NERC Open Research Archive
sharing our research

Centre for Ecology & Hydrology
NATURAL ENVIRONMENT RESEARCH COUNCIL

Article (refereed) - postprint

Douglas, Grant B.; Lurling, Miquel; Spears, Bryan M. 2016. **Assessment of changes in potential nutrient limitation in an impounded river after application of lanthanum-modified bentonite** [in special issue: Geo-engineering to manage eutrophication in lakes].

Crown Copyright © 2016
This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
(cc) BY-NC-ND

This version available http://nora.nerc.ac.uk/516401/

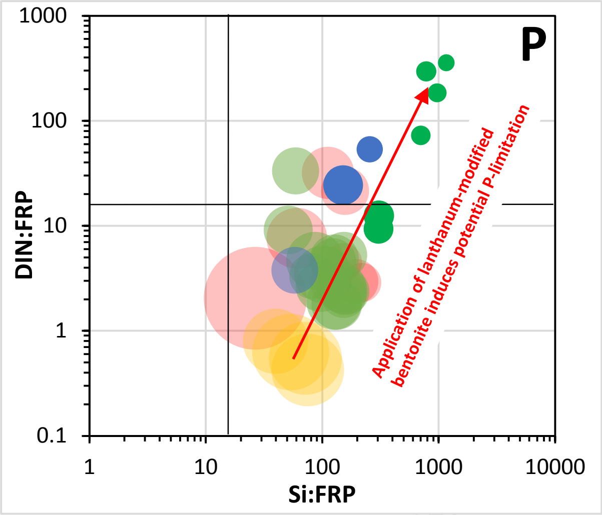
NERC has developed NORA to enable users to access research outputs wholly or partially funded by NERC. Copyright and other rights for material on this site are retained by the rights owners. Users should read the terms and conditions of use of this material at http://nora.nerc.ac.uk/policies.html#access

NOTICE: this is the author's version of a work that was accepted for publication in *Water Research*. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in *Water Research* (2016), 97. 47-54. 10.1016/j.watres.2016.02.005

www.elsevier.com/

Contact CEH NORA team at
noraceh@ceh.ac.uk

The NERC and CEH trademarks and logos ('the Trademarks') are registered trademarks of NERC in the UK and other countries, and may not be used without the prior written consent of the Trademark owner.


P
1000
100
10
1
0.1
DIN:FRP
1
10
100
1000
10000
Si:FRP
Application of lanthanum-modified bentonite induces potential P-limitation

Assessment of changes in potential nutrient limitation in an impounded river after application of lanthanum-modified bentonite.

Grant B. Douglas[a*], Miquel Lurling[b] and Bryan M. Spears[c]

[a)]CSIRO Land and Water, Perth, WA, Australia

[b)]Department of Environmental Sciences, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands

[c)]Centre for Ecology and Hydrology, Penicuik, Midlothian, Scotland, UK, EH26 0QB

*Corresponding author
Dr Grant Douglas
Senior Principal Research Scientist
CSIRO Land and Water Flagship
Private Bag 5, Wembley, WA
6913
Australia
Email: grant.douglas@csiro.au

Abstract

With the advent of phosphorus (P)-adsorbent materials and techniques to address eutrophication in aquatic systems there is a need to develop interpretive techniques to rapidly assess changes in potential nutrient limitation. In a trial application of the P-adsorbent, lanthanum-modified bentonite (LMB) to an impounded section of the Canning River, Western Australia, a combination of potential P, nitrogen (N) and silicon (Si) nutrient limitation diagrams based on dissolved molar nutrient ratios and actual dissolved nutrient concentrations have been used to interpret trial outcomes. Application of LMB resulted in rapid and effective removal of filterable reactive P (FRP) from the water column and also effectively intercepted FRP released from bottom sediments until the advent of a major unseasonal flood event. A shift from potential N-limitation to potential P-limitation also occurred in surface waters. In the absence of other factors, the reduction in FRP was likely to be sufficient to induce actual nutrient limitation of phytoplankton growth. The outcomes of this experiment underpins the concept that, where possible in the short-term, in managing eutrophication the focus should not be on the limiting nutrient under eutrophic conditions (here N), but the one that can be made limiting most rapidly and cost-effectively (P).

Highlights

Application of lanthanum-modified bentonite (LMB) resulted in rapid P reduction

Phosphorus generated from bottom sediments effectively intercepted

Application of LMB may induce P-limitation with respect to algal growth

Keywords

nutrient limitation, lanthanum-modified bentonite

1. Introduction

The interception of the nutrients phosphorus (P), nitrogen (N), and silicon (Si) derived from bottom sediments (e.g. Spears et al., 2008; Arai et al., 2012; Anthony and Lewis, 2012, Zhu et al, 2012) concurrent with, or even long after the reduction of external nutrient loading, constitutes a major on-going challenge in the management of eutrophic aquatic systems. In the quest to better manage internal loading of nutrients in freshwater aquatic systems, novel P-adsorbent materials such as lanthanum-modified bentonite (LMB) have been developed (Douglas et al., 1999; Douglas patent, Douglas et al., 2004; Robb et al., 2003).

Since its development and commercialisation, LMB has been applied to over 200 aquatic systems internationally. Varying degrees of success have been achieved related to the efficient manufacture and application of the LMB, calculation of effective dose rates, and hence longevity (Meis et al., 2013), and confounding effects due to factors such as on-going external nutrient inputs (Lürling and Van Oosterhaut, 2012; Copetti et al, this issue).

One of the key questions still to be addressed at the field scale, to date, is whether P-limitation of the phytoplankton is created or enhanced following LMB application? This type of independent assessment relies primarily on two factors, that of changes in the relative molar ratios of the three key nutrients, N, P and Si and also the absolute dissolved concentrations of these nutrients that occur as a result of the application of LMB (e.g. Justic et al, 1995a, b). While phytoplankton nutrient limitation bioassays may also address the question of potential nutrient limitation, and are considered a powerful adjunct to the approach presented here, they are generally time consuming and expensive and may also constitute an imperfect assessment tool. Alternatively, the use of nutrient ratios constitutes a rapid assessment tool with higher frequency detection and analysis leading to the generation of close to real-time data over large spatial scales. In an attempt to better understand the effects of the application of LMB on changes in potential for nutrient limitation in freshwater aquatic systems, we have re-examined the results of the first intensively monitored major trial of LMB that occurred in the Canning River in Western Australia in 2000 (Douglas et al., 2001). The methods applied here can be readily transferred to the analysis of changes in potential nutrient limitation in other freshwater aquatic systems where LMB or other P-absorptive material have been applied.

