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Short Communication

Assessing chlorophyll–*a* and water quality dynamics in arid–zone temporary pan systems along a disturbance gradient

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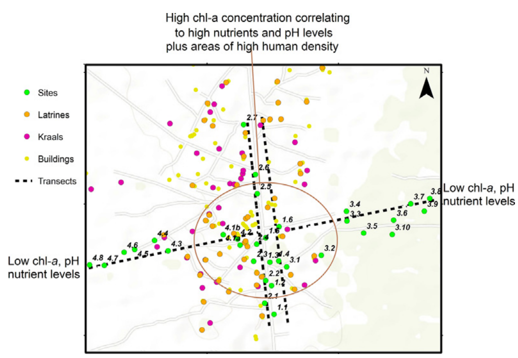
HIGHLIGHTS

- Disturbed pans had elevated pH, nutrients and dissolved oxygen.
- Chlorophyll–*a* concentration increased with surface area, and disturbance gradient.
- Anthropogenic activities had an overall effect on the pan water quality.
- Continuous monitoring strategies should be established to understand nutrient dynamics.

GRAPHICAL ABSTRACT



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ABSTRACT

Temporary pans are susceptible to various anthropogenic effects such as pollution, resource extraction, and land use intensification. However, given their small endorheic nature, they are almost entirely influenced by activities close to their internally drained catchments. Human–mediated nutrient enrichment within the pans can lead to eutrophication, resulting in increased primary productivity and decreased associated alpha diversity. The Khakhea–Bray Transboundary Aquifer region and the pan systems that characterise the area are understudied area with no records available of the biodiversity therein. Additionally, the pans are a major water source for the people in these areas. This study assessed differences in nutrients (*i.e.*, ammonium, phosphates) and their effect on chlorophyll–*a* (chl–*a*) concentrations in pans along a disturbance gradient in the Khakhea–Bray Transboundary Aquifer region, South Africa. Physicochemical variables, nutrients, and chl–*a* were measured from 33 pans representing variable anthropogenic exposure during the cool–dry season in May 2022. Five environmental variables (*i.e.*, temperature, pH, dissolved oxygen, ammonium, and phosphates) showed significant differences between the undisturbed and disturbed pans. The disturbed pans generally had elevated pH, ammonium, phosphates and dissolved oxygen compared to the undisturbed pans. A strong positive relationship was observed between chl–*a* and temperature, pH, dissolved oxygen, phosphates and ammonium. Chlorophyll–*a* concentration increased as surface area, and the distance from kraals, buildings and latrines decreased. Anthropogenic activities were found to have an overall effect on the pan water quality within the Khakhea–Bray Transboundary Aquifer region. Therefore, continuous monitoring strategies should be established

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to better understand the nutrient dynamics through time and the effect that this may have on productivity and diversity in these small endorheic systems.

1. Introduction

Globally temporary endorheic wetlands make up many surface waters in both arid and semi–arid regions such as Australia, Africa, Europe, and North America (Roshier et al., 2001; Calhoun et al., 2017; Nhiwatiwa et al., 2017a; Mpakairi et al., 2022a). Endorheic depressions in wetlands referred to as pans in South Africa are also common in France (with vernal pools representing 0.05 % of the natural habitat), Europe and the USA. These temporary systems are classified as wetlands but are often overlooked during monitoring and research (Williams, 2006; Bird et al., 2019). In southern Africa, geomorphic features and climatic conditions have given rise to one of the highest densities of temporary pans (Goudie and Wells, 1995; Bird et al., 2019). Temporary pans vary in size and hydroperiods (Williams, 2012). The hydroperiod is the main driver of these pan systems, often resulting in a unique biotic community characterised by a number of specialist plant and animal species only found within these systems (Calhoun et al., 2017; Brendonck et al., 2022). Anthropogenic effects such as pollution, resource extraction and land use intensification (Human et al., 2018; Dube et al., 2020; Wasserman and Dalu, 2022) are increasingly prevalent with implications for primary and secondary productivity, and associated ecosystem functioning in these systems.

