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Reference:

Rebelo Alanna Jane, Emsens Willem-Jan, Esler Karen J., Meire Patrick.- Quantification of water purification in South African palmiet wetlands
Water science and technology - ISSN 0273-1223 - 78:5(2018), p. 1199-1207
Full text (Publisher's DOI): <https://doi.org/10.2166/WST.2018.389>
To cite this reference: <https://hdl.handle.net/10067/1546850151162165141>

Quantification of water purification in South African Palmiet Wetlands

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AJR conceived the study, AJR performed data analysis, AJR wrote the manuscript and KJE, PM, WE, contributed and edited it.

Keywords: agricultural runoff, channel erosion, degradation, fen, self-purification capacity, valley-bottom wetland

Abstract

Despite the importance of water purification to society, it is one of the more difficult wetland ecosystem services to quantify. It remains an issue in ecosystem service assessments where rapid estimates are needed, and poor-quality indicators are over used. We attempted to quantify the water purification service of South African palmiet wetlands; valley-bottom peatlands highly threatened by agriculture. First, we performed an instantaneous catchment-scale ‘mass balance’ sampling approach, which compared the fate of various water quality parameters over degraded and pristine sections of palmiet wetlands. We found that pristine palmiet wetlands acted as a sink for water, major cations, anions, dissolved silicon and nutrients; though there was relatively high variation in these trends. There are important limitations to this catchment-scale approach, including the fact that at this large scale there are multiple mechanisms (internal wetland processes as well as external inputs) at work which are impossible to untangle with limited data. Therefore, secondly, we performed a small, field-scale field survey of a wetland fragment to corroborate the catchment-scale results. There was a reasonable level of agreement between the results of the two techniques. We conclude that it appears possible to estimate the water purification function of these valley-bottom wetlands using this catchment-scale approach.

Introduction

Wetlands are considered to be one of the most important types of ecological infrastructure to society in terms of the ecosystem services they provide (Russi et al., 2013). The type of wetland, landscape configuration and hydrological connectivity have been cited to be important in determining the type and magnitude of ecosystem services that will be provided (Moor et al., 2017). Valley-bottom and floodplain wetlands in particular, due to a combination of their position in the landscape and their composition (alluvium, peat beds and vegetation), have been shown to attenuate flood events (Rebelo et al., 2015), mitigate water pollution (Fisher and Acreman, 2004), sequester carbon (Mitsch et al., 2013), retain sediment (Venterink et al., 2006), provide clean water and food for local communities (Schuyt, 2005) and provide a host of other cultural ecosystem services underpinned by their high biodiversity (Raymond et al., 2009). Despite their value, the complexity of wetland ecology has resulted in wetlands being the least studied system in terms of ecosystem services (de Bello et al., 2010). Water purification is noted to be one of three key ecosystem service complexes provided by wetlands (Moor et al., 2017). However, it is difficult to quantify wetland water purification in the field (as opposed to artificial wetlands) given the internal complexity of wetland ecosystems (Jordan et al., 2003).

Water purification, sometimes referred to as 'water quality' in ecosystem service studies, has been estimated in many different ways (Boerema et al., 2017). Besides rapid assessments or scores, the simplest way to attempt to quantify water purification is to measure either physical or chemical properties of a water body at one point in time, focussing on parameters of interest and known thresholds for these parameters (Boerema et al., 2017; Kandziora et al., 2013). Other studies use modelling techniques: investigating nutrient retention at a catchment-scale, using the InVEST model or modelling nutrient retention, export or turnover rates in vegetation or in the ecosystem itself (Bai et al., 2011; Boerema et al., 2017). Some studies measure properties of the soil (nutrients or elements of interest), nutrient retention in vegetation or nutrient removal potential of particular land-covers (Boerema et al., 2017). Lastly, other studies quantify processes such as decomposition rates and net primary productivity, relating these to water purification (Boerema et al., 2017; Kandziora et al., 2013). Ultimately many of these methods can be problematic because they study water quality, or impacts on water quality, rather than the water purification function of a particular ecosystem, or are modelled estimates, often not validated (Boerema et al., 2017). However, quantitative water and nutrient budgets of wetlands are difficult and costly because of high variation amongst wetlands as well as within wetlands, due largely to interannual variation in rainfall (Jordan et al., 2003). Therefore, there is a need for a compromise between full water and nutrient budgets and the inadequate rapid assessments of water quality when estimating the ecosystem service: water purification.

In South Africa, the value of valley-bottom/flood-plain wetlands in terms of water purification has often been overlooked in favour of their fertile soils for potential food provision. Therefore South African wetlands and associated river systems are in a

critical state, with over 65% reported to be damaged, and 50% estimated to have been destroyed (Nel et al., 2007). Increasing concern over the loss of water-related ecosystem services following wetland degradation (mainly in terms of water provision, but also of water purification) has prompted conservation and restoration efforts in South Africa. South African Palmiet wetlands are a type of unchannelled valley-bottom wetland with peat layers ranging between 0.5 to 10 m deep (Job, 2014; Sieben, 2012). Palmiet wetlands are named after the plant species that dominates the system: *Prionium serratum*. Palmiet is a super-dominant ecosystem engineer (species that significantly modify their environment in their favour) and peat-forming species (Sieben, 2012). However there has been little research done on these unique wetlands, and there is little understanding of their structure and functioning. Therefore, in the face of the threats to these wetlands, there is an urgency to better understand these systems and the ecosystem services they provide. In this study, we attempt to quantify the ecosystem service of 'water purification' in South African palmiet wetlands. We investigate how water quality changes spatially in three of these wetlands subjected to agricultural pollution at a catchment-scale, as well as in a small-scale field survey. We ask the following research question: do pristine palmiet wetlands act as a sink for pollutants (nutrients and metals) linked to agricultural fertilizer application?

