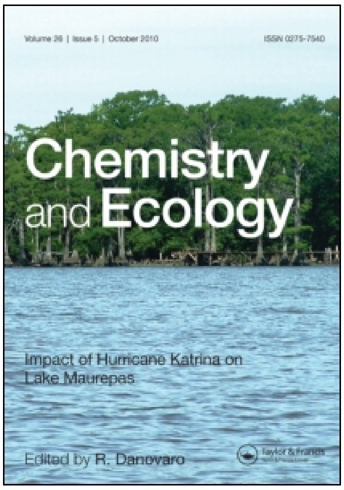

**Chemistry and Ecology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

# Differential release of nitrogen and phosphorus from anoxic sediments

Darren S. Baldwin[a]; Janice Williams[a]
[a] Murray-Darling Freshwater Research Centre, Wodonga, Australia

**To cite this Article** Baldwin, Darren S. and Williams, Janice(2007) 'Differential release of nitrogen and phosphorus from anoxic sediments', Chemistry and Ecology, 23: 3, 243 — 249

**To link to this Article: DOI:** 10.1080/02757540701339364

**URL:** http://dx.doi.org/10.1080/02757540701339364

*Chemistry and Ecology*
Vol. 23, No. 3, June 2007, 243–249

# Differential release of nitrogen and phosphorus from anoxic sediments

DARREN S. BALDWIN* and JANICE WILLIAMS

Murray-Darling Freshwater Research Centre, PO Box 991, Wodonga, Australia

*(Received 18 September 2006; in final form 10 January 2007)*

Release of dissolved $NH_4^+$, $NO_x$, filterable reactive P, Fe(II), and $S^{2-}$ from reservoir sediments under anoxic conditions were measured using mesocosms. The sediments were a net sink for $NO_x$, but were a net source of both ammonia and Fe(II). Unexpectedly, the sediments did not release reactive P to any great extent over the 28 d of the experiment. This resulted in an increase in the ratio of dissolved inorganic nitrogen to filterable reactive phosphorus in the overlying water over time. Maintaining a high concentration of dissolved inorganic nitrogen to filterable reactive phosphorus ratios in the overlying water column is a potential method for minimizing the occurrence of cyanobacterial blooms. Therefore, understanding the underlying mechanisms responsible for the retention of P has implications for the ongoing management of the reservoir.

*Keywords*: Sediment; Nutrient; Cyanobacteria; Anoxia

## 1. Introduction

Blooms of toxic cyanobacteria affect the usability of water resources; during blooms, water may not be fit for human or stock consumption, or for recreation activities that rely on primary contact with the water (e.g. swimming) [1]. There are a number of factors that determine the algal community structure in a lake or water-storage reservoir including light, temperature, mixing, and nutrient status [1]. Although still contentious [2], a number of studies have suggested that cyanobacteria dominate other species only when the ratio of dissolved inorganic nitrogen (diN—ammonia+nitrate) to filterable reactive phosphate (frP—a surrogate measure of orthophosphate) is low [3]. For example, in a mesocosm experiment, cyanobacteria were dominant when the diN:frP ratio was less than 10:1 (by mass) and did not occur when the ratio was greater than about 15:1 [3]. Sediments are both the major source and sink for nutrients in many aquatic ecosystems, and sediment processes can strongly influence the concentration of nutrients in the overlying water column and hence the ratio of N:P.

Lake Hume is a large water-storage reservoir in south-eastern Australia. Generally, physical conditions in the water storage are conducive to the formation of cyanobacterial blooms [4],

---

*Corresponding author. Email: darren.baldwin@csiro.au

*Chemistry and Ecology*
ISSN 0275-7540 print/ISSN 1029-0370 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02757540701339364

but cyanobacterial blooms rarely occur in the storage [5]. As part of a larger study on why there are only sporadic occurrences of cyanobacterial blooms in this reservoir, we examined the uptake and release of nutrients from the reservoir's sediments. The reservoir stratifies on a yearly basis, and so there are extended periods when the sediments will be totally anoxic [6]. Based on our observations on this and other water storages, we hypothesized that the diN:frP ratio in the water column would decrease under anoxic conditions—which should favour cyanobacteria. Previously, we have shown that in this particular reservoir, most available nitrate in the overlying water column is rapidly lost through denitrification following the onset of anoxia [7]. Conversely, the release of frP from anoxic sediments in other water bodies is well documented. Phosphate ions bound to iron minerals in the sediment can be solubilized under anaerobic conditions, either directly by iron-reducing bacteria or indirectly through the actions of sulfate-reducing bacteria [8]. Iron-reducing bacteria reduce particulate ferric minerals to dissolved ferrous ions, releasing any P bound to the mineral surface [9]. Sulfate-reducing bacteria reduce sulfate to sulfide; sulfide is a strong enough reducing agent to also reduce ferric minerals [10].