2. Methods

2.1. *Trial location*

The Canning River located in urban Perth, Western Australia, is seasonally impounded by the use of a removable weir to maintain water in its mid to upper sections (see Robb et al., 2003 for location). An upstream water supply reservoir and riparian water abstraction results in little to no flow upstream of the weir during the period of impoundment (October–May). Water depths for 2 km behind the weir generally range from 1 to 3 m and up to 5 m. The Canning River in the region of the LMB application is mainly fresh due to substantial freshwater inputs during winter. During summer water temperatures may reach 26 C at the bottom and 29 C at the surface. Thermal stratification leads to sustained hypoxic and sometimes anoxic conditions that may lead to remobilisation of a substantial nutrient inventory contained within the bottom sediments.

2.2. *Sampling and monitoring*

An extensive monitoring program was established for the LMB trial with water samples collected from surface and bottom waters for analysis of filterable reactive P (FRP), total nitrogen (TN), dissolved inorganic nitrogen (DIN = NO_x, + NH_3, where NO_x = NO_3 + NO_2), total P (TP), silicate (SiO_2-Si), dissolved organic carbon (DOC) and chlorophyll *a* concentrations. Analysis of samples were performed according to American Public Health Association Standards (APHA, 1998). Measurements of physical variables such as temperature, conductivity, pH and dissolved oxygen (DO) were taken with Hydrolab multi-probe sondes. Data on FRP, DIN and SiO_2-Si from the Canning River trial of LMB in 2000 is contained in Douglas et al, (2001) and is plotted as a time series over the 136 days of the trial.

2.3. Application of Lanthanum Modified Bentonite (LMB)

A total of 20 tonnes of LMB was applied on day 8 of the trial in early January 2000 as a slurry to the surface of the water column over a 400 m section of the Canning River and allowed to settle to form a thin reactive capping of a theoretical 1 mm in thickness on the bottom sediments. The LMB-treated section was separated from an upstream Control section using partially submerged canvas curtains. These curtains were designed primarily to restrict bottom water exchange between the sections while allowing boat access through a central portion submerged approximately 0.5m below the river surface. A second 5 tonne quantity of LMB was applied in late April 2000 (day 114). The LMB was applied in linear sections via spray heads mounted on a boom at the rear of the boat after dilution with Canning River water in a manifold to dilute to a *ca.* 10% w/w solids concentration. The LMB remained suspended in the water column between spray runs constituting a marker for subsequent runs which were overlapped by approximately 1m to allow for lateral dispersion of the LMB suspension between individual applications.

Only a narrow range of surface and bottom pH occurred in the Control surface (6.8-7.7) and bottom (6.6-7.5) and LMB-treated surface (6.9-7.9) and bottom (6.6-7.6) waters throughout the duration of the field trial. Following application of the LMB, pH varied by <0.1 to 0.3 pH units in the surface and bottom waters, respectively, relative to the Control section. Transient changes in Secchi depth from approximately 0.9 to 1.3 m in the Control section to approximately 0.2 to 0.8 m in the LMB-treated section occurred for 1-2 days following LMB application. Chlorophyll-a concentrations were similarly low in surface waters in both the

Control and LMB-treated sections, (range both 3 to 40 µg L^{-1}, mean 12 ± 8 and 12 ± 9 µg L^{-1} respectively) throughout the period of the trial.

2.4. Analysis of potential nutrient limitation

The analysis of potential nutrient limitation applied here are based on those developed by Justic et al., (1995 a, b) in a study of changes in potential nutrient limitation in the Adriatic Sea and Trommer et al., (2013) in a study of a North Atlantic coastal ecosystem. Briefly, dissolved nutrient (DIN, FRP, SiO_2-Si) data have been converted to molar ratios and plotted in binary diagrams separated into quadrants using lines of nutrient ratios based on the Redfield ratio (C:N:Si:P = 106:16:15:1). A quadrant signifying a potential for nutrient limitation has been designated using P, N or Si.

3. Results

3.1.Canning River hydrology

The LMB trial was characterised by the occurrence of unseasonal rainfall and resultant increased river flow soon after application on day 8 (Figure 1). This unseasonal rainfall and flow fifteen days into the trial and only eight days after LMB application introduced an added complexity into the trial monitoring. On this basis, the trial was divided up into five sections: Pre-LMB application (days 1 to 7), Post-LMB application (days 8 to 16), Flood flow (days 17 to 48), Post flood (days 49 to 112) and Flow resumes (days 113 to 139). These sections are depicted in Figure 1 and are used in the analysis and discussion of potential nutrient limitation.

3.2.Filterable reactive P concentrations

Average concentrations of FRP in the bottom waters throughout the trial ranged from below detection limits (<0.005 mg L^{-1}) to maxima of *ca.* 0.1 mg L^{-1} in the LMB sections. In the Control section bottom water FRP concentrations ranged from 0.02 to 0.2 mg L^{-1} (Figure 2a).

In the eight days immediately prior to the application of LMB, average FRP concentrations in bottom waters at each section were approximately 0.05 mg L^{-1}. Upon the application of LMB on day 8, average bottom water FRP concentrations declined to below detection limits in all sections (Figure 2a).

With the onset of increased flow after rainfall on day 18 average bottom water FRP concentrations increased with the greatest increase in the Control section. After the main flow on day 25 and during the subsequent period of elevated flow, FRP concentrations in the LMB-treated section intermittently exceeded that of the Control section. After day 53, bottom water FRP concentrations in the LMB-treated section also remained at or below that of the Control section until the advent of three substantial rainfall/flow events (peak flow on days 115, 123 and 136) late in the trial. These flow events resulted in displacement of water in the LMB-treated section by water from the Control section further upstream.

Average FRP concentrations in surface waters displayed a similar temporal pattern and concentration range to that of the bottom waters (Figure 2a). The only substantial difference between the surface and bottom waters was the simultaneous, large increase in average FRP concentrations in all sections during the small flood event that commenced on day 15, one day after the completion of the LMB application. Average FRP concentrations in the surface waters ranged from below detection limits in the LMB-treated sections to maxima of *ca.* 0.16 mg L^{-1} in the LMB-treated section and between *ca.* 0.01 and 0.17 mg L^{-1} in the Control section. All surface water FRP maxima occurred simultaneously on day 18 during a higher flow event.

3.3. Dissolved Inorganic Nitrogen (DIN = NH_3 + NO_x): Dissolved NH_3 concentrations

Average surface water NH_3 concentrations ranged between *ca.* 0.0 - 0.5 mg L^{-1} over the period of the Canning River trial (Figure 2b). The highest average surface water concentrations occurred in the LMB-treated section during the period of application of the LMB. Thereafter surface water concentrations were similar between the LMB-treated and Control sections and were generally in the range of 0.05-0.1 mg L^{-1}. These periods of lower NH_3 concentrations in the surface waters were, however, punctuated by higher NH_3 concentrations of *ca.* 0.10-0.15 mg L^{-1} which had a close temporal relationship to periods of rainfall/increased flow and low dissolved oxygen concentrations in the trial area.

