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OPINION

A novel model for cyanobacteria bloom formation: the critical role of anoxia and ferrous iron

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SUMMARY

1. A novel conceptual model linking anoxia, phosphorus (P), nitrogen (N), iron (Fe) and sulphate to the formation of noxious filamentous and colonial cyanobacteria blooms is presented that reconciles seemingly contradictory ideas about the roles of P, N and Fe in bloom formation.

2. The model has several critical concepts: (i) P regulates biomass and productivity in fresh waters until excessive loading renders a system N-limited or light-limited, but it is the availability of ferrous ions (Fe^{2+}) that regulates the ability of cyanobacteria to compete with its eukaryotic competitors; (ii) Fe^{2+} diffusing from anoxic sediments is a major Fe source for cyanobacteria, which acquire it by migrating downwards into Fe^{2+}-rich anoxic waters from oxygenated waters; and (iii) subsequent cyanobacterial siderophore production provides a supply of Fe^{3+} for reduction at cyanobacteria cell membranes that leads to very low Fe^{3+} concentrations in the mixing zone.

3. When light and temperature are physiologically suitable for cyanobacteria growth, bloom onset is regulated by the onset of internal Fe^{2+} loading which in turn is controlled by anoxia, reducible Fe content of surface sediments and sulphate reduction rate.

4. This conceptual model provides the basis for improving the success of approaches to eutrophication management because of its far-reaching explanatory power over the wide range of conditions where noxious cyanobacteria blooms have been observed.

Keywords: cyanobacteria, eutrophication, freshwaters, nuisance algae, nutrient cycling

Introduction

Freshwater cyanobacteria blooms of filamentous and 'matrix' colonial species (hereafter called cyanobacteria) remain a significant global problem in spite of decades of research and billions of dollars spent on nutrient removal to reduce primary productivity (Steffensen, 2008). We define the word 'bloom' here to mean dominance by cyanobacteria (i.e. >50% of the phytoplankton biomass) regardless of whether surface accumulation occurs. Specific problems of cyanobacteria blooms include the production of toxic or otherwise unpleasant taste and odour compounds, accumulation of surface scum and anoxia leading to fish kills, all of which are expensive to mitigate (Wilhelm *et al.*, 2006; Havens, 2008; Smith, Boyer & Zimba, 2008). We have learned a great deal about eutrophication in the last 50 years and achieved major successes in controlling, even reversing, eutrophication in many systems (Jeppesen *et al.*, 2005). Nevertheless, the problem persists and in some regions appears to be worsening (Carey, Weathers & Cottingham, 2008; Winter *et al.*, 2011; Michalak *et al.*, 2013).

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Management of affected waters would be greatly aided by improved scientific understanding of the underlying causative mechanisms for cyanobacteria bloom formation.

While total phosphorus (TP) and total nitrogen (TN) concentrations are positively correlated with the magnitude and duration of cyanobacteria blooms and are clearly very strong risk factors, the reason why large cyanobacteria are often rare in nutrient-poor (oligotrophic) waters, yet manage to displace their eukaryotic competitors in nutrient-rich (mesotrophic and eutrophic) waters (Watson, McCauley & Downing, 1997; Downing, Watson & McCauley, 2001), has not been clearly established. We cannot predict with any certainty when a cyanobacteria bloom will begin once temperatures are warm enough to support growth or the duration of a bloom except through empirical observations from previous years. Nor do we know why the problem is worsening in some mesotrophic systems.

Clearly, the predictive state of cyanobacteria science is unsatisfactory. This dissatisfaction may have contributed to the recent debate challenging the supremacy of the P paradigm in eutrophication management. Wurtsbaugh, Lewis, Paerl and their colleagues argue that N plays a major role alongside P in promoting cyanobacteria blooms and that both N and P should be controlled (Lewis & Wurtsbaugh, 2008; Lewis, Wurtsbaugh & Paerl, 2011; Paerl, Hall & Calandrino, 2011a; Paerl *et al.*, 2011b). This argument has been vigorously challenged in return by Schindler and his colleagues who claim that controlling N to control cyanobacteria will not work because N-fixation by cyanobacteria will compensate to a large extent for induced N shortages (Schindler *et al.*, 2008; Schindler & Hecky, 2009; Paterson *et al.*, 2011). The outcome of this on-going debate can be expected to influence the direction of billions of dollars in public expenditures to remedy nutrient loading.

The dominant line of research thinking for the last 50 years with respect to factors that control cyanobacteria bloom formation has focused mainly on P and N and, to a lesser extent, temperature and light, although other factors have, from time to time, been hypothesised, including molybdenum (Cole *et al.*, 1993) and iron (Fe; Wilhelm, 1995). Judging by the quantity of literature published in recent years, many scientists must feel that looking at P and N one more time from a different angle could shine enough light to solve the mystery of cyanobacteria dominance in nutrient-enriched waters. This has not happened and we are quite pessimistic that it will ever happen without new thinking. A reviewer reminded us of a quote attributed to Albert Einstein, 'The definition of insanity is doing the same thing over and over again and expecting different results'.

Our purpose here is to present a novel model that does *not* supplant the important roles of P and N as major macronutrients, but instead weaves additional ideas into older ones to create a novel and more comprehensive conceptual framework with much more explanatory power that spans the range of conditions where cyanobacteria blooms have been observed. Although in early stages of testing, the large amount of indirect and some direct evidence strongly suggests that the coupled biogeochemical/physiological model proposed here is worth presenting to a larger audience at this stage to expedite the full range of scientific scrutiny and testing necessary for further development.

What do we know with reasonable certainty?

Our state of knowledge of the causative factors of cyanobacteria blooms is incomplete. We know that recruitment of cyanobacteria *via* akinete germination and activation of overwintering vegetative cells in oxic sediments is light- and temperature-dependent (Head, Jones & Bailey-Watts, 1999a; Brunberg & Blomqvist, 2003) and that they need nutrients to support population growth. We know that freshwater pelagic cyanobacteria are ubiquitous, capable of dominating nutrient-rich waters globally (Paerl & Paul, 2012) in both soft and hardwaters (Marino *et al.*, 1990; Codd *et al.*, 2005; Paterson *et al.*, 2011) with one major exception. Pelagic forms are 'conspicuously absent' from phytoplankton communities of polar regions, while benthic forms are common (Rautio *et al.*, 2011; Vincent & Quesada, 2012).

We know that with sufficient P enrichment, cyanobacteria blooms are almost certain to occur and that there is a lesser risk of cyanobacteria dominating oligotrophic and mesotrophic waters (Downing *et al.*, 2001).

We know that N-fixing cyanobacteria often dominate the phytoplankton community when N is limiting (Smith, 1983; Havens *et al.*, 2003), but we do not know why non-N-fixing cyanobacteria such as *Microcystis* dominate nutrient-rich waters when N availability is sufficient (Xu *et al.*, 2010).

We know that as an oligotrophic lake becomes eutrophic, P regulates phytoplankton biomass and productivity (Hecky & Kilham, 1988; Watson *et al.*, 1997) until P loading becomes excessive relative to N loading. However, the only conclusion we can draw about the role of P in promoting cyanobacteria dominance is that high P concentrations are a strong risk factor for cyanobacteria bloom formation (Downing *et al.*, 2001) because the

causal mechanism between P and bloom formation has eluded us. In summary, we do not know how P or high N : P loading ratios specifically influence the outcome of competition between cyanobacteria and eukaryotic algae.

Conventional wisdom says that cyanobacteria populations are small in oligotrophic waters because they are poor competitors for P; that is, they have lower P transport affinities at low P than eukaryotic algae and are therefore excluded from the phytoplankton community (Tilman *et al.*, 1986) [affinity is defined as the slope of a transport rate versus P concentration curve at very low P, which is equivalent to the ratio of maximum transport rate/half saturation constant in Michaelis–Menten kinetics (Molot & Brown, 1986)]. This argument is consistent with resource-partitioning theory that states that when species are limited by the same nutrient, only one species can dominate the community, and it will be the one with the superior nutrient sequestering ability (Taylor & Williams, 1975; Titman, 1976; Sommer, 1993). Many eutrophication models employ this P acquisition concept by assuming the following: first, a low P transport affinity for cyanobacteria and a higher affinity for eukaryotes at low P concentrations to simulate observed eukaryotic-dominated communities typical of oligotrophic waters, and second, that cyanobacteria have higher uptake rates than eukaryotes at higher P concentrations to allow model cyanobacteria populations to dominate at higher P (e.g. Scavia, Lang & Kitchell, 1988). However, evidence from laboratory and field studies shows that cyanobacteria and picocyanobacteria (bacteria-sized cyanobacteria that are single celled or attached to each other without a mucilaginous sheath and which lack a buoyancy mechanism) have higher P affinities than their eukaryotic competitors (Molot & Brown, 1986; Wagner, Falkner & Falkner, 1995; Aubriot & Bonilla, 2012) and thus should dominate low P systems. Since this P affinity evidence is contrary to the low P affinity hypothesis, eutrophication phytoplankton models such as those just described are wrong, but the models persist in their current form because there are no better alternatives.

The critical role of ferrous iron

Asking why cyanobacteria are absent from oligotrophic systems is as important as asking how they dominate eutrophic systems: they are two sides of the same mechanism. Clearly, something other than P kinetics prevents cyanobacteria from dominating phytoplankton communities in oligotrophic waters, and this factor may explain both their absence from some systems and their abundance in others.