## 2. Material and methods

Lake Hume is a large water-storage reservoir on the Murray River near Albury, south eastern Australia (36° 14′ S, 147° 15′ E). At full capacity ($3.04 \times 10^9\,\mathrm{m}^3$), the lake has a surface area of $202.5\,\mathrm{km}^2$ and a maximum depth of 41.4 m. At the time of sampling, the lake was not stratified, but the lake stratifies annually in summer and early autumn; with a thermocline at about 8–10 m [6]. The lake is fed by two major tributaries, the Murray River, which flows in from the north-east, and the Mitta Mitta River that flows in from the south-east. Triplicate sediment samples were taken from three sites on the lake, corresponding to the Murray River arm (figure 1, Site 1), the central part of the lake (figure 1, Site 2) and the Mitta Mitta River arm of the lake (figure 1, Site 3), during the austral spring using an Eckman grab in 10–15 m of water. All sediment samples had a thin (about 1–3 mm) layer of oxidized iron at the surface, but no evidence of oxidation below this layer.

Following sampling, the samples were gently mixed to disrupt the surface oxidized layer, $500\,\mathrm{cm}^3$ of the fine sediment from each grab sample was immediately transferred into purpose-built 2 l microcosm chambers [11], and the chambers were then quickly filled to overflowing with lake water that had been autoclaved, degassed, and stored in gas-tight containers the previous day. The mesocosms were then sealed, stored underwater to minimize gas transfer

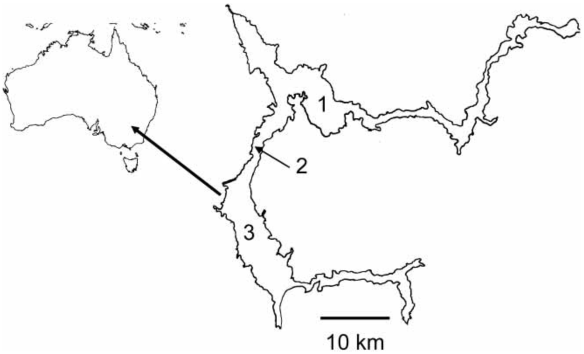

Figure 1. Lake Hume, showing the sampling sites.

into the mesocosm, transported back to the laboratory, and stored under water at 20 °C for the length of the experiment. Water samples were taken at time 0 (immediately after sealing) and 1, 3, 6, 15, 21, and 28 d after sampling.

Following gentle mixing [11]; water samples were taken by syringe, filtered through 0.45 μm syringe filters, and preserved. Samples for nutrient analysis were preserved by freezing. $NH_4^+$ was analysed using the phenate method, oxides of nitrogen ($NO_3^- + NO_2^-$) were analysed using the automated cadmium reduction method, and $PO_4^{3-}$ was analysed by the molybdenum blue method [12] simultaneously on a Lachat Quickchem 8000 auto analyser. Samples for sulfide analysis were preserved with zinc acetate and stored frozen. Analyses were performed using the modified methylene blue method on a Varian Carey 1E UV-Vis spectrophotometer [13]. Samples for Fe(II) analysis were preserved with one drop of concentrated, ultra-pure HCl and stored frozen. The samples were analysed using the colorimetric ferrozine technique also using a Varian Carey spectrophotometer [14]. (Fe(II) samples were not analysed for time = 0.) All errors quoted are the standard error.

## 3. Results

The uptake or release of each of the analytes followed a similar pattern for each of the replicate samples at each of the three sites. However, the within-site variability in the magnitude of change was greater than the between-site variability. Therefore, in the following analysis, the results from each of the nine samples have been combined.

The sediments were a net source of ammonia (figure 2). Rates of ammonia release from the sediments were highly variable, with final concentrations of ammonium ions in the overlying water varying from between about 500 and 3000 μg l$^{-1}$. However, the patterns of release of ammonia from each sediment sample were similar and could be modelled using a first-order rate equation:

$$[NH_4^+] = [NH_4^+]_{max}(1 - e^{-kt}), \tag{1}$$

where $[NH_4^+]_{max}$ is the maximum concentration of ammonium ions in the mesocosm, $k$ is the first-order rate constant, and $t$ is time. Fitting the model to the combined data for the whole of lake ($r^2 = 0.97$) gave an average $[NH_4^+]_{max}$ of 1700 (±140) μg N l$^{-1}$ and a first-order rate constant of 0.095 (±0.019) day$^{-1}$.

