RESEARCH ARTICLE



Water and sediment chemistry drivers of chlorophyll-*a* dynamics within a Ramsar declared floodplain pan wetland system

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Abstract

Floodplain pans are hydrologically dynamic in nature and characterised by variables such as chlorophyll-a (chl-a), water, and sediment chemistry over their hydroperiods. The present study investigated the spatio-temporal variations in water and sediment physico-chemical, and chlorophyll-a concentration characteristics of six floodplain pans found in the Ramsar declared Makuleke wetlands, Kruger National Park, South Africa. The water and sediment physico-chemical variable values were generally elevated during the high-water period, whereas chlorophyll-a concentrations varied across pans and hydroperiod. Benthic chl-a concentration significantly varied across pans with concentrations ranging from 161 to 1036.2 mg m². The two-way ANOVA showed significant differences in benthic chl-a concentration among hydroperiods, and no significant differences were observed in pelagic chl-a across pans and hydroperiods. Generally, pelagic and benthic chl-a concentration increased as water and sediment chemistry variables increased. Furthermore, three sediment variables, i.e. pH, calcium, and magnesium, and water conductivity were found to be significant in structuring benthic chlorophyll-a dynamics in pans. However, none of the sediment and water variables had a significant effect on pelagic chl-a. Hydroperiod had a significant effect on influencing chl-a concentration, with high and low water level periods being characterised by low and high chl-a concentration, respectively. The *n*-MDS results showed strong overlaps in chl-*a* biomass among the Makuleke floodplain pans across hydroperiods. The increasing chl-a concentration in these floodplain pans due to potential bioturbation effects as a result of large mammals could potentially lead to eutrophication, which in turn could affect the system's primary productivity and aquatic biota. Therefore, it is important to establish a continuous monitoring programme on these pans to inform sound management decisions.

Keywords Kruger National Park · Hydroperiod · Ramsar wetlands · Sediment metals · Phytobenthos

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Introduction

Floodplain wetland pans are regions of high productivity dependent on flood pulses (Acosta et al. 2020; O'Brien et al. 2021). These systems have been described as sabkhas, vleis, pans, playas, playa lakes and saline lakes, whereas in southern Africa, the term 'pan' refers to as closed or endorheic basins (Yechieli and Wood 2002). These wetlands are habitats for various plants and animals (Tripp and Crosman 2021) while providing a range of ecosystem services such as flood attenuation, water storage, and purification (Zhao et al. 2016; Dalu et al. 2020). Despite the essential ecosystem services, floodplains are considered among the most threatened freshwater environments, due to pollution from increasing anthropogenic impacts such as poorly managed agricultural activities, wastewater discharges, and urbanisation (Chen et al. 2018; Aguinaga et al. 2019; Cuthbert et al. 2019). These systems are often located in the middle or lower reaches of river systems and are characterised by a drop in the velocity of water as it spreads over the dissipative floodplain. As such, these environments can accumulate pollutants while having negative implications on living plant and animal organisms (Jiang et al. 2013; Dalu and Chauke 2020; Rahman and Singh 2020).

Phytoplankton is a critical component of primary production in floodplain wetlands (Molinari et al. 2021) as it contributes to aquatic food-web dynamics (Thuy et al. 2018). Phytoplankton also plays important roles in the biogeochemical cycles of many elements in these systems through uptake, incorporation, or production during photosynthesis and nitrogen fixation (Basu and Mackey 2018). As unicellular photosynthetic organisms, phytoplankton are primarily driven by light and nutrients (Dalu and Wasserman 2018; Hopkins et al. 2021). One of the primary reasons for measuring phytoplanktonic biomass is to estimate primary production rates. The total chlorophyll-a (chl-a) concentration is the most widely used proxy for phytoplankton biomass because it is coloured, specific to, and shared by all primary producers (Huot et al. 2007). Over the years, studies on phytoplankton assessments focused on marine, coastal, and inland water bodies; however, studies on the wetland ecology, especially those that are located in national parks, have been understudied in the global south, in particular, southern Africa.

The study of chl-*a* in relation to sediment chemistry dynamics in floodplain wetlands is important because sediments can potentially indicate the levels of contamination in various floodplain pans across different hydroperiods (Dalu et al. 2020). Sediments can also provide information on different human activities that are taking or have taken place in a particular catchment where floodplain wetlands are located (Singh et al. 1997; Taylor and Owens 2009; Dalu and Wasserman 2022). In natural aquatic environments, sediments are the main sink for various metals, but due to changes in environmental conditions such as pH, water temperature, and oxygen redox potential, sediments can potentially act as a source of metals (Neumann et al. 1998; Chon et al. 2012; Li et al. 2020). Metal elements entering the aquatic systems can accumulate in the benthic sediments, subject to sediments' absorptive capacity and textural composition (Kuriata-Potasznik et al. 2016).

The present study focuses on the Makuleke floodplain pans, a Ramsar-declared wetland system (wetlands containing representative, rare or unique biological diversity and designated to be of international importance) in the northern Kruger National Park, South Africa. Previous studies done in the area have focused on macroinvertebrate diversity (Fernandes et al. 2015; Dyamond 2017), water quality issues (Kock 2017), and pan hydrology and ecology (Nesbitt, 2014). At present, no information exists for chl-*a*, benthic sediment metals, and water dynamics within the region. Ultimately, research that seeks to assess benthic and pelagic chl-*a* in relation to water and sediment chemistry dynamics in floodplain pans as a case study to evaluate the spatiotemporal dynamics of chl-*a* in relation to water and sediment chemistry in the Kruger National Park.

The study specifically addresses benthic and pelagic chla, water and sediment metal dynamics across hydroperiods among various pan systems in the Makuleke floodplain. The main aim of the study was to assess the following: (i) the overall ecosystem health among pans and hydroperiod, (ii) chlorophyll-a concentrations in relation to various physico-chemical parameters across various floodplain pans to determine potential drivers of phytoplankton biomass, and (iii) the spatio-temporal variation of chl-a based on hydroperiod (water level) and environmental variables. We hypothesised that (i) the pans' ecosystem health will deteriorate during low water period since there would be high metal accumulations on benthic sediments, and (ii) the hydroperiod (water level) would have greater implications for phytoplankton biomass across all the pans due to variation in physico-chemical parameters and fluctuating metals input during low and high water period.