The model presented here has several critical concepts. We accept that P regulates biomass and productivity except in systems with very high concentrations relative to N (N is discussed below). Importantly, we also propose that the availability of ferrous iron, Fe^{2+}, regulates the ability of cyanobacteria to compete with eukaryotic competitors. Further, the scarcity of Fe^{2+} in P-limited oxygenated waters severely limits cyanobacteria growth unless supplemented by migrating down into Fe^{2+}-rich anoxic waters enriched by internal loading from anoxic surface sediments (Fig. 1).

Evidence for the ecological importance of Fe^{2+} to bloom formation was provided by Molot *et al.* (2010) who prevented a cyanobacteria bloom in P-enriched mesocosms in eutrophic Lake 227 in the Experimental Lakes Area by adding oxine which would have oxidised Fe^{2+} and chelated Fe^{3+}. The inhibitory effect of oxine was reversed in laboratory cultures in one of two chlorophytes by adding Fe, but growth of two oxine-exposed cyanobacteria could not be re-established with Fe additions. Their results suggest that cyanobacteria can transport Fe^{2+} but not Fe^{3+} across their cell membrane (see also Hopkinson & Morel, 2009; Kranzler *et al.*, 2011, 2013; Dang *et al.*, 2012).

Free Fe^{2+} is very soluble in anoxic waters but is present only in vanishingly small concentrations in circumneutral oxygenated waters because it is rapidly oxidised to Fe^{3+}. Fe^{3+} is the most common form of Fe in non-acidic oxygenated waters, but it is not very soluble. However, total dissolved Fe concentrations (typically defined as that which passes through a 0.2- or 0.45-μm filter) are usually much higher in fresh waters because of complexation of Fe^{3+} and Fe^{2+} to dissolved organic matter (DOM; Ghassemi & Christman, 1968; Curtis,

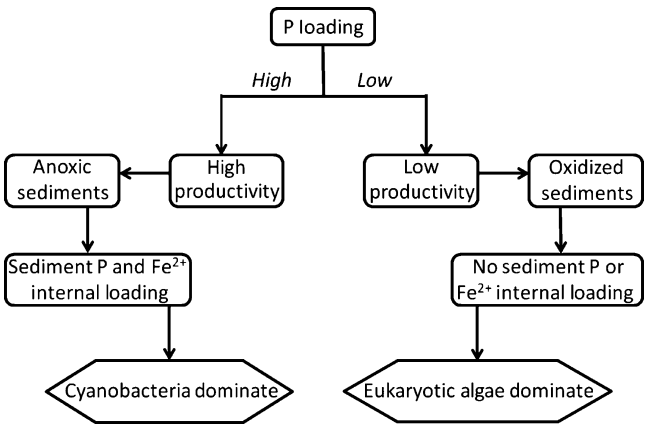

Fig. 1 Simplified conceptual diagram of the modified phosphorus eutrophication model of cyanobacteria bloom formation for systems lacking naturally anoxic surficial sediments. The only factor controlling Fe^{2+} production shown here is anoxia at the sediment water interface.

1993; Molot & Dillon, 2003). Therefore, most if not all of the Fe in the mixing layer is biologically unavailable to cyanobacteria without dissociation and reduction steps prior to transport across the inner membrane.

Cyanobacteria also have higher Fe requirements than their eukaryotic competitors with N-fixation imposing an even higher Fe demand (Table 1). This, coupled to an inability to transport Fe^{3+}, may induce Fe limitation in cyanobacteria in waters lacking a large Fe^{2+} pool. We hypothesise that internal Fe^{2+} loading in nutrient-rich waters prevents Fe limitation. Some eukaryotic algae appear able to transport Fe^{3+} (Molot *et al.*, 2010) and some employ phagotrophy as a mechanism for acquiring Fe (Maranger, Bird & Price, 1998), which, combined with a lower Fe demand, probably prevents Fe limitation in eukaryotic algae.

Sources of Fe^{2+}

Fe^{2+}-specific transport and high metabolic Fe requirements do not by themselves guarantee that cyanobacteria are Fe-limited. Fe limitation is more likely if the rate of supply of Fe^{2+} is low. In systems lacking internal Fe^{2+} loading from anoxic sediments, the major sources of Fe^{2+} are extracellular photoreduction of Fe^{+3} complexed to DOM (Zepp, Faust & Hoigne, 1992; Voelker, Morel & Sulzberger, 1997) and biological reduction of Fe^{+3} at the cell membrane (Kranzler *et al.*, 2011, 2013; Fig. 2). We postulate that rapid reoxidation by dissolved oxygen above pH 6 outside cells and in the periplasmic space decreases the availability of Fe^{2+} derived from photoreduction and biological reduction for transport across the cell membrane. This follows from a consideration of the high reactivity of Fe^{2+} with dissolved oxygen: 80% of Fe^{2+} is oxidised within 1 or 2 min at pH 7.6 in a solution in atmospheric equilibrium (Morgan & Lahav, 2007). Note that the dissolved oxygen concentration in equilibrium with the atmosphere during the summer is about 250 μM, whereas the concentration of Fe^{2+} in the periplasmic space between the outer and inner membrane is probably many orders of magnitude smaller at circumneutral pH.

Table 1 Summary of published Fe:C and Fe:P quotients (μmol mol^{-1}) for eukaryotic phytoplankton and N-fixing and non-N-fixing cyanobacteria, including picocyanobacteria, under a variety of growing conditions. Quotients for some heterotrophic pelagic bacteria are also shown. Data presented here are for low Fe when both low Fe and high Fe culture conditions are available. Fe concentrations may be overestimated because of potential Fe adsorption to cell walls (Tovar-Sanchez *et al.*, 2003; Tang & Morel, 2006)

Eukaryotes	Non-N-fixing	N-fixing	References
	0.15–0.24[1]	15.3[1]	Raven (1988)
	Trichodesmium 5.2	*Trichodesmium* 13.5	Kusta, Sañudo-Wilhemy & Carpenter (2003)
	Crocosphaera: 0.76–6.5 Mean 16.7 ± 18.0 *Trichodesmium* culture: 14.7 & 138.2 Mean 76.5	*Crocosphaera*: 7.3–96.7 Mean 36.2 ± 28.7 *Trichodesmium* culture: 12.4–176.7 Mean 91.4 ± 65.4 *Trichodesmium* field: 13.8–85.9 Mean 66.1 ± 39.0	Tuit, Waterbury & Ravizza (2004)
		Trichodesmium 13 (total Fe) 3.1 (Ti washed)	Berman-Frank *et al.* (2001)
		Trichodesmium 27 *Anabaena* 0.4 *Cyanothece* 0.08	Berman-Frank *et al.* (2007)
Thalassiosira 3–7			Sunda, Swift & Huntsman (1991)
Thalassiosira 0.65–14			Maldonado & Price (1996)
Thalassiosira 6–12			Price (2005)
Marine field phytoplankton 4.4 ± 0.8	Heterotrophic marine bacteria 9.1 ± 1.5		Tortell, Maldonado & Price (1996)
Marine field phytoplankton 3.7 ± 2.3	Cyanobacteria N-fixing capability not stated 19 Heterotrophic bacteria 6.65 ± 2.5		Tortell *et al.* (1999)
Thalassiosira 8–11		*Trichodesmium* 11–28	Glass, Wolfe-Simon & Anbar (2009)
Fe : P ratio: 10^{-34}–10^{-4} oceanic $10^{-3.1}$–10^{-2} coastal	Fe : P ratio: $10^{-2.7}$–$10^{-1.4}$ picocyanobacteria *Synechococcus*		Brand (1991)

[1]Dry weight converted to C by assuming 50% of dry weight was C.

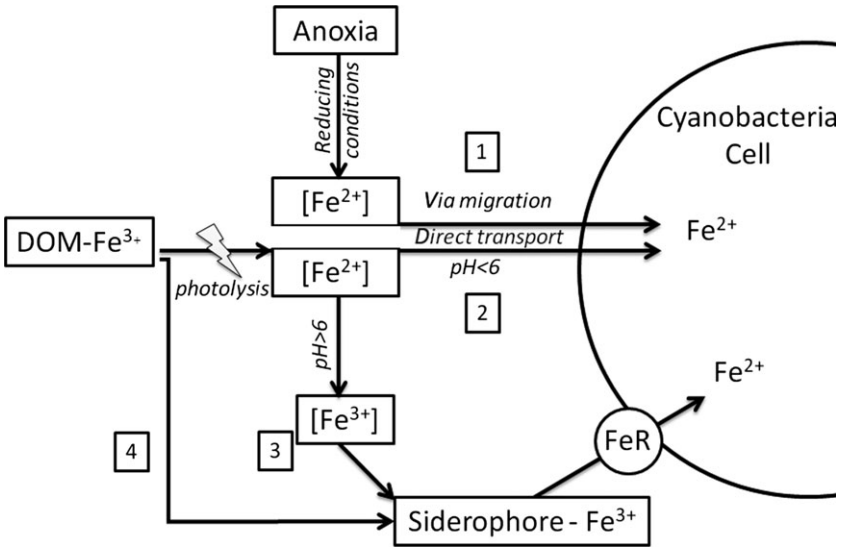

Fig. 2 The processes that promote Fe delivery to cyanobacteria and thereby promote cyanobacteria dominance in lakes. (1) Anoxia: systems with anoxic sediments will experience Fe^{2+} flux into anoxic waters. Migrating cyanobacteria can acquire Fe^{2+} for direct transport into cells. (2) Photoreduction: DOM-Fe^{3+} can be photo-reduced, giving rise to Fe^{2+} that is available for direct Fe^{2+} transport into phytoplankton cells, but the transport rate is pH dependent. Acidity affects rates of abiotic oxidation by dissolved O_2 and at pH <6 Fe re-oxidation may be low enough to give rise to a pool of transportable Fe^{2+}. At higher pH, much of it is probably re-oxidised before transport. (3) and (4) Fe-scavenging (or acquisition) system: siderophores are produced by cyanobacteria that can (3) bind free soluble Fe^{3+} and (4) cleave Fe^{3+} from DOM complexes. Scavenged Fe^{3+} is then delivered to the cell membrane, creating a pool of Fe only accessible by cyanobacteria. Fe^{3+} is reduced by the Fe reducing system (FeR) before transport across the inner membrane. The Fe^{2+} pool is shown as two separate pools – in anoxic waters (internal loading) and in the mixing layer (photo-reduction).