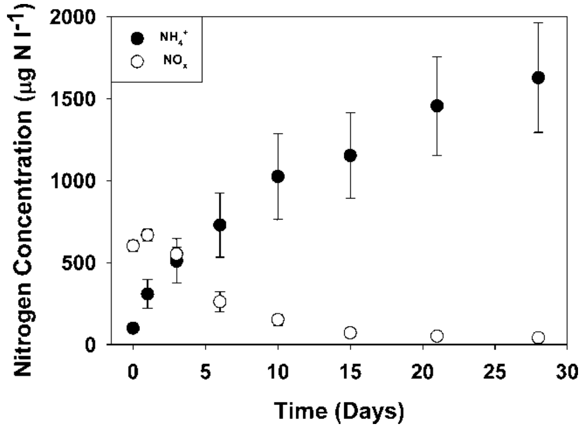

Figure 2. Mean concentrations of $NH_4^+$ and $NO_x$ in the mesocosms over time. Error bars show the standard error ($n = 9$).

The sediments were a net sink for $NO_x$ (figure 2). Following a slight initial increase in $NO_x$, the concentration declined rapidly in all mesocosms—reaching a final concentration of $<100\,\mu g\,l^{-1}$. $NO_x$ loss could also be modelled using a first-order rate equation of the type:

$$[NO_x] = [NO_x]_{\text{initial}} e^{-kt}, \qquad (2)$$

where $[NO_x]_{\text{initial}}$ is the initial concentration of nitrate in solution, $k$ is the first-order rate constant, and $t$ is time. Fitting the model to the combined data for the whole of lake ($r^2 = 0.98$) gave an average initial concentration of 810 (±50) $\mu g\,N\,l^{-1}$ and a first-order rate constant of 0.16 (±0.02) $d^{-1}$.

It is not possible to tell whether or not sulfate reduction was occurring. The average sulfide concentration in the overlying water fell from about 60 $\mu g\,S\,l^{-1}$ at the start of the experiment to about 20 $\mu g\,S\,l^{-1}$ by day 6 but had returned to levels of about 50 $\mu g\,S\,l^{-1}$ by day 10, where they remained for the rest of the experiment (data not shown).

Iron reduction was clearly occurring in the sediments (figure 3). After a short initial lag phase (varying from 3–10 d, depending on the sample), the concentration of ferrous ion in the overlying water continued to increase over the length of the experiment, reaching final concentrations

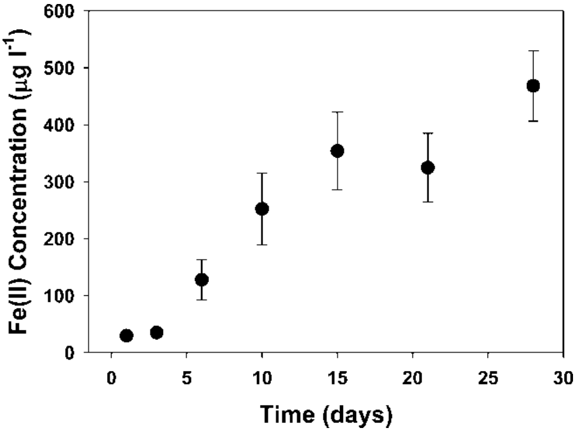

Figure 3. Mean concentrations of Fe(II) in the mesocosms over time. Error bars show the standard error ($n = 9$).

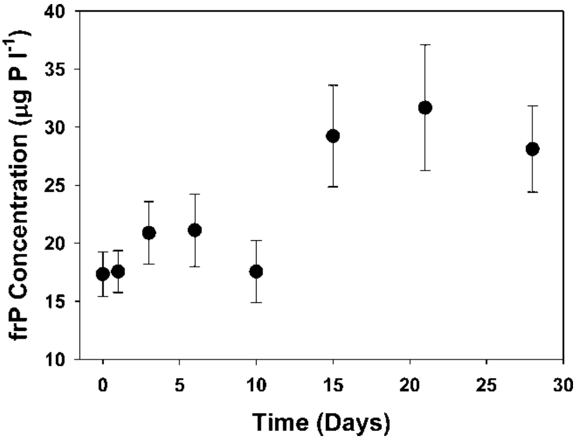

Figure 4. Mean concentrations of filterable reactive phosphate in the mesocosms over time. Error bars show the standard error ($n = 9$).

of between about 150 and 800 $\mu$g $Fe^{2+}$ $l^{-1}$. Although iron reduction was occurring, this did not result in a significant concomitant release of srP (figure 4). Although the P concentration increased slightly in some mesocosms, it actually declined over time in others. Overall, in the first 10 d of the experiment, the average srP concentration in the mesocosms was about 15–20 $\mu$g P $l^{-1}$, increasing to about 30 $\mu$g P $l^{-1}$ by day 15, where it remained until the end of the experiment.