Methods

Study sites

Palmiet wetlands occur in valley-bottoms throughout the Cape Floristic Region of South Africa. This Region is characterised by oligotrophic and acidic soils due to the highly leached dystrophic lithosols associated with the sandstone mountains of the Cape Supergroup. Therefore, palmiet wetlands are naturally slightly acidic systems. Three palmiet wetlands were selected as study sites in three different catchments throughout the Cape Floristic Region: the Theewaterskloof and Goukou wetlands (Western Cape) and the Kromme wetland (Eastern Cape) (**Fig. 1**). The catchments are of varying sizes, the Theewaterskloof the smallest, and the Kromme the largest. All wetlands have been transformed to some degree, all with some level of channel erosion; invasion of alien trees (especially in tributaries) and the Goukou and Kromme are situated in an agricultural context, receiving runoff from liming and fertilizers (**Fig. 1**). This impact tends to intensify in a downstream direction, with the least impact upstream in the catchment, and the greatest impact (most transformed wetlands) downstream. The Theewaterskloof catchment had agriculture upstream prior to the building of the impoundment that supplies the metropolis of City of Cape Town. The land upstream of the impoundment is now part of a nature reserve.

Figure 1. The three study palmiet wetlands in their respective catchments (back areas labelled 1-3) in the Cape Floristic Region of South Africa (light green). Provinces are indicated with gray lines in the map of South Africa. Catchment boundaries are represented by solid black lines. The three insets may not show the catchment boundary due to the small size of the wetland relative to the catchment. Invasion by alien trees is represented in solid black in the insets, whereas 'headcut' refers to gully erosion. The direction of riverflow within each catchment is indicated by arrows. Water quality sampling points are indicated with red points in each catchment.

Study design

We used two approaches to estimate the water purification ability of South African palmiet wetlands: firstly, a catchment-scale analysis of three wetlands, and secondly a small field survey. To quantify the service of water purification at a catchment-scale, we compared the ability of relatively pristine (least disturbed in terms of gully erosion) wetland sections to attenuate pollution with that of wetland sections that had lost their ecological infrastructure through degradation by channel erosion. In the field survey we attempted to follow pollutants through one wetland fragment to see whether they were exported from the wetland or whether the wetland attenuated them at this smaller, field-scale.

Catchment Analysis

We collected water samples in September 2014 at 21 points throughout the three study catchments containing valley-bottom palmiet wetlands (**Fig. 1**). These points were opportunistically selected as locations where all the surface water moving through the wetland could be sampled. Therefore, these points were either places where the wetland had become channelized and all the surface water was directed through one

main channel or places where multiple small channels were evident and accessible along a cross section of the wetland. Finally, we selected 19 of the 21 points for further analysis. At each water quality sampling point we estimated discharge by measuring channel area (averaging cross sectional depth and width measurements) and flow velocity of the surface using the float method, as the water level was often too shallow for use of a flow velocity meter. A correction factor of 0.9 was used to correct surface flow velocity to average flow velocity. Water quality parameters were selected according to their potential link to fertilizer or pesticide application by adjacent agriculture. In situ, we measured pH (water), electrical conductivity and temperature using a MultiLine F/Set-3 meter (WTW, Germany). Also in the field, we filtered (0.45 μm) and preserved samples for analysis of multiple parameters which were analysed later in the lab. The concentration of phosphate ($\text{PO}_4^{3-}\text{-P}$), sulphate ($\text{SO}_4^{2-}\text{-S}$), nitrate ($\text{NO}_3^-\text{-N}$), ammonium ($\text{NH}_4^+\text{-N}$), total phosphorus (P-tot), total Kjeldahl nitrogen (Kj-N) and chloride (Cl^-) were measured on a continuous -flow analyzer (CFA) (SKALAR: SAN++). Total dissolved K, Na, Mg, Ca, Fe, Cu, Mn, Zn and Al were acidified with HNO_3 and concentrations thereof -as well as total dissolved Si- were measured on an Inductively Coupled Plasma Spectrometer using Optical Emission Spectroscopy (ICP-OES) (Thermo Scientific, type: iCAP6300 Duo). Chemical oxygen demand was measured according ISO15705 using the LCI500 kit and the DR2800 spectrophotometer (ISO, 2002).

Field Survey

In April 2015 we conducted a more detailed field experiment in the Kromme Catchment to examine the effects we had seen at a catchment-scale at a smaller, field-scale. The study site included a small patch of relatively pristine wetland (approximately 300 m by 70 m of uneroded palmiet wetland vegetation) surrounded by intensive irrigated agriculture applying fertilizers at high rates (**Fig. 2**). A channel entered the wetland patch from a degraded section of the wetland (all alluvium washed away) and then dispersed through the wetland (i.e. there was no more noticeable channel within the wetland as the alluvium and peatbeds were intact). The pristine palmiet wetland fragment ended at a concrete weir which was constructed to protect this remaining wetland from headcut erosion approaching from downstream. Nine water quality samples were taken in the channel entering the wetland (degraded section), another nine samples were taken 30 m apart along a transect through the relatively pristine part of the wetland and eight samples were taken at various points at the outflow (above and below the weir) (**Fig. 2**). In this field survey, the same parameters were used as from the catchment-scale analysis, but in addition dissolved organic carbon was also measured by UV/persulfate oxidation on a CFA (Gershey et al., 1979).