Many physical and biological factors determine water quality within these temporary pan systems (Henri et al., 2014; Park and Hwang, 2016; Nhiwatiwa et al., 2017a). The physical and chemical conditions within these pan systems reflect the land use patterns and physical characteristics of the landscapes in which they are found (Morrice et al., 2008). Human disturbances around the pan systems can lead to changes in the water quality, and in turn, this can change the diversity within these systems (Nhiwatiwa et al., 2017b). The endorheic nature of these pans, and reduced water flow (in and out), coupled with the shallowness of these pan systems, make them more vulnerable and susceptible to anthropogenic impacts (Henri et al., 2014). Human–mediated nutrient enrichment within the pans can lead to adverse effects such as eutrophication, which promotes plant and algal growth. Nutrient enrichment degrades aquatic ecosystems and impairs water viability for consumption, industry, agriculture, recreation, and other purposes (Carpenter et al., 1998). Water nutrient analyses provide information on the ecological integrity of the water resources at a specific time. The water quality and trophic status of these ecosystems can be monitored using chlorophyll–*a*, as an algal parameter in conjunction with other environmental indicators (Omar, 2010).

Although a water quality classification system was developed for pans (De Klerk et al., 2016), very few studies (*e.g.*, Bird and Day, 2014; Dube et al., 2020) have specifically looked at the effects that anthropogenic activities have on water quality within temporary pans in South Africa. The current study aimed to assess how differences in nutrient (*i.e.*, ammonium, phosphates) concentrations and anthropogenic activities affect chl–*a* concentration variation among pans in the Khakhea–Bray Transboundary Aquifer region. Overall, we hypothesized that anthropogenic activities near human settlement areas would result in significantly higher chl–*a* and nutrient concentrations. Generating information on the effect of anthropogenic activities on water quality of pans in temporary wetlands will help develop assessment tools to better monitor human impacts across temporary wetland ecosystems and aid in the prioritization of temporary wetlands for conservation.

2. Methods

2.1. Study area

The study was carried out in the Khakhea–Bray Transboundary Aquifer region, located on the border of Botswana and South Africa in the Northwest Province, as part of a more extensive investigation. The Khakhea–Bray Transboundary Aquifer region is characterised by numerous temporary pans, which cover an area of about 29,700 km^2. The underlying geology is dominated by a rocky outcrop comprising of Campbell–Rand dolomites (Turton et al., 2006). The area's climate is semi–arid, with low annual rainfall (approximately 376 mm per annum average) (Mpakairi et al., 2022b). The pan systems in the Khakhea Bray Transboundary Aquifer Region lose water through evaporation and infiltration, with infiltration contributing partly to groundwater recharge. The pan systems also constitute a significant source of potable water for the local households and drinking water for the livestock (C.P. Mungenge, pers. observ.).

The study took place during the cool–dry season in May 2022. Site selection was based on the presence of high densities of pans near human settlements (Fig. 1). Within the chosen study region, a line transect of 1.5 km along the main road was measured. Two perpendicular transects 1.3 km long each from the road were also measured (Fig. 1). All human structures, namely buildings, latrines, and kraals, were identified within 200 m of the transect line. Within the area, 33 pans were identified and designated as either undisturbed or disturbed. Undisturbed pans were all pans located >500 m from the road transect that did not have any human structure observed within a 400 m buffer. Disturbed pans were found <500 m from the road and had human structures within a 400 m buffer. The GPS coordinates of the 33 pans (14 undisturbed, 19 disturbed) and all associated human structures were collected in the field. These coordinates were then used to measure the distance of each of the pans from the nearest human structure and anthropogenic activity. The distances and the surface area of each pan were measured using the Google Earth Pro Desktop version 9.172.0.0. As such, three measurements (distance to the nearest anthropogenic disturbance type) were associated with each pan based on the nearby human structures.

2.2. Physico–chemical analysis

At the centre of each pan, temperature (°C), pH, conductivity (μS cm^{-1}), turbidity (NTU), TDS (mg L^{-1}), salinity (ppm), percentage oxygen saturation and dissolved oxygen (mg L^{-1}) were measured at a depth of 1 m from the surface using an AquaRead multiparameter meter (Model AP–700 and AP–800, AquaRead Ltd, UK). 250 mL of water ($n = 2$) was collected in plastic containers from each pan for nutrient analysis and stored on ice. Nutrients (*i.e.*, phosphates and ammonium) were analyzed using a multiparameter benchtop photometer (Hanna Instruments Model HI83300) whereby ammonium (Photometer range 0–10 ± 0.04 mg L^{-1} accuracy, resolution 0.01 mg L^{-1}) was determined through the Nessler method, phosphates (photometer range 0–30 mg L^{-1} ± 1.0 mg L^{-1} accuracy, resolution of 0.1 mg L^{-1}) through the amino acid method and nitrates (photometer range 0–30 ± 0.5 mg L^{-1} accuracy, resolution, resolution 0.1 mg L^{-1}) through the cadmium reduction method (Dalu et al., 2019).