Average bottom water NH_3 concentrations were in general approximately two to three times higher than average surface water concentrations (Figure 2b). Average NH_3 concentrations in the LMB-treated section attained a maximum concentration of *ca.* 1.1 mg L^{-1} on day 24 before rapidly declining to average concentrations below 0.2 mg L^{-1} (Figure 2b).

As in the surface waters, high average bottom water NH_3 concentrations were in general associated either with periods of low DO concentrations and/or periods of rainfall/increased flow. Short periods of increased NH_3 concentration in the LMB-treated section corresponded to either a sharp decline in DO concentration (*e.g.* day 73) and/or periods of increased flow later in the field trial. Furthermore, the high NH_3 concentrations also corresponded to the period of initially higher bottom water salinity which was present prior to the commencement of the trial and continued until the first rainfall/flow event.

3.4. Dissolved Inorganic Nitrogen (DIN = NH_3 + NO_x): Oxidised nitrogen (NO_x = NO_3-N + NO_2-N)

Average concentrations of oxidised nitrogen (NO_x) displayed similar patterns in both surface and bottom waters, although maximum concentrations in surface waters were generally 2-3 times higher than in bottom waters (Figure 2b). Prior to and immediately after the application of the LMB there was little change in average NO_x concentration relative to the Control section with all average concentrations low (<0.02 mg L^{-1}). During the flow events with maxima on day 19 and 25, NO_x concentrations increased to approximately 0.5 mg L^{-1} (Figure 2b).

After the major flow event which peaked on day 25, average NO_x concentrations remained low until a major increase in average concentration on day 101 in the LMB-treated section relative to the Control section which only increased marginally. In surface waters, the average concentration was *ca.* 0.45 mg L^{-1} in the LMB-treated section (Figure 2b). Correspondingly, a similar pattern of average NO_x concentrations occurred in bottom waters, albeit higher than the surface waters with maximum concentrations of *ca.* 1.6 mg L^{-1} in the LMB-treated section while NO_x concentration in the Control section were lower (*ca.* 0.05 mg L^{-1}, Figure 2b). These increases in average NO_x concentrations on day 101 were not temporally related to increases in flow as in earlier periods of high NO_x concentration. There were substantial corresponding increases, however, in DO concentrations in the LMB-treated section relative to the Control section during this period (Figure 2b).

3.5. Dissolved silica

Average surface water concentrations of SiO_2-Si declined dramatically in the period immediately prior to the application of LMB from *ca.* 4.0-7.0 mg L^{-1} to *ca.* 2.0-2.5 mg L^{-1} (Figure 2c). In surface waters immediately after the application of the LMB there were similar SiO_2-Si concentrations between the LMB-treated and Control sections.

After the major flood event 25 days into the trial, average dissolved silica concentrations increased to *ca.* 5mg L^{-1} in all sections. Thereafter, dissolved silica concentrations decreased at all sections until *ca.* day 80 where there were two periods where average concentrations of dissolved silica were substantially higher in the Control section than in the LMB-treated sections. During a later period of the trial average dissolved silica concentrations in bottom waters at the Control section were approximately 40% higher than in the LMB-treated section.

Average bottom water concentrations of dissolved silica declined by a similar magnitude to surface waters (from *ca.* 4.5-6.5mg L^{-1} to 2.5-3.0 mg L^{-1}) in the period immediately prior to the application of the LMB (Figure, 2c). After application, however, average dissolved silica concentrations in the LMB-treated sections were substantially higher until the advent of the major flood event 25 days into the trial. Thereafter, average dissolved silica concentrations in bottom waters, with some minor exceptions generally declined over the remainder of the trial in a similar manner to surface waters with concentrations as low as 1.5-2.5 mg L^{-1} during the latter stages of the field trial (Figure 2c).

3.6. Changes in nutrient ratios following LMB application

A summary of dissolved molar nutrient ratios for DIN/FRP, Si/FRP and Si/DIN ($\mu \pm 1\sigma$) for Control surface and bottom waters and LMB-treated surface and bottom water sections for the Canning River trial are given in Table 1. In the period immediately prior to the application of LMB to the Canning River, both the Control and LMB-treated sections show similar average molar nutrient ratios and standard deviations in surface and bottom waters.

Upon the application of LMB, average DIN.FRP molar ratios increase from 0.6 ± 0.2 to 141 ± 141 and 4 ± 3 to 298 ± 292 in surface and bottom waters respectively. The DIN/FRP ratios, however, remained similar in the Control surface and bottom waters. Large increases in the Si/FRP molar ratio in surface and bottom waters in the LMB treated section and a large increase in the Si/FRP molar ratio also occur in the LMB-treated bottom waters.

With the advent of increased flow on day 17, surface and bottom waters in both the Control and LMB-treated sections become similar again for the duration of increase flows until day 48 (Figure 1, Table 1) signifying complete displacement of water from both sections. In the

Post-flood interval from days 49 to 112, and albeit with some variation around the average, DIN/FRP molar ratios are higher in the surface (6 ± 8), but more notably in the bottom (16 ± 35) waters of the LMB-treated section relative to the Control section with similarly low DIN/FRP molar ratios of 2 ± 1 and 3 ± 1 in surface and bottom waters respectively. Upon resumption of flow in day 113 until the termination of the field trial on day 136, a wide range of average nutrient ratios and variability is evident.

4. Discussion

4.1. Key factors to consider in potential nutrient limitation.

Although a large, unseasonal flood event compromised the intended longevity of the LMB trial in the Canning River, considerable information on changes in nutrient concentrations and the potential for nutrient limitation of primary production and changes due to the application of LMB can be gleaned. In correctly interpreting the nutrient limitation status of the Canning River trial and changes induced by the application of LMB, however, two factors must be considered.

The first is the actual nutrient molar ratios which indicates the potential for a nutrient to become limiting. To this end, bivariate plots of nutrient molar ratios facilitate a broad overview of not only changes induced by the application of the LMB to the Canning River, but also the potential for shifts in potential nutrient limitation of phytoplankton in a dynamic environment that experienced unseasonal flow shortly after LMB application.

