Seasonal variations of water and sediment quality parameters in endorheic reed pans on the Mpumalanga Highveld

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Abstract

The Mpumalanga Lakes District consists of approximately 320 pans, of which less than 3% are classified as reed pans. There is limited information available on reed pans and as a result they are at risk of various anthropogenic activities, for example mining and agriculture. Four reed pans were selected and assessed to determine seasonal trends of a variety of water and sediment quality parameters. The study took place over one seasonal cycle from 2008–2009; samples were collected seasonally to account for various hydrological extremes. Water samples were collected and their nutrient and chlorophyll *a* concentrations were determined, while various other water quality parameters were measured *in situ*. Sediment samples were analysed for physical and chemical properties, namely, grain size and organic carbon content. The seasonal changes in concentrations of As, Cr, Cu, Fe, Pb, Mn, Mo, Ni, Se, Sr, U and Zn were also analysed within the surface water and sediment. Increased nutrient concentrations within the water were evident during spring and summer at some of the sites, which influenced other water quality variables, e.g., dissolved oxygen and pH. Seasonal trends in metal concentrations were influenced by the prevailing environmental conditions (e.g., rainfall) experienced at the selected sites as well as physical and chemical properties (e.g., grain size and organic carbon content). This study showed distinct seasonal variability of water and sediment quality parameters in endorheic reed pans on the Mpumalanga Highveld. There is a need for further studies on all of the different types of pans in terms of their water and sediment quality. This type of information will allow for a sound and defensible scientific basis for the assessment of likely impacts (e.g., eutrophication), the evaluation of the significance of these impacts, and the design of remedial and preventative measures.

Keywords: depressional wetlands, endorheic wetlands, eutrophication, metal concentrations, nutrients, reed pans

Introduction

Globally, wetland loss has been estimated to be around 50%, whilst approximately 35 to 50% of wetlands are thought to have already been lost or severely degraded in South Africa (Dini, 2004; DWAF, 2004). Pans are classified in South Africa as depressional, endorheic wetlands, which are also found throughout the world (Goudie and Wells, 1995). These wetlands could otherwise be classified as palustrine or lacustrine, but also possess additional features such as having a flat basin floor and no outlet (Dini et al., 1998). In South Africa, most pans are situated in the north-western regions in areas with a mean annual rainfall of 500 mm (Goudie and Thomas, 1985). Reed pans, classified as a particular type of pan, are usually defined as pans containing dense colonies of reeds and sedges (Cowan and Van Riet, 1998), with a floating reed-covered mat within the pan, and usually with high water levels maintained throughout the year (Grundling et al., 2003).

Aquatic ecosystems in South Africa, including wetlands, are being threatened by unsustainable social and economic activities, for example cultivation, industrial developments, mining and overgrazing (DWAF, 2004). The main stressors of concern are usually toxic heavy and/or trace metal contamination, as well as nutrient enrichment (CSIR, 2010). These stressors can have a direct impact on an aquatic environment, including water and sediment quality (Driscoll, 1985; Winterbourne et al., 2000; Dise et al., 2001; CSIR, 2010).

In South Africa, the conservation of aquatic resources is of critical importance (Taylor et al., 2007; Ashton et al., 2008), and the need for conservation is increasing as a result of a decline in water quality of aquatic ecosystems due to increased pollution (Ashton et al., 2008). If allowed to deteriorate, the quality of water can adversely affect not only the aquatic ecosystem of the specific water resource, but the quality of groundwater as well (Shaw and Thomas, 1989; CSIR, 2010). According to Dallas and Day (1993), water quality is one of the most important factors which influence an aquatic ecosystem's integrity, as the distribution of aquatic freshwater organisms is controlled mainly by water quality characteristics, including dissolved oxygen, acidity and nutrient content.

Sediments are regarded as a sink for a wide range of contaminants, such as metals. This poses a threat to the aquatic environment, because sediments usually contain pollutant concentrations that are far higher than those of the overlying water (Tessier and Campbell, 1987; Bervoets et al., 1994; Williamson et al., 1996). This occurs as a result of long-term inputs of pollutants into the sediment which then bind to sediment particles and organic matter (Newman and Watling, 2007).

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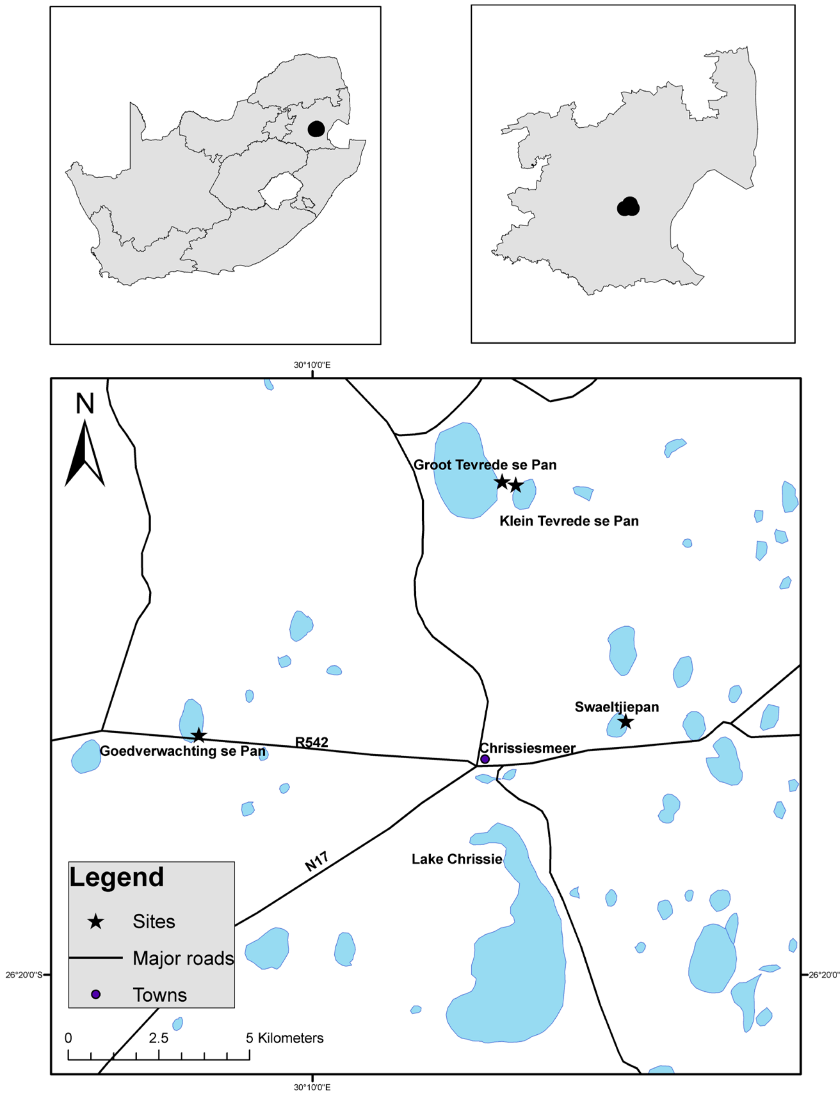

Figure 1
A map of the study area indicating the location of the specific sampling sites in South Africa (top left), in Mpumalanga (top right), and in the proximity of Lake Chrissie (bottom)

Important sediment quality characteristics that govern the sediment concentrations of these pollutants include organic carbon content and grain size (Berkman et al., 1986; Hellawell, 1986; Walling and Moorehead, 1989).