2.3. Chlorophyll–*a* analysis

Chlorophyll–concentrations were determined by taking 250 mL of each water sample filtered through a 0.7 μm Whatman glass fiber filter (Ø = 47 mm). The filters were placed in plastic zip–lock bags and stored on ice in the field. The filters were then stored at −20 °C until extraction. Each filter was extracted in 10 mL of 90 % acetone in the dark for 24 h. Chlorophyll–*a* concentration was then determined fluorometrically using a Turner 10 AU fluorometer. Absorbances were taken for each sample before and after adding two drops of 1 N HCl (Holm-Hansen and Riemann, 1978; Gusha et al., 2021). Chlorophyll–*a* concentrations were then

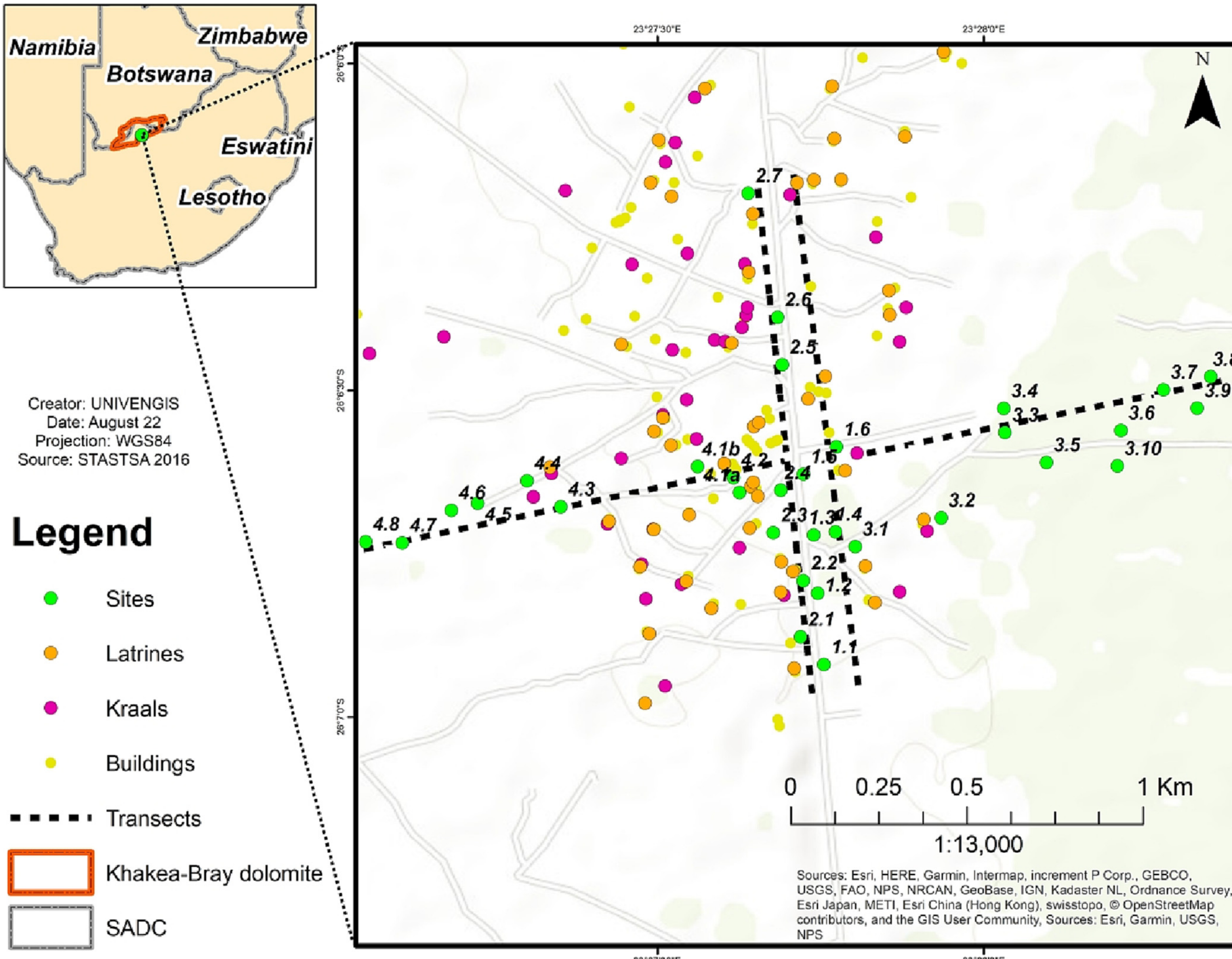

Fig. 1. Map showing the 33 sampled pans (in green) in May 2022 in the southern section of the Khakhea–Bray Transboundary Aquifer region and the various anthropogenic activities around the pans.

calculated following the Environmental Protection Agency (EPA) method 445.0 (Arar and Collins, 1997):

$$chl - a\left(\text{mg L}^{-1}\right) = \left(\frac{a}{V}\right) \times (F_o - F_a) \times C$$

where chl–*a* (mgL^{-1}) is the chl–*a* concentration in mg L^{-1}, “a” is the quantity of acetone used for extraction in mL, V is the quantity of water filtered in mL, F_o is the chl–*a* reading before acidification with 1 N HCl (hydrochloric acid), F_a is the chl–*a* reading after acidification with 1 N HCl (hydrochloric acid), and C is the constant value (0.325).

2.4. Data analysis

ESRI ArcGIS 10.8 software was used for symbolization using proportional circles for the pH, ammonium, phosphate and chl–*a* concentrations in the 33 pans that were sampled. A two–sample *t*–test was used to determine the environmental variables' differences between the undisturbed and disturbed pans. All the measured variables