The second factor to consider is the absolute nutrient concentrations. Nutrient ratios, particularly those for N and P have been used to predict the prevalence of nuisance cyanobacteria, with a TN:TP of <13 favouring cyanobacteria (Smith, 1983). However, the resulting phytoplankton biomass and species composition will be quite different in a scenario with TN of 1 μg L^{-1} and TP 0.1μg L^{-1} and a scenario with 10 mg N L^{-1} and 1 mg P L^{-1}; both having equal N:P ratio of 10. This latter point becomes important where nutrient limitation may be indicated based on molar ratios, but where in practical terms prevailing nutrient concentrations may be sufficient to support the growth of substantial phytoplankton biomass until the supply of one or more nutrients is exhausted and effectively becomes limiting. On this basis, limiting nutrients concentrations of FRP < ~3 µg L^{-1} (0.1 µM), DIN < 14 µg L^{-1} (1.0 µM) and Si < 56 µg L^{-1} (2.0 µM) have been selected as documented in Justic et al (1995a, b) as indicative of likely nutrient limitation in the absence of other critical factors that may influence phytoplankton biomass or species composition such as light or micronutrient limitation. The complex interplay between absolute nutrient concentrations, nutrient species and ratios remains a subject of considerable research (e.g. Hecky and Kilham, 1988; Maberly et al., 2002; Kolzau et al., 2014).

4.2. Alteration of nutrient limitation status following LMB application

Prior to the application of LMB (Pre-LMB, Figure 3), neither potential P- or Si-limitation was indicated. In contrast, however, surface water nutrient ratios indicated the potential for N-limitation with samples occupying the N-limitation quadrant. However, N-limitation was not indicated for bottom waters. This difference in the potential for N-limitation in the bottom waters may reflect re-supply of DIN from internal loading (Figure 2b) in addition to the persistence of stratification.

Average DIN concentrations of 20 ± 4 µg L^{-1} and low DIN/FRP molar nutrient ratios in the surface waters indicate a likelihood of actual N-limitation prior to the application of the LMB. However, the presence of N-fixing cyanobacteria within the Canning River during spring and summer may mean that little N-limitation occurred for these phytoplankton species.

Immediately following the application of LMB, a major shift to potential P-limitation is indicated by a shift in nutrient ratios into the P-limitation quadrant for the majority of surface and all bottom waters (Figure 3) with substantial increases in DIN/FRP ratios in the LMB-treated section relative to the Control section (Table 1). Average FRP concentrations in the surface and bottom waters were reduced from 76 ± 10 µg L^{-1} to 7 µg L^{-1} ± 4 µg L^{-1} and 44 µg L^{-1} ± 3 µg L^{-1} to 6 µg L^{-1} ± 4 µg L^{-1}, respectively. This corresponds to a reduction of approximately 91% FRP for both the surface and bottom waters. These reductions substantially reduced the average FRP concentrations indicating the potential for actual P-limitation throughout the entire water column.

As a consequence of the application of LMB and the likelihood of P-limitation, there is a substantial shift away from potential N-limitation (Figure 3) that is augmented in bottom waters in particular by a substantial increase in DIN following the application of LMB (Figure 2b).

The potential for Si-limitation remained similar in both surface and bottom waters following the application of LMB. Concurrent shifts are apparent, however, in Si/FRP molar ratios which move to substantially higher ratios, often approaching an order of magnitude and a reduction in Si/DIN molar ratios which may decrease by a similar extent (Table 1). These changes reflect the decline in FRP and the increase in DIN concentrations, particularly in bottom waters, that were associated with this application of LMB.

4.3. Factors influencing a shift towards P-limitation following LMB application

With the onset of a major, unseasonal flood event commencing day 17 and defined as finishing on day 48 when flows returned to average spring/summer magnitude, complete displacement of the water column occurred within the LMB treated section. Hence, changes in the nutrient concentration and nutrient molar ratios reflected the composition of influx from the catchment upstream of the trial site. As might be expected, a range of FRP, DIN and Si concentrations and nutrient ratios were present corresponding to different catchment sources and dilution factors common over a hydrograph. Nonetheless, only a few samples reflected the potential for P-limitation, and none for DIN or Si limitation. In practice, however, high average FRP concentrations of 47 µg L^{-1} ± 42 µg L to 54 µg L ± 28 µg L in the surface and bottom waters during this period indicated little likelihood of actual P-limitation, while increased turbidity and reduced water temperatures would have reduced the likelihood of substantial phytoplankton biomass.

Upon the cessation of substantial flow and renaissance of quiescent conditions within the trial area, the observed nutrient ratios, particularly in the surface waters assumed a condition intermediate between those prior to and immediately after the application of the LMB. Similarly, data indicating the potential for N- and Si-limitation occupied similar areas of the nutrient limitation plots between pre- and post-LMB application conditions. Bottom waters, however, were generally similar to the nutrient status prior to the application of the LMB following the cessation of the high rainfall event. This status may reflect the resumption of stratification and the (partial) burial or physical displacement of the LMB during the flood event. This would allow an unmodified flux of FRP to emanate from the bottom sediments, possibly from recently (re)deposited sediment, similar to that of pre-LMB application conditions, re-setting the former nutrient flux status. Nonetheless, it is apparent that FRP concentrations remain lower than observed in the Control section of the Canning River trial (Figure 2a) from day 48 to 112 suggesting that the LMB although (partially) buried was capable of intercepting FRP release from bed sediments during this period.

With the resumption of flow on day 113 until the cessation of the trial on day 136, nutrient ratios displayed variability similar to that observed within the earlier, unseasonal, flood event again reflecting the diversity of nutrient inputs from the upper catchment. During this period, lower absolute nutrient concentrations reflect both the source and dilution of nutrient inputs as described above.

4.4. Wider implications of the Canning River results for the N versus P debate

The results presented in this study are also important in view of a vexed debate on how to manage eutrophication. The paradigm of P control as most effective in managing eutrophication (Golterman, 1975; Schindler et al., 2008; Schindler, 2012) has been challenged based on nutrient addition experiments showing that both N and P addition yield more phytoplankton biomass than single nutrient additions (e.g. Lewis and Wurtsbaugh, 2008; Xu et al., 2010; Lewis et al., 2011). In addition, several studies showed that N limitation is widespread in eutrophic waters, as was the case in Canning River prior to LMB addition, and this has led to the assumption that N should be controlled (e.g. Conley et al., 2009; Paerl and Otten, 2013; Glibert et al., 2014; Paerl et al., 2014). Based on the latter studies, recently the EPA produced a “facts sheet” stating that both N and P should be reduced to prevent eutrophication and the proliferation of harmful algal blooms (EPA, 2015). The dual limitation paradigm is also supported by other researchers (e.g. Paerl et al., 2001), particularly where excessive loading of both P and N occurs in eutrophic systems. However, as evidenced from this study some critical comments need to be made in relation to the assertion that N control is needed to manage eutrophication.