In South Africa, almost 10% of wetlands are thought to be peatlands (Joosten and Clarke, 2002; Millenium Ecosystem Assessment, 2005). These peatlands are usually valley bottom fens, whilst some may be found in hill slope seepage areas and inter-dune depressions (Grundling et al., 2003). Reed pans, including one of the sites selected in this study, have been confirmed to contain peat (Grundling et al., 2003). The interaction between organic material and pollutants, as well as the rarity of peatlands in South Africa, highlights the importance of understanding the functioning of reed pan systems

The aim of this study was to determine the seasonal variation of a selection of water and sediment quality parameters within selected reed pans, thereby creating a baseline from which to determine the possible impact of land use activities on the water and sediment quality of reed pans. This study also aspires to contribute to a better understanding of the functioning of reed pans, by evaluating the seasonal changes in important sediment and water quality parameters, and, in so doing, aid in the future management and conservation of reed pans.

Materials and methods

Study area and site selection

This study was conducted in the Mpumalanga Province, South Africa, near Lake Chrissie (26° 16’ 52.02”S; 30° 12’ 38.92”E), within the so-called Mpumalanga Lakes District (MLD). The MLD is subjected to warm, wet summer weather and cold, dry winters, but, unlike other pan fields, the MLD is situated in a relatively humid area with a mean annual rainfall of approximately 800–1 000 mm and a mean annual potential evaporation of approximately 1 600–1 800 mm (Schulze, 1997). The MLD is located at approximately 1 700 m amsl and is located in the middle of an extensive drainage system between the Usutu, Vaal, Olifants, Komati and Mpuluzi catchments (McCarthy et al., 2007). Samples were collected seasonally (2008–2009) to reflect 4 different seasons, namely, autumn (AUT), winter (WIN), spring (SPR) and summer (SUM), at 4 selected reed pans (Fig. 1). These four reed pans, namely, Klein Tevrede se Pan (KT), Groot Tevrede se Pan (GT), Goedverwachting se Pan (GO) and Swaeltjie Pan (SW), were selected due to their accessibility as well as the fact that they experience anthropogenic impacts to varying degrees, predominantly by agriculture and livestock.

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Water

The *in situ* water quality parameters, namely, pH, electrical conductivity and dissolved oxygen, were measured on site using Eutech Instrument's handheld water quality meters. Water samples (approximately 1 ℓ) were collected in triplicate using pre-cleaned polypropylene containers. The bottles were first rinsed 3 times with water from the specific site before the water sample was taken from approximately 10 cm below the surface. These bottles were filled to the brim and kept in a cold, dark environment to minimise the risk of chemical and biological processes occurring in the bottle whilst in transit to the laboratory. In the laboratory the water samples were analysed for the following variables: ammonium (NH_4^+); nitrate (NO_3^-); nitrite (NO_2^-) and phosphate (PO_4^{3-}). These variables were chosen as reasonable indicators of increased nutrient enrichment. They were analysed according to the Merck Spectroquant Guidelines and analysed using a Merck Spectroquant Photometer SQ 118.

The analysis of the concentrations of various dissolved metals was also carried out on the water samples using an inductively coupled plasma optical emission spectrometer (ICP-OES), as well as an inductively coupled plasma mass spectrometer (ICP-MS). The following metals were analysed as indicators of the dynamics of metal concentrations within reed pans: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), strontium (Sr), uranium (U) and zinc (Zn).

Chlorophyll *a* concentrations were determined within 24 h of being sampled according to the procedure described by of Sartory and Grobbelaar (1984) and DWAF (1992), after which the concentrations were calculated according to the equations described by Lorenzen (1967).

Sediment

Sediment samples were collected in triplicate according to the methods described in USEPA (2001), from a pre-selected area in the pan, at a water depth of approximately 1 m. Sediment samples were transferred into pre-cleaned containers and stored in a freezer until analysis could be performed, in order to prevent the loss of organic matter through digestion by invertebrates and organic decomposition. In the laboratory, excess water was carefully removed from the samples using a syringe, to prevent the loss of fine sediment, and subsequently homogenised.

Sub-samples were weighed, dried (at 60°C for 96 h) and weighed again to determine the moisture content. These dried sediment samples were then homogenised and used to determine the following: firstly, a thoroughly homogenised sub-sample of the sediment sample was taken and the organic carbon content was determined (prior to particle size determination) using the method of Stecko and Bendell-Young (2000); secondly, the total concentration of selected metals (same metals as for the water samples) present in the sediment samples was determined by digesting a known amount of dried sediment according to the Milestone Method for Soil (DG-EN-12) (Tessier et al.,1984; Cid et al., 2002). The metal analyses of the digested soil samples were carried out using ICP-OES and ICP-MS instrumentation. All of the sediment concentrations are reported as dry weight. Finally, the particle size distribution of a known amount of the dried sediment samples was determined using an Endecott sieve system (sieve sizes ranging from 4 000 µm to 53 µm) and classified according to the classification used by Cyrus et al. (2000).

Quality control and quality assurance protocols were followed with each batch of samples through the inclusion of blanks, certified reference materials and matrix spikes, as well as by doing a standard calibration run. All sediment and water samples were analysed in triplicate (triplicate analysis of each original triplicate-collected sample) against known standards. Calibration was carried out using matrix matched calibration standards. Analytical accuracy for sediment analysis was determined using a certified standard reference material from Resource Technology Corporation and CN Schmidt BV: Trace Elements on Fresh Water Sediments (CNS392-050). The percentage recoveries for the standards and certified reference materials were within an acceptable range (< 10% deviation).

Statistical analysis

Seasonal differences within the water and sediment were determined using a two-way analysis of variance (ANOVA). If Levene's test of equality of variance gave a result of $p > 0.05$, it was assumed that the test showed equal variance and Scheffe's *post hoc* multiple comparison test was then performed. If the Levene's test showed $p < 0.05$, it was assumed that there was unequal variance and Dunnette's T3 *post hoc* multiple comparison test was then performed. Significance was assumed as a probability level of $p \leq 0.05$. These descriptive statistics were determined using Predictive Analytics SoftWare (PASW) Statistics Version 18 Software.

Piper diagrams were used to graphically represent the chemistry of the water samples at each site. These diagrams plot cations and anions as separate ternary plots and are mainly used to show the clustering of data points, which indicates whether or not samples have similar chemical compositions in terms of their major ions. Piper diagrams are particularly useful in illustrating distinct water quality populations (Piper, 1944; Appelo and Postma, 1993), which may then be described according to their cationic and anionic distributions. These diagrams were constructed using Aquachem Water Quality Analysis Software Version 5.1.

Results

Water

Nutrients and in situ *water quality parameters*

The results for all of the water quality parameters measured are summarised and presented in Fig. 2. The seasonal trend of nutrient enrichment at the four reed pans is presented as total inorganic nitrogen (TIN), expressed as the sum of NH_4^+; NO_3^- and NO_2^-, as well as total inorganic phosphorus (TP), expressed as PO_4^{3-}. Although few seasonal trends can be observed with regard to nutrient levels (Fig. 2 A–D), TP concentrations were found to be highest during SUM (between 0.46 mg/ℓ to 0.07 mg/ℓ) at all of sites and decreased towards WIN (between 0.14 mg/ℓ to 0.01 mg/ℓ). From the results it can also be seen that TIN was high throughout the year in GO (~ 9 mg/ℓ), whilst the rest of the sites had relatively lower TIN values (~ ≤ 5 mg/ℓ). Total inorganic phosphorus concentrations were also highest at GO (~ 0.25 mg/ℓ) when compared to the rest of the sites (~ ≤ 0.06 mg/ℓ).