had skewed distributions except for pH. Therefore, all the other variables were log (x + 1) transformed, excluding percentage oxygen saturation, which was square root transformed. A correlation analysis was then done to compare the relationships between chl–*a* and all the other variables measured. The test and analysis were carried out using the software package STATISTICA version 14.0.0.15 (TIBCO Software Inc., 2020).

3. Results

Environmental variables varied between the undisturbed and disturbed pans. Nitrate concentrations in all sampled pans were all below detectable limits, highlighting that nitrate levels in the pans are low. As such, nitrates were not included in further analyses. The *t*–tests comparing environmental variables measured for the two groups of pans showed that temperature, pH, dissolved oxygen, ammonium, and phosphate levels were significantly different between the undisturbed and disturbed pans. Disturbed pans generally had higher pH (mean ± standard deviation: 9 ± 0.5), ammonium (1.9 ± 0.6 mg L^{-1}), phosphates (0.74 ± 0.4 mg L^{-1}) and dissolved oxygen (6.9 ± 1.5 mg L^{-1}) levels compared with the undisturbed pans (Fig. 2). Salinity levels were low across all the pans (<0.05 mg L^{-1}). The undisturbed pans showed higher total dissolved solids (107.6 ± 96.6 mg L^{-1}) and turbidity (46.8 ± 85.2 NTU) levels. The disturbed pans had slightly higher chl–*a* concentrations (mean ± standard deviation: 0.11 ± 0.2 mg L^{-1}) than the undisturbed pans (0.08 ± 0.1 mg L^{-1}) but this was not found to be significant ($p > 0.05$) (Table 1, Fig. 2).

In all 33 pans, there was a strong significant positive relationship between chl–*a* and temperature, pH, turbidity and ammonia. Strong negative relationships were observed between chl–*a* and phosphates, distance to the