Materials and methods

Study area

The study was carried out in six floodplain wetland pans in the Pafuri section within the Makuleke Ramsar declared wetland site, Kruger National Park, South Africa (Fig. 1).



Fig. 1 Location of study sites (Nyavadi (A), Jachacha (B), Mapimbi (C), Nghila (D), Mambvumbvanyi (E), and Nwambi floodplain pans (F)) within the north Makuleke wetlands, Pafuri area, Kruger National Park, South Africa

The low hydroperiod (LW) sampling was done during the hot-dry months (September and December) when the pans were at their lowest water levels, whereas the high hydroperiod (HW) was done during the hot-wet when pans were at full capacity (March and April). The pans were chosen based on various characteristics such as perenniality, hydroperiod, location, and biodiversity. For instance, Nyavadi pan is one of the biggest in the Makuleke wetlands and is situated in savanna grasslands. Mapimbi and Nghila pans are situated very close (50 m \sim 1 km) to the confluence of the Limpopo and Luvuvhu rivers, making their perenniality last longer. Pans such as Mambvumbvanyi and Nwambi have high bird diversity and a high abundance of crocodiles, while both are situated in the fever tree forest (Vachellia xanthophloea). Lastly, Jachacha and Nwambi pans are permanent pans containing water throughout the year. These pans were devoid of aquatic vegetation with Mambvumbvanyi pan only having a few marginal aquatic vegetation on one small section. All these pans are utilised as water sources by large mammals such as elephants, hippopotamuses, and many other species. Sampling sites in all the pans were randomly selected along a perpendicular gradient to represent the pan (i.e. two edges, one middle (closer to the middle depending on animals present)). From each pan, three sites were chosen as sampling points for environmental variables and benthic sediments by wading in as these were not deep systems, with sampling taking place in September 2020 (LW1), April 2021 (HW1), December 2021 (LW2), and March 2022 (HW2). September 2020 and December 2021 were considered low-water (LW) periods, while April 2021 and March 2022 were considered high-water (HW) periods. Sampling was also done within the macrophyte belt if present.

In the Pafuri area, there are undulating plains with a variety of sedimentary and volcanic rocks (and the soils that go with them) as well as alluvial floodplains (Venter et al. 2003). The local vegetation and hydrology of the study area are determined by the underlying geological formations. On crests and in the middle of slopes, soils range from extremely shallow brown and black calcareous clay and loam on basalt to shallow to deep red and yellow-brown coarse to fine sands on sandstone. Greyish brown and deep black calcareous clays (shallow to moderately deep) are found on the lower slopes, and deep red alluviums are found in the valley bottoms (Venter et al. 2003). The forest ecosystem occupies the Limpopo River's margins and occurs as a belt on river alluvium areas, with Phragmites mauritianus in the river channel close to Nghila and Mapimbi pan. Away from the forest belt of the Limpopo River, Colophospermum mopane and Commiphora glandulosa dominate the broad-leaved dry bushveld Savanna region on shallow calcareous clays. *Burkea africana* and *Pseudolachnostylis maprouneifolia* grow in the deep sands, while combretum grows in the shallow, stony sands. Wooded areas interspersed with grasslands and dry thickets can be found, as can woodlands composed of *Androstachys johnsonii* and *Croton pseudopulchellus*, as well as areas dominated by *Afzelia quanzensis* and *Euclea divinorum* (Venter et al. 2003).

The average annual rainfall for the Pafuri region area is low: 375–420 mm year⁻¹, but more importantly, rainfall is highly variable, with an inter-annual coefficient of variation of 35% (variation of rainfall from year to year) (Venter et al. 2003). Precipitation occurs due to the intertropical convergence moving southward, though the Mozambiquan current also has a potential impact on the Kruger National Park (Venter et al. 2003). Over the past 3000 years, a good paleoclimate record has been developed for the region, reflecting the correlation between global temperature anomalies and correlations with rainfall for the summer rainfall in the region (Holmgren et al. 1999).

Water quality variables

During each sampling event, at each site, environmental parameters such as pH, conductivity (μ S cm⁻¹), total dissolved solids (ppm), salinity (ppm), resistivity (Ω), oxygen reduction potential (mV), and temperature (°C) (n=3 per site per each sampling event) were measured by immersing a portable multi-parameter probe (PCTestr 35, Eutech/Oakton Instruments, Singapore) into the water and results recorded in situ at each sampling site.

Sediment chemistry variables

The benthic sediments were collected using acid-washed wooden splints, and each integrated sample was placed in new polyethylene Ziplock bags to avoid cross contamination. The composite sediment samples were immediately packed in a cooler box with ice and transported to the University of Venda Pollution laboratory for analysis within 24 h. In the laboratory, the samples were oven-dried at 60 °C for 72 h to a constant weight before being disaggregated in a porcelain mortar. The dried sediment samples were then homogenised using a riffle splitter, and thereafter, a sediment subsample of 0.5 kg was separated and sent to BEMLAB, Cape Town, for further analysis. The pH, phosphorus (P), ammonium (NH₄⁺), potassium (K), calcium (Ca), magnesium (Mg), sodium (Na), copper (Cu), zinc (Zn), manganese (Mn), boron (B), iron (Fe), carbon (C), sulphur (S), and sediment organic matter (SOM) concentrations were quantified for each pan and hydroperiod as described in detail by Makherana et al. (2022). Briefly, for each sediment core, elements such as K, Mg, Na Ca, Cu, Zn, Mn, B, Fe, and S were measured using an Inductively coupled plasma atomic emission spectroscopy (ICPMS) instrument (see Rice 2012 for detailed methodology), while the ammonia and phosphorus were analysed using a SEAL AutoAnalyzer 3 high resolution and Bray–2 extract as described by Bray and Kurtz (1945).