It can be seen from Fig. 2 E-F that at KT and GO an increase in chlorophyll *a* concentrations was noticed in SUM and especially SPR (approximately 25 µg/ℓ and 60 µg/ℓ, respectively),

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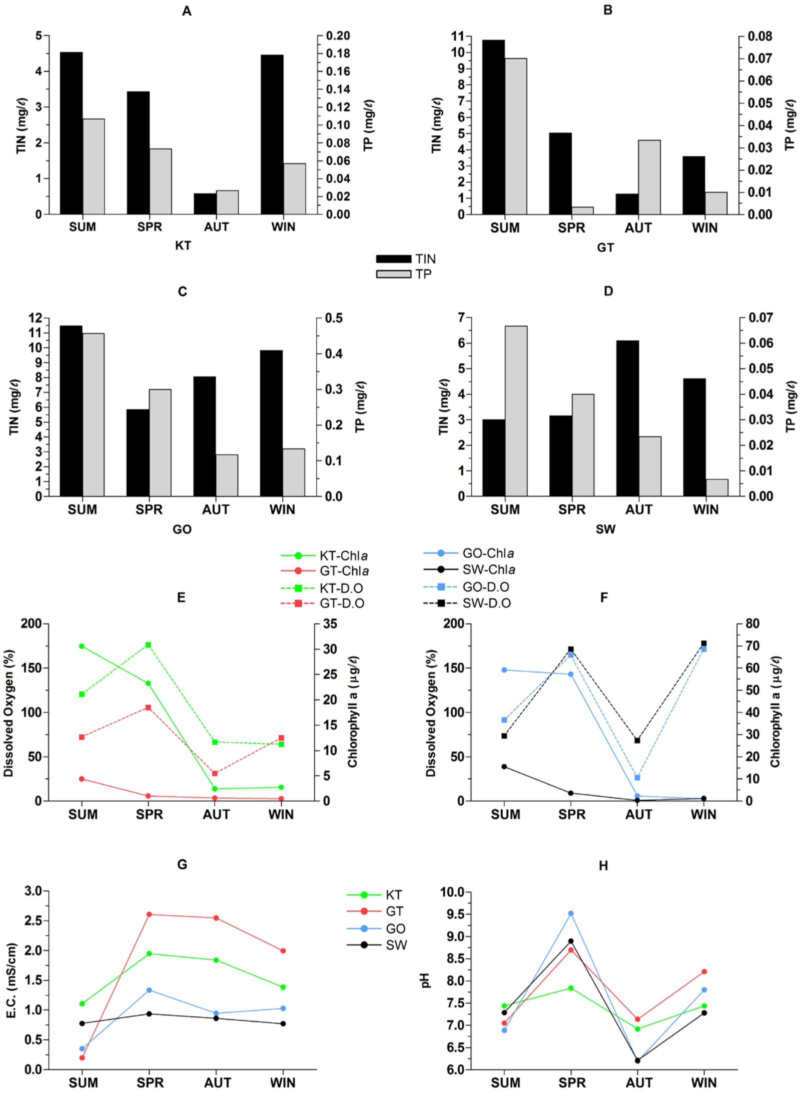

Figure 2
Seasonal fluctuations in TIN (total inorganic nitrogen), TP (total inorganic phosphorus), chlorophyll a, dissolved oxygen, electrical conductivity (EC) and pH for the four reed pans.
KT - Klein Tevrede se Pan
GT - Groot Tevrede se Pan
GO - Goedverwachting se Pan
SW - Swaeltjie Pan
AUT - autumn
WIN - winter
SPR - spring
SUM - summer

followed by a decrease in AUT and WIN (< 5 µg/ℓ). Two of the reed pans, GT and SW, had lower chlorophyll *a* concentrations throughout the year (~ 1.65 µg/ℓ and ~ 5.20 µg/ℓ, respectively) when compared to KT and GO (~ 14.75 µg/ℓ and ~ 29.99 µg/ℓ, respectively). Dissolved oxygen generally increased during SPR and WIN at the four different pans. The conductivity values measured (Fig. 2 G) indicate a decrease during SUM, after which it remains relatively constant for WIN, AUT and SPR. Sites KT and GT had relatively high conductivity values when compared to the other sites, whereas the conductivity values at SW were below 1 mS/cm throughout the different seasons. With regard to the pH values measured at the different sites (Fig. 2 H), all of the sites showed the same seasonal trend with increased pH levels observed during SPR and WIN. All of the pH levels measured at the four pans ranged between 6 and 9, with only a single value exceeding this range.

Piper diagrams (Fig. 3) were drawn to illustrate the seasonal variability of the chemical water composition (in terms of the major cations and anions) at each of the four reed pans. According to these diagrams, the ternary cation plot of all of the sites indicate year round Mg^{2+} and $Na^{+}+K^{+}$ dominance, whilst the ternary anion plot showed mainly SO_4^{2-} and Cl^{-} dominance. Thus, with the exception of GT during SUM, mostly saline conditions were experienced at the different sites. Hence these four reed pans have very similar major ion water chemistry.

Dissolved metal concentrations

The seasonal variation of the dissolved metal concentrations within the water bodies of the four reed pans was measured and the seasons in which the maximum (and respective minimum) metal concentrations occurred at a particular site are illustrated in Fig. 4. The maximum concentrations of most of the metals analysed in the surface waters of the four reed pans were reached during AUT and SUM and were generally significantly different ($p < 0.05$) to the concentrations of these metals found during the other two seasons. Where metals did not conform to these trends, the metals that had their maximum concentrations during WIN and SPR generally differed significantly ($p < 0.05$) from the corresponding concentrations found during AUT and SUM. Thus, in contrast to the other selected metals, the maximum concentrations for selenium, strontium and uranium were recorded in WIN and SPR.

Sediment

Sediment properties

The various sediment characteristics that influence the availability of metals in sediment are presented in Fig. 5. The sediment samples from the four pans were found to consist

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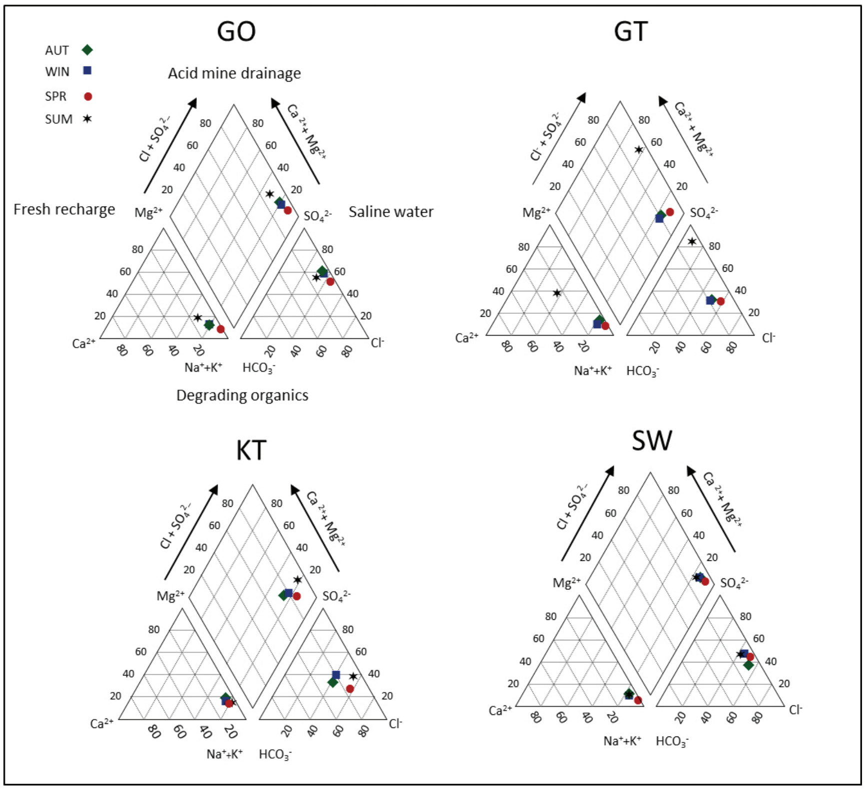

Figure 3
Piper diagrams showing the seasonal variation of the mean values for the macro-ion chemical constituents recorded at the four reed pans selected in this study. Symbols: see Fig. 2.