## 4. Discussion

The sediments from Lake Hume exhibit a differential release of N and P under anoxic conditions. This differential release in turn affects the ratio of diN:frP in the overlying water column. At the beginning of the mesocosm experiment, the ratio of diN:frP (by weight) was 44 (±6):1, and after 28 d of incubation under anoxic conditions, the ratio had increased to 71 (±17):1, well above levels that favour species other than cyanobacteria [3].

The response of $NO_x$ is consistent with earlier measurements of denitrification in sediments from this reservoir. Previously, we have shown a rapid loss of nitrate from solution under anoxic conditions—with about 75% of the nitrate converted to $N_2$ through denitrification [7]. Similarly, the net release of ammonia from the sediments is consistent with other studies [15]. Under anoxic conditions, ammonia can be produced through the mineralization of organic matter (ammonification) or microbially mediated dissimilatory nitrate reduction to ammonia (DNRA) [16]. Given that the rate of loss of nitrate from the water column was different from the rate of formation of ammonia, and the net ammonia production was about 2.5 times greater than the amount of nitrate lost, this would suggest that DNRA is not an important pathway for anoxic ammonia release from these sediments. The rate of ammonia release from sediments in the current studies is similar to other studies of ammonia release from water-storage sediments [15].

The release of srP from the sediments under anoxic conditions is significantly less than would be predicted from earlier studies on P release from reservoir sediments [15, 17]; previous studies have reported rates of sediment P release at least two orders of magnitude greater than that observed in this study [15, 17].

The reason behind the lack of sedimentary P release is unknown. Previous studies on P speciation of sediments from this reservoir have shown that a substantial amount of P is associated with iron minerals [18]. The current study clearly shows that iron reduction was occurring in the sediments, and so we should expect concomitant P release. It is possible that the sediment P dynamics in the current study is similar to that described by Roden and Edmonds [19]. They suggested that P displaced from the reduction of iron minerals may react with the reduced iron, either adsorbing to ferrous oxyhydroxides in the sediment or alternatively precipitating out as ferrous phosphate minerals. They suggest that only when sulfate reduction is occurring will P be released from the sediment—the sulfide produced from sulfate reduction displaces phosphate from the ferrous minerals [19]. In the current study, there was no clear evidence that sulfate reduction was occurring in the sediments. The sulfide concentration in the overlying water was generally low and actually declined during the first half of the experiment. If this hypothesis is correct, significant P release will only occur if sulfate reduction in the sediments is stimulated (e.g. by the addition of sulfate).

An alternate hypothesis to explain the lack of P release is that the sediments still contained oxidized Fe minerals. P released through iron reduction reabsorbs onto non-reduced iron minerals in the sediments [8]. If this hypothesis is correct, then P release from the sediments will only occur once all of the iron minerals in the sediment that can adsorb phosphate have been reduced.

However, differentiating between the two mechanisms has important ramifications for the reservoir managers. Lake Hume is used both for raw drinking-water supply and primary contact recreation. There have only been four periods in the last 70 yr when significant algal blooms occurred in Lake Hume (immediately following commissioning in the 1930s, 1973, 1981–1982, and 2002–2005) [4], but minimizing cyanobacterial blooms is a key management priority for the lake. One control mechanism is to maintain a high diN:frP ratio, which in turn means limiting the release of P from the sediments. If sulfate reduction is the principal driver of anoxic sediment P release, then strategies need to be explored to limit the delivery of S to the lake. If retention by oxidized Fe in the sediments is retarding the release of P, then strategies need to be explored that maximize the oxidation of the sediments. Differentiating between the two mechanisms is not a trivial exercise, as sulfate reduction can also lead to iron reduction and/or displacement of adsorbed P from oxidized iron minerals [10]. One possible approach would be to conduct a detailed study of shifts in iron mineralogy following the onset of anoxic conditions using $^{57}$Fe Mössbauer spectroscopy [20].