Determining chlorophyll-a in pans

Pelagic chlorophyll-a

Two 250 mL water samples were collected from each pan and placed on ice. Pelagic chlorophyll-*a* concentrations were determined as a proxy for quantifying phytoplankton biomass from all six sampled pans. Both water samples from each pan were filtered and analysed separately. In the laboratory, samples from each pan were filtered (vacuum < 5 cm Hg) through 0.7-µm pore size (diameter 47 mm) GIC Scientific glass fibre filters. After filtering, the water was inserted in 15-mL centrifuge tubes containing 10 mL of 90% acetone solution and then stored in a freezer for at least 24 h to allow for chl-*a* extraction (see Lorenzen 1967 methodology). After 24 h, samples were removed from the freezer and centrifuged at 3000 rpm for 10 min before 2 mL was extracted from each sample to measure absorbance at the wavelength of 665 nm and 750 nm using a SPECTRO star NANO (BMG LabTech GmbH, Ortenberg).

Chlorophyll-*a* was calculated using the following formula:

$$Chl - a (mgm^{2}) = \frac{11.4 \times K \times ((665b - 750b) - (665a - 750a)) \times Ve}{Vf \times L}$$

where L is the cuvette light path (1 cm), Ve is the extraction volume (10 mL), and Vf is the filtered volume (0.25 L). K is 2.43, b is the absorbance before acidification, and a is the absorbance after acidification.

Benthic chlorophyll-a

Benthic algal core samples (volume = 16.1 cm^3) were collected from each site (n = 2) at each pan, using a Perspex sediment corer of 20-mm internal diameter inserted by hand into the sediment. About 20 mL of 90% acetone was inoculated into the container with the sediment sample, swirled in the vortex, and the container with the sample was put in a freezer at -20 °C for 24 h for chlorophyll extraction. After 24 h, samples were removed from the freezer and centrifuged at 3000 rpm for 10 min before 2 mL was extracted from each sample to measure absorbance at the wavelength of 665 nm and 750 nm using a SPECTRO star NANO (BMG LabTech GmbH, Ortenberg) following Human et al. (2018). To measure the absorbance, a 1-cm quartz cuvette was used before and after acidification with 0.01 M hydrochloric acid. We calculated benthic chl-*a* for each core on each site in the pan.

Benthic chlorophyll–*a* concentration was calculated based on Sartory and Grobbelaar (1984) using the following formula:

Results

$$Chl - a (mgm^2) = \frac{(\text{Absorbance correction})((665b - 750b) - (665a - 750a)) \times Ve}{A_1 \times L}$$

where L is the cuvette light path (cm) (1 cm), A_1 is the sample collection area (0.0161 m²), Ve is the volume of extract (L), Absorbance correction is 26.7, b is the absorbance before acidification, and *a* is the absorbance after acidification.

Data analysis

Differences in chl-a, water variables, and sediment chemistry among various pans and hydroperiod (i.e. low-water and high-water period) were tested using a two-way ANOVA after the data was found to meet all the assumptions of parametric tests based on the homogeneity of variances and normality. Pairwise comparisons were analysed for significant (p < 0.05) variables among the pans and hydroperiod. These tests were performed in SPSS v25.0 for Windows software (SPSS Inc. 2017). To determine whether the ecosystem health based on chl-a (log [x+1] transformed) variables differed among floodplain pans (i.e. Nyavadi, Mambvumbvanyi, Jachacha, Mapimbi, Nghila, and Nwambi) and hydroperiod (i.e. low-water and high-water period) (Wu et al. 2023), we used a distance-based PERMutational Analysis of Variance (PERMANOVA; Anderson, 2001) in PRIMER v6 add-on package PERMANOVA + (Anderson, Gorley, and Clarke, 2008). Each term in the analysis was tested using 9999 permutations, with significant terms being investigated using a pair-wise comparison based on the PERMANOVA t-statistic (Anderson et al. 2008).

Multivariate regression was successfully performed to get a statistical model by many authors (Ghasemi and Saaidpour 2007). In this study, a multivariate regression model was employed to determine the most important variables responsible for the variation in sediment quality, water quality, and chlorophyll-*a* concentrations.

To further evaluate changes in chl-*a* among pans and hydroperiods within the Makuleke floodplain, a non-metric multidimensional scaling (n-MDS) analysis with Euclidean dissimilarity as a measure of distance was carried out using PC-ORD version 5.10 in quick and dirty mode (Kruskal and Wish 1978). We further elucidated the relationship between the dependent and independent variables by conducting Spearman correlation analysis in SPSS v25.0 (SPSS Inc. 2017) to precisely determine the relationships between chl-*a* and independent variables.

Physical and chemical properties of water and sediment

During our first sampling in September 2020 (low water period), Nyavadi pan had no water (i.e. dry); therefore, none of the water parameters were recorded in this pan (see Table 1). pH, conductivity, salinity, and TDS were generally high during the low water period at Jachacha and Mapimbi, with pH in these pans being slightly alkaline during low water as it ranged from a mean average of 7.6 to 9.2 (Table 1). High oxygen redox potential and resistivity concentration were recorded during the high water period at Nyavadi and Nwambi, respectively (Table 1). Benthic chl-a ranged from a mean of 161 to 954 mg m² in the high water period, whereas in the low water period, it ranged from 319 to 916 mg m^2 . Generally, a low concentration of pelagic chl-a was observed in all pans-during both hydroperiods, ranging from a mean of 2.6 to 6.4 μ g L⁻¹ during the low water level and 3.7 to 8.2 μ g L⁻¹ during the high water level period (Table 1).

Twelve sediment variables (i.e. pH, P, Ca, Mg, K, Na, Cu, Zn, Mn, Fe, C, and S) showed significant differences (p < 0.05) across all pans, whereas six variables (i.e. P, NH₄⁺, Cu, Mn, Fe, and C) were significantly different (p < 0.05) across hydroperiods (Table 2). Seven sediment variables (pH, NH₄⁺, Mg, K, Na, Cu, and S) differed significantly (p < 0.05) between studied floodplain pans and hydroperiod (Table 2), whereas all water variables (i.e. pH, conductivity, total dissolved solids, salinity, resistivity, and temperature) differed significantly (p < 0.05) across the pans and hydroperiods except for oxygen redox potential, which only showed significant differences among the study pans (Table 2).