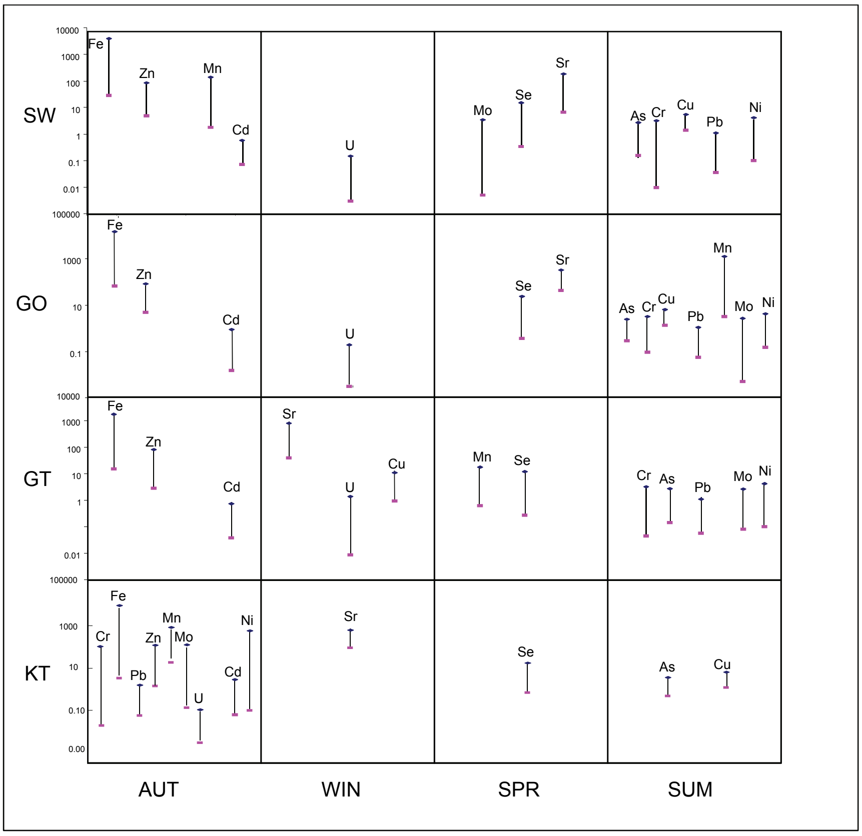

Figure 4
Seasonal variation of the maximum (■) and minimum (■) range of metal concentrations measured in the water (µg/ℓ) of the four selected reed pans. Symbols: see Fig. 2.

mainly of medium-sized sand that has grain sizes of 500–212 µm. The coarse sand (4 000–2 000 µm) and gravel (> 4 000 µm) fractions at GO seemed to increase during SPR and SUM. From these results (Fig. 5) it can be seen that the organic carbon content of the sediments at all four pans was highest during AUT. The organic carbon contribution found in the sediment usually exceeded 10%.

Metal concentrations within the sediment

The metal concentrations within the sediment samples are presented in Fig. 6, to indicate seasonal variation in terms of maximum metal concentrations, and corresponding minimum concentrations. The maximum concentration of most of the metals analysed was found during the AUT and SPR seasons and was generally not significantly different from the concentrations recorded in the other two seasons in all four of the pans. Where there were instances where certain metal concentrations did not conform to this trend, with maximum concentrations being reached during WIN or SUM, the difference between these concentrations and those found during AUT and SPR was generally found to be non-significant. Across all of the different seasons, the sediment samples from the four pans were found to have metal concentrations higher than those recorded in the overlying water.

Discussion

Seasonal changes of water quality parameters in the surface waters of reed pans

Eutrophication has been defined as the process whereby an ecosystem is organically enriched through an increase of nutrients (Nixon, 1995), either naturally or anthropogenically (Rast and Thornton, 1996). These increased nutrient concentrations ultimately result in the progressive degradation of an aquatic ecosystem (Carpenter et al., 1998). According to Heathwaite (1993), the key nutrients that control the trophic status of freshwater systems are nitrogen (N) and phosphorus (P). Although no clear seasonal trend could be established for TIN concentrations, our results showed TP concentrations to be the highest during the summer months,