Figure 2. (a) The map of South Africa indicates the location of the Kromme catchment (red box) within the Cape Floristic Region (green shaded area) -also see **Fig. 1**. (b) The Kromme River inset shows the location of the study transect (red box). (c) The transect used for the field survey in the Kromme Catchment, South Africa. Points indicate water sampling points; yellow indicates degraded and red indicates pristine parts of the wetland; white indicates points at the outflow of the weir. The river flows approximately west to east, indicated by the arrows.

Analysis

For the catchment-scale analysis, we used an instantaneous ‘mass balance’ type sampling approach to estimate changes in water quality over wetland sections (sections of wetland between sampling points) (**Plate A1, Plate A2**). Therefore, at each sampling point, the quantity (mg/s) of each water quality parameter entering the wetland was calculated by multiplying its concentration (mg/l) by the discharge (l/s). This was not done for conductivity and pH. Where there were multiple channels or tributaries, these were taken into consideration in calculations by adding these quantities to that of the water entering the wetland section via the main channel (**Plate A2**). Each wetland section was classified as either ‘degraded’ or ‘pristine’ according to one criterion: the physical condition of the wetland (whether gully or channel erosion was evident at a large scale, and whether the alluvium had been washed away). The nine wetland sections were therefore classified into six pristine sections and three degraded ones (furthest downstream): one in the Goukou and two in the Kromme (**Plate A1**). For each of these nine wetland sections, the change in water quality was calculated for each parameter by subtracting the quantity (concentration*discharge) of each parameter

199 leaving the wetland section, from the quantity entering it. If that value was positive, it
200 indicated that the parameter was decreasing, or that the wetland section was a net sink
201 for that parameter (either the parameter was being used by internal wetland processes,
202 or it was being deposited). If negative, the parameter was increasing, or the wetland
203 section was a net source for that parameter (exporting that parameter).

204 To test whether the water purification ability of wetlands differed between degraded
205 and pristine wetland sections, we fitted linear mixed models taking wetland (site) into
206 account. We used the lme4 package in R (Bates et al., 2015). Wetland was entered as a
207 random effect to account for the dependence between observations from within the
208 same wetland/catchment. Degradation and the interaction between wetland and
209 degradation were entered as fixed effects. First, the significance of the interaction was
210 tested by comparing the fit of this model to a reduced model with only the main effect.
211 This could not be done for the Theewaterskloof wetland, since we had no degraded
212 sections there. Where the interaction term was significant, we could not test for the
213 effect of degradation. In the case of non-significant interaction, we excluded it from the
214 model and tested the significance of the main effect: degradation. Significance was
215 tested using an F-test with Kenward-Roger correction for degrees of freedom, as
216 implemented in the “pbKRtest” package of R.

217 For the field survey, we correlated each parameter against distance through the wetland
218 fragment to see whether these parameters changed significantly passing through the
219 pristine wetland. All nine samples entering the wetland were averaged, as well as all
220 eight samples downstream of the wetland, yielding a sample size of 11. We used
221 Spearman Correlations in R. If the correlation was strongly and significantly negative,
222 the wetland fragment is acting as a sink for the parameter. If the correlation was
223 strongly and significantly positive, the wetland fragment is acting as a source for the
224 parameter.

Results

Catchment Analysis

On average, pristine palmet wetlands tended to act as a sink for water, base cations (total dissolved Ca, K, Mg, Na), anions (total dissolved Cl⁻ and SO₄²⁻), dissolved Si, and nutrients (total phosphorus and Kjeldahl nitrogen), though there was relatively high variation in these trends (**Table 1, Table A1**). The pH of the water of pristine wetlands ranged from 4.3 to 7.7. Where water from agricultural runoff entered a wetland patch (typically with a higher than natural pH), pH was observed to decrease through the wetland patch in most cases. Similarly, chemical oxygen demand decreased over these pristine wetland sections. Conductivity was the only parameter that increased over the pristine sections of palmet wetland. Degraded wetland patches behaved differently from pristine ones, though not significantly so. These sections of eroded wetland tended to export water, cations, anions, dissolved silicon, and Kjeldahl nitrogen. Additionally, pH, conductivity and chemical oxygen demand tended to increase over these wetland sections, though there was also large variation in these trends.

Table 1. Summary results for change in quantity (concentration g/l * discharge l/s) of water quality parameters (mean ± standard deviation) across degraded and pristine sections of valley-bottom palmet wetlands. Values used to calculate means and standard deviations are presented in **Table A1** (degraded n=3, pristine n=6). Negative values indicate that wetlands are a net source of a parameter, and positive values indicate a net sink. For discharge, pH, conductivity and chemical oxygen demand, negative values indicate an increase and positive values a decrease. Statistics are results from linear mixed models and F tests. Significant parameters are highlighted in bold. NS: not significant; NT: not tested (interaction effects significant). Water quality parameters not presented here can be found in **Table A4**.