It has been claimed that “*in controlling excessive algal growth, it is important to know which element limits the expansion of algal populations when their growth stops because of nutrient depletion*” (Lewis et al., 2011). In the case of the Canning River this was N, but efficient methods for *in situ* immobilisation for N are generally not currently achievable in many systems or rates of in-situ denitrification may not be sufficient. In subsequent years in the Canning River, however, artificial oxygenation has been used in a coordinated approach to induce nitrification-denitrification to reduce water column DIN concurrently with other LMB applications whilst also maintaining oxygenated conditions less conducive to bottom sediment P release. Results over the past decade suggest that this combined approach may yield the best outcome in terms of reduced nutrients and phytoplankton biomass. Importantly, there are few, if any documented cases where N reduction, alone, has alleviated eutrophication in a freshwater ecosystem. In contrast, many cases have shown that reducing P, alone, can strongly reduce eutrophication effects including the occurrence of harmful algal blooms (Schindler, 2012).

With respect to our study, there are two important aspects to consider. First, when eutrophication symptoms appear, the ecosystem has already generally experienced years of ongoing nutrient loading and has changed in such a way that straightforward diversion of nutrient inflows will not result in rapid recovery, which may take decades to centuries (Sharpley et al., 2014). The legacy inventory of P in bottom sediments causes hysteresis and delay in recovery that make additional in-lake measures to manage sediment P release necessary to evoke rapid rehabilitation of eutrophic lakes and ponds (Cooke et al., 2005). Secondly, it is evident from Liebig’s law of the minimum that only one element needs to be controlled to reduce harmful algal blooms; not two. In theory, this could be any element, but in general, only P can be reduced effectively through formation of poorly to insoluble salts with aluminium, calcium, iron, lanthanum or other cations. This was postulated over 40 years ago: “*It is not important whether phosphate is currently the limiting factor or not, or even that it has ever been so; it is the only essential element that can easily be made to limit algal growth*” (Golterman, 1975). The call for dual N and P reduction is founded on an apparent misinterpretation of the necessity for all nutrients to be present in abundance to support an algal bloom, but the limitation of only one is necessary to manage and reduce eutrophication symptoms. The Canning River experiment evidently showed that a system under N-limitation, caused by relative enrichment in P, and suffering from persistent algal blooms, could be brought to P limitation effectively.

The current advice for dual N and P reductions (EPA, 2015), in practice, means merely an external load reduction. Controlling external inputs is crucial as is demonstrated from the rainfall load experienced in the Canning River experiment. However, the effective management of eutrophication can be achieved with combinations of catchment and in-situ system measures The application of solid phase P sorbents, such as the LMB, is not recommended in open systems with ongoing external nutrient loading, but seems suited for lakes and ponds with small, diffuse P loads and legacy inventory of labile P stored in the sediment (Copetti et al., this issue; Spears et al., this issue).

The Canning River LMB experiment indicates that, where possible, in managing eutrophication the focus should not be exclusively on the limiting nutrient under eutrophic conditions (here N), but the one that can be made limiting most rapidly and cost-effectively (P). This is particularly so in the short-term (e.g. a single year) where the reduction in P concentrations inducted by LMB application may be sufficient to substantially reduce phytoplankton biomass. Nevertheless, in the medium to longer term, dual N-P limitation should be implemented where practical and cost effective. These measures should be implemented such that the effects of the new catchment nutrient inputs, if not effectively managed, or the effects of in-situ nutrients derived via internal loading from bottom sediments, both of which are capable of supporting phytoplankton growth, are minimised.

5. Conclusions

Interpretation of nutrient ratios and concentrations in a trial of lanthanum-modified bentonite (LMB) in the Canning River, Western Australia has demonstrated that:

- the application of LMB can result in a rapid and effective removal of FRP from the water column and can effectively intercept and capture FRP released from bottom sediments;
- a shift from potential N-limitation to potential P-limitation occurred due to the application of LMB;
- following the application of LMB, a reduction in FRP within the treated section of the Canning River may have been sufficient to induce (in the absence of other limiting factors) actual nutrient limitation of phytoplankton growth.
- nutrient limitation diagrams constitute a simple and rapid method to interpret changes in the potential for nutrient limitation of phytoplankton after the application of P-absorbent materials.

6. Acknowledgements

G. Douglas gratefully acknowledges the support of both CSIRO and the Western Australia Department of Water in funding the research and development of lanthanum-modified bentonite. The excellent comments of two anonymous reviewers were incorporated into the manuscript.

7. References

Anthony, J.L., Lewis Jr, W.M. 2012. Low boundary layer response and temperature dependence of nitrogen and phosphorus releases from oxic sediments of an oligotrophic lakes. Aquatic Sci., 74, 611-617.

Arai, H., Fukushima, T, Komastu, K., 2012. Increase in silicon concentrations and release from suspended solids and bottom sediments in Lake Kasumigaura, Japan. Limnology 2012, 81-95.

Conley, D.J., Paerl, H.W., Howarth, R.W., Boesch, D.F., Seitzinger, S.P., Havens, K.E., Lancelot, C., Likens, G.E., 2009. Controlling eutrophication: Nitrogen and phosphorus. Science 323, 1014–1015.

Cooke, G.D., Welch, E.B., Peterson, S.A., Nichols, S.A., 2005. Restoration and management of lakes and reservoirs. CRC Press,Taylor & Francis Group, Boca Raton.

Copetti, D, Finsterle, K., Marziali, L., Stefani, F., Tartari, G., Douglas, G., Reitzel, K., Spears, B. M., Winfield, I. J., Crosa, G., D'Haese, P., Lürling. M., 2015. Eutrophication management in surface waters using lanthanum-modified bentonite: a review. Water Research (submitted).

Douglas, G.B., Adeney, J.A and Robb, M., 1999. A Novel Technique for Reducing Bioavailable Phosphorus. International Association Water Quality Conference on Diffuse Pollution 517-523.

Douglas, G.B., Robb, M.S., Coad, D.N., Ford, P.W., 2004. A Review of Solid Phase Adsorbents for the Removal of Phosphorous from Natural and Wastewaters. Phosphorous in Environmental Technology: Principles and Applications, E. Valsami-Jones, Editor. 2004, WA. p. 291-320.

Douglas, G. B. & J. A. Adeney, 2001. 2000 Canning River PhoslockTM trial. Confidential report prepared for Water and Rivers Commission. CSIRO Land and Water Report January, 2001, 75 pp.