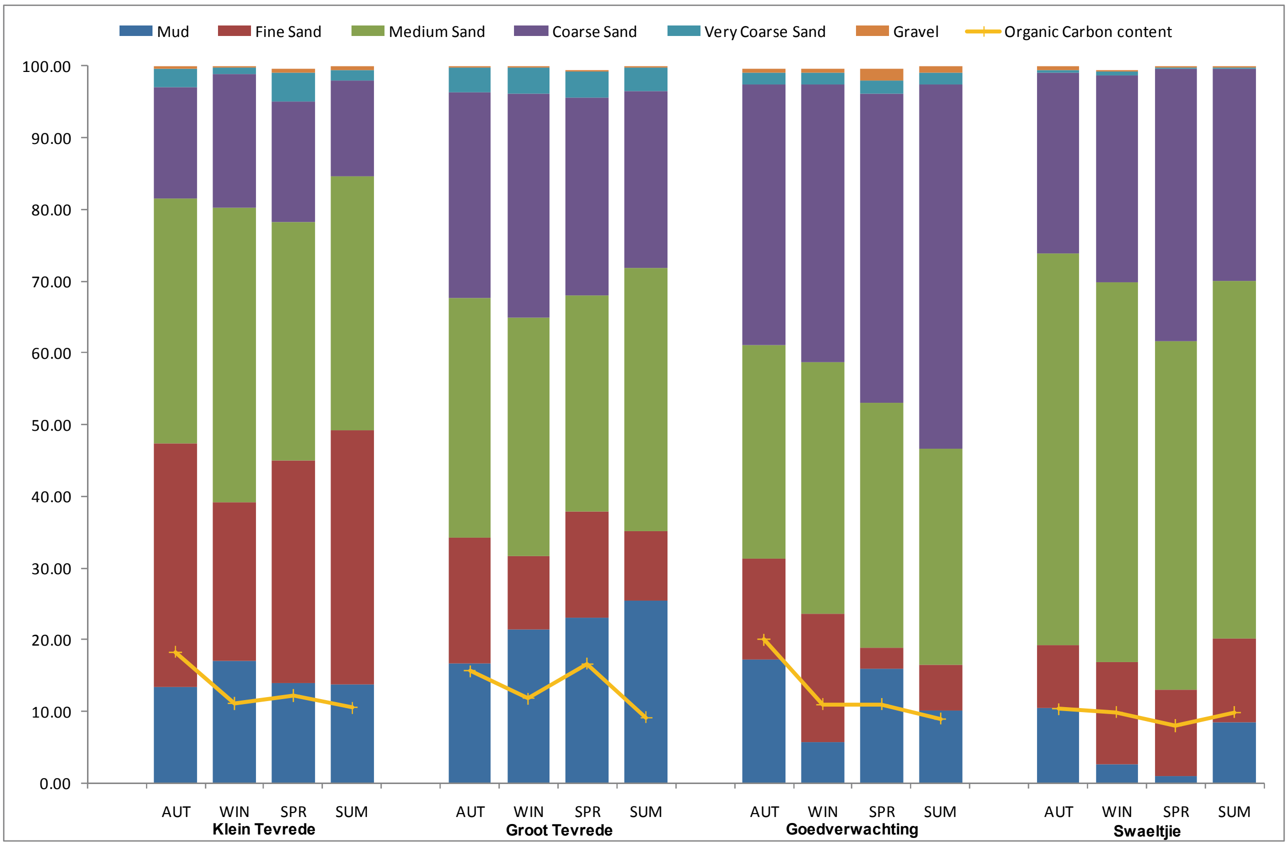

Figure 5
The sediment characteristics analysed in the four selected reed pans. AUT - autumn, WIN - winter, SPR - spring, SUM - summer.

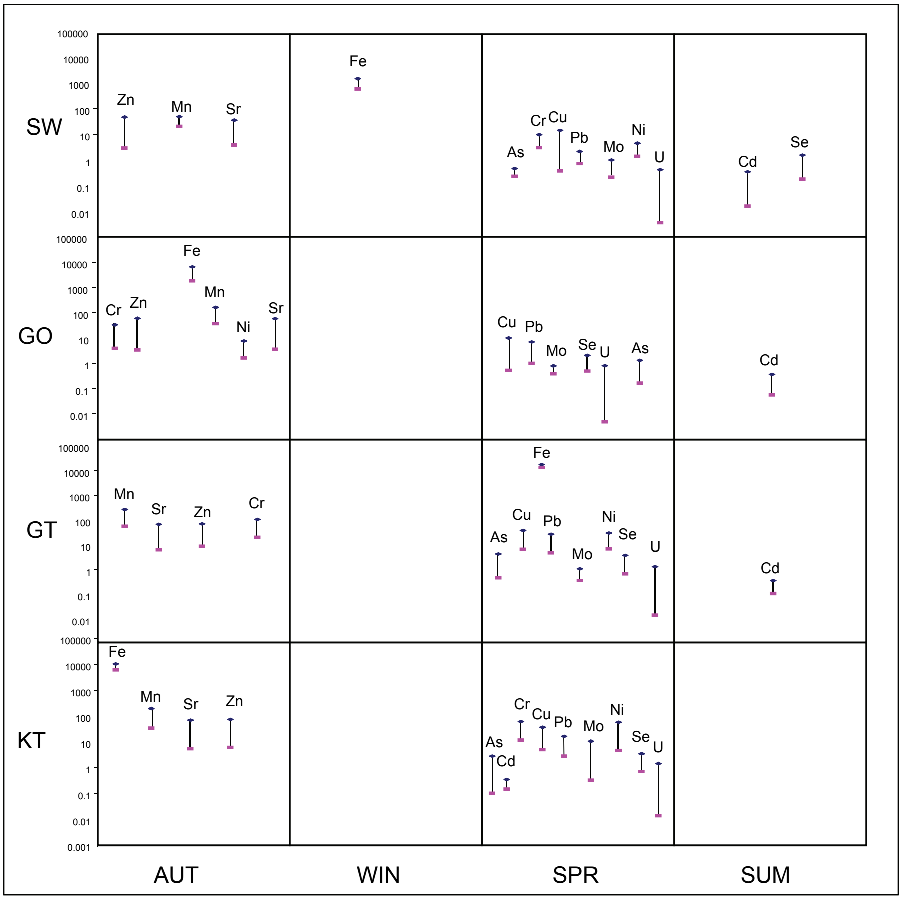

Figure 6
Seasonal variation of the maximum (■) and minimum (■) range of metal concentrations measured in the sediment (μg/g) of the four reed pans selected. Symbols: see Fig. 2.

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subsequently decreasing towards the winter months. Both TIN and TP concentrations were relatively high at GO throughout the different seasons studied, compared to the other sites. Studies have shown P to be the most important limiting nutrient in the process of eutrophication; therefore, GO is probably the site which is most at risk of eutrophication, because of its higher seasonal TP content (Mainstone and Parr, 2002). One of the main non-point sources of TIN and TP is agricultural practices (Walmsley, 2000). This is the result of the addition of more nutrients, in the form of fertilisers, than are removed as produce (Carpenter et al., 1998). The runoff, containing dissolved nutrients, from these types of activities tends to be intermittent in nature, and as a result nutrient concentrations in runoff are often at their highest during high runoff conditions, which are linked seasonally to fertiliser application and rainfall (Carpenter et al., 1998; McNaught and O'Keefe, 2005; De Villiers and Thiart, 2007). This explains the seasonal trend observed for the TP, and to a degree TIN, within the water bodies of the four pans. This also explains why GO had higher concentrations than the other reed pans, with regard to TIN and TP, as a visible increase in surrounding agricultural practices was observed in the catchment of GO when compared to the other reed pans.

Eutrophication can impact water quality and the health of aquatic systems (Hoagland and Franti, 2008) and results in, among other, the depletion of oxygen and the accumulation of metabolic products, as well as the development of cyanobacterial blooms (Oberholster and Ashton, 2008). From our results it can be seen that GO and KT showed a relatively similar seasonal trend with regard to dissolved oxygen concentrations, as with their chlorophyll *a* concentrations, with the exception of the WIN concentration at GO. These chlorophyll *a* concentrations increased during SPR and SUM when there is an increase in productivity (Dallas and Day, 1993), which corresponds to the large amounts of algae (*Gonium* sp.) observed at GO during SUM, and results in an increase in dissolved oxygen concentrations. When the season changes to AUT/WIN the decomposition of organic material and the chemical breakdown of pollutants can result in a decrease in oxygen (Schmitz, 1996; Paisley et al., 2003; Graham and Louw, 2009). The increase in dissolved oxygen concentration seen at GO during WIN is due to the fact that a decrease in temperature can lead to an increase in dissolved oxygen (Graham and Louw, 2009). The use of dissolved oxygen measurements are generally also complicated by the amount of movement in the water through events such as wind stirring. The current level of eutrophication in GO does not appear to have a detrimental effect on the dissolved oxygen concentration and therefore ecosystem health.

On the other hand, the dissolved oxygen concentration trend of GT and SW has an almost inverse relationship with the respective chlorophyll *a* concentrations. There is a gradual decrease in chlorophyll *a* concentrations at these two sites from SUM to WIN, with the dissolved oxygen concentrations having distinct increases during SPR (due to increased photosynthesis and rainfall) and WIN (due to a decrease in temperature and wind stirring) (Dallas and Day, 1993; Graham and Louw, 2009). The lower concentrations of chlorophyll *a* at GT and SW, when compared to GO and KT, may be as a result of a lower degree of surrounding agricultural land use observed at these sites, resulting in lower TP inputs due to agriculture. (Carpenter et al., 1998; McNaught and O'Keefe, 2005; De Villiers and Thiart, 2007).