Chlorophyll-a dynamics

The Makuleke Wetland ecosystem health based on the chl-*a* differed significantly among floodplain pans (PER-MANOVA, Pseudo– $F_{(1,61)}$ =4.671, *p* < 0.001) (see Table 3). Using pairwise comparisons, we found significant pairwise differences (*p* < 0.05) for all pans with the exception of Jachacha vs Nghila, Jachacha vs Mapimbi, and Mambvumbvanyi vs Nwambi which were not significantly different (*p* > 0.05) (Table 3).

During the low water period, the mean pelagic chl-a for Nyavadi, Jachacha and Nwambi were 4.5, 6.4 and 2.6 µg

and benthic) variables (mean \pm SD) measured in floodplain pans ($n=6$) during LW (low water) and HW	
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Pans	Nyavadi		Jachacha		Mambvumbvany.		Nghila		Mapimbi	-	Nwambi	
Variables	LW	MH	LW	ММ	LW	MH	TM	MH	LW	HW I	LW	MH
Sediments												
Hq	7.1 ± 0.0	7.2 ± 0.0	7.2 ± 0.1	7.1 ± 0.1	6.9 ± 1.8	5.6 ± 0.4	7.4 ± 0.1	7.5 ± 0.2	7.1 ± 0.0	6.9 ± 0.2	5.7 ± 1.0	5.6 ± 0.4
$P (mg \\ kg^{-1})$	275.2 ± 48.4	299.5±15.6	165.3 ± 61.2	235.8 ± 27.2	71.6 ± 62.2	33.2 ± 5.2	118.4 ± 31.9	119.5 ± 19.9	68.1 ±27.8	78.8±12.5	34.2 ± 16.0	23.9 ± 3.1
NH4 (mg kg ⁻¹)	61.7 ± 12.1	140.6 ± 80.4	82.9±82.0	103 ± 2.3	72.8±93.6	119.2 ± 59.9	40.6 ± 37.6	63.9 ±78.8	107.3 ± 29.3	100.8 ± 48.2	84.9±5.4	111.6±9.1
Ca (mg kg^-l)	26.9 ± 5.4	25.7 ± 10.7	13.1 ± 2.3	22.3 ± 2.2	8.9±5.2	18.1 ± 2.1	17.6 ± 8.4	10.2 ± 0.2	21.6 ± 4.2	16.2 ± 10.0	13.5 ± 10.7	8.4±2.7
${\mathop{\rm Mg}}_{\mathop{\rm kg} olimits}(\mathop{\rm mg} olimits)$	22.4 ± 10.6	19.3 ± 10.9	13.7 ± 2.1	14.4 ± 0.7	2.1 ± 1.0	10.3 ± 2.1	8.8±2.6	6.2 ± 1.3	13.1 ± 3.1	8.5±4.7	7.2±5.5	3.9 ± 0.5
$\substack{K \ (mg}{kg^{-1}})$	1.9 ± 0.7	1.9 ± 0.7	1.18 ± 0.2	1.1 ± 0.3	0.8 ± 0.1	1.4 ± 0.1	0.9 ± 0.3	0.5 ± 0.1	1.1 ± 0.1	0.8 ± 0.3	1.1 ± 0.5	0.7 ± 0.3
Na (mg kg^-l)	6 ± 0.6	4.5±4.7	17.3 ± 10.6	3.7 ± 1.2	8.9±12.4	0.7 ± 0.4	3.5 ± 1.0	1.2 ± 0.6	2.7±0.2	1.5 ± 1.3	0.7 ± 0.6	0.7 ± 0.6
Cu (mg kg^{-1})	13.7 ± 5.4	13.9 ± 4.7	10.9 ± 1.6	11.4 ± 5.3	6.9±5.9	27.9 ± 4.9	7.2 ± 5.3	2.4 ± 1.4	10.8 ± 5.9	12.3 ± 7.0	20.3 ± 11.0	13.7 ± 2.3
Zn (mg kg^-l)	0.9 ± 0.4	0.8 ± 0.1	0.8 ± 0.2	0.7 ± 0.3	1.3 ± 0.5	3.4 ± 0.3	0.9 ± 0.2	0.4 ± 0.0	1.1 ± 0.1	1.1 ± 0.3	2.7 ± 0.3	2.2 ± 0.3
${\mathop{\rm Mn}} ({\mathop{\rm mg}} {\mathop{\rm kg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} {\mathop{\rm Hg}} $	174.3 ± 1.8	144.1 ± 36.5	197 ± 0.7	169.3 ± 25.1	114.6 ± 130.7	540.8±27.2	130.1 ± 21.0	90.8 ± 19.8	242.3±88.7	205.8 ± 129.7	358.3 ± 175.7	416.5 ± 13.4
B (mg kg^{-1})	1.1 ± 0.3	0.6 ± 0.1	2.0 ± 1.1	0.7 ± 0.0	2.5±2.6	1.2 ± 0.2	1.4 ± 0.0	0.5 ± 0.5	0.8 ± 0.1	0.7 ± 0.0	0.9 ± 0.4	0.9 ± 0.2
Fe (mg kg^{-1})	148 ± 2.8	148.7 ± 37.1	254.1 ± 157.6	299.1 ±240.1	407.5 ± 507.0	833±127.3	128.1 ± 96.1	88.4±38.1	298.5 ± 4.2	395.5 ± 12.0	703.5 ± 248.2	622.5 ± 196.6
$C (mg kg^{-1})$	1.7 ± 0.9	1.8 ± 0.8	0.8 ± 0.4	1.9 ± 1.6	0.7±0.6	3.3 ± 1.3	0.6 ± 0.1	0.3 ± 0.1	1.52 ± 0.8	1.4 ± 0.7	2.7±0.7	1.5 ± 1.1
${ m S}~({ m mg}~{ m kg}^{-1})$	28.9 ± 8.7	36.9 ± 23.7	125.9 ± 135.1	50.1 ± 33.1	70±85.5	21.2 ± 2.7	46.4 ± 13.2	22.5±26.6	272.6±219.6	80.5 ± 59.8	33.7±9.2	17.3±77
SOM (%) Water	30.8 ± 26.5	55.5 ± 9.0	83.3±19.6	52.3 ± 14.2	65.8 ±24.4	68.4 ±30.1	34.8±8.9	75.1±1.7	67.9 ± 10.8	79.1±7.0	59.2±15.7	55.7±31.5
Hq	5.6 ± 0.3	7.6 ± 0.6	9.2 ± 0.2	8.7 ± 0.2	8.4 ± 1.4	8.2 ± 0.1	8.5 ± 1.4	9.2 ± 0.4	8.3 ± 1.2	7.9 ± 0.5	6.6 ± 1.1	7.6 ± 0.1
ORP (mV)	43.9 ±2.3	148.8 ± 87.5	111.6 ± 40.1	106 ± 33.6	134.1 ± 34.2	83.4±18.3	87.8 ± 14	121.7 ± 95	149.6±2.7	106.2 ± 3.7	71.3 ± 33.2	79.3±20.8
Conduc- tivity $(\mu S \ cm^{-1})$	142.1±3.3	278.8±6.3	1395.6±1830.6	240.1 ± 19.7	678±711.3	495.5 ± 318.5	1860.5 ± 2415.5	813.7±218	1813.5±2395.0	558.5 ± 343.8	321.7±194.7	321.2±197.1
(mqq)	7.1 ±0.2	164.9 ± 0.9	764.5 ± 1068.4	146.9 ± 0.3	346.4±477.5	270.2 ± 133.7	9.5 ± 2.0	484.7±79.6	1305.1 ± 1839.9	253.1 ± 223.2	126.6 ± 166.1	173.9±79.1
Salinity (ppm)	341 ± 32.5	286.3 ± 198.9	745.7 ± 926.7	372.8 ± 43.5	399.8±217.5	246.9 ± 150.4	307.8 ± 134.2	432.1±137.1	981.3±1233.5	305.5 ± 130.1	235 ± 18.6	292.1 ± 96.0
Resistiv- ity (Ω)	435.4 ± 13.9	313.8 ± 13.1	236.6±166.2	199.2 ± 94.2	434.2±425.1	219.4±25.8	221.1 ± 135.8	574.3±497.9	160.6±44.7	136.3 ± 20.8	1177.7 ± 1252.0	334.8 ± 168.0

