paulo. 411–414.

GARSTANG M, ELLERY WN, MCCARTHY TS, SCHOLES MC, SCHOLES RJ, SWAP RJ and TYSON PD (1998) The contribution of aerosol- and water-borne nutrients to the functioning of the Okavango Delta. *S. Afr. J. Sci.* **94** (5) 223.

GIESKE A (1997) Modelling outflow from the Jao/Boro River system in the Okavango Delta, Botswana. *J. Hydrol.* **193** 214–239. https://doi.org/10.1016/S0022-1694(96)03147-2

GIESKE A (1996) Vegetation-driven groundwater recharge below Okavango Delta, Botswana as a solute sink mechanism - an indicative model. *Botsw. J. Earth Sci.* **3** 33–37.

GONDWE M and MASAMBA WL (2014) Spatial and temporal dynamics of diffusive methane emissions in the Okavango Delta, northern Botswana, Africa. *Wetlands Ecol. Manage.* **22** (1) 63–78. https://doi.org/10.1007/s11273-013-9323-5

GUMBRICHT T, MCCARTHY J and MCCARTHY TS (2004b) Channels, wetlands and islands in the Okavango Delta, Botswana, and their relation to hydrological and sedimentological processes. *Earth Surf. Processes Landforms* **29** (1) 15–29. https://doi.org/10.1002/esp.1008

GUMBRICHT T and MCCARTHY TS (2003) Spatial patterns of islands and salt crusts in the Okavango Delta, Botswana. *S. Afr. Geol. J.* **85** (2) 164–169. https://doi.org/10.1080/03736245.2003.9713797

GUMBRICHT T, MCCARTHY TS and BAUER P (2004a) The micro-topography of the wetlands of the Okavango Delta, Botswana. *Earth Surf. Processes Landforms* **30** (1) 27–39. https://doi.org/10.1002/esp.1124

HUMPHRIES MS, KINDNESS A, ELLERY WN and HUGHES JC (2010) Water chemistry and effect of evapotranspiration on chemical sedimentation on the Mkuze River floodplain, South Africa. *J. Arid Environ.* **75** (6) 555–565. https://doi.org/10.1016/j.jaridenv.2011.01.013

HUMPHRIES MS, KINDNESS A, ELLERY WN, HUGHES JC, BOND JK and BARNES KB (2011) Vegetation influences on groundwater salinity and chemical heterogeneity in a freshwater, recharge floodplain wetland, South Africa. *J. Hydrol.* **411** (1–2) 130–139. https://doi.org/10.1016/j.jhydrol.2011.09.041

JAVAUX M and VANCLOOSTER M (2006) Scale-dependency of the hydraulic properties of a variably saturated heterogeneous sandy subsoil. *J. Hydrol.* **327** 376–388. https://doi.org/10.1016/j.jhydrol.2005.11.040

KRAH M, MCCARTHY TS, ANNEGARN H and RAMBERG L (2004) Airborne dust deposition in the Okavango Delta, Botswana, and its impact on landforms. *Earth Surf. Processes Landforms* **29** (5) 565–577. https://doi.org/10.1002/esp.1051

KRAH M, MCCARTHY TS, HUNTSMAN-MAPILA P, WOLSKI P, ANNEGARN H and SETHEBE K (2006) Nutrient budget in the seasonal wetland of the Okavango Delta, Botswana. *Wetlands Ecol. Manage.* **14** (3) 253–267. https://doi.org/10.1007/s11273-005-1115-0

MACKAY A, DAVIDSON T, WOLSKI P, MAZEBEDI R, MASAMBA WL, HUNTSMAN-MAPILA P and TODD M (2011) Spatial and seasonal variability in surface water chemistry in the Okavango Delta, Botswana: A multivariate approach. *Wetlands* **31** (5) 815–829. https://doi.org/10.1007/s13157-011-0196-1

MASAMBA WRL and MUZILA A (2005) Spatial and seasonal variation of major cation and selected trace metal ion concentrations in the Okavango-Maunachira-Khwai channels of the Okavango Delta. *Botsw. Notes Rec.* **37** 218–226.

MCCARTHY J, GUMBRICHT T, MCCARTHY TS, FROST PE, WESSELS K and SEIDEL F (2004) Flooding patterns in the Okavango wetland in Botswana, between 1972 and 2000. *Ambio* **7** 453–457.

MCCARTHY T, ELLERY W and ELLERY K (1993) Vegetation-induced, subsurface precipitation of carbonates as an aggradational process in the permanent swamps of the Okavango (Delta) fan, Botswana. *Chem. Geol.* **107** (1–2) 111–131. https://doi.org/10.1016/0009-2541(93)90105-R

MCCARTHY TS and ELLERY WN (1994) The effect of vegetation on soil and ground water chemistry and hydrology of islands in the seasonal swamps of the Okavango fan, Botswana. *J. Hydrol.* **154** (1–4) 169–193. https://doi.org/10.1016/0022-1694(94)90216-X

MCCARTHY TS and ELLERY WN (1998) The Okavango Delta. *Trans. R. Soc. S. Afr.* 53 (2) 157–182. https://doi.org/10.1080/00359199809520384

MCCARTHY TS and ELLERY WN (1995) Sedimentation on the distal reaches of the Okavango fan, Botswana, and its bearing on calcrete and silcrete (ganister) formation. *J. Sediment Res. A* **A65** (1) 77–90.