Overcoming Fe limitation requires a large source of Fe^{2+} that we suggest can be supplied by internally loaded Fe^{2+} from anoxic sediments; that is, Fe^{2+} diffusing upwards from microbial reduction of Fe^{3+} oxyhydroxides (Cook, 1984; Davison, 1993). Anoxic sediments are characteristic of nutrient-rich waters (Nürnberg, 2004), and indeed, Trimbee and Prepas (1988) argued 25 years ago that anoxia was a pre-condition for cyanobacteria blooms in eutrophic waters. Several studies have noted that warm temperatures and stable water columns promote cyanobacteria blooms in eutrophic waters (Paerl, 1988; Zhang & Prepas, 1996), conditions that concurrently promote anoxia.

Fe^{2+} transported upward from anoxic sediments remains in reduced form until it reaches oxygenated waters where it is rapidly reoxidised to Fe^{3+}. Hence, to acquire internally loaded Fe^{2+} before reoxidation, cyanobacteria must migrate downwards into anoxic waters below the mixed layer. Migration velocities appear to be large enough to reach anoxic areas in many systems, but data are limited (Table 2). Migration downwards into anoxic waters has been observed (Camacho *et al.*, 1996; Camacho, Vicente & Miracle, 2000; Gervais *et al.*, 2003) as well as acquisition of P during migration (Head, Jones & Bailey-Watts, 1999b). *Aphanizomenon* has been observed migrating upwards in the anoxic hypolimnion of Lake 227 in the Experimental Lakes Area in northwestern Ontario below the metalimnion (Fig. 3). Maximum concentrations of upwardly migrating filaments were repeatedly measured at 6.5 m in this 10-m-deep lake (2.5 m below the metalimnion). While we do not know whether *Aphanizomenon* in Lake 227 acquires hypolimnetic Fe^{2+} or whether it uses anoxygenic photosynthesis, cyanobacteria do use the latter elsewhere (Garlick, Oren & Padan, 1977). However, $\delta^{15}N$ and $\delta^{13}C$ signatures in particulate organic matter at 6 and 8 m indicate both biological use of N and C fixation (J. Venkiteswaran & S. Schiff, unpubl. data) by cyanobacteria, sulfur bacteria or chemoautotrophs.

Acquiring Fe with siderophores

Siderophores are low molecular weight, high-affinity Fe^{3+} chelators produced by some fungi and bacteria, including cyanobacteria (Neilands, 1995; Hopkinson & Morel, 2009). Picocyanobacteria do not appear to produce siderophores, although some *Synechococcus* can (Kranzler *et al.*, 2013), but may have the ability to access siderophore-bound Fe^{3+} (Hopkinson & Morel, 2009). A reduction step to free the bound Fe^{3+} and transport it

Table 2 Summary of published cyanobacteria migration rates and distances

Notes	References
90% of *Microcystis* colonies in Vinkeveen Lake, Netherlands, were upwardly buoyant at 8 m. Most colonies found in shallower waters less than 5 m	Ibelings, Mur & Walsby (1991)
Cyanobacteria in Cauldshiels Loch, Scotland, found migrating upward at 11 m, just below thermocline but perhaps still in metalimnion. These colonies were found to transport P from hypolimnion to epilimnion	Head *et al.* (1999b)
Velocities of *Microcystis* colonies from surface of Lake Okaro, New Zealand, were measured in a graduated cylinder. Sinking velocities after 24 h of illumination averaged 52 ± 13 m day^{-1}, and rising velocities after 24 h of darkness averaged 58 m day^{-1}. These would likely differ in a more turbulent environment	Walsby & McAllister (1987)
Small individual filaments of *Oscillatoria agardhii* in Lake Gjersjoen, Norway, a lake with an anoxic hypolimnion, moved less than 10 cm day^{-1}, but when aggregated into larger colonies (~3 mm in diameter) had a rising rate of 24 m day^{-1} and a sinking rate of up to 89 m day^{-1}. The proportion of positively buoyant filaments increased with depth: at 10 m depth (3 m below the bottom of the metalimnion), 100% were positively buoyant, at 8.5 m depth, 85% of the filaments collected were positively buoyant, and at 4 m depth (top of the metalimnion), 39% were positively buoyant	Walsby, Utkilen & Johnsen (1983)

into the cell as Fe^{2+} is probably necessary (Boukhalfa & Crumbliss, 2002; Harrington & Crumbliss, 2009; Kranzler *et al.*, 2013).

Siderophores are designed to scavenge Fe^{3+} (but not Fe^{2+}) from the surrounding environment in Fe-limited conditions and increase the supply rate of Fe^{3+} to cells (Wilhelm & Trick, 1994). This strategy locks Fe^{3+} into siderophore-bound complexes that are unavailable to other algae that do not have a siderophore-Fe uptake system and may act to limit their population growth. Indeed, Sorichetti, Creed and Trick (2014a) found that siderophores lower 'free' (modelled) Fe^{3+} to extremely low concentrations. Siderophores do not appear to be responsible for initiating blooms but could be essential in maintaining them by limiting eukaryotic access to Fe (Murphy, Lean & Nalewajko, 1976). Siderophores may also help cyanobacteria survive through extended periods of low Fe^{2+} availability.

Factors regulating internal Fe^{2+} loading

Anoxia

The redox potential at the sediment/water interface must be low enough to facilitate microbial Fe reduction in surface sediments with diffusion of Fe^{2+} into overlying waters of stratified lakes or into the boundary layer above the sediment/water interface in shallow polymictic systems. A low redox potential requires both anoxia and nitrate depletion because aerobic and anaerobic respiration raise the redox potential to levels that prevent Fe reduction.

Reducible Fe content in sediments and sulphate concentrations

If Fe^{2+} availability is a major factor required for the onset of cyanobacterial dominance, then factors that control internal Fe^{2+} loading rates once anoxia develops are critical to bloom formation. An important factor controlling this Fe^{2+} supply is the reducible Fe content (assumed to be primarily Fe^{3+} oxyhydroxides) in surficial sediments and its rate of reduction under anoxic conditions. The reducible Fe content is typically controlled by the settling of particulate Fe to surface sediments and sediment diagenesis processes involving dissolution, diffusion and precipitation of Fe (Wersin *et al.*, 1991). Reducible Fe is redox sensitive and therefore may decline after anoxia begins if the reduction/dissolution rate exceeds the rate of new inputs.

The reducible Fe content can have a large range in fresh waters. Loh *et al.* (2013) reported a range from 0.22 to 78.0 μmoles Fe (g dry wgt)$^{-1}$ in three Canadian hardwater lakes, while the range was 2.9–123.7 μmoles Fe (g dry wgt)$^{-1}$ in five softwater lakes in central Ontario (Powe *et al.*, 2013).

A second factor is the competing mechanisms that remove Fe $^{2+}$ from sediment pore waters or the overlying water column. Fe^{2+} can be sequestered in ferrous phosphate or ferrous sulphides and carbonates or complexed to organic matter. Ferrous phosphate has been identified in freshwater sediments (Emerson & Widmer, 1978; Manning, Murphy & Prepas, 1991). While the extent to which its formation can limit internal Fe^{2+} loading is unclear, its formation appears to be inhibited by sulphide (Katsev *et al.*, 2006). Ferrous carbonate is considered very rare in freshwater sediments and can only occur in anoxic environments with high pCO_2, low dissolved sulphide and a high Fe/Ca ratio to prevent calcite formation (Bernard & Symonds, 1989).