Table 1 (cc	ontinued)											
Pans	Nyavadi		Jachacha		Mambvumbvany		Nghila		Mapimbi		Nwambi	
Variables	LW H	M	LW	MH	LW	MH	LW	MH	LW	MH	TM	Mł
Temp (°C)	30.9 ± 1.1	26.6±2.7	33.7±8.4	29.7 ± 1.8	33.4±4.3	25.1 ± 0.2	31.6 ± 8.5	27.1 ± 0.2	29.9 ± 1.8	26.2 ± 0.9	28.7 ± 1.9	25.7 ± 1.1
Chl-a												
Benthic (mg m ²)	1036.2 ± 1232.7	161 ± 101.5	916.3±1219.1	751.8 ± 394.8	599.5±662.1	858.5±285.9	318.6 ± 393.6	953.9±346.5	417.5 ± 560.7	166.3 ±56.9	<i>77</i> 4.5 ± 927.0	480.5±248.8
Pelagic (μg L ⁻¹)	4.5 ± 1.7	3.7 ± 3.5	6.4±6.6	8.2±3.7	2.9±3.4	4.6 ±2.6	3.7 ± 4.4	5.7±0.2	5.3 ± 3.2	6.3 ±7.3	2.6 ± 1.5	7.1 ±4.4

L–1, respectively, whereas during the high water period, the mean pelagic chl–a for Nyavadi, Jachacha and Nwambi were 3.7, 8.2 and 7.1, respectively.

Benthic chlorophyll-a concentration varied from pan to pan, with the highest mean concentration recorded as 916.3 mg m² in Jachacha and the lowest being 318.6 mg m² in Nyavadi during the low water period. During the high water period, the lowest mean concentration of chla was recorded at Mapimbi pan (166.3 mg m²⁾ with the highest at Nyavadi pan (1 036.2 mg m²) (Fig. 2b). Benthic chl-a concentrations were high in Nyavadi, Mambvumbvanyi, Nghila, and Mapimbi during the high water periods and low in Nyavadi and Nwambi during the low water periods (Fig. 1b). Using two-way ANOVA, we observed significant differences in benthic chl-a concentration among hydroperiod (F = 15.666, p < 0.001); however, no significant differences were observed on pelagic chl-a in pans (F = 0.942, p = 0.473) and hydroperiod (F = 3.854, p = 0.036) (Table 2).

Relationship between benthic and pelagic chlorophyll-a with physicochemical variables

Using multivariate regression analyses, significant relationships (p < 0.05) between benthic chlorophyll-a concentration and sediments parameters (i.e. K, Ca, and Mg) and water oxygen redox potential were observed for hydroperiod, whereas significant relationships (p < 0.05) between benthic chlorophyll-a concentration and sediment calcium and water conductivity were recorded for floodplain pans (Table 4). Additionally, all optimised multivariate regression models had shown no significant differences in chl-a and other variables. The overall regression model for benthic chl-aacross hydroperiod was significant, $F_{(24,21)}=2.49$, p < 0.001, $R^2=0.74$.

The regression analyses showed no significant relationships (p < 0.05) between pelagic chlorophyll-*a* concentration and sediment variables across the hydroperiod and pans which has been attested by all water variables which showed no significant ($F_{(24,21)} = 0.75$, p < 0.75, $R^2 = 0.46$) difference against pelagic chl-*a* among hydroperiods with the overall regression.

Pelagic chl-*a* was significantly positively correlated (r=0.46, p<0.05) with NH₄⁺ (sediment variable), and negatively correlated with conductivity (water variable) (r=-0.30, p<0.05). There was a highly significant positive correlation (p<0.01) between benthic chl-*a* and conductivity, indicating that there was covariance between nutrients and inorganic contaminants during the flood season (high water period) (Table 5).