	Degraded	Pristine	Statistics
Discharge (l/s)	-240.0±377.45	401.2±865.92	NS
pH	-1.0±0.89	0.2±0.92	NS
Conductivity (uS/cm)	-410.9±587.24	-65.1±131.28	NT
Ca (g/s)	-2.5±2.53	0.1±0.33	F=5.72, ndf=1, ddf=6.36, p=0.05
K (g/s)	-0.9±0.94	4.3±10.46	F=5.69, ndf=1, ddf=5.00, p=0.06
Mg (g/s)	-3.7±4.00	0.2±0.46	F=5.52, ndf=1, ddf=6.20, p=0.06
Na (g/s)	-28.8±32.07	1.4±3.79	F=5.55, ndf=1, ddf=6.14, p=0.06
Cl(g/s)	-47.7±51.54	5.6±13.45	F=5.56, ndf=1, ddf=6.20, p=0.06
SO ₄ (g/s)	-6.1±7.74	2.2±5.37	NT
Si (g/s)	-0.4±1.19	0.7±1.40	NS
Chemical Oxygen Demand (g/s)	-4.7±6.31	2.7±7.31	NS
Total P (g/s)	0.0±0.08	0.1±0.15	NS
Kjeldahl N (g/s)	-0.2±0.31	0.2±0.50	NS

Field Survey

Results show that at this point in time, this Kromme wetland fragment acted as a sink for dissolved K, dissolved organic carbon and Al (**Table 2**). pH also decreased significantly

(6.96 to 6.12) along the length of the wetland, becoming slightly more acidic (Rho=-0.72, p<0.05). However, it is noteworthy that the gradients of each of these parameters are relatively flat, except for K (m=-0.45). At first glance, this wetland fragment seemed to be a source of the following parameters: Ca, Mg, Na and DSi, as all parameters have quite strong correlations (Rho = $\pm$ 0.69-0.77). However, the gradients are quite flat (m<0.04), except for Na which has a gradient of 0.18. Low gradients would suggest little change over the wetland fragment. Conductivity, Cl⁻, Fe, SO₄²⁻, chemical oxygen demand, and nutrients (total phosphorus and Kjeldahl nitrogen) did not change significantly over the 300 m stretch.

Table 2. Change in water quality parameters over distance downstream in a field survey of the Kromme Wetland, South Africa. Spearman's Rho and statistics indicate significance of the gradient (gradient of the relationship between each parameter and distance), indicating the relevance of the relationship (steeper gradient indicates more change, a gentler gradient indicates less). In this case, negative values indicate that this wetland is acting as a net sink for a parameter (decreasing); positive values indicate a net source (increasing). See **Table A3** for absolute values. Significant parameters are highlighted with bold text. NS: not significant.

	Rho	Spearman Statistics	Gradient (m)
pH	-0.72	S = 491.36, p-value = 0.01	-0.07
Conductivity (uS/cm)	-0.09	NS	-0.34
Ca (mg/l)	0.76	S = 68.09, p-value = 0.004	0.04
K (mg/l)	-0.79	S = 512.19, p-value = 0.002	-0.45
Mg (mg/l)	0.76	S = 69.72, p-value = 0.004	0.00
Na (mg/l)	0.69	S = 89.31, p-value = 0.01	0.18
Cl (mg/l)	-0.07	NS	-0.13
Fe (mg/l)	0.26	NS	0.01
Zn (mg Zn/l)	0.67	S = 95.60, p-value = 0.02	0.00
Al (mg Al/l)	-0.75	S = 500.07, p-value = 0.005	0.00
Si (mg/l)	0.77	S = 64.72, p-value = 0.003	0.03
SO ₄ (mg/l)	0.21	NS	0.05
Chemical Oxygen Demand (g/s)	-0.36	NS	-0.39
Total P (mg/l)	0.24	NS	0.00
Kjeldahl N (mg/l)	-0.51	NS	-0.01
Dissolved Organic Carbon (mg/l)	-0.65	S = 470.65, p-value = 0.02	-0.08

Discussion

Overall palmiet wetland systems are oligotrophic, therefore it is noteworthy that the absolute concentrations of each parameter are quite low during low flow periods (**Table A2**), and are not of concern in terms of exceeding national water quality regulations for toxicity (DWAF, 1996). Across all three catchments, results are similar in that pristine wetlands tended to act as sinks for most parameters during low flow, including water, mostly accompanied by a decrease in pH across the length of the wetland and an increase in conductivity. We can only speculate as to the mechanisms behind the attenuation of these parameters as these may be a complex combination of internal wetland processes and external inputs from agriculture. In terms of water (discharge) being taken up by the wetland, it may be that the wetland is facilitating percolation into aquifers (de Haan, 2016; Job, 2014). It may also be a simple effect of

transpiration by wetland vegetation which is known to use relatively large amounts of water (Rebelo, 2012). Most likely it is a combination of these factors. Ultimately the partitioning of water between the various stages of the hydrological cycle in these wetlands will have a large impact on that of the various water quality parameters measured in this study.

The results of the instantaneous catchment 'mass balance' analysis show that wetlands in good condition tend to act as a sink for base cations (Ca, Mg, K). The field survey confirms this for K, but in this case the other two cations do not seem to change over the length of the wetland. It appears that these wetlands are acting as a sink for base cations resulting in an overall decrease in pH along the wetland section. This may possibly be linked to two conflicting mechanisms: first, liming practises from agriculture causing a spike in base cations and carbonates and a concomitant increase in pH in degraded wetland stretches (Beukes et al., 2012), and second, an increase in CO₂ in the wetland due to respiration of wetland vegetation and microbes in the soil (Trumbore, 2000), or the release of humic acids upon decomposition, causing a decrease in pH further down the wetland (Keller et al., 2009). The disappearance of nutrients (total phosphorus, potassium and Kjeldahl nitrogen), other ions, and dissolved silicon may be explained to some extent by plant uptake (Fisher and Acreman, 2004), microbial immobilization within the wetlands or adsorption to and retention by the soil (Fisher and Acreman, 2004).