## Acknowledgements

This study was commissioned by the Lake Hume Blue-Green Algae Abatement Program Project Working Group. We would like to thank J. Pengelly for the N and P analyses; Drs Rodger Croome, Rod Oliver, Vlad Matveev, Brad Sherman, and Alison Mitchell for valuable discussions on algal blooms in Lake Hume; and Dr Ewen Silvester for commenting on an earlier version of this manuscript.

## References

[1] R. Oliver, G. Ganf. Freshwater blooms. In *The Ecology of Cyanobacteria: Their Diversity in Time and Space*, B. Whitton, M. Potts (Eds), pp. 149–194, Kluwer Academic, Dordrecht, Netherlands (2000).

[2] C. Reynolds. What factors influence the species composition of phytoplankton in lakes of different trophic status? *Hydrobiol.*, **369**/**370**, 11 (1998).

[3] V.H. Smith, S.J. Bennett. Nitrogen:phosphorus supply ratios and phytoplankton community structure in lakes. *Arch. Hydrobiol.*, **146**, 37 (1999).

[4] D.S. Baldwin, R. Croome, V. Matveev, A. Mitchell, R. Oliver, B. Sherman, J. Williams. *Cyanobacterial (Blue-Green Algal) Blooms in Lake Hume*, pp. 8–9, Lake Hume Algal Taskforce, Albury, Australia (2006).

[5] Matveev, V. and Matveeva, L., Seasonal succession and long-term stability of the pelagic community in a productive Australian reservoir. *Mar. Freshw. Res.*, **56**, 1137 (2005).

[6] B. Sherman. *Hume Reservoir Thermal Monitoring and Modelling—Final Report*, p. 20, State Water, Sydney (2005).

[7] A.M. Mitchell, D.S. Baldwin. The effects of sediment desiccation on the potential for nitrification, denitrification, and methanogenesis in an Australian reservoir. *Hydrobiol.*, **392**, 3 (1999).

[8] D.S. Baldwin, A.M. Mitchell, J. Olley. Pollutant–sediment interactions: sorption, reactivity and transport of phosphorus. In *Agriculture, Hydrology and Water Quality*, P.M. Haygarth, S.C. Jarvis (Eds), pp. 265–280, CABI, Wallingford, UK (2002).

[9] W. Einsel, Uber die beziehungen des eisenkreislaufs zum phosphatkreislauf im eutrophen See. *Arch. Hydrobiol.*, **29**, 664 (1936).

[10] B. Boström, J.M. Andersen, S. Fleischer, M. Jansson. Exchange of phosphorus across the sediment–water interface. *Hydrobiol.*, **170**, 229 (1988).

[11] D.S. Baldwin, G.N. Rees, A.M. Mitchell, G. Watson. Spatial and temporal variability of nitrogen dynamics in an upland stream before and after a drought. *Mar. Freshw. Res.*, **56**, 457 (2005).

[12] American Public Health Association. *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC (1992).

[13] J.D. Cline. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.*, **14**, 454 (1969).

[14] J. Sorenson J. Reduction of ferric iron in anaerobic, marine sediment and interaction with reduction of nitrate and sulfate. *Appl. Environ. Microbiol.*, **43**, 319 (1982).

[15] W.H. Nowlin, J.L. Evarts M.J. Vanni. Release and potential fates of nitrogen and phosphorus from sediments in a eutrophic reservoir. *Freshw. Biol.*, **50**, 301 (2005).

[16] S. Rysgaard, N. Risgaard-Petersen, L.P. Nielsen, N.P. Reusbech. Nitrification and denitrification in lake and estuarine sediments measured by the 15 N dilution technique and isotope pairing. *Appl. Environ. Microbiol*, 59, 2093 (1993).

[17] A.M. Mitchell, D.S. Baldwin. The effects of desiccation/oxidation on the potential for bacterially mediated P release from sediments. *Limnol. Oceanogr.*, **43**, 481 (1998).

[18] D.S. Baldwin. The phosphorus composition of a diverse series of Australian sediments, *Hydrobiologia*, **335**, 63 (1996).

[19] E.E. Roden, J.W. Edmonds. Phosphate mobilization in iron-rich anaerobic sediments: Microbial Fe(III) oxide reduction versus iron-sulfide formation. *Arch. Hydrobiol.*, **139**, 347 (1997).

[20] F.C. Hawthorne. Mossbauer spectroscopy. In *Spectroscopic Methods in Mineralogy and Geology*, F.C. Hawthorne (Ed.), *Rev. Mineral.*, 18, pp. 255–340 (1988).