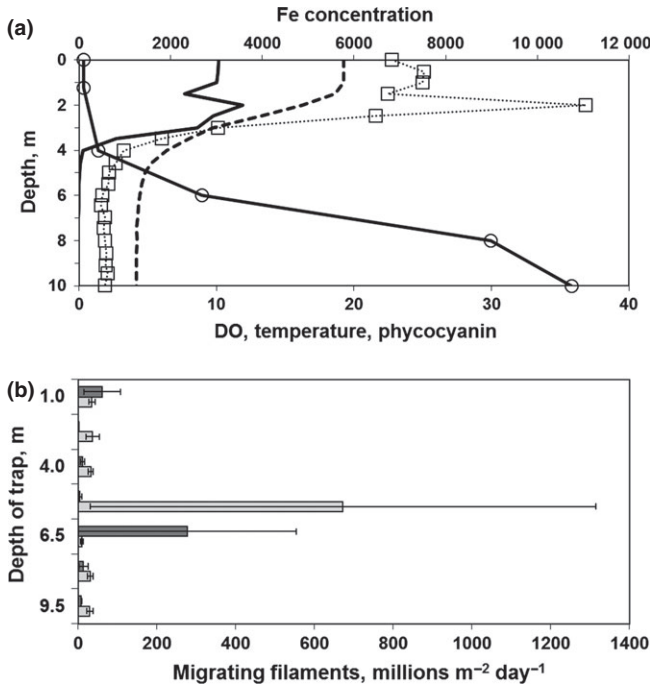

Fig. 3 Cyanobacteria migration in Lake 227. (a) Lower axis: dissolved oxygen (DO, mg L^{-1}; solid line), temperature (°C; dashed line) and phycocyanin concentration (relative fluorescence units; squares) and upper axis: total reactive Fe concentration (μg L^{-1}, circles) in Lake 227 on 28 June 2011. (b) Number of migrating *Aphanizomenon* filaments during 24 h period on 28–29 June 2011. Upward migration: dark bars, downward migration: light bars. Error bars are standard errors with n = 4. Data from by S. McCabe and L. Molot.

Sulphate reduction to sulphide can limit Fe^{2+} diffusion rates from anoxic sediments because of insoluble iron sulphide formation (Carignan & Tessier, 1988). Hence, lakes in which the sulphide formation rate is high enough to prevent Fe^{2+} diffusion should not experience a cyanobacteria bloom. The sulphate reduction rate is limited by the sulphate diffusion rate at concentrations less than 3 mM (which includes non-saline freshwater systems), but not at 28 mM typical of open ocean waters (Boudreau & Westrich, 1984). Hence, sulphate reduction rates will be greater in marine sediments than in freshwater sediments at a given organic matter deposition rate. Indirect evidence for the influence of sulphate reduction rate on internal Fe^{2+} loading comes from marine sediments, which have significantly higher internal soluble P loading than freshwater systems, probably because of a much higher formation rate of iron sulphide (Caraco, Cole & Likens, 1990; Blomqvist, Gunnars & Elmgren, 2004). A high rate of iron sulphide formation limits formation of insoluble Fe phosphate (because of the sulphide's higher solubility product), in turn permitting higher internal P loading. In a study of saline lakes in Alberta, cyanobacteria were absent from the most saline (65 mM), which was also hypereutrophic, but present in others with less sulphate (1.7–23 mM; Marino *et al.*, 1990). However, significant Fe^{2+} removal as ferrous carbonate cannot be ruled out because of the high lake pH (9.6).

There is little quantitative information on relationships between sulphate concentration, reducible Fe content and internal Fe^{2+} loading. Loh *et al.* (2013) explored empirical relationships between Fe release rate, sediment Fe fractions and sulphate concentration in batch incubations of lake sediment cores, but these relationships should be treated with caution because sulphate rapidly disappeared in the first few days due to sulphate reduction. It could be informative to consider the ratio of reducible Fe to sulphate concentration in overlying water, *R*, as a potential indicator of cyanobacteria bloom formation in fresh waters when the sediment/water interface becomes anoxic. High *R* is an indication of Fe^{2+} internal loading and could be associated with bloom situations, whereas no internal loading or cyanobacteria dominance should occur low at *R*. The range of *R* in eight Canadian lakes discussed above, all of which have experienced cyanobacteria dominance or near dominance at certain times of the year, was 3–1709 μmoles Fe (g dry wgt)$^{-1}$ mM^{-1} sulphate. We note that cyanobacteria were dominant when *R* exceeded 8. In cyanobacteria-dominated Lake 227, epilimnetic sulphate concentrations are very low (<0.03 mM) and the reducible Fe content, while not known, is probably very high because hypolimnetic dissolved Fe concentrations are very high (>15 μM at the beginning of the 2006 bloom 2 m below the metalimnetic/hypolimnetic boundary; Molot *et al.*, 2010). Hence, *R* is probably very high.

Sulphide-mediated Fe limitation may explain why N-fixation rates vary along a salinity gradient. If internal Fe^{2+} loading in anoxic systems declines with increasing salinity (sulphate generally increases with salinity), we should expect to find N-fixation rates changing along a salinity gradient with rates lowest in ocean waters, intermediate in brackish and higher in fresh waters because of increasing Fe limitation with salinity. Reported N-fixation ranges (mmoles N m^{-2} year^{-1}) are 0.14–6.4 for oceans, 0.9–129 for estuaries and 14–657 for eutrophic lakes (Howarth *et al.*, 1988). The ranges overlap to some extent, but the maximum reported rates for each type of system span two orders of magnitude (6.4–657 mmoles N m^{-2} year^{-1}), implying that Fe^{2+} may be less available in more saline waters. Some of the variability was probably caused by varying degrees of N deficit, residence time (Nixon *et al.*, 1996) and the many assumptions used to calculate annual rates from short-term measurements.

Nevertheless, the negative relationship between salinity (i.e. sulphate) and maximum N-fixation estimates for each type of ecosystem is consistent with the central role of Fe^{2+} hypothesised in this model.

There is very little information on reducible Fe levels in marine sediments. Reducible Fe in surface sediments at two shallow Danish coastal sites in the Kattegat region (Jensen & Thamdrup, 1993) was 95 μmoles (g dry wt)$^{-1}$, similar to the highest value of 124 μmoles (g dry wt)$^{-1}$ measured in the Canadian lakes. Assuming an open ocean sulphate concentration of 28 mM, *R* for these Danish sites was 3.4 μmoles Fe (g dry wgt)$^{-1}$ mM^{-1} sulphate, a low value consistent with absence of blooms in the Canadian lakes. More information on reducible Fe content and sulphate concentrations in fresh waters, coastal regions and estuaries would be useful in testing the use of *R* as an indicator of conditions suitable for cyanobacteria dominance.

Two alternative explanations (but not mutually exclusive) involving the relationship between salinity/sulphate and N-fixation are as follows: (i) high sulphate concentrations may interfere with nitrogenase activity in brackish water cyanobacteria (Stal, Staal & Villbrandt, 1999), and (ii) increased water density associated with higher salinity may slow downward migration rates, thereby lengthening the time it takes to acquire Fe^{2+} although higher salinity should increase upward migration rates.

Basin morphometry and depth of anoxia affect Fe^{2+} availability and accessibility

Anoxic zones enriched with Fe^{2+} must be accessible to migrating cyanobacteria for blooms to occur. It is highly unlikely that marine sediments in ocean regions removed from coastal areas with restricted circulation or freshwater sediments in the deepest part of deep lakes meet this criterion because anoxic zones may be too deep; that is, too far below the mixing zone. However, coastal regions and lakes have shallow sediments located along the sides of their basins and, hence, internally loaded Fe^{2+} in inshore regions with anoxic surficial sediments could be accessible when mixing conditions permit.

Although sampling stations are typically located in the deepest part of inland lakes, inshore regions can play an important role. For example, Hamilton Harbour (at the western end of Lake Ontario) at the central station (24 m maximum depth) was completely anoxic below 18 m and had less than 1 mg L^{-1} O_2 below 15 m on 23 June 2010 (Fig. 4a). However, at an inshore site (12 m depth), anoxia occurred just above the sediment/water interface at 12 m and O_2 was less than 1 mg L^{-1} below 11 m. Thus, completely anoxic water was *c.* 6 m closer to the surface, and hypoxic water was 4 m closer to the surface at the inshore site compared with the centre of the Harbour. Clearly, the top of the anoxic layer in the hypolimnion was not strictly horizontal throughout the harbour as it appears to have curved upward inshore. Hence, an anoxic sediment/water interface is more likely to occur closer to the bottom of the metalimnion inshore than offshore, and Fe^{2+} produced in inshore regions could contribute to bloom formation when mixing conditions permit.

Cyanobacterial blooms are also observed in eutrophic polymictic systems even though bottom waters may not be anoxic. Polymictic systems do not thermally stratify for any great duration but have boundary layers at the sediment/water interface that could contain accessible Fe^{2+}. Internal P loading occurs in polymictic systems (Jensen & Andersen, 1992; Ramm & Scheps, 1997), suggesting that the sediment/water interface is anoxic at least periodically when winds are calm (Loewen, Ackerman & Hamblin, 2007; Bryant *et al*., 2010), perhaps developing at night when photosynthetic production of dissolved oxygen stops, and thus may contain Fe^{2+}. When winds are calm, the boundary layer thickness will increase (Bryant *et al*., 2010) and will be large enough for cyanobacteria to obtain nutrients should they migrate the short distance to the sediment/water interface. Cyanobacteria blooms in western and central Lake Erie appear to originate inshore in areas that have polymictic behaviour (shallow and not stratified, for example, Maumee Bay, Sandusky Bay; Millie *et al*., 2009).