Two of the three degraded wetlands are sources of most parameters which should be indicative of the loss of water purification function of these wetlands (**Table A1**). This may either be through excessive pollution from agricultural runoff that has saturated the water purification ability of the wetlands, or may be indicative of peat degradation which results in the release of large quantities of dissolved substances (Laine et al., 2013). That degraded wetlands appear to export water (are a net source of water) may possibly be explained by the gully erosion drawing down the water table, resulting in groundwater discharge. However this may also be a function of the hydrogeomorphology of different zones of the system and would need further research to confirm. In the case of the third degraded wetland, which appears to be largely acting as a sink for many parameters, it is known that there is high water abstraction in this region of the catchment (Rebelo, 2012). Due to the fact that this is illegal and there are therefore no data, this is not accounted for in the instantaneous 'mass balance' and this could explain why these results seem contradictory. This wetland section was also a much larger area, suggesting that this technique works better for smaller areas or scales.

Although there are clear differences between degraded and pristine wetland sections, there are important limitations to this approach which need to be considered. Firstly, we have only one snapshot in time, and therefore have no idea of temporal variation in water purification within these wetlands (Jordan et al., 2003). Secondly, channel structure is simplified and assumptions are made for discharge calculations, therefore

affecting the instantaneous ‘mass balance’ results. Thirdly, results are highly sensitive to discharge and discharge has relatively high uncertainty. Additionally a large amount of discharge is in the form of subsurface water flow which was not measured in this study (de Haan, 2016). Fourthly, little is known about abstraction for irrigation, and frequency and amount of fertilizer and lime application at catchment-scales. Lastly, the full extent of the water purification ability of a wetland cannot be calculated unless its capacity is exceeded by pollution, at which point its capacity would decline (Fisher and Acreman, 2004; Mitsch and Gossilink, 2000). Therefore, the attempts to measure water purification of pristine wetlands are likely to be underestimates.

Due to the uncertainty present in a catchment-scale approach, we conducted a field survey to investigate the water purification function of these valley-bottom wetlands in more detail at a smaller, field-scale. There is a good level of agreement between the findings of the catchment-scale study and the field survey. Similar results show that at the time of sampling, this wetland fragment also seemed to act as a sink for K, Kjeldahl nitrogen and Al. Most significantly, pH also decreased along this stretch of wetland by almost 1 unit over only 300 m. Dissolved organic carbon was not measured in the catchment-scale study, however in this field survey it was found to decrease over the stretch of pristine wetland. Since high concentrations of dissolved organic carbon may be indicative of decomposition (Freeman et al., 2004), the fact that this wetland acts as a sink for this parameter would suggest that this wetland is not suffering drainage (Evans et al., 2016; although see Kalbitz and Geyer, 2002). Contrary to the catchment-scale study, some parameters seemed to be exported from the wetland, most notably Na. It is interesting that this wetland seems to be a source of Na as this could be occurring as a result of the change in pH. Excess H ions may replace certain base cations on the soil adsorption complex, thereby releasing them.

Conclusion

There was a good level of agreement between the results of the catchment-scale study conducted in 2014, and a smaller, field-scale survey done in 2015. From these results, it appears possible to estimate the water purification function of these valley-bottom wetlands, though with some level of uncertainty. This method could be interesting for ecosystem service studies as it quantifies the ecosystem service itself rather than water quality, or impacts to water quality (a disservice). From this research, these palmiet wetlands appear able to store water or aid percolation into groundwater, as well as act as a sink for pollutants (nutrients and metals) linked to agricultural fertilizer application. However much is still unknown, including detailed information on the water balance, and the role of sediments and their response to various parameters. This is a key area for future research. The temporal variation of palmiet wetlands as sinks for pollutants, as well as the full potential of these wetlands as sinks, is not measured. This would be an interesting area for further research in light of the urgency to protect these wetlands from further degradation.

Acknowledgements

This work was supported by the Erasmus Mundus Programme (European Commission); the Applied Centre for Climate and Earth System Science (ACCESS), a Consolidoc grant (Stellenbosch University) and GreenMatter, South Africa. Thank you to Byron-Mahieu van der Linde for essential assistance in the field, Mr Tom van der Spiet for laboratory assistance and anonymous reviewers for improving the manuscript. Research was conducted under permit number: 0052-AAA008-00019 (Cape Nature). Thank you to the anonymous reviewers for valuable suggestions to improve the manuscript.

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1 **Appendix**

Plate A1. The three wetlands and the sections considered in this study (locations of the catchments can be seen in **Fig. 1**). Theewaterskloof wetland, 1.6km in length (1 section), the Goukou wetland, 15km in length (4 sections), and the Kromme wetland, 30 km in length (4 sections). Red boxes indicate degraded wetland sections, green boxes indicate pristine wetland sections according to the criteria of channel erosion.

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Plate A2: Schematic models for the ‘mass balance’ type approach used to quantify water purification in this study. Sampling points and wetland names correspond to those in **Figure 1** and **Plate A1**. ‘In’ represents the water entering the stretch of wetland (labelled on the left), and ‘out’ indicates the water leaving the stretch of wetland being investigated. Separate cross sections indicate tributaries joining the main wetland. Wetlands with peatlands intact are represented by the colour green, while wetlands degraded by alien invasion (peat beds more/less intact) are in yellow. Brown lines indicates that the wetland has become channelized. More than one channel is indicative of braided channels in the wetland. Unsampld channels are given with stippled lines. Gray indicates a canal, or impoundment in the wetland.

Table A1. Results from the instantaneous ‘mass balance’ sampling for three palmiet wetlands: Theewaterskloof (1 section), Goukou (4 sections), and Kromme (4 sections) wetlands. Parameters are all reported as change over the stretch of wetland, i.e. inflow – outflow, all given in g/s (parameter g/l * discharge l/s) except for pH, conductivity (uS/cm) and discharge (l/s). Negative values (red) indicate that the wetland is a source for that parameter (or that it increases), positive values (green) indicate that the wetland is a sink for that parameter (or that it decreases).