EPA, U.S. Environmental Protection Agency. Preventing Eutrophication: Scientific Support for Dual Nutrient Criteria (EPA publication 820-S-15-001, 2015; http://www2.epa.gov/sites/production/files/documents/nandpfactsheet.pdf).

Glibert, P.M., Maranger, R., Sobota, D.J., Bouwman, L., 2014. The Haber Bosch–harmful algal bloom (HB–HAB) link. Environ. Res. Lett. 9, 105001.

Golterman, H.L., 1975. Physiological limnology (Developments in Water Science 2, Elsevier, Amsterdam-Oxford-New York, 1975), p. 385.

Hecky, R.E. and Kilham, P., 1988. Nutrient limitation of phytoplankton in freshwater and marine environments: A review of recent evidence on the effects of enrichment. Limnol. Oceangr., 33, 796-822.

Jeff, S., Hunter, K., Vandergucht, D., Hudson, J., 2012. Photochemical mineralisation of dissolved organic nitrogen to ammonia in prarie lakes. Hydrobiologia, 693, 71-80/

Johnson, Z.C., Warwick, J.J., Schumer, R., 2015. A numerical investigation of the potential impact of stream restoration on in-stream N removal. Ecol. Engineer., 83, 96-107.

Justic, D., Rabalais, N.N., Turner, R.E., Dortch, Q., 1995a. Changes in nutrient structure of river-dominated, coastal waters: stoichoimetric nutrient balance and its consequences. Estuarine, Coastal and Shelf Science 40, 339-356.

Justic, D., Rabalais, N.N., Turner, R.E., 1995b. Stoichoimetric nutrient balance and origin of coastal eutrophication. Marine Pollution Bulletin 30, 41-46.

Kolzau, S., Wiedner, C., Rucker, J., Kohler, J., Kohler, A., Dolman, A.M., 2014. Seasonal Patterns of Nitrogen and Phosphorus Limitation in Four German Lakes and the

Predictability of Limitation Status from Ambient Nutrient Concentrations. PLoS ONE, 9, e96065, doi:10.1371/journal.pone.0096065.

Lewis, Jr., W.M., Wurtsbaugh, W.A., 2008. Control of Lacustrine Phytoplankton by Nutrients: Erosion of the Phosphorus Paradigm. Internat. Rev. Hydrobiol. 93(4-5), 446–465.

Lewis, Jr., W.M., Wurtsbaugh, W.A., Paerl, H.W., 2011. Rationale for Control of Anthropogenic Nitrogen and Phosphorus to Reduce Eutrophication of Inland Waters. Environ. Sci. Technol. 45, 10300–10305.

Lürling, M., Van Oosterhout, F., 2012. Case study on the efficacy of a lanthanum-enriched clay (Phoslock®) in controlling eutrophication in Lake Het Groene Eiland (The Netherlands). Hydrobiologia, 710, 253-263.

Maberly, S.C., King, L., Dent, M.M., Jones, R.I., Gibson, C.E., 2002. Nutrient limitation of phytoplankton and periphyton growth in upland lakes. Freshwater Biology, 47, 2136-2152.

Meis, S., Spears, B.M., Maberly, S.C., Perkins, R.G., 2013. Assessing the mode of action of Phoslock® in the control of phosphorus release from the bed sediments in a shallow lake (Loch Flemington, UK). Wat. Res. 47, 4460-4473.

Paerl, H.W., Gardner, W.S., McCarthy, M.J., Peierls, B.L., Wilhelm, S.W., 2014. Algal blooms: Noteworthy nitrogen. Science 346, 175.

Paerl, H.W., Otten, T.G., 2013. Harmful Cyanobacterial Blooms: Causes, Consequences, and Controls. Microb. Ecol. 65, 995–1010.

Paerl, H.W., Xu, H., McCarthy, M.J., Zhu, G., Qin, B, Li., Y. and Gardner, W.S., 2011. Controlling harmful cyanobacterial blooms in a hypereutrophic lake (Lake Taihu, China): The need for a dual nutrient (N & P) management strategy. Water Research, 45, 1973-1983.

Robb, M., Greenop, B., Goss, Z., Douglas, G., Adeney, J., 2003. Application of Phoslock®, an innovative phosphorus binding clay, to two Western Australian waterways: preliminary findings. Hydrobiologia 494 (1-3), 237-243.

Schindler, D.W., 2012. The dilemma of controlling cultural eutrophication of lakes Proc. R. Soc. B 279, 4322–4333.

Schindler, D.W., Hecky, R.E., Findlay, D.L., Stainton, M.P., Parker, B.R., Paterson, M., Beaty, K.G., Lyng, M., Kasian, S.E.M., 2008. Eutrophication of lakes cannot be controlled by reducing nitrogen input: Results of a 37 year whole ecosystem experiment. Proc. Natl. Acad. Sci. U.S.A. 105, 11254–11258).

Sharpley, A., Jarvie, H.P., Buda, A., May, L., Spears, B.M., Kleinman, P., 2013. Phosphorus Legacy: Overcoming the Effects of Past Management Practices to Mitigate Future Water Quality Impairment. Journal of Environmental Quality. Vol. 42 No. 5, p. 1308-1326.

Spears, B.M., Carvalho, L., Perkins, R. and Paterson, D.M., 2008. Effects of light on sediment nutrient flux and water column nutrient stoichiometry in a shallow lake. Water Research 42, 977-986.

Spears, B.M., Mackay, E.B., Yasseri, S., Gunn, I.D.M., Waters, K.E., Andrews, C., Cole, S., de Ville, M., Kelly, A., Meis, S., Moore, A.L., Nürnberg, G., van Oosterhout, F. Pitt, J.-A., Madgwick, G., Woods, H.J., Lürling, M., this issue. Lake responses following lanthanum-modified bentonite (Phoslock®) application: a meta-analysis of water quality and aquatic macrophyte responses across 18 lakes. Water Research.

Trommer, G., Leynaert, A., Klein, C., Naegelen, A., Beker, B., 2013. Phytoplankton phosphorus limitation in a North Atlantic coastal ecosystem not predicted by nutrient load. Journal of Plankton Research 35(6), 1207-1219.

Xu, H., Paerl, H.W., Qin, B., Zhu, G., Gao, G., 2010. Nitrogen and phosphorus inputs control phytoplankton growth in eutrophic Lake Taihu, China. Limnol. Oceanogr., 55(1), 2010, 420–432.

Zhu, M.Y., Zhu, G.W., Zhao, L.L., Yao, X., Zhang, Y, Gao, G., Qin, B., 2012. Influence of algal bloom degradation on nutrient release at the sediment-water interface in Lake Taihu, China. Environ. Sci. Pollut. Res., 20, 1803-1811.