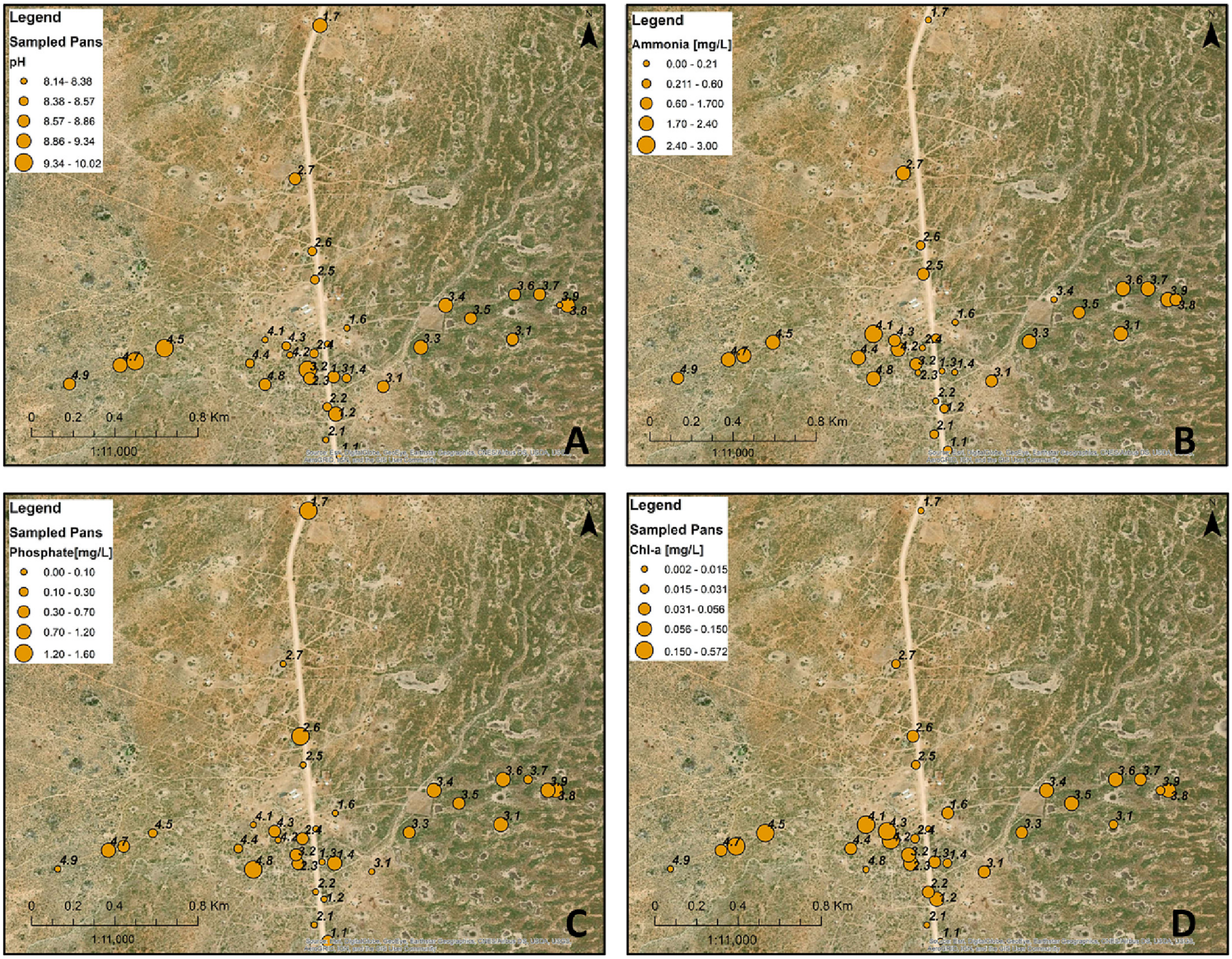

Fig. 2. Maps showing different environmental variables measured across the 33 pans in May 2022: (A) pH, (B) ammonium, (C) phosphates (D) chlorophyll–*a* concentration.

nearest latrines, kraals and buildings and surface area of each pan (Table 2). Conductivity, TDS, salinity, and dissolved oxygen were not significantly correlated ($p > 0.05$) with chl–*a* concentrations in the pans (Table 2).

4. Discussion

The present study found significant differences in the pH, temperature, dissolved oxygen, ammonium, and phosphate concentrations overall between the undisturbed and disturbed pans. All these five variables were higher in the disturbed pans than the undisturbed pans. The higher temperatures recorded in the disturbed pans, when compared to the undisturbed pans, are likely attributed to anthropogenic activities within the temporary pan systems of the Khakhea Bray Transboundary Aquifer Region.

Table 1
Summary of pairwise comparisons (*t*–test) of environmental variables (mean ± standard deviation) between the undisturbed and the disturbed pans. Significant values ($p < 0.05$) are indicated in bold.