		Small scale	Medium scale				Large scale			
Parameter	Unit	Theewaterskloof	Goukou A	Goukou B	Goukou C	Goukou D	Kromme A	Kromme B	Kromme C	Kromme D
Wetland type:		Pristine	Pristine	Pristine	Pristine	Degraded	Pristine	Pristine	Degraded	Degraded
Discharge	l/s	2154.38	99.77	-133.86	191.43	-180.92	1.37	93.88	104.35	-643.57
pH	-	1.31	0.91	-0.6	-0.94	-1.59	0.90	-0.09	-1.47	0.00
Conductivity	uS/cm	22.33	-7.60	-28.30	-330.20	-1089.00	-31.50	-15.50	-74.25	-69.50
Ca	g/s	0.73	0.04	-0.14	-0.11	-4.56	-0.07	0.14	0.31	-3.32
K	g/s	25.65	0.19	-0.16	-0.04	-1.39	0.14	0.04	0.17	-1.52
Mg	g/s	1.02	0.09	-0.28	-0.03	-7.28	-0.12	0.29	0.63	-4.35
Fe	g/s	0.11	0.01	-0.24	0.21	0.00	0.00	0.02	0.02	-0.39
Dissolved Si	g/s	3.37	0.28	-0.56	0.71	-0.22	-0.17	0.34	0.62	-1.73
Zn	g/s	0.09	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Cu	g/s	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	g/s	0.22	0.00	-0.08	0.10	0.00	-0.01	0.01	0.02	-0.03
Mn	g/s	0.02	0.01	0.00	0.00	-0.01	0.00	0.00	0.00	-0.01
Na	g/s	8.68	0.72	-1.98	-0.22	-58.93	-0.64	1.89	4.92	-32.36
Cl	g/s	32.62	1.61	-3.60	0.62	-90.20	-1.23	3.80	9.62	-62.53
SO42-	g/s	12.86	0.30	-1.83	1.88	-14.23	0.04	-0.19	1.19	-5.29
Chemical Oxygen Demand	g/s	14.19	1.21	-7.14	7.44	-4.59	-0.50	0.87	1.58	-11.04
Total P	g/s	0.37	0.01	-0.02	0.02	-0.02	0.00	0.02	0.03	-0.12
Kjeldahl N	g/s	1.20	0.04	-0.16	0.15	-0.11	0.00	0.04	0.10	-0.52
PO4-P	g/s	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.01	-0.02
NH4-N	g/s	0.13	0.01	-0.02	0.02	0.00	0.00	0.01	0.01	-0.04
NO3-N	g/s	-0.04	-0.01	0.01	-0.02	0.03	0.00	0.00	0.07	-0.13

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Table A2. Water quality parameters for three palmiet wetlands: Theewaterskloof, Goukou, and Kromme wetlands. Acronyms: DO – dissolved oxygen, COD – chemical oxygen demand. For sampling locations see **Plate A1**. Discharge is already corrected for roughness (factor 0.9).

Parameter	Unit	T13	T14	T15	T16	T17	T18	G16	G17	G18	G19	G20	G21	G22
		-	-	-	-	-	-	-	-	-	-	-	-	-
Latitude	DD	33.95385	33.94853	33.95408	33.96129	33.96176	33.96304	34.00427	34.02128	34.02810	34.02528	34.05346	34.06521	34.09241
Longitude	DD	19.17013	19.16915	19.17163	19.16731	19.16830	19.17091	21.41524	21.40761	21.38020	21.37960	21.33817	21.34151	21.29403
pH	-	6.5	8.1	7.1	7.0	7.7	5.8	5.5	4.5	5.1	4.3	6.2	6.4	7.9
Conductivity	µS/cm	40.0	59.0	30.0	28.0	30.0	52.0	72.1	79.7	108.0	85.2	541.0	649.0	1684.0
Discharge	l/s	-	2946	-	90	216	90	154	54	188	222	60	90	270
DO	mg/l	55.3	77.1	86.6	95.0	67.0	103.0	83.0	73.0	101.6	103.0	103.1	76.1	93.2
Ca	mg/l	0.39	0.32	0.32	0.27	0.28	0.31	0.39	0.44	0.88	0.45	3.85	6.67	18.76
K	mg/l	3.32	9.12	3.60	2.11	1.86	0.13	1.98	2.04	1.43	0.52	2.09	6.45	6.80
Mg	mg/l	0.49	0.47	0.49	0.41	0.46	0.50	0.97	1.08	1.79	1.13	9.24	11.21	30.41
Fe	mg/l	1.00	0.14	0.19	0.30	0.30	0.60	0.18	0.39	1.40	0.37	0.69	1.49	0.40
DSi	mg/l	0.99	1.63	1.73	1.90	1.74	1.82	2.82	2.84	3.79	2.36	1.90	2.26	1.51
Zn	mg/l	0.01	0.03	0.02	0.01	0.01	0.01	0.01	0.00	0.02	0.05	0.01	0.01	0.00
Cu	mg/l	0.001	0.001	0.001	0.003	0.001	0.001	0.001	0.001	0.001	0.000	0.001	0.001	0.001
Al	mg/l	0.31	0.11	0.11	0.22	0.13	0.12	0.09	0.23	0.52	0.25	0.06	0.08	0.02
Mn	mg/l	0.01	0.01	0.01	0.01	0.01	0.02	0.06	0.01	0.02	0.02	0.05	0.06	0.04
Na	mg/l	3.30	3.90	3.91	3.08	3.62	3.81	7.43	7.91	12.79	9.06	69.46	82.51	243.80
Cl	mg/l	12.30	13.70	10.60	8.40	9.10	12.80	16.90	18.30	24.40	17.80	133.70	140.90	379.40
SO ₄ ²⁻	mg/l	19.90	7.50	19.00	16.40	11.00	8.50	2.90	2.70	10.50	5.00	17.50	12.90	57.40
COD	mg/l	34.70	10.90	9.46	63.70	10.80	9.96	14.40	18.50	43.30	26.90	7.76	30.90	24.70
Total P Kjeldahl	mg/l	0.20	0.17	0.17	0.22	0.17	0.17	0.14	0.13	0.15	0.15	0.17	0.39	0.20
N	mg/l	1.17	0.61	0.52	1.55	0.52	0.51	0.41	0.41	0.98	0.63	0.45	1.08	0.69
PO ₄ -P	mg/l	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.09	0.03
NH ₄ -N	mg/l	0.06	0.05	0.04	0.04	0.02	0.03	0.05	0.02	0.11	0.03	0.03	0.07	0.03
NO ₃ -N	mg/l	0.01	0.01	0.06	0.11	0.11	0.00	0.01	0.20	0.02	0.00	0.04	0.41	0.00