Anoxia is not limited to eutrophic systems. In a study of five oligotrophic, softwater embayments with natural anoxia along the Georgian Bay (Great Lakes) coast in Ontario, Canada, cyanobacteria dominated three of the five and were 14–27% of the phytoplankton biomass in the other two embayments (Powe *et al*., 2013). Biomass was low and internal P loading did not occur in two of the embayments dominated by cyanobacteria. It was concluded that P was not a factor in determining cyanobacteria dominance in these systems. Notably, anoxia and internal Fe^{2+} loading coincided with or preceded dominance, consistent with the model proposed here. Clearly, oligotrophic waters are not immune to cyanobacteria dominance, and the critical concept of the role of Fe^{2+} apparently holds over a wide trophic range.

Timing of bloom formation

Once light and temperature become physiologically favourable for cyanobacteria growth, our model predicts

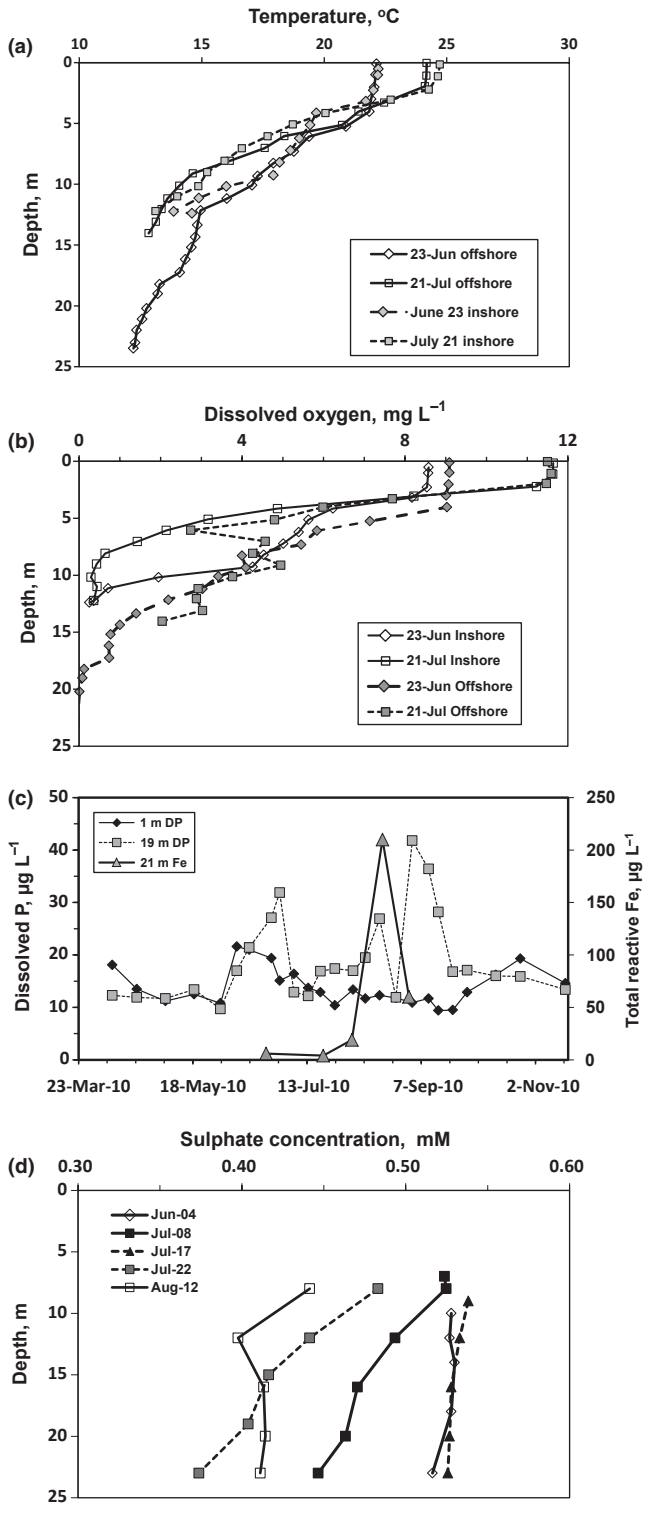

Fig. 4 Profiles in Hamilton Harbour: (a) temperature profiles at the deep (1001) and inshore (909) stations (note cooling between 23 June and 21 July 2010); (b) dissolved oxygen profiles at the deep and inshore stations in 2010; (c) dissolved P (0.45 µM filter) at 1 m and 19 m and total reactive Fe at 21 m at the deep station in 2010; (d) sulphate concentrations on four different dates in 2009 at the deep station. Data from S. Watson (Environment Canada).

that bloom onset is regulated by the onset of internal Fe loading, which in turn is controlled by the development of anoxia, reducible Fe content of surface sediments and sulphate reduction rate. These factors, presented in Fig. 5 as a decision tree, may explain variation in timing of bloom onset between years and among lakes. For example, cyanobacteria blooms begin in softwater Lake 227 in north-western Ontario in mid-June, *c.* 6 weeks after ice-out (Molot *et al.*, 2010) although biogeochemical conditions are optimal after ice-out in early May when sampling begins (the hypolimnion is anoxic, hypolimnetic Fe concentrations are very high (Molot *et al.*, 2010) and hypolimnetic sulphate concentrations are very low (<0.02 mM) in mid-May). Bloom onset appears to have coincided with warming of the top 2 m of the epilimnion to *c.* 15–20 °C.

In contrast, cyanobacteria blooms typically begin much later much further south in hardwater Hamilton Harbour (Lake Ontario), typically in mid-August several months after surface waters temperatures have increased above 15 °C. The delay in Hamilton Harbour may be related to a delay in internal Fe^{2+} loading. An anoxic episode in June 2010 was accompanied by internal P loading, but not by internal Fe loading or a cyanobacteria bloom (Fig. 4a,b). The June episode was interrupted by a seiche, following which anoxia was re-established in July and internal Fe loading was then observed in early August followed by a cyanobacteria bloom 2 weeks later. Sulphate was not measured in the Harbour in 2010, but concentrations typically range from 0.42 to 0.63 mM unless disturbed by a seiche which imports oxygenated, low sulphate hypolimnetic water from Lake Ontario (*c.* 0.27 mM sulphate; data from Environment Canada). Figure 4c illustrates this: in 2009, sulphate declined throughout the water column below 10 m between 4 June and 8 July, increased to *c.* 4 June levels by 17 July and then rapidly decreased again over the next 5 days. High rates of iron sulphide formation are consistent with high levels of acid extractable Fe found in surface sediments in the harbour (Loh *et al.*, 2013). It is not known whether the reducible Fe content increased as the summer progressed, but a combination of increasing reducible Fe and lower sulphate in late summer might have increased *R* to a level capable of initiating a bloom.

Is N important? Yes but…

Both P and N are important as macronutrients to all phytoplankton species, without which cell growth is impossible. Algal cells require more N than P [the