The correlation of benthic chl-*a* and variables such as Cu and Fe in sediment was significant (p < 0.01), whereby

Table 2Two-way analysesof variance (ANOVA)conducted based on sedimentparameters, water variables,and chlorophyll-a for pansand hydroperiod. Bold valuesindicate significant differencesat p < 0.05

Dependent variable		Pans		Hydrope	riod	Pans×hyc	lroperiod
		F	р	F	р	F	р
Sediment							
pН		8.024	< 0.001	3.331	0.054	11.871	< 0.001
P		6.214	< 0.001	6.763	0.005	0.625	0.764
NH4		1.863	0.14	7.483	0.003	3.78	0.005
К		23.402	< 0.001	2.679	0.09	3.379	0.009
Ca		22.884	< 0.001	5.721	0.01	10.35	< 0.001
Mg		9.869	< 0.001	5.282	0.013	8.242	< 0.001
Na		20.615	< 0.001	1.531	0.238	13.156	< 0.001
Cu		32.549	< 0.001	33.951	< 0.001	7.352	< 0.001
Zn		8.76	< 0.001	0.532	0.595	1.217	0.332
Mn		8.624	< 0.001	15.564	< 0.001	3.538	0.007
В		2.837	0.039	5.075	0.015	3.092	0.014
Fe		20.832	< 0.001	9.325	0.001	2.699	0.026
С		6.37	0.001	11.215	< 0.001	1.681	0.151
S		7.101	< 0.001	2.123	0.143	4.517	0.002
SOM		0.982	0.45	3.752	0.039	0.88	0.556
Water							
pН		4.244	< 0.001	5.754	< 0.001	3.448	0.008
ORP (mV)		17.046	< 0.001	6.192	0.007	5.496	< 0.001
Conductivity (µS	$S \text{ cm}^{-1}$)	10.208	< 0.001	10.086	< 0.001	8.034	< 0.001
TDS (ppm)		17.194	< 0.001	11.331	< 0.001	21.294	< 0.001
Salinity (ppm)		24.879	< 0.001	13.823	< 0.001	8.587	< 0.001
Resistivity (Ω)		11.837	< 0.001	23.695	< 0.001	12.275	< 0.001
Temp (°C)		13.096	< 0.001	6.849	< 0.001	12.444	< 0.001
Chlorophyll-a							
Benthic (mg m ²)	1	2.032	0.112	15.666	< 0.001	1.004	0.465
Pelagic (µg L ⁻¹)		0.942	0.473	3.854	0.036	1.387	0.25
Pans	Jachacha	Mamb	vumbvanyi	Nghila	Mapimbi	Nwambi	Nyavadi
Jachacha	1.000	0.022		0.052	0.111	< 0.001	0.010
Mambvumbvanyi	1.836	1.000		0.002	0.043	0.184	< 0.001
Nghila	1.608	2.332		1.000	0.033	< 0.001	0.001
Mapimbi	1.369	1.630		1.674	1.000	0.005	0.005

Table 3 Pairwise comparisonresults for the PERMANOVAhighlighting the t (white) andp values (grey) for pans. Boldvalues indicate significantdifferences at p < 0.05

r=0.31 and r=0.30, respectively. Both these elements may cause serious metal pollution in sediment. There was no significant correlation (p > 0.05) between other sediment chemistry variables and chl-a in the floodplain pans. However, there was a significant positive correlation (p < 0.05) between benthic chl-a and water variables such as TDS, salinity, and water temperature (Table 5), indicating that benthic chl-a increases with an increase in TDS, salinity, and water temperature, which indirectly shows that benthic chl-a may be driven/influenced by the concentrations of physicochemical parameters of water.

Nwambi

Nyavadi

2.642

1.980

1.243

2.724

The phytoplankton biomass in the Makuleke floodplain pans revealed a spatial variation of chlorophyll based on sites. The n-MDS ordination results showed that pans were variably separated in terms of nutrient input that drives chl-a concentrations (Fig. 3). Observation on n-MDS showed that variables such as Fe, Zn, Mn, C, and Cu had a positive influence on chl-a concentration across all the pans (i.e. with an exception for Banyini) and hydroperiod (Fig. 3). Metals Mg, Ca, and K had a strong positive influence on Banyini pan chl-aconcentration. The n-MDS vectors showed sediment pH,

2.182

3.090

< 0.001

1

1.000

4.180

2.902

2.910

Fig. 2 Mean pelagic (**a**) and benthic (**b**) chlorophyll-*a* concentrations across six floodplain wetland pans during low and high water periods in the Makuleke wetlands, Kruger National Park



Na, and P having a negative association with some pan sites from Mambvumbvanyi and Jachacha, whereas water variables such as ORP, conductivity, pH, and salinity were negatively associated with some sites of Mapimbi pan (Fig. 3). Most of the pans resembled different behaviours of chl-a, except for two pans (i.e. Mambvumbvanyi and Nghila) which showed a unique placement in ordination (grouped together), suggesting higher chl-a levels than other pans (Fig. 3). Furthermore, we also observed a slight difference in chl-a concentration of Nyavadi pan (uniquely displaced), which suggests the variability in phytoplankton biomass as compared to other pans (i.e. Nwambi, Mapimbi, Nghila, and Jachacha). High hydroperiod chl-a concentrations were strongly positively associated with sediment variables (i.e. Mg, Ca, K, Fe, Zn, C, Mn, Cu), whereas the low hydroperiod was positively (i.e. Mg, Ca, K, Fe, Zn, C, Mn, Cu) and negatively (i.e. sediment pH, Na, and P; water ORP, conductivity, pH, and salinity) (Fig. 3). In essence, the hydroperiods showed overlaps (Fig. 3).