Variable	Undisturbed pans	Disturbed pans	*p*
Temperature (°C)	20.8 ± 3.1	22.9 ± 1.9	**<0.001**
pH	8.6 ± 0.4	9.0 ± 0.5	**<0.001**
Conductivity (μS cm^{-1})	173.2 ± 160.3	144.6 ± 33.0	0.145
Turbidity (NTU)	46.79 ± 85.2	37.8 ± 68.6	0.319
Total dissolved solids (mg L^{-1})	107.6 ± 96.6	93.4 ± 19.7	0.193
Salinity (ppm)	0.04 ± 0.02	0.05 ± 0.01	0.217
Percentage oxygen saturation	66.0 ± 17.2	85.2 ± 23.2	**<0.001**
Dissolved oxygen (mg L^{-1})	5.3 ± 1.2	6.90 ± 1.5	**<0.001**
Ammonium (mg L^{-1})	0.86 ± 0.9	1.90 ± 0.6	**<0.001**
Phosphates (mg L^{-1})	0.39 ± 0.5	0.74 ± 0.4	**0.020**
Chlorophyll–a (mg L^{-1})	0.08 ± 0.1	0.11 ± 0.2	0.209
Total surface area (m2)	816.5 ± 735.6	1092.7 ± 735.1	0.154

Table 2
Summary of correlation analysis comparing relationships between chlorophyll–*a* and all the other environmental variables. Significant relationships ($p < 0.05$) are highlighted in bold.

Pair of variables	Spearman R	*p*
Chlorophyll–*a* *vs* temperature	**0.529**	**0.029**
Chlorophyll–*a* *vs* pH	**0.571**	**0.017**
Chlorophyll–*a* *vs* conductivity	−0.051	0.844
Chlorophyll–*a* *vs* turbidity	**0.593**	**0.012**
Chlorophyll–*a* *vs* total dissolved solids	−0.049	0.852
Chlorophyll–*a* *vs* salinity	−0.424	0.090
Chlorophyll–*a* *vs* %dissolved oxygen	0.019	0.474
Chlorophyll–*a* *vs* dissolved oxygen	0.328	0.198
Chlorophyll–*a* *vs* ammonium	**0.534**	**0.027**
Chlorophyll–*a* *vs* phosphate	**−0.502**	**0.040**
Chlorophyll–*a* *vs* distance to the nearest latrines	**−0.566**	**0.018**
Chlorophyll–*a* *vs* distance to the nearest Kraals	**−0.730**	**<0.001**
Chlorophyll–*a* *vs* distance to the nearest buildings	**−0.551**	**0.022**
Chlorophyll–*a* *vs* surface area	**−0.617**	**0.008**

Most of the disturbed pans were surrounded by bare ground since the land had been cleared for construction and domestic activities, exposing the terrestrial environment to higher levels of solar radiation. In comparison, the undisturbed pans were bordered by a matrix of trees and shrubs, that overshadowed the banks of the pans. The slightly higher pH in the disturbed pans may also indicate pollution from the various human activities around the pans. Although the disturbed pans had a slightly high value of dissolved oxygen, the oxygen levels measured in all the pans in general was considered good since, for most natural freshwater systems, any concentration above 5 mg L^{-1} is considered healthy (Dalu et al., 2013).

The below–detectable levels of nitrates after the inundation of sediment from a semi–arid area have been observed previously in a study by Arce et al. (2015). For our study the pans were sampled soon after the rains when they contained water. It is likely that nitrates levels that accumulate in sediment during the periods of desiccation are low and are immediately processed after inundation *via* denitrification, rather than being released into the water. The reduction of nitrates in the water stimulates production of ammonium which can be preferably assimilated by organisms in the water (Dortch, 1990). Ammonium was detectable in the pans, and it was found that ammonium, phosphate and chl–*a* concentrations were higher in the disturbed pans than in the undisturbed pans. These results show a similar pattern to Dube et al. (2020) where chl–*a* and ammonium concentrations were found to be high in pans in the Ndumo communal area, indicating different levels of anthropogenic activities in close proximity to pans.

The present study also examined the relationship between several environmental variables and chl–*a* concentrations to elucidate potential indicator for the impacts of the anthropogenic activities. Temperature, pH and ammonium were found to drive the chl–*a* concentrations in the pan systems, with strong positive relationships between these three variables and chl–*a*. The strong relationship between chl–*a* and temperature has been shown in other studies (Pieterse and Van Vuuren, 1997) since temperature influences the rate of chemical reactions within aquatic systems. This may also explain why the smaller pans had higher concentrations of chl–*a* as the smaller surface area resulted in the pan heating up faster, thereby facilitating higher algal production (Nhiwatiwa and Dalu, 2017). The chl–*a* concentration is highly dependent on the nutrient concentration as these nutrients (*i.e.*, nitrogen, phosphorous) are essential for primary plant production. In this study, the strong relationship between ammonium and chl–*a* may suggest that these pans are nitrogen–limited aquatic ecosystems. Further studies over an extended period should be conducted to validate our findings.