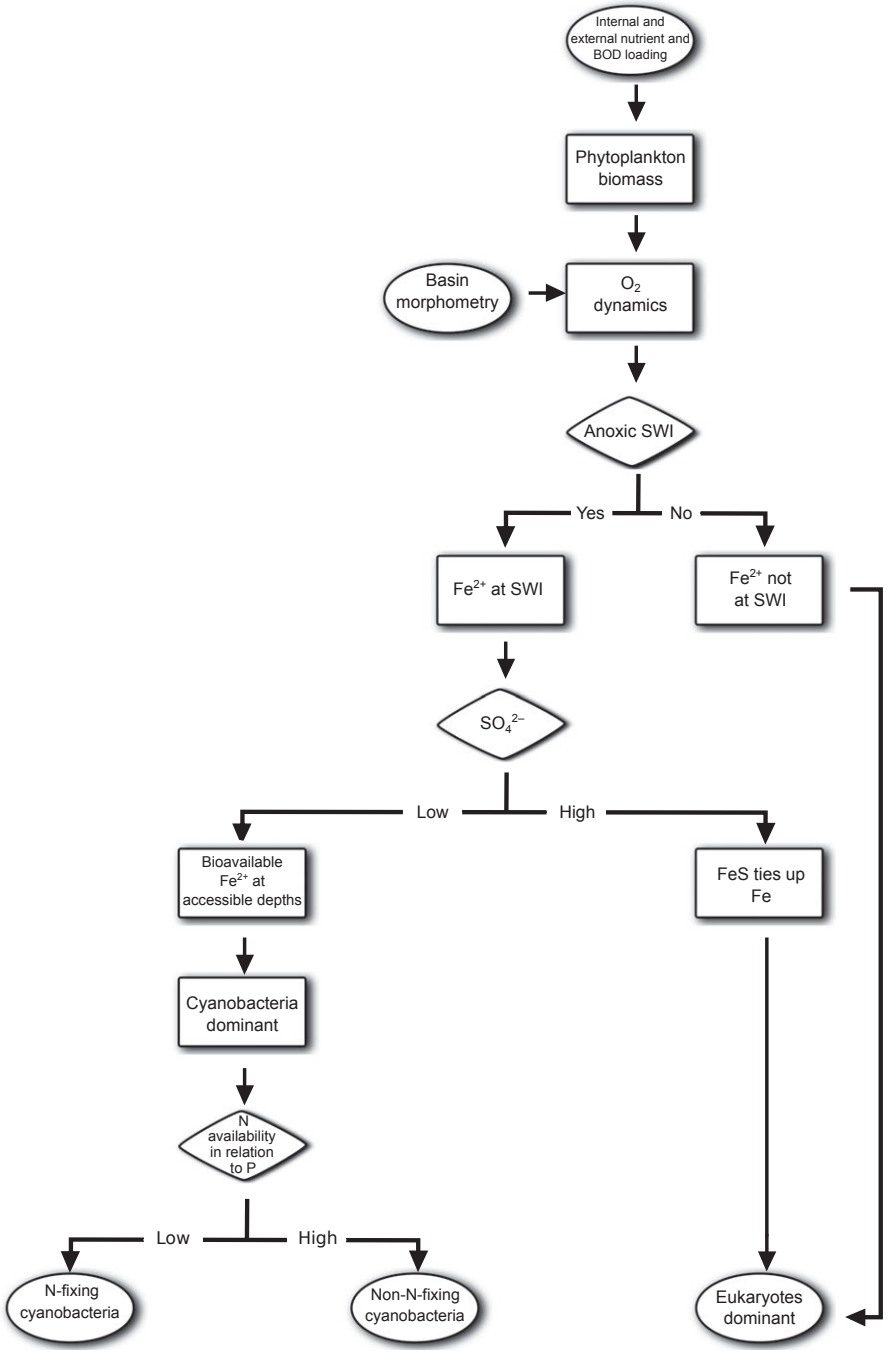

Fig. 5 Decision tree for biogeochemical processes promoting cyanobacteria bloom formation. Ovals represent the start and finishing points in the tree, rectangles are major processes and concentrations, and diamonds are critical decision points. The first critical junction at the top is whether or not anoxia occurs and if so, whether microbial reduction in Fe^{3+} to Fe^{2+} loading occurs. At the next critical junction, sulphate plays a role in determining internal Fe^{2+} loading and thus whether the phytoplankton is dominated by cyanobacteria or eukaryotic algae. BOD – biochemical oxygen demand; SWI – sediment/water interface.

stoichiometric molar N : P quotient is conventionally set at 16 : 1 (Redfield, Ketchum & Richards, 1963), and while the ratio varies considerably among species, it is always greater than 1 (Klausmeier *et al.*, 2004; Walve & Larsson, 2007)]. Nutrient inputs to culturally eutrophic lakes typically include both P and N although the N : P ratio of inputs varies such that productivity in eutrophic lakes is P-limited in some and N-limited in others. However, P management has been emphasised to reduce algal blooms for three reasons: (i) most oligotrophic freshwater systems are P-limited (Hecky, Campbell & Hendzel, 1993), (ii) cyanobacteria dominance of oligotrophic P-limited systems is (or has been) rare (Downing *et al.*, 2001), and (iii) it is easier and cheaper to remove P from waste water treatment plant effluent than N. Nevertheless, it has been argued in recent years that both P and N controls are needed to limit cyanobacteria biomass in eutrophic fresh waters rather than controlling P alone (Conley *et al.*, 2009; Paerl & Scott, 2010; Lewis *et al.*, 2011; Paerl *et al.*, 2011a and b).

The model presented here, however, suggests that implementing anthropogenic N controls to induce N-limitation either alone or concomitant with P controls will have limited impact on cyanobacteria *dominance* in fresh waters unless Fe^{2+} availability is greatly restricted by preventing anoxia at the sediment/water interface. If anoxia and internal Fe^{2+} loading are not prevented, N-limitation will favour N-fixing cyanobacteria that will fix N to compensate for the loss of anthropogenic N.

We note that large blooms of N-fixing *Aphanizomenon* comprising up to 90% of the phytoplankton biomass consistently occurred in Lake 227 throughout the 23 years after experimental N inputs ceased (Paterson *et al.*, 2011). The hypolimnion is anoxic shortly after ice-off, and the high rate of internal Fe loading provides the Fe^{2+} necessary to support a large, N-fixing population (Molot *et al.*, 2010). Heterocyst abundance has been increasing since 1990 when N additions stopped, perhaps in response to gradual loss of legacy N in sediments (Paterson *et al.*, 2011). These long-term results are consistent with the proposed central roles of anoxia and internal Fe^{2+} loading in promoting cyanobacteria dominance.

Studies have found low nitrate concentrations to be associated with cyanobacteria blooms (McQueen & Lean, 1987; Nürnberg, 2007) leading some to argue that the cause of bloom formation is that an inorganic N pool with high ammonia and low nitrate favours N acquisition by cyanobacteria, whereas the reverse favours N acquisition by eukaryotic algae (Blomqvist, Pettersson & Hyenstrand, 1994). However, there is a plausible alternative explanation for the correlation between cyanobacteria blooms and low nitrate: anoxia promotes denitrification and prevents nitrification, and hence, nitrate concentrations will be low (Keeney, Chen & Graetz, 1971), but it is the associated internal Fe^{2+} loading that is directly responsible for cyanobacteria dominance.

Picocyanobacteria

Our model explains why freshwater picocyanobacteria, with similar Fe requirements to larger non-N-fixing cyanobacteria, coexist in oligotrophic waters with eukaryotic algae. Freshwater picoplankton (which consists of bacteria-sized cyanobacteria and eukaryotic species) make up 0–90% of algal abundance in oligotrophic systems (Vörös *et al.*, 1998; Bell & Kalff, 2001; Callieri & Stockner, 2002; Callieri *et al.*, 2007). This observation raises the questions of what mechanism allows this co-existence to occur and what mechanism accounts for larger cyanobacteria dominating eutrophic systems rather than picocyanobacteria?

Resource-partitioning theory predicts that co-existence is possible under equilibrium conditions when two phytoplankton species are limited by different nutrients (Taylor & Williams, 1975; Titman, 1976; Sommer, 1993). Since studies show that eukaryotic phytoplankton are usually limited by P in oligotrophic waters, there are two nutrient-based explanations that may account for their co-existence with picocyanobacteria.

1. Both groups are P-limited. Although picocyanobacteria have higher P transport affinities than eukaryotic algae (Molot & Brown, 1986) and should dominate, higher grazing pressure on picocyanobacteria could lead to co-existence (Cavender-Bares *et al.*, 1999; Mann & Chisholm, 2000).

2. The two groups are limited by different nutrients: Fe limitation of picocyanobacteria and P-limitation of eukaryotes and thus co-existence is permitted according to resource-partitioning theory. Picocyanobacteria have higher Fe requirements than eukaryotic algae, leading to Fe limitation in apparently P-limited oligotrophic and mesotrophic systems (Twiss, Auclair & Charlton, 2000; McKay *et al.*, 2005), similar to some marine systems (Brand, 1991; Sunda & Huntsman, 1995; Maldonado & Price, 1999).

In either the P or dual P and Fe-limited scenarios, small species may occupy the cyanobacterial niche in oligotrophic waters because severe nutrient limitation favours small cells with high surface area/volume ratios (Smith & Kalff, 1983; Sunda & Huntsman, 1995). What remains to be explained is how larger cyanobacteria outcompete picocyanobacteria as nutrient enrichment increases. Perhaps the ability of larger cyanobacteria to migrate into anoxic waters to take advantage of a large Fe^{2+} pool gives them a competitive advantage over non-migratory picocyanobacteria. However, several supplemental mechanisms may also be involved: (i) selective grazing of picocyanobacteria may suppress the population, (ii) secretion of siderophores by larger cyanobacteria which picocyanobacteria may not be able to utilise may leave picocyanobacteria unable to obtain sufficient Fe for growth, and (iii) secretion of allelogenic compounds by larger cyanobacteria may impair growth of other phytoplankton (Keating, 1977, 1978). Evidence for either (2) or (3) comes from preliminary studies showing that nutrient-enriched filtrate from spent *Anabaena* cultures limits *Synechoccocus* growth, but the reverse does not occur (Fig. 6; Sorichetti *et al.*, 2014b).

Cyanobacteria dominance in acidified lakes

We hypothesised that rapid re-oxidation above pH 6 by dissolved oxygen outside cells and in the periplasmic

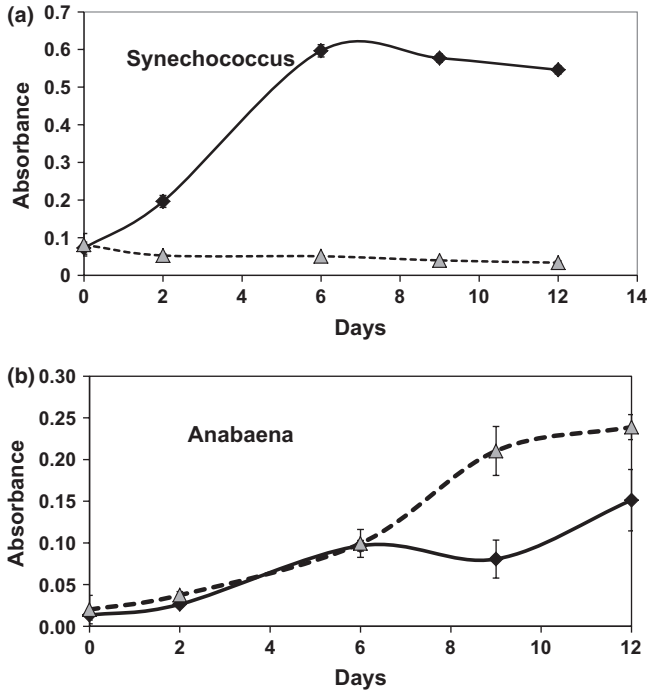

Fig. 6 Growth (mean absorbance at 672 nm ± standard error) of (a) *Synechococcus leopoliensis* (CPCC 102) in spent *Anabaena* sp. (CPCC 64) media filtrate and (b) growth of *Anabaena* in spent *Synechococcus* media compared to control cultures in synthetic media. Grey triangles – cultures in spent media; black diamonds – controls. All cultures were grown under continuous illumination at 24 °C in Bold 3M media with 0.05 μM Fe and 172 μM P. Spent media were amended with 0.05 μM Fe and 172 μM P before re-use. Error bars are standard errors with $n = 3$. Data from by S. McCabe and L. Molot.

space decreases the availability of Fe^{2+} derived from photoreduction and biological reduction for transport across the inner cell membrane (see *Sources of Fe^{2+}* section above). It follows that Fe^{2+} supply rates may be higher in acidic waters in systems lacking anoxic sediments because acidity inhibits rapid reoxidation of Fe^{2+} to Fe^{3+} by dissolved oxygen. For example, 80% of Fe^{2+} is abiotically oxidised within 1 or 2 min at pH 7.6 but takes more than 8 h at pH 5 at atmospheric equilibrium (Morgan & Lahav, 2007). There is indirect evidence in support of this because acid-tolerant cyanobacteria species such as *Rhabdoderma* and *Merismopedia* often dominate oligotrophic, atmospherically acidified lakes (Molot, Heintsch & Nicholls, 1990; Anderson, Blomqvist & Renberg, 1997).