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Table A2 continued...

Parameter	Units	K13	K14	K15	K16	K17	K18	K19	K20	K21
Latitude	DD	-33.867281	-33.878272	-33.884728	-33.884458	-33.91684517	-33.91649776	-33.919075	-33.950278	-33.90894277
Longitude	DD	24.016944	24.053292	24.070878	24.072269	24.19655124	24.19803219	24.208031	24.339311	24.1592335
pH	-	6.5	5.6	5.6	5.8	6.7	7.1	7.5	7.3	5.9
Conductivity	µS/cm	129.9	161.4	179.8	174.0	1144.0	237.0	262.0	319.0	173.6
Discharge	l/s	124	122	26	31	-	162	149	155	231
DO	mg/l	87.0	99.0	90.4	94.0	91.2	90.6	71.0	75.0	87.5
Ca	mg/l	1.00	1.56	1.81	2.04	27.86	3.18	3.66	4.27	1.53
K	mg/l	1.68	0.58	0.70	1.13	6.67	1.37	1.82	1.97	0.80
Mg	mg/l	2.01	3.00	2.87	2.76	39.40	4.12	4.75	5.60	2.91
Fe	mg/l	0.17	0.21	0.20	0.18	3.61	0.38	0.39	0.51	0.13
DSi	mg/l	2.29	3.67	3.82	3.70	1.68	3.00	3.19	2.27	2.62
Zn	mg/l	0.01	0.04	0.01	0.05	0.01	0.07	0.04	0.01	0.02
Cu	mg/l	0.001	0.001	0.000	0.000	0.002	0.001	0.001	0.001	0.001
Al	mg/l	0.05	0.09	0.08	0.06	0.02	0.02	0.02	0.03	0.07
Mn	mg/l	0.01	0.00	0.00	0.01	0.50	0.01	0.05	0.01	0.01
Na	mg/l	15.47	20.85	23.75	23.03	124.70	30.29	32.42	41.61	22.23
Cl	mg/l	30.90	41.30	43.70	44.10	247.00	58.30	62.20	80.40	43.60
SO ₄ ²⁻	mg/l	2.30	2.00	1.30	27.30	7.30	6.00	4.50	6.80	3.90
COD	mg/l	5.35	9.50	10.60	10.10	99.10	6.87	8.82	14.10	6.54
Total P	mg/l	0.16	0.16	0.15	0.15	0.16	0.15	0.15	0.16	0.14
Kjeldahl N	mg/l	0.45	0.47	0.52	0.65	4.06	0.47	0.77	0.67	0.44
PO ₄ -P	mg/l	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
NH ₄ -N	mg/l	0.03	0.05	0.02	0.03	2.18	0.08	0.13	0.05	0.05
NO ₃ -N	mg/l	0.00	0.02	0.00	0.02	0.02	0.28	0.03	0.17	0.33

28 **Table A3.** Absolute values for water quality parameters for the field survey, Kromme Wetland, South Africa. Points are numbered from left to right from **Fig. 2**. All
 29 parameters are given in mg/l besides pH, distance (m) and electrical conductivity (uS/cm). COD: chemical oxygen demand, DOC: dissolved organic carbon.