MCCARTHY TS, ELLERY WN, ROGERS KH, CAIRNCROSS B and ELLERY K (1986) The roles of sedimentation and plant growth in changing flow patterns in the Okavango Delta, Botswana. *S. Afr. J. Sci.* **82** (10) 579–584.

MCCARTHY TS, MCIVER JR and CAIRNCROSS B (1986) Carbonate accumulation on islands in the Okavango Delta, Botswana. *S. Afr. J. Sci.* **82** (10) 588–591.

MITSCH WJ and GOSSELINK JG (2007) *Wetlands*. John Wiley and Sons, Inc, New York, USA.

MLADENOV N, MCKNIGHT D, WOLSKI P and RAMBERG L (2005) Effects of annual flooding on dissolved organic carbon dynamics within a pristine wetland, the Okavango Delta, Botswana. *Wetlands* **25** (3) 622–638. https://doi.org/10.1672/0277-5212(2005)025[0622:EOAFOD]2.0.CO;2

MLADENOV N, WOLSKI P, HETTIARACHCHI GM, MURRAY-HUDSON M, ENRIQUEZ H, DAMARAJU S, GALKADUWA MB, MCKNIGHT DM and MASAMBA W (2014) Abiotic and biotic factors influencing the mobility of arsenic in groundwater of a through-flow island in the Okavango Delta, Botswana. *J. Hydrol.* **518** (Part C) 326–341. https://doi.org/10.1016/j.jhydrol.2013.09.026

Okavango Delta Monitoring & Forecasting (2015) URL:http://www.okavangodata.ub.bw/ori/monitoring/water/index.php (Accessed 15 November 2015).

OSMAN KT (2014) *Soil Degradation, Conservation and Remediation*. Springer, The Netherlands. 248. https://doi.org/10.1007/978-94-007-7590-9

R DEVELOPMENT CORE TEAM (2012) R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0. URL: http://www.R-project.org/

RAMBERG L and WOLSKI P (2008) Growing islands and sinking solutes: Processes maintaining the endorheic Okavango Delta as a freshwater system. *Plant Ecol.* **196** (2) 215–231. https://doi.org/10.1007/s11258-007-9346-1

REDDY RK and DELAUNE RD (2008) *Biogeochemistry of Wetlands: Science and Applications*. CRC Press, Boca Raton, Florida.

SAWULA G and MARTINS E (1991) Major ion chemistry of the lower Boro River, Okavango Delta, Botswana. *Freshwater Biol.* **26** (3) 481–493. https://doi.org/10.1111/j.1365-2427.1991.tb01413.x

SCHOELYNCK J, SCHALLER J, STRUYF E, WOLSKI P, CONLEY DJ, MOSIMANE K, VAN PELT D, MURRAY-HUDSON M, MEIRE P and FRINGS P (2015) The trapping of organic matter within plant patches in the channels of the Okavango Delta: A matter of quality. Manuscript submitted for publication.

STARK JR, HANSON PE, GOLDSTEIN RM, FALLON JD, FONG AL, LEE KE, KROENING SE and ANDREWS WJ (2000) Water quality in upper Mississippi River basin, Minnesota, Wisconsin, South Dakota, Iowa, and North Dakota, 1995-98. United States Geological Survey, Washington DC. 35 pp.

STRUYF E, MOSIMANE K, VAN PELT D, MURRAY-HUDSON M, MEIRE P, FRINGS P, WOLSKI P, SCHALLER J, GONDWE JM, SCHOELYNCK J and CONLEY DJ (2015) The role of vegetation in the Okavango Delta silica sink. *Wetlands* **35** (1) 171–181. https://doi.org/10.1007/s13157-014-0607-1

WEST DT, VAN AS JG and VAN AS LL (2015) Surface water quality in the Okavango Delta panhandle, Botswana. *Afr. J. Aquat. Sci.* **40** (4) 359–372. https://doi.org/10.2989/16085914.2015.1104288

WETZEL PR, VAN DER VALK AG, NEWMAN S, GAWLIK DE, GANN TT, CORONADO-MOLINA CA, CHILDERS DL and SKLAR FH (2005) Maintaining tree islands in the Florida Everglades: Nutrient redistribution is the key. *Front. Ecol. Environ.* **3** (7) 370–376. https://doi.org/10.1890/1540-9295(2005)003[0370:MTIITF]2.0.CO;2

WILSON BH and DINÇER T (1976) An introduction to the hydrology and hydrography of the Okavango Delta. In: *Symposium on the Okavango Delta and its Future Utilization*, 30 August to 2 September 1976, Gaborone.

WOLSKI P and SAVENIJE H (2006) Dynamics of surface and groundwater interactions in the floodplain system of the Okavango Delta, Botswana. *J. Hydrol.* **320** 283–301. https://doi.org/10.1016/j.jhydrol.2005.07.027

WOLSKI P, SAVENIJE HHG, MURRAY-HUDSON M and GUMBRICHT T (2006) Modelling of the flooding in the Okavango Delta, Botswana, using a hybrid reservoir-GIS model. *J. Hydrol.* **331** (1–2) 58–72. https://doi.org/10.1016/j.jhydrol.2006.04.040