In this study, chl–*a* concentrations in the pans increased with decreasing phosphates and decreasing distances from each pan to the identified associated anthropogenic activity, namely latrines, kraals, and buildings. This meant that the pans influenced by the various anthropogenic disturbances showed higher chl–*a* concentrations and, higher algal growth when compared to the undisturbed pans. Proximity to kraals was the major factor driving the chl–*a* concentrations in the pans. Most of the pans observed in the Khakhea Bray Transboundary Aquifer region were frequented by livestock. Cattle typically enter water systems to drink, and the activity is often associated with urination and defecation within or near these temporary systems, with implications for primary productivity dynamics (Buxton et al., 2020). The cattle have unrestricted access to the temporary pans and tend to be attracted to the water and the presence of forage material (Hughes et al., 2016). Fecal contamination from grazing livestock results in higher ammonium concentrations in the pans closer to the homesteads (Collins and Rutherford, 2004). The pit latrines represented the primary means for human–waste disposal within the study site. The leaching of ammonium and nitrates from the pit latrines into the groundwater that feeds the pans results in high levels of nitrogen–containing compounds (ammonium) in the disturbed pans close to the homesteads and thus represents a major threat to these systems. Similar studies have also shown that contamination is particularly high (particularly with nitrates and coliform bacteria) when the aquifer is located five meters below the pit latrines (Love et al., 2005; Templeton et al., 2015).

Chlorophyll–*a* concentration was also driven by the proximity of the pans to buildings and homesteads. Pollution problems from domestic point sources, which lead to excessive nutrient enrichment, are an ever–growing threat (Dudgeon et al., 2006). For this study, waste dumping was prevalent in the sampled area given the lack of appropriate waste disposal facilities. Dry pans are used as dumping sites with plastics and even baby diapers. Once inundation occurs after the wet season, the waste is seen within these pans (C.P. Mungenge, pers. observ.). The endorheic nature of the pans allows no outward drainage or flushing which can cause an accumulation of nutrients, from the latrines, livestock waste and waste pollution, within these systems (Henri et al., 2014; Nhiwatiwa et al., 2019).

Freshwater systems are threatened globally by overexploitation, pollution, and destruction and/or degradation of habitat (Dudgeon et al., 2006; De Villiers, 2007; Reid et al., 2019). This is problematic as wetlands are often biodiversity hotspots that support high densities and diversities of wildlife (Calhoun et al., 2017). Nutrient enrichment (particularly phosphorous and nitrogen) associated with anthropogenic activities can therefore alter algal production within aquatic ecosystems and have detrimental consequences on these systems (Chislock et al., 2013). Anthropogenic–mediated changes to temporary wetlands can alter hydroperiods (Euliss and Mushet, 2004) leading to compositional changes of biotic communities, altered predation pressure, invasions and altered biogeochemical cycles which can disrupt ecosystem functioning and of the loss of ecosystem services.

5. Conclusions

As we hypothesized, the pans with human disturbances had higher nutrient concentrations, and these anthropogenic activities did impact the nutrient concentration dynamics and chl–*a* concentrations of temporary pans. Proximity to kraals had the highest influence on the chl–*a* in the pans. Continuous monitoring strategies need to be established to better understand the nutrient dynamics over time, especially since the Khakhea Bray Transboundary Aquifer Region pan systems are an understudied area and a major water source for the people in the area.

CRediT authorship contribution statement

Chipo P. Mungenge: Formal analysis, Methodology, Data curation, Investigation, Validation, Visualization, Writing – original draft, Writing – review & editing. **Ryan J. Wasserman:** Methodology, Visualization, Investigation, Supervision, Writing – original draft, Writing – review & editing. **Farai Dondofema:** Methodology, Investigation, Visualization, Formal analysis, Funding acquisition, Writing – review & editing. **Chad Keates:** Visualization, Methodology, Investigation, Writing – review & editing. **Fannie M. Masina:** Methodology, Investigation, Writing – review & editing. **Tatenda Dalu:** Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Funding acquisition, Supervision, Resources, Validation, Visualization, Writing – original draft, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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