Point	Latitude	Longitude	Distance	pH	Conductivity	Ca	K	Mg	Na	Cl	Fe	Zn	Al	DSi	SO ₄ ²⁻	COD	Total P	Kj N	DOC
1	33°55'5.91"S	24°12'8.81"E	0	6.34	150	1.8	1.3	2.7	21.0	37	0.33	0.003	0.078	2.8	4	18.6	<0,02	0.82	-
2	33°55'6.39"S	24°12'10.19"E	0	6.77	160	1.8	4.2	2.7	20.8	40	0.32	0.003	0.085	2.8	4	19.2	<0,02	0.32	5.6
3	33°55'6.96"S	24°12'10.09"E	0	6.69	158	1.8	4.9	2.7	20.7	40	0.24	0.003	0.077	2.8	<4	20.9	<0,02	0.44	6.2
4	33°55'7.10"S	24°12'10.39"E	0	6.31	153	1.8	1.7	2.7	20.9	36	0.33	0.003	0.084	2.7	4	19.2	<0,02	0.53	-
5	33°55'7.30"S	24°12'10.72"E	0	6.35	176	1.8	8.5	2.7	20.9	43	0.33	0.007	0.084	2.8	<4	17.7	<0,02	0.73	5.7
6	33°55'7.08"S	24°12'11.10"E	0	7.18	193	1.8	13.1	2.7	20.9	48	0.31	0.003	0.08	2.7	<4	21.0	<0,02	0.35	6.3
7	33°55'7.60"S	24°12'11.12"E	0	6.57	165	1.8	2.8	2.7	20.9	37	0.33	0.009	0.085	2.8	4	21.4	<0,02	0.36	5.8
8	33°55'7.58"S	24°12'11.74"E	0	6.28	252	1.8	28.1	2.7	21.0	61	0.31	0.002	0.078	2.8	4	24.3	<0,02	0.37	6.3
9	33°55'7.66"S	24°12'12.72"E	0	6.38	154	1.7	2.5	2.6	20.7	38	0.30	0.004	0.089	2.8	4	21.2	<0,02	2.05	5.4
10	33°55'8.39"S	24°12'18.96"E	30	6.96	168	1.9	7.3	2.7	21.6	43	0.21	0.002	0.067	2.8	<4	24.0	0.02	0.63	7.0
11	33°55'8.39"S	24°12'20.20"E	60	6.98	153	1.8	2.5	2.7	21.0	38	0.34	0.004	0.073	2.8	<4	21.4	0.02	0.48	6.6
12	33°55'8.38"S	24°12'21.46"E	90	6.81	156	1.9	1.3	2.8	21.2	38	0.39	0.002	0.067	2.8	<4	19.5	<0,02	0.40	6.6
13	33°55'8.37"S	24°12'22.51"E	120	6.51	170	2.0	2.5	2.9	21.9	39	0.69	0.004	0.062	2.8	5	27.6	0.04	0.63	7.2
14	33°55'8.32"S	24°12'23.76"E	150	6.33	171	2.1	1.9	2.9	21.9	39	0.32	0.002	0.052	2.8	5	27.4	0.04	0.66	6.9
15	33°55'8.40"S	24°12'24.66"E	180	6.08	182	2.5	2.0	3.4	23.9	43	3.07	0.012	0.072	3.3	5	24.0	0.02	0.46	6.7
16	33°55'8.52"S	24°12'25.51"E	210	6.1	167	2.2	1.5	3.1	23.0	40	0.33	0.002	0.046	3.0	<4	20.6	0.03	0.54	5.9
17	33°55'8.63"S	24°12'26.79"E	240	6.12	173	2.2	1.8	3.1	23.0	40	0.41	0.005	0.043	3.0	<4	21.9	0.04	0.53	5.8
18	33°55'8.53"S	24°12'28.15"E	270	6.12	174	2.2	1.3	3.0	22.9	40	0.28	0.002	0.043	3.1	<4	20.7	0.02	0.45	5.7
19	33°55'8.37"S	24°12'28.96"E	300	6.56	157	2.2	1.9	3.1	22.8	41	0.33	0.004	0.051	3.0	<4	16.2	0.03	0.39	6.0
20	33°55'8.64"S	24°12'29.00"E	300	6.2	159	2.3	1.5	3.1	23.0	40	0.48	0.012	0.057	3.0	12	14.5	0.03	0.64	5.9
21	33°55'8.83"S	24°12'28.96"E	300	6.18	161	2.3	1.3	3.1	23.2	39	0.39	0.003	0.046	3.1	<4	16.7	0.03	0.60	6.1
22	33°55'9.03"S	24°12'29.00"E	300	6.17	163	2.3	1.3	3.2	23.6	41	0.27	0.010	0.042	3.0	<4	16.4	0.03	0.48	5.5
23	33°55'8.21"S	24°12'29.73"E	330	6.21	150	2.0	1.2	2.9	21.7	37	0.25	0.003	0.046	2.9	<4	16.8	0.02	0.32	5.3
24	33°55'8.59"S	24°12'29.76"E	330	6.15	149	2.1	1.1	2.9	21.9	39	0.39	0.008	0.056	2.9	<4	17.0	0.02	0.30	5.4
25	33°55'8.34"S	24°12'30.66"E	330	6.14	151	2.1	1.1	2.9	21.9	38	0.47	0.004	0.093	2.8	<4	19.4	<0,02	0.33	6.7
26	33°55'8.67"S	24°12'30.70"E	330	6.18	149	2.1	1.3	2.9	21.7	39	0.33	0.011	0.059	2.9	<4	20.0	0.02	0.43	5.9

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34 **Table A4.** Summary results for change in quantity (concentration g/l * discharge l/s) of water quality parameters (mean ± standard deviation) across degraded and pristine
35 sections of valley-bottom palmiet wetlands for those parameters not presented in **Table 1**. Values used to calculate means and standard deviations are presented in **Table**
36 **A1** (degraded n=3, pristine n=6). Negative values indicate that wetlands are a net source of a parameter, and positive values indicate a net sink. Statistics are results from
37 linear mixed models and F tests. Significant parameters are highlighted in bold. NS: not significant.

	Degraded	Pristine	Statistics
Fe (g/s)	-0.1±0.23	0.0±0.15	NS
Zn (g/s)	0.0±0.00	0.0±0.04	NS
Cu (g/s)	0.0±0.00	0.0±0.00	NS
Al (g/s)	0.0±0.02	0.0±0.11	NS
Mn (g/s)	0.0±0.00	0.0±0.01	NS
PO4-P (g/s)	0.0±0.01	0.0±0.03	NS
NH4-N (g/s)	0.0±0.02	0.0±0.05	NS
NO3-N (g/s)	0.0±0.11	0.0±0.02	NS

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