Table 1. Summary of nutrient molar ratios in control and LMB-treated sections of the Canning River trial.

Section/ratio	CS DIN/FRP	CS Si/FRP	CS Si/DIN	CB DIN/FRP	CB Si/FRP	CB Si/DIN
Pre-LMB	1.0 ± 0.3	108 ± 27	122 ± 54	4 ± 4	122 ± 40	56 ± 36
Post-LMB	2.2 ± 0.7	87 ± 12	42 ± 15	8 ± 10	93 ± 25	27 ± 21
Flood flow	10 ± 12	128 ± 70	36 ± 34	10 ± 10	83 ± 41	22 ± 28
Post flood	3 ± 1	104 ± 48	47 ± 27	2 ± 1	67 ± 28	33 ± 20
Flow resumes	19 ± 15	63 ± 93	5 ± 8	25 ± 22	143 ± 95	9 ± 6
Section/ratio	LMB S DIN/FRP	LMB S Si/FRP	LMB S Si/DIN	LMB B DIN/FRP	LMB B Si/FRP	LMB B Si/DIN
Pre-LMB	0.6 ± 0.2	60 ± 16	111 ± 55	4 ± 3	107 ± 30	35 ± 23
Post-LMB	141 ± 141	640 ± 360	12 ± 12	298 ± 292	824 ± 692	3 ± 1
Flood flow	10 ± 11	130 ± 64	31 ± 28	35 ± 36	132 ± 62	11 ± 20
Post flood	6 ± 8	117 ± 36	40 ± 25	16 ± 35	110 ± 34	29 ± 23
Flow resumes	21 ± 25	121 ± 55	33 ± 39	49 ± 53	119 ± 84	32 ± 47

CS = Control Surface

CB = Control Bottom

LMB S = Lanthanum-Modified Bentonite Surface

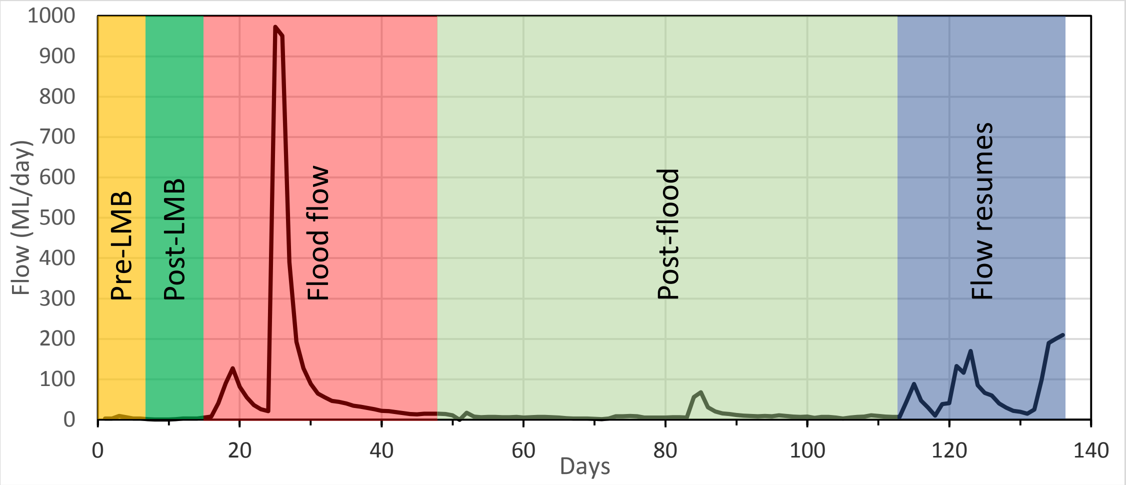
LMB B = Lanthanum-Modified Bentonite Bottom

Figure Captions

Figure 1. Flow (ML day^{-1}) throughout the Canning River LMB trial divided up into five sections: Pre-LMB application (days 1 to 7), Post-LMB application (days 8 to 16), Flood flow (days 17 to 48), Post flood (days 49 to 112) and Flow resumes (days 113 to 136).

Figure 2 (a) Filterable reactive P (FRP), (b) Dissolved inorganic nitrogen (DIN) and, (c) dissolved silica concentrations for surface and bottom waters in Control and LMB-treated sections.

Figure 3. Potential nutrient limitation ratio plots. for surface waters (above) and bottom waters (below) for the Canning River LMB trial. Colours as per Figure 1 for periods: Pre-LMB 🟨, Post-LMB 🟩, Flood flow 🟥, Post flood 🟩, Flow resumes 🟦. Symbol size signifies relative nutrient concentrations. The letter for P, N or Si define quadrants of potential nutrient limitation.


Flow (ML/day)
1000
900
800
700
600
500
400
300
200
100
0
Pre-LMB
Post-LMB
Flood flow
Post-flood
Flow resumes
0
20
40
60
80
100
120
140
Days