Discussion

The floodplain pans in the Makuleke wetlands, Kruger National Park are characterised by shallow water bodies with varying concentrations of chlorophyll-*a*, water, and sediment parameters. Using field data collection, we quantified relationships between algal productivity (using chl-*a* as a proxy (i.e. benthic and pelagic)) and environmental variables (i.e. water and sediments variables) in tropical floodplain wetlands across hydroperiod

Variables Benthic chl-a					Pelagic c	hl-a		
	β	SE	t	р	β	SE	t	р
Sediment variables	3							
pH	1.01	0.33	3.032	0.006	0.41	0.57	0.728	0.475
Р	-0.60	0.30	-2.022	0.056	0.06	0.47	0.136	0.893
NH_4^+	-0.01	0.20	-0.063	0.950	0.21	0.28	0.754	0.459
Κ	-3.46	3.67	-0.943	0.357	1.50	5.38	0.279	0.783
Ca	- 1.65	0.42	-3.932	0.001	-0.34	0.80	-0.424	0.676
Mg	1.87	0.62	2.997	0.007	-0.14	1.07	-0.126	0.901
Na	-0.58	0.34	- 1.699	0.104	0.01	0.52	0.021	0.984
Cu	0.34	0.46	0.729	0.474	-0.20	0.67	-0.293	0.773
Zn	0.22	0.58	0.376	0.711	-1.05	0.80	-1.314	0.203
Mn	0.26	0.32	0.809	0.428	0.57	0.45	1.254	0.224
В	0.42	0.27	1.58	0.129	0.02	0.40	0.040	0.969
Fe	-0.23	0.38	-0.598	0.556	0.66	0.54	1.230	0.232
С	0.28	0.28	0.994	0.332	0.20	0.42	0.482	0.635
S	0.16	0.25	0.656	0.519	-0.05	0.36	-0.135	0.894
SOM	-0.28	0.16	-1.76	0.093	-0.08	0.25	-0.328	0.747
Water variables								
pН	0.25	0.27	0.951	0.352	-0.01	0.39	-0.020	0.984
ORP	0.03	0.19	0.179	0.860	-0.20	0.27	-0.728	0.474
Conductivity	-0.80	0.33	-2.467	0.022	-0.23	0.53	-0.443	0.662
TDS	-0.49	0.75	-0.650	0.523	0.11	1.09	0.102	0.920
Salinity	0.28	0.82	0.336	0.740	-0.05	1.18	-0.045	0.964
Resistivity	0.02	0.17	0.142	0.888	-0.01	0.24	-0.026	0.979
Temperature	0.30	0.21	1.434	0.166	-0.06	0.31	-0.201	0.843
Pelagic chl-a	0.01	0.15	0.060	0.950	0.02	0.31	0.057	0.955

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(high water period season and low water period). The results showed that water parameters (i.e. conductivity) and sediment variables (i.e. pH, Ca, and Mg) influenced benthic chl-a dynamics within the pans. This could be due to the fact that Mg is a proportionately important macro-nutrient essential for phytoplankton growth, resulting in the propagation of chlorophyll-a concentrations rising within the pans (El-Otify 2015; Ahmed et al. 2020). Benthic chl-a concentration varied among the high water and low water periods, with marginally higher chl-a concentrations during the high water period. The longer inundation period during the high water could have led to enhanced growth of phytoplankton in the pans (Dalu et al. 2022). In agreement, the present study shows that during the low water period, phytoplankton growth was lower, suggesting low input of nutrients during this period.

The increased phytoplankton biomass in wetland systems is a clear indicator of eutrophication, which tends to reduce biodiversity and negatively impact food web structure in aquatic ecosystems (Liu et al. 2020a; Puthiyottil et al. 2021; Gentine et al. 2022). In our study, chla concentrations were found to be minimal and not to cause detrimental effects to these systems' biodiversity. The present study supports our first and second hypotheses that chl-a concentrations will vary across pans and hydroperiods, given that all sampled pans are located at different zones with different nutrient inputs. It can also be noted that seasonality does play a significant role in driving phytoplankton dynamics in the Makuleke floodplain because changes in pan sizes largely influence the growth and propagation of algae in wetlands. This is similar to the study done by Amorim et al. (2019), which reported algal blooms as a result of increased rainfall and increased water levels within pans. Furthermore, the Kruger National Park is dominated by a diversity of wild animals, with high densities of megafauna, which increase nutrient levels within the pans through urine and faecal deposition, while directly resuspending benthic algae within pans (Diana et al. 1991; Smith and Schindler 2009; Khan and Mohammad 2014). This is attested by the Pearson correlation results which indicated a positive association of variables such as salinity and TDS with benthos and NH_4^+ with pelagic chl-*a*, suggesting that megafauna can potentially cause mixing of nutrients, resulting in phytoplankton biomass changes within the pans.

Table 5 Spearman correlation for benthic and pelagic chlorophyll-*a* against sediment and water chemistry variables. Bold values indicate significance at p < 0.05

Variable	Benthic cl	hl-a	Pelagic ch	Pelagic chl-a	
	r	р	r	р	
Sediments					
pН	-0.07	0.623	-0.02	0.896	
Р	-0.19	0.214	-0.06	0.679	
NH_4^+	0.22	0.151	0.46	0.039	
K	0.16	0.301	-0.11	0.484	
Ca	0.01	0.944	-0.14	0.372	
Mg	0.13	0.397	-0.06	0.718	
Κ	0.15	0.311	-0.11	0.48	
Na	0.16	0.299	-0.01	0.965	
Cu	0.31	0.001	-0.04	0.81	
Zn	0.10	0.491	-0.13	0.396	
Mn	0.26	0.083	0.07	0.651	
В	-0.13	0.403	-0.26	0.087	
Fe	0.30	0.001	0.18	0.236	
С	0.09	0.566	-0.01	0.962	
S	-0.07	0.648	-0.03	0.832	
SOM	-0.19	0.211	-0.10	0.516	
Water variables					
pН	-0.16	0.282	-0.06	0.716	
ORP	-0.19	0.196	-0.09	0.547	
Conductivity	-0.43	0.003	-0.30	0.041	
TDS	-0.34	0.019	-0.18	0.235	
Salinity	-0.35	0.018	-0.20	0.173	
Resistivity	-0.14	0.372	-0.23	0.118	
Temperature	0.41	0.004	0.18	0.241	
Benthic chl-a			0.33	0.025	

Based on our findings, the majority of the metals found in the benthic sediments come from natural bedrock and from the adjacent Limpopo and Luvuvhu Rivers. The potential processes occurring within and outside the park that may influence the metals include the following: (a) the metals in the subsurface rocks can potentially leach to surface water bodies (Villafane et al. 2012), (b) the majority of the metals in pans are emanating from the adjacent Limpopo and Luvuvhu River via subsurface flow (Anand et al. 2016) and get deposited into the pans, and (c) the rainfall has the potential to carry metals from far areas (outside the park) and deposit them into the pans through surface runoff (Qiao et al. 2022). The concentrations of metals in pans sediments are low relative to published literature for the Makuleke wetlands system (Nortjé et al. 2012; Dyamond 2017); however, a study conducted by Dalu et al. (2020) identified very high metal concentration for K, Ca, and Mg in Nylsvlei Wetlands system (a Ramsar wetland site), suggesting that the Makuleke wetlands are subjected to very minimal threats.