Seasonal variation of other water quality parameters (e.g., electrical conductivity and pH) showed that conductivity at all of the study sites stayed relatively similar during WIN, AUT and SPR, but decreased during SUM (Fig. 2 G) as increased rainfall resulted in a dilution effect (Marneweck, 2004). Overall, the conductivity values of KT, GT and GO varied between 0.20 mS/cm and 2.61 mS/cm, thus mostly indicating relatively brackish conditions as most measurements are above 1 mS/cm (Morrison et al., 2001). The conductivity values at SW, on the other hand, varied between 0.77 mS/cm and 0.94 mS/cm, indicating electrolyte-rich water (Taylor et al., 2007). The above-mentioned salinity gradients at the various pans are also evident from the Piper diagram (Fig. 3), as the dominance of $Na^+ + K^+$, Mg^{2+} and $SO_4^{2-} + Cl^-$ indicates year-round saline conditions. In the MLD, the bedrock of pans belong predominantly to the Vryheid Formation, which forms part of the Ecca Group that is composed, *inter alia*, of feldspathic sandstones intercalated with lesser shale and siltstone (Wellington, 1955; Johnson et al., 2006; McCarthy et al., 2007). Geological strata are known to contribute to the increase in cations and anions through groundwater discharge; for example, limestones form efficient aquifers that introduce minerals such as Mg^{2+}, whilst metamorphic or igneous rocks contribute to Na^+, K^+, SO_4^{2-} and Cl^- in the surface waters (Appelo and Postma, 2005). The relatively similar conductivity values measured during the lower rainfall periods, namely AUT and WIN, may be an indication of the relative importance of groundwater discharge in reed pans. This is because evaporation, in the absence of consistent groundwater discharge, would have a concentrating effect in pans, resulting in higher conductivity values. This is in contradiction to the relatively high water levels observed throughout all of the seasons during this study, as well as in previous studies of reed pans (Grundling et al., 2003; Marneweck, 2004). It would thus appear that the consistent groundwater discharge aids in offsetting the evaporation taking place in reed pans.

The measured pH levels showed a clear seasonal trend which varied between 6 and 9. Maximum pH values occurred in SPR, and minimum pH values were recorded in AUT. The decrease in pH observed during SUM is likely due to increased rainfall, whilst the increase in pH seen during SPR is most likely a result of increased photosynthesis of the aquatic vegetation (including algae), which causes an increase in the pH of standing water (Barkay et al., 1989; Mason et al., 1995; DWAF, 1996a, b; Ravichandran, 2004). This increase in pH corresponds with the increase in chlorophyll *a* concentrations seen during this period. Thus, it can be seen that at GO, which is most influenced by nutrient enrichment, the increase in pH during SPR is more marked in relation to the other sites (Fig. 2).

The dissolved metal concentrations measured in the water of the four reed pans showed distinct seasonal trends. From Fig. 4 it was evident that the maximum concentration of most of the metals occurred during AUT and SUM, whilst other metals, namely Se, Sr and U, had high concentrations during WIN and SPR. This may be an indication that Se, Sr and U are sourced mainly from the groundwater discharge within reed pans as opposed to surface runoff. This is due to the fact that seasonal changes in metal concentrations are influenced by a variety of factors, including total hardness, organic matter, water temperature, dissolved oxygen, pH, increased rainfall and suspended material (Hellawell, 1986). Hence, increased rainfall during SUM would dissolve and transport metals from the surrounding watershed into the water column of the pans, which starts tailing off in AUT, and results in the higher metal concentrations measured during these seasons (ANZECC and ARMCANZ, 2000). Currently, there are no guideline values available for the water quality variables in depressional

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wetlands in South Africa, and as a result it is not possible to determine whether any threshold values are being exceeded within these systems.

Seasonal changes of sediment quality parameters in the underlying sediment of reed pans

The physical properties of sediment, such as grain size, play a vital role in transportation and sedimentation processes (ANZECC and ARMCANZ, 2000). The smaller the grain size the higher the surface area of the specific sediment particle, thus increasing its ability to adsorb various contaminants such as metals (ANZECC and ARMCANZ, 2000). Our results showed that the sediment found within these pans consisted mainly of a grain size between 500 and 212 µm. No distinct seasonal changes were noticed with regard to grain size. The study site, GO, was the only site that showed increased grain sizes exceeding 2 mm during SUM. This may be due to erosion taking place within the pan's catchment as a result of the increased agricultural practices mentioned earlier. Such changes can impact biotic communities (Hill, 2005), as well as the bioavailability of substances such as metals (Bervoets and Blust, 2003; Newman and Watling, 2007).

Throughout the four seasons the amount of organic carbon found in the sediment of the four reed pans (Fig. 6) was close to or above 10%. As a result, these sediments can be classified as organic, according to the guidelines set for South Africa (Kotze et al., 1996). The organic carbon content was highest during AUT and SPR, which is as a result of the decay of vegetation found within these pans (Grundling and Dada, 1999; Graham and Louw, 2009). An increase in organic matter influences the concentrations of various compounds within the sediment (ANZECC and ARMCANZ, 2000). It was observed that the four reed pans selected for this study contained a variety of free-floating, emergent-floating, emergent and submerged aquatic plants. These plants are important sources of organic material which, under the right circumstances, can contribute to the formation of peat found in these systems (Grundling and Dada, 1999; Richards, 2001; Grundling et al., 2003).

The metal concentrations found within the sediment of the four reed pans showed a seasonal trend which corresponded to the seasonal profile of the organic carbon content within the sediment. The organic carbon content of sediments has been shown to influence the concentrations of various compounds, including metals (Hellawell, 1986; ANZECC and ARMCANZ, 2000). This is an important consideration which needs to be taken into account during any decision making-process dealing with pans containing peat (e.g. reed pans), as this will have a profound impact on the potential toxicity of pollutants within these systems.

The seasonal trend observed in the sediment also complements the trend noticed in the surface waters. Metals bound to sediment particles are generally in thermodynamic equilibrium with their corresponding pore waters; this involves the use of the adsorption sites on the individual sediment particles or organic material (ANZECC and ARMCANZ, 2000). As a result, diffusion of these contaminants takes place naturally when the concentration in the overlying water is less than that of the pore water. Thus, during SUM, when increased rainfall would create a concentration gradient, metals are diffused out of the sediment pore water and into the overlying water column. Here the organic content of sediments also plays an important role through the decomposition of organic material which releases metals from the sediment (ANZECC and ARMCANZ, 2000; Schumacher, 2002).

The analysis of the sediments in the four reed pans selected also confirmed the claims of previous studies that sediments contain higher metal concentrations than those found in the overlying water. This is because metals are introduced into the sediment by physical, chemical and biological processes which are able to accumulate metals over time (Tessier and Campbell, 1987; ANZECC and ARMCANZ, 2000). Thus, seasonal changes in metal concentrations within the sediment of reed pans are likely, as a result of the properties of the metals (e.g., their solubility), the environment of the pan (e.g., increased rainfall), and the properties of the sediment (e.g., organic carbon content) (ANZECC and ARMCANZ, 2000). With no guideline values available for sediments within depressional wetlands in South Africa, threshold values will need to be established so as to determine the potential toxicity of pollutants (e.g., metals) within reed pans (given their distinctive nature) resulting from increased additions of pollutants over time.