Interestingly, reduction in sulphate concentrations as a result of SO_2 emission controls might increase the risk of cyanobacteria dominance in lakes with low reducible Fe content by significantly increasing internal Fe^{2+} loading (in effect, increasing R), particularly if climate change exacerbates the risk of late summer and autumn anoxia through longer ice-free and thermally stratified periods (Futter, 2003; Stainsby *et al.*, 2011).

Management relevance

Our model has significant potential to improve eutrophication management because it improves our ability to intervene judiciously.

Nutrient management guidelines

Current maximum acceptable P concentrations and their associated P loading guidelines (e.g. tonnes $year^{-1}$ for a given system) to prevent cyanobacteria blooms are empirical, based on past experience. For example, the maximum P concentration guideline in the Province of Ontario is 20 μg L^{-1} (Ontario Ministry of Environment & Energy, 1994). If P loading criteria are set to prevent cyanobacteria blooms, they should be set at levels that leave sediments oxidised to the greatest extent practicable to prevent internal Fe^{2+} loading. P criteria may need to be adjusted downward if anoxia at the sediment/water interface becomes more prevalent under a warmer climate.

Tertiary treatment

Our model suggests that use of iron-based coagulating agents to remove phosphate from waste water effluent should be reconsidered if the use of these compounds leads to a build-up of reducible Fe in sediments.

In-lake treatment

Our model suggests that in-lake chemical and aeration treatments to reduce the risk of cyanobacterial bloom formation should also be reconsidered. For example, would whole-lake treatment with aluminium or polyaluminium sulphate (Welch & Schrieve, 1994; Lewandowski, Schauser & Hupfer, 2003; Gibbs, Hickey & Özkundakci, 2011; Jancula & Maršálek, 2011) be more effective than, say, Fe^{3+}-chloride treatment? (Cooke *et al.*, 1993; Wisniewski, 1999) Aluminium hydroxide is not redox sensitive and will not release adsorbed P from anoxic sediments, while the additional sulphate could increase formation of ferrous sulphides and lower internal Fe loading, depending on background sulphate concentrations and the magnitude of the chemical treatment. In contrast, Fe^{3+}-chloride will increase the reducible Fe content in sediments, and, if anoxia is not controlled, reduction of the new Fe will release adsorbed P and Fe^{2+} into overlying waters, leading to

cyanobacteria dominance (Kleeberg, Herzog & Hupfer, 2013). Other redox-insensitive materials are also available for in-lake treatment (see, for example, Gibbs *et al.*, 2011).

Hypolimnetic aeration has had some success in mitigating cyanobacteria blooms (Prepas *et al.*, 1997). Hypolimnetic aerators could be designed to increase oxygen delivery to sediments to suppress internal loading as well as maintain minimum oxygen concentrations in overlying water (Singleton & Little, 2006). Alternatively, the upper part of the water column could be aerated (Hudnell *et al.*, 2010) if it can be shown that increased turbulence in the mixing zone disrupts vertical migration into anoxic regions.

Research challenges and knowledge gaps

Our model presents many experimental challenges. It is challenging to test cyanobacteria for Fe limitation when they are rare in a system, especially when small samples are used to run assays, because samples may not include any cyanobacteria or their populations may be too small to displace their competitors within the experimental timeframe. When cyanobacteria are abundant, an Fe-stress test may no longer be relevant. Standard bottle nutrient-enrichment assays add Fe^{3+}, not Fe^{2+}, with chelators to keep Fe^{3+} in solution, but choice of chelator may affect outcomes (Molot *et al.*, 2010).

A knowledge gap is the minimum extracellular Fe^{2+} concentrations needed to establish dominance. However, measuring Fe^{2+} colorimetrically is problematic because of significant autoreduction of Fe^{3+} to Fe^{2+} in the presence of dissolved humic matter and a high detection limit (Verschoor & Molot, 2013). Special precautions must also be taken to exclude oxygen during sampling, transport, fixation and measurement.

It would be very useful to know migration rates and maximum migration distances under a range of mixing conditions and migration frequencies for different cyanobacteria species. There are very few relevant studies, and the data contained therein are helpful only to a modest extent (Table 2).

We have presented a strong argument for a novel model linking anoxia, P, N, Fe^{2+}, sulphate and cyanobacteria migration to cyanobacteria bloom formation across three gradients – nutrients, salinity and acidity – which reconciles seemingly contradictory ideas about the roles of P, N and Fe in bloom formation. The model has far-reaching explanatory power and generates many testable hypotheses, some of which are listed below (some may require development of new methods).

1. In systems lacking anoxic surficial sediments, the rate of Fe^{2+} reoxidation in the water column is too high to permit cyanobacteria dominance when pH exceeds 6 but is low enough to permit their dominance in systems with pH <5.5.

2. Cyanobacteria migrate into anoxic waters to acquire sufficient Fe^{2+} to support population growth in non-acidified lakes.

3. There is a maximum depth below which a given cyanobacteria species cannot migrate.

4. *R* is a strong predictor of cyanobacteria dominance in non-acidified lakes with anoxic sediments.

5. Cyanobacteria use siderophores (Fe-scavenging compounds) to promote cyanobacteria population growth in non-acidified lakes.

6. Reductions in nitrogen loading will have minimal impact on cyanobacteria dominance unless the spatial and temporal extent of sediment anoxia is significantly decreased.

7. In systems without anoxic surficial sediments and with very low Fe and very low P concentrations, the large surface area/volume ratio of picocyanobacteria gives them a competitive advantage over larger cyanobacteria.

While the collective weight of evidence from indirect and direct field and laboratory studies in support of this model is compelling, much more work is urgently needed to test it because cyanobacteria bloom formation is a pressing environmental health issue. We hope investigators will be encouraged by this article to begin examining new ideas.

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References

Anderson N., Blomqvist P. & Renberg I. (1997) An experimental and palaeoecological study of algal responses to lake acidification and liming in three central Swedish lakes. *European Journal of Phycology*, **32**, 35–48.

Aubriot L. & Bonilla S. (2012) Rapid regulation of phosphate uptake in freshwater cyanobacterial blooms. *Aquatic Microbial Ecology*, **67**, 251–263.

Bell T. & Kalff J. (2001) The contribution of picophytoplankton in marine and freshwater systems of different trophic status and depth. *Limnology and Oceanography*, **46**, 1243–1248.

Berman-Frank I., Cullen J., Shaked Y., Sherrell R. & Falkowski P. (2001) Iron availability, cellular iron quotas, and nitrogen fixation in Trichodesmium. *Limnology and Oceanography*, **46**, 1249–1260.

Berman-Frank I., Quigg A., Finkel Z.V., Irwin A.J. & Haramaty L. (2007) Nitrogen-fixation stargetgies and Fe requirements in cyanobacteria. *Limnology and Oceanography*, **52**, 2260–2269.

Bernard A. & Symonds R.B. (1989) The significance of siderite in the sediments from Lake Nyos, Cameroon. *Journal of Volcanology and Geothermal Research*, **39**, 187–194.

Blomqvist P., Pettersson A. & Hyenstrand P. (1994) Ammonium-nitrogen – a key regulatory factor causing dominance of non-nitrogen-fixing cyanobacteria in aquatic systems. *Archiv für Hydrobiologie*, **132**, 141–164.

Blomqvist S., Gunnars A. & Elmgren R. (2004) Why the limiting nutrient differs between temperate coastal seas and freshwater lakes: a matter of salt. *Limnology and Oceanography*, **49**, 2236–2241.

Boudreau B. & Westrich J. (1984) The dependence of bacterial sulfate reduction on sulfate concentration in marine sediments. *Geochimica et Cosmochimica Acta*, **48**, 2503–2516.

Boukhalfa H. & Crumbliss A.L. (2002) Chemical aspects of siderophore mediated iron transport. *BioMetals*, **15**, 325–339.

Brand L. (1991) Minimum iron requirements of marine phytoplankton and the implications for the biogeochemical control of new production. *Limnology and Oceanography*, **36**, 1756–1771.