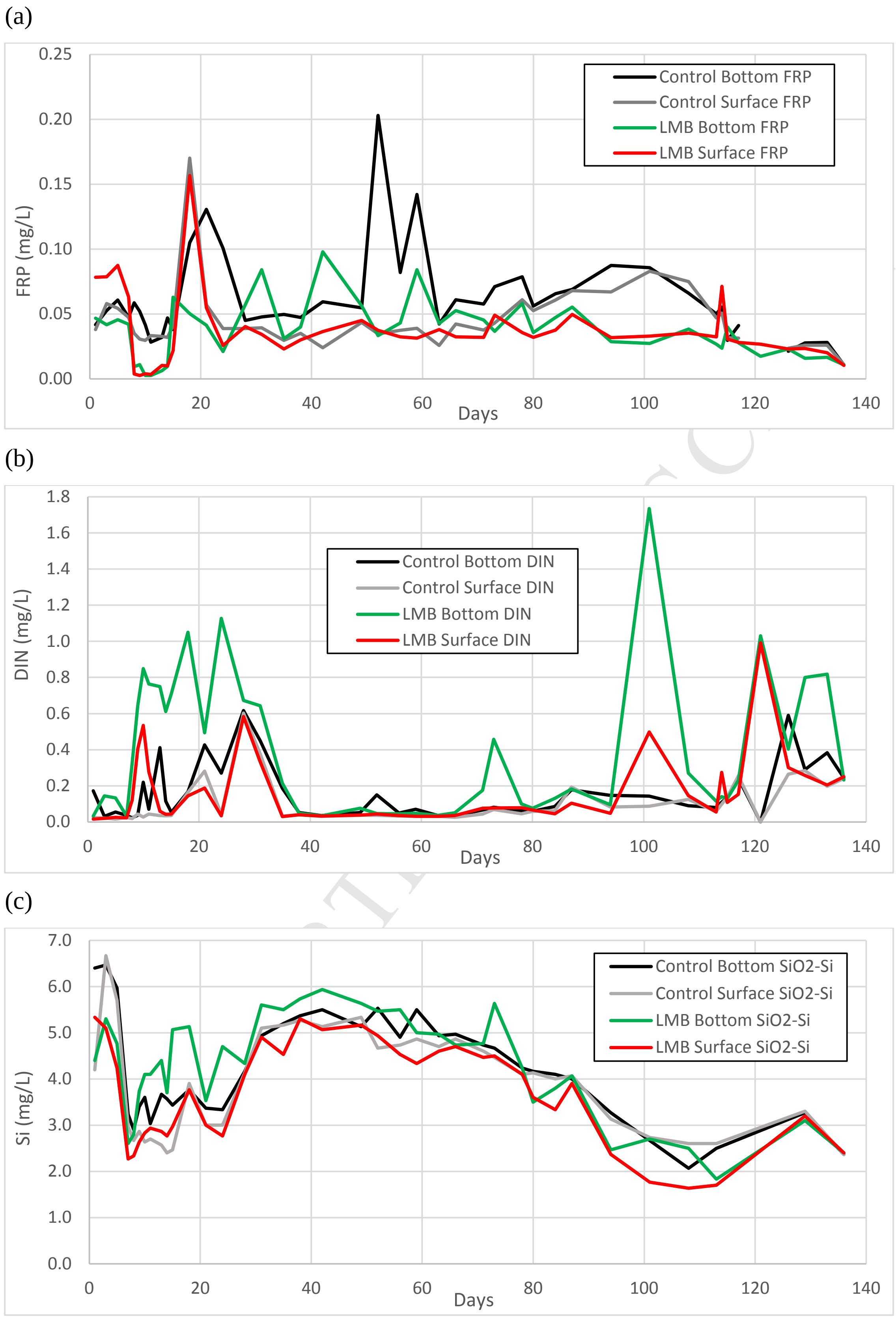
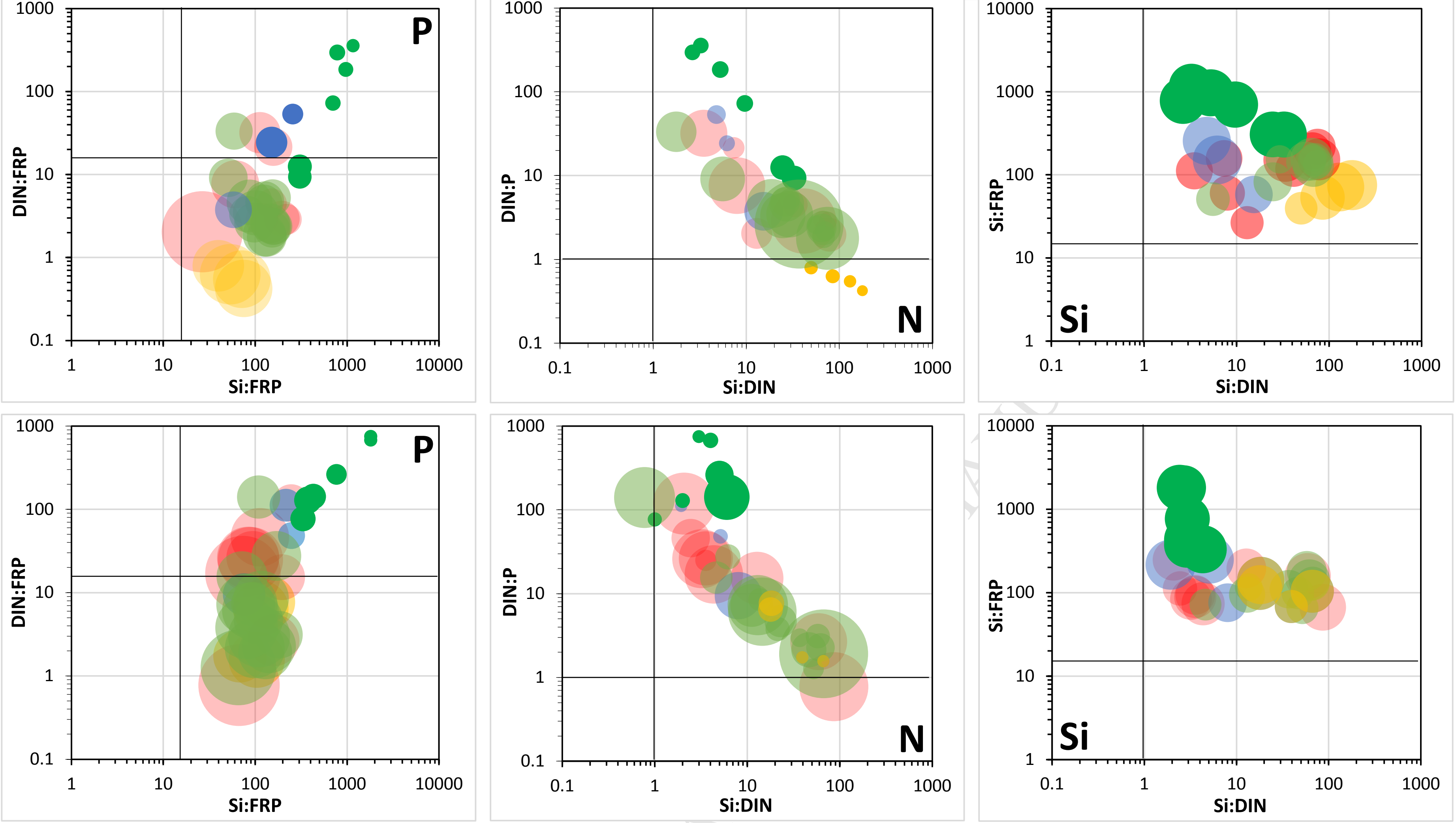


Figure 2 (a) Filterable reactive P (FRP), (b) Dissolved inorganic nitrogen (DIN) and, (c) dissolved silica concentrations for surface and bottom waters in Control and LMB-treated sections.


P
DIN:FRP
Si:FRP
1000
100
10
1
0.1
1
10
100
1000
10000
N
DIN:P
Si:DIN
0.1
1
10
100
1000
Si
Si:FRP
Si:DIN
10000
1000
100
10
1
P
DIN:FRP
Si:FRP
N
DIN:P
Si:DIN
Si
Si:FRP
Si:DIN

Highlights

Application of LMB resulted in rapid reduction of phosphorus

Phosphorus generated from bottom sediments effectively intercepted

Nutrient ratios used to assess changes in potential nutrient limitation