Conclusion

The study showed that there are distinct seasonal trends with regard to a variety of water and sediment quality parameters within reed pans. The interrelationships between a variety of factors (measured within the water and sediment, respectively) were also evident. By contributing to an understanding of the seasonal variability of these parameters, this study can aid in properly defining reed pans and illustrating some of their seasonal attributes. This information may be useful in future studies on reed pans as baseline data, as well as to other studies relating to depressional wetlands other than reed pans. The results from this study highlighted important considerations for managing reed pan systems, for example, the importance of their high organic content with regard to pollutant toxicity. Further studies on reed pans are needed to properly ascertain the hydrological functioning of these systems, for example, groundwater recharge-discharge status, as well as to determine suitable threshold values, so as to properly guide decision making in the face of ever-increasing impacts from surrounding land uses.

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References

ANZECC and ARMCANZ (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality. National Water Quality Management Strategy. Vol. 1–2. Australian and New Zealand Environment and Conservation Council and the Agriculture and Resource Management Council of Australia and New Zealand.

APPELO CAJ and POSTMA D (1993) *Geochemistry, Groundwater and Pollution*. AA Balkema, Rotterdam.

APPELO CAJ and POSTMA D (2005) *Geochemistry, Groundwater and Pollution* (2^{nd} edn.). AA Balkema, Rotterdam.

ASHTON PJ, HARDWICK D and BREEN CM (2008) Changes in water availability and demand within South Africa's shared river

http://dx.doi.org/10.4314/wsa.v38i5.3
Available on website http://www.wrc.org.za
ISSN 0378-4738 (Print) = Water SA Vol. 38 No. 5 October 2012
ISSN 1816-7950 (On-line) = Water SA Vol. 38 No. 5 October 2012

basins as determinants of regional social-ecological resilience. In: Burns MJ and Weaver A (eds.) *Exploring Sustainability Science: A Southern African Perspective*. Stellenbosch University Press, Stellenbosch, South Africa.

BARKAY T, LIEBERT C and GILLMAN M (1989) Environmental significance of the potential for mer(Tn21)-mediated reduction of Hg^{2+} to Hg^0 in natural waters. *Appl. Environ. Microbiol.* **55** 1196–2002.

BERKMAN HE, RABENI CF and BOYLE TP (1986) Biomonitors of stream quality in agricultural areas: fish versus invertebrate. *Environ. Manage*. **10** 413–419.

BERVOETS L and BLUST R (2003) Metal concentrations in water, sediment and gudgeon (*Gobio gobio*) from a pollution gradient: relationship with fish condition factor. *Environ. Pollut*. **126** 9–19.

BERVOETS L, PANIS L and VERHEYEN R (1994) Trace metal levels in water, sediments and *Chironomus gr. thumni*, from different water courses in Flanders (Belgium). *Chemosphere* **29** 1591–1601.

CARPENTER SR, CARACO NF, CORRELL DL, HOWARTH RW, SHARPLEY and SMITH VH (1998) Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecol. Appl*. **8** 559–568.

CID BP, GONZALEZ MD and GOMEZ EF (2002) Comparison of single extraction procedures, using either conventional shaking or microwave heating, and the Tessier sequential extraction method for the fractionation of heavy metals from environmental samples. *Analyst* **127** 681–688.

COWAN GI and VAN RIET W (1998) A directory of South African wetlands. Department of Environmental Affairs and Tourism, Pretoria, South Africa.

CSIR (2010) A CSIR Perspective on Water in South Africa. CSIR Report No. CSIR/NRE/PW/IR/2011/0012/A. CSIR, Pretoria.

CYRUS DP, WEPENER V, MACKAY CF, CILLIERS PM, WEERTS SP and VILJOEN A (2000) The Effect of Interbasin Transfer on the Hydrochemistry, Benthic Invertebrates and Ichthyofauna of the Mhlathuze Estuary and Lake Nsenzi. WRC Report No. 722/1/00. Water Research Commission, Pretoria.

DALLAS HF and DAY JA (1993) The Effect of Water Quality Variables on Riverine Ecosystems: A Review. WRC Report No. TT 61/93. Water Research Commission, Pretoria.

DE VILLIERS S and THIART C (2007) The nutrient status of South African rivers: concentrations, trends and fluxes from the 1970s to 2005. *S. Afr. J. Sci.* **103** 343–349.

DINI J (2004) Restoring wetlands and healing a nation: South Africa's Working for Wetlands programme. South African National Biodiversity Institute, South Africa.

DINI J, COWAN G and GOODMAN P (1998) South African national wetland inventory: proposed wetland classification system for South Africa. Department of Environmental Affairs and Tourism, Pretoria, South Africa.

DISE NB, MATZNER E, ARMBRUSTER M and MACDONALD J (2001) Aluminium output fluxes from forest ecosystems in Europe: A regional assessment. *J. Environ. Qual*. **30** 1747–1756.

DRISCOLL CT (1985) Aluminium in acidic water: chemistry, transport and effects. *Environ. Health Perspect* **63** 93–104.

DWAF (DEPARTMENT OF WATER AFFAIRS AND FORESTRY, SOUTH AFRICA) (1992) Analytical Methods Manual. Technical Report No. 151. Department of Water Affairs and Forestry, Pretoria, South Africa.

DWAF (DEPARTMENT OF WATER AFFAIRS AND FORESTRY, SOUTH AFRICA) (1996a) South African Water Quality Guidelines. **7**: Aquatic Ecosystems (1st edn.). Department of Water Affairs and Forestry, Pretoria, South Africa.

DWAF (DEPARTMENT OF WATER AFFAIRS AND FORESTRY, SOUTH AFRICA) (1996b) South African Water Quality Guidelines. **1**: Domestic Use (2nd edn.). Department of Water Affairs and Forestry, Pretoria, South Africa.

DWAF (DEPARTMENT OF WATER AFFAIRS AND FORESTRY, SOUTH AFRICA) (2004) Development of a framework for the assessment of wetland ecological integrity in South Africa. Report No. 0000/00/REQ/0904. Resource Quality Services, Department of Water Affairs and Forestry, Pretoria, South Africa.

GOUDIE AS and THOMAS DSG (1985) Pans in Southern Africa with particular reference to South Africa and Zimbabwe. *Zeitschrift für Geomorphologie* **29** 1–19.

GOUDIE AS and WELLS GL (1995) The nature, distribution and formation of pans in arid zones. *Earth-Sci. Rev*. **38** 1–69.

GRAHAM M and LOUW MD (2009) River ecoclassification. Manual for ecostatus determination version 2. Module G: Index of habitat integrity. Section 2: Model photo guide. WRC Report No. TT 378/09. Water Research Commission, Pretoria.

GRUNDLING P-L and DADA R (1999) Peatlands of South Africa. A booklet produced by the Council for Geoscience, Pretoria, South Africa. Printed by Share-Net for environmental education.

GRUNDLING P-L, LINSTRÖM A, GROBLER R AND ENGELBRECHT J (2003) The Tevredenpan peatland complex of the Mpumalanga Lakes District. In: Couwenberg J and Joosten H (eds.) *International Mire Conservation Group Newsletter Issue 2007/3*. International Mire Conservation Group.

HEATHWAITE A L (1993) The impact of agriculture on dissolved nitrogen and phosphorus cycling in temperate ecosystems. *Chem. Ecol*. **8** 217–231.

HELLAWELL JM (1986) *Biological Indicators of Freshwater Pollution and Environmental Management*. Elsevier Applied Science Publishers, London.

HILL L (2005) Elands Catchment Comprehensive Reserve Determination Study, Mpumalanga Province, Ecological Classification and Ecological Water Requirements (Quantity) Workshop Report. Report No. ENV-P-C 2004-019. CSIR, Pretoria.