The significant differences observed between few variables (pH, Ca, Mg, and NH_4^+) and chl-*a* concentration suggested that the metals that have accumulated in sediments could potentially influence phytoplankton biomass in the water column with changes in the hydroperiod dynamics. According to Acosta et al. (2011), flooding duration events may result in the uneven distribution of metals across wetlands systems, suggesting that water level plays a significant role in driving metal concentrations while altering soil physicochemical properties, such as salinity, which would additionally change metal mobility in sediments (Bai et al. 2018).

In most tropical regions, rainfall plays a critical role in affecting physicochemical parameters and in the transfer of metals from the catchment land and irrigable lands to flood-plain pans (Ullah et al. 2023), which could lead to increased primary productivity during the high water period. It can also be noted that the levels of metals and chl-*a* are generally also influenced by other indirect factors (condition of the nearby rivers) and direct factors (geological substrate and animals that are found in the park) (Maslukah et al. 2019; Liu et al. 2020b). Furthermore, the increasing chl-*a* concentration in these floodplain pans may also be due to potential bioturbation effects as a result of large mammals that visit the pans periodically in search of drinking water.

In the current study, *n*-MDS ordination showed that several elements such as Fe, Zn, Mn, C, and Cu were important in influencing variation in chl-a concentration among pans and across hydroperiods. A similar study by Anas et al. (2015) found that the presence of metals such as Mn. Fe. and Cu concentrations in wetland sediment increased with an increase in the phytoplankton biomass. Experimental evidence by Coale (1991) suggests that some metals such as Mn, Fe, and Cu could produce inhibitory effects on phytoplankton biomass at elevated concentrations, through limiting nutrients (i.e. phosphorus and nitrogen) concentrations present in the water media. In agreement to our second hypothesis, we found that water variables such as salinity, conductivity, pH, and ORP were also important in influencing the chl-a concentration within pans and hydroperiods. Similarly, studies (e.g. Inyang and Wang 2020; Xiao et al. 2020; Ma et al. 2022) conducted in wetlands have highlighted that variables such as salinity, conductivity, pH, and ORP are the main drivers of phytoplankton biomass and can potentially influence primary productivity. The presence of high salinity in the pans may be associated with nitrogen and other ion input which emanates from the Luvuvhu and Limpopo river catchments, while conductivity and pH increased due to bioturbation during the different hydroperiods resulting in chl-a concentration differences.

Fluctuations in water levels are also known to promote pond diversity (Anton-Pardo et al. 2016), which may be a part of normal water regime variation. Such natural changes are typical intermittent for temporary ponds, since their



Fig. 3 The *n*-MDS ordination of the chlorophyll-*a* concentration across floodplain wetland pans and hydroperiod with physical and chemical properties vectors in the Makuleke wetlands, Kruger National Park

water level may change drastically due to processes in the water cycle (i.e. precipitation, evaporation, and runoff). Long-term fluctuations make it easier for small bodies of water, such as pans, to disappear, leading to water deficits (Wolnicki et al. 2008). A study by Pires et al. (2021) and Canisius et al. (2019), which examined wetland systems in Brazil, found that the water level intermittent in temporal wetlands is the major factor that contributes to differentiation in the macroinvertebrate and fish communities. This emphasises the strong effect of hydroperiod on organisms inhabiting small water bodies. Furthermore, an experimental study on temporary pond ecosystems by Zokan and Drake (2015) has also indicated that besides predation, demographic constraints due to wetland drying play a key role in structuring zooplankton communities, suggesting that water level can potentially alter the composition and functioning of small temporal pans. Moreover, water level changes affect the plankton community's richness and composition (Yang et al. 2021).

The present study attempts to detect the physicochemical properties of water, chl-*a* dynamics, and metal concentration in the sediment of Makuleke floodplain pans in the Kruger National Park. The results of this study observed a significant positive relationship between benthic chl-*a* and Mg suggesting a positive interaction of that metal with phytoplankton biomass. The potential increased concentration of Mg within pans during high water period will likely disrupt the wetland food web, resulting to deterioration of wetland biodiversity. Hence, strict management actions should be considered to protect the ecological sustainability of these

floodplain pans. Boeckman (2007) also found that spatiotemporal characteristics in ephemeral wetlands greatly influence the phytoplankton biomass. Thus, exploring changes in water levels over time is crucial to comprehending how phytoplankton responds to these changes in wetlands systems.

Conclusions

In conclusion, the study results indicated that water and sediment chemistry variables influenced pelagic and benthic chla concentrations in pans. We further observed that there are no major human activities occurring inside the park which could potentially impact these systems; however, more monitoring is required as water coming from the catchment could result in increased metal and nutrient pollution and enrichment. Between the hydroperiods, there were significant differences in sediment variables such as pH, NH₄⁺, Cu, Mn, Fe, and C. The latter variables play a significant role in driving the benthic chl-a within the pans especially during high water periods (see Table 2). We found that the results from the present study have the potential to elucidate long-term trends in the ecosystem health of floodplain pans. Despite water variables differing significantly across pans and hydroperiods, this study did not find any of the water parameters tested to be major drivers of pelagic chl-a across pans. We, therefore, recommend future studies that will determine the possible sources of metals found in the pans of the Makuleke floodplain pans, with much focus being given to the hydrological dynamics of these floodplain systems.

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Data availability Data will be made available on request.

Declarations

Ethical approval The data for this study was collected in accordance with the Kruger National Park permit (KNP Permit Reference no. DALT1635) and ethical clearance for the present study was approved by the University of Venda Research committee (Ethical clearance No. SES/20/ERM/14/1611).

Consent to participate All authors have agreed to participate in this paper.

Consent for publication All authors have agreed to publish this paper.

Conflict of interest The authors declare no competing interests.

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