HOAGLAND KD and FRANTI TG (2008) Eutrophication. In: Trimble SW (ed.) *Encyclopedia of Water Science* (2nd edn.). CRC Press, Boca Raton

JOHNSON MR, VAN VUUREN CJ, VISSER JNJ, COLE DI, WICKENS H DE V, CHRISTIE ADM, ROBERTS DL and BRANDL G (2006) Sedimentary rocks of the Karoo Supergroup. In: Johnson MR, Anhaeusser CR and Thomas RJ (eds.) *The Geology of South Africa*. Geological Society of South Africa, Johannesburg/Council for Geoscience, Pretoria, South Africa.

JOOSTEN H and CLARKE D (2002) Wise use of mires and peatlands: Background principles including a framework for decision-making. Prepared for International Mire Conservation Group and International Peat Society. Saarijärvi, Finland.

KOTZE DC, KLUG JR, HUGHES JC and BREEN CM (1996) Improved criteria for classifying hydric soils in South Africa. *S. Afr. J. Plant Soil*. **13** 67–73.

LORENZEN CJ (1967) Determination of chlorophyll and pheopigments: spectrophotometric equations. *Limnol. Oceanogr.* **12** 343–346.

MILLENIUM ECOSYSTEM ASSESSMENT (2005) *Ecosystems and Human Well-Being: Wetlands and Water Synthesis*. World Resource Institute, Washington, DC.

MAINSTONE CP and PARR W (2002) Phosphorus in rivers – ecology and management. *Sci. Total Environ*. **282–283** 25–47.

MARNEWECK G (2004) Reserve determination methods for pans. In: DWAF (2004) Development of a framework for the assessment of wetland ecological integrity in South Africa. Report No. 0000/00/REQ/0904. Resource Quality Services, Department of Water Affairs and Forestry, Pretoria, South Africa.

MASON RP, MOREL FMM and HEMOND HF (1995) The role of microorganisms in elemental mercury formation in natural water. *Environ. Sci. Technol*. **80** 775–787.

McCARTHY TS, CAIRNCROSS B, HUIZENGA J-M AND BATCHELOR A (2007) Conservation of the Mpumalanga Lakes District. Technical Report. School of Geosciences, University of the Witwatersrand. Department of Geology, University of Johannesburg. Wetland Consulting Services (Pty) Ltd.

McNAUGHT AS and O'KEEFE DM (2005) Natural and anthropogenic sources of nutrient and sediment to a Great Lakes tributary stream. *Verh. Internat. Limnol*. **29** 997–1004.

MORRISON G, FATOKI OS, PERSSON L and EKBERG A (2001) Assessment of the impact of point source pollution from the Keiskammahoek Sewage Treatment Plant on the Keiskamma River – pH, electrical conductivity, oxygen-demanding substance (COD) and nutrients. *Water SA* **27** 475–480.

NEWMAN BK and WATLING RJ (2007) Definition of baseline metal concentrations for assessing metal enrichment of sediment from

the south-eastern Cape coastline of South Africa. *Water SA* **33** 675–692.
NIXON SW (1995) Coastal marine eutrophication: A definition, social causes, and future concerns. *Ophelia* **41** 199–219.
OBERHOLSTER PJ and ASHTON PJ (2008) State of the nation: An overview of the current status of water quality and eutrophication in South African rivers and reservoirs. CSIR Report No. CSIR/NRE/WR/IR/2008/0075/C. CSIR, Pretoria.
PAISLEY MF, WALLEY WJ, NIKHADE J and DILS R (2003) Identification of the key biological indicators of nutrient enrichment in rivers for use in predictive/diagnostic models. Theme 8: Aquatic Ecology and Dangerous Substances. In: Bruen M (ed.) *Diffuse Pollution and Basin Management. Proceedings of the 7th International Specialised IWA Conference, Dublin, Ireland*. ISBN: 1902277767.
PIPER AM (1944) A graphic procedure in the geochemical interpretation of water analyses. *Trans. Am. Geophys. Union* **25** 914–928.
RAST W and THORNTON JA (1996) Trends in eutrophication research and control. *Hydrol. Processes.* **10** 295–313.
RAVICHANDRAN M (2004) Interactions between mercury and dissolved organic matter – a review. *Chemosphere* **55** 319–331.
RICHARDS LT (2001) A guide to wetland identification, delineation and wetland functions. Unpublished Magister Artum in Environmental Management dissertation. Rand Afrikaans University, South Africa.
SARTORY DP and GROBBELAAR JU (1984) Extraction of chlorophyll *a* from freshwater phytoplankton for spectrophotometric analysis. *Hydrobiologia* **114** 177–187.
SCHMITZ RJ (1996) *Introduction to Water Pollution Biology*. Gulf Publishing Company, Houston.
SCHULZE RE (1997) South African atlas of agrohydrology and -climatology. WRC Report No. TT 82/96. Water Research Commission, Pretoria.
SCHUMACHER BA (2002) Methods for the determination of total organic carbon (TOC) in soils and sediments. NCEAC-1282, EMASC-001. Ecological Risk Assessment Support Center, Office of Water, US Environmental Protection Agency, Washington, DC.
SHAW PA and THOMAS DSG (1989) Playas, pans and salt lakes. In: Thomas DSG (ed.) *Arid Zone Geomorphology*. Belhaven Press, London.
STECKO JRP and BENDELL-YOUNG LI (2000) Contrasting the geochemistry of suspended particulate matter and deposited sediments within an estuary. *Appl. Geochem.* **15** 753–775.
TAYLOR JC, HARDING WR and ARCHIBALD CGM (2007) An Illustrated Guide to Some Common Diatom Species from South Africa. WRC Report No. TT 282/07. Water Research Commission, Pretoria.
TAYLOR JC, PRYGIEL J, VOSLOO A and DE LA REY PA (2007) Can diatom-based pollution indices be used for biomonitoring in South Africa? A case study of the Crocodile West and Marico water management area. *Hydrobiologia* **592** 455–464.
TESSIER A and CAMPBELL PGC (1987) Partitioning of trace metals in sediments: relationships with bioavailability. *Hydrobiologia* **149** 43–52.
TESSIER A, CAMPBELL PGC, AUCLAIR JC and BISSON M (1984) Relationships between the partitioning of trace metals in sediments and their accumulation in the tissues of the freshwater mollusc *Elliptio complanata* in a mining area. *Can. J. Fish. Aquat. Sci.* **41** 1463–1472.
USEPA (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY) (2001) Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual. EPA 823-B-01-002. Office of Water, United States Environmental Protection Agency, Washington, DC.
WALLING DE and MOOREHEAD PW (1989) The particle size characteristics of fluvial suspended sediment: an overview. *Hydrobiologia* **176/177** 125-149.
WALMSLEY RD (2000) Perspectives on Eutrophication of surface water: Policy/Research Needs in South Africa. WRC Report No. KV 129/00. Water Research Commission, Pretoria.
WELLINGTON JH (1955) South Africa – a geographic study. *Phys. Geogr.* **1** 474–481.
WILLIAMSON RB, VAN DAM LF, BELL RG, GRENN MO and KIM JP (1996) Heavy metal and suspended sediment fluxes from a contaminated intertidal inlet (Manukau Harbour, New Zealand). *Mar. Pollut. Bull.* **32** 812–822.
WINTERBOURNE MJ, MCDIFFETT WF and EPPLEY SJ (2000) Aluminium and iron burdens of aquatic biota in New Zealand streams contaminated by acid mine drainage: effects of trophic level. *Sci. Total Environ.* **254** 45–54.

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