Brunberg A.-K. & Blomqvist P. (2003) Recruitment of *Microcystis* (Cyanophyceae) from lake sediments: the importance of littoral inocula. *Journal of Phycology*, **39**, 58–63.

Bryant L.D., Lorrai C., McGinnis D.F., Brand A., Wüest A. & Little J.C. (2010) Variable sediment oxygen uptake in response to dynamic forcing. *Limnology and Oceanography*, **55**, 950–964.

Callieri C., Modenutti B., Queimalinos C., Bertoni R. & Balseiro E. (2007) Production and biomass of picophytoplankton and larger autotrophs in Andean ultraoligotrophic lakes: differences in light harvesting efficiency in deep layers. *Aquatic Ecology*, **41**, 511–523.

Callieri C. & Stockner J.G. (2002) Freshwater autotrophic picoplankton: a review. *Journal of Limnology*, **61**, 1–14.

Camacho A., Garcia-Pichel F., Vicente E. & Castenholz R.W. (1996) Adaptation to sulfide and to the underwater light field in three cyanobacterial isolates from Lake Arcas (Spain). *FEMS Microbiology Ecology*, **21**, 293–301.

Camacho A., Vicente E. & Miracle M. (2000) Ecology of a deep-living *Oscillatoria* (=*Planktothrix*) population in the sulphide-rich waters of a Spanish karstic lake. *Archiv für Hydrobiologie*, **148**, 333–355.

Caraco N.F., Cole J.J. & Likens G.E. (1990) A comparison of phosphorus immobilization in sediments of freshwater and coastal marine systems. *Biogeochemistry*, **9**, 277–290.

Carey C.C., Weathers K.C. & Cottingham K.L. (2008) *Gloeotrichia echinulata* blooms in an oligotrophic lake: helpful insights from eutrophic lakes. *Journal of Plankton Research*, **30**, 893–904.

Carignan R. & Tessier A. (1988) The co-diagenesis of sulfur and iron in acid lake sediments of southwestern Québec. *Geochimica Cosmochmica Acta*, **52**, 1179–1188.

Cavender-Bares K., Mann E., Chisholm S., Ondrusek M. & Bidigare R. (1999) Differential response of equatorial Pacific phytoplankton to iron fertilization. *Limnology and Oceanography*, **44**, 237–246.

Codd G.A., Azevrdo S.M.F.O., Bagchi S.N., Burch M.D., Carmichael W.W., Harding W.R. *et al.* (2005) CYANONET. A global network for cyanobacterial bloom and toxin risk assessment. Initial situation assessment and recommendations. IHP-VI Technical Documents in Hydrology No. 76, UNESCO, Paris.

Cole J.J., Lane J., Marino R. & Howarth R. (1993) Molybdenum assimilation by cyanobacteria and phytoplankton in freshwater and salt-water. *Limnology and Oceanography*, **38**, 25–35.

Conley D.J., Paerl H.W., Howarth R.W., Boesch D.F., Seitzinger S.P., Havens K.E. *et al.* (2009) Controlling eutrophication: nitrogen and phosphorus. *Science*, **323**, 1014–1015.

Cook R.B. (1984) Distributions of ferrous iron and sulfide in an anoxic hypolimnion. *Canadian Journal of Fisheries and Aquatic Sciences*, **41**, 286–293.

Cooke G.D., Welch E.B., Martin A.B., Fulmer D.G., Hyde J.B. & Schrieve G.D. (1993) Effectiveness of Al, Ca, and Fe salts for control of internal phosphorus loading in shallow and deep lakes. *Hydrobiologia*, **253**, 323–335.

Curtis P.J. (1993) Effect of dissolved organic carbon on ^{59}Fe scavenging. *Limnology and Oceanography*, **38**, 1554–1561.

Dang T.C., Fujii M., Rose A.L., Bligh M. & Waite T.D. (2012) Characteristics of the freshwater cyanobacterium *Microcystis aeruginosa* grown in iron-limited continuous culture. *Applied and Environmental Microbiology*, **78**, 1574–1583.

Davison W. (1993) Iron and manganese in lakes. *Earth-Science Reviews*, **34**, 119–163.

Downing J.A., Watson S.B. & McCauley E. (2001) Predicting cyanobacteria dominance in lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, **58**, 1905–1908.

Emerson S. & Widmer G. (1978) Early diagenesis in anaerobic lake sediments – II. Thermodynamic and kinetic factors controlling the formation of iron phosphate. *Geochimica et Cosmochimica Acta*, **42**, 1307–1316.

Futter M.N. (2003) Patterns and trends in southern Ontario lake ice phenology. *Environmental Monitoring and Assessment*, **88**, 431–444.

Garlick S., Oren A. & Padan E. (1977) Occurrence of facultative anoxygenic photosynthesis among filamentous and

unicellular cyanobacteria. *Journal of Bacteriology*, **129**, 623–629.

Gervais F., Siedel U., Heilmann B., Weithoff G., Heisig-Gunkel G. & Nicklisch A. (2003) Small-scale vertical distribution of phytoplankton, nutrients and sulphide below the oxycline of a mesotrophic lake. *Journal of Plankton Research*, **25**, 273–278.

Ghassemi M. & Christman R.F. (1968) Properties of the yellow organic acids of natural waters. *Limnology and Oceanography*, **13**, 583–597.

Gibbs M.M., Hickey C.W. & Özkundakci D. (2011) Sustainability assessment and comparison of efficacy of four P-inactivation agents for managing internal phosphorus loads in lakes: sediment incubations. *Hydrobiologia*, **658**, 253–275.

Glass J.B., Wolfe-Simon F.W. & Anbar A.D. (2009) Coevolution of metal availability and nitrogen assimilation in cyanobacteria and algae. *Geobiology*, **7**, 100–123.

Harrington J.M. & Crumbliss A.L. (2009) The redox hypothesis in siderophore-mediated iron uptake. *BioMetals*, **22**, 679–689.

Havens K.E. (2008) Cyanobacteria blooms: effects on aquatic ecosystems. *Advances in Experimental Medicine and Biology*, **619**, 733–747.

Havens K.E., James R., East T. & Smith V. (2003) N: P ratios, light limitation, and cyanobacterial dominance in a subtropical lake impacted by non-point source nutrient pollution. *Environmental Pollution*, **122**, 379–390.

Head R.M., Jones R.I. & Bailey-Watts A.E. (1999a) An assessment of the influence of recruitment from the sediment on the development of planktonic populations of cyanobacteria in a temperate mesotrophic lake. *Freshwater Biology*, **41**, 759–769.

Head R.M., Jones R.I. & Bailey-Watts A.E. (1999b) Vertical movements by planktonic cyanobacteria and the translocation of phosphorus: implications for lake restoration. *Aquatic Conservation: Marine and Freshwater Ecosystems*, **9**, 111–120.

Hecky R.E., Campbell P. & Hendzel L. (1993) The stoichiometry of carbon, nitrogen, and phosphorus in particulate matter of lakes and oceans. *Limnology and Oceanography*, **38**, 709–724.

Hecky R.E. & Kilham P. (1988) Nutrient limitation of phytoplankton in freshwater and marine environments: a review of recent evidence on the effects of enrichment. *Limnology and Oceanography*, **33**(4, part 2), 796–822.

Hopkinson B.M. & Morel F.M.M. (2009) The role of siderophores in iron acquisition by photosynthetic marine microorganisms. *BioMetals*, **22**, 659–669.

Howarth R.W., Marino R., Lane J.M. & Cole J.J. (1988) Nitrogen-fixation in fresh-water, estuarine, and marine ecosystems. 1. Rates and importance. *Limnology and Oceanography*, **33**, 669–687.

Hudnell H.K., Jones C., Labisi B., Lucero V., Hill D.R. & Eilers J. (2010) Freshwater harmful algal bloom (FHAB) suppression with solar powered circulation (SPC). *Harmful Algae*, **9**, 208–217.

Ibelings B.W., Mur L.R. & Walsby A.E. (1991) Diurnal changes in buoyancy and vertical distribution in populations of *Microcystis* in two shallow lakes. *Journal of Plankton Research*, **13**, 419–436.

Jancula D. & Maršálek B. (2011) Critical review of actually available chemical compounds for prevention and management of cyanobacterial blooms. *Chemosphere*, **85**, 1415–1422.

Jensen H. & Andersen F. (1992) Importance of temperature, nitrate, and pH for phosphate release from aerobic sediments of 4 shallow, eutrophic lakes. *Limnology and Oceanography*, **37**, 577–589.

Jensen H. & Thamdrup B. (1993) Iron-bound phosphorus in marine-sediments as measured by bicarbonate-dithionite extraction. *Hydrobiologia*, **253**, 47–59.

Jeppesen E., Sondergaard M., Jensen J., Havens K., Anneville O., Carvalho L. *et al.* (2005) Lake responses to reduced nutrient loading – an analysis of contemporary long-term data from 35 case studies. *Freshwater Biology*, **50**, 1747–1771.

Katsev S., Tsandev I., L'Heureux I. & Rancourt D.G. (2006) Factors controlling long-term phosphorus efflux from lake sediments: exploratory reactive-transport modeling. *Chemical Geology*, **234**, 127–147.

Keating K. (1977) Allelopathic Influence on blue-green bloom sequence in a eutrophic lake. *Science*, **196**, 885–887.

Keating K. (1978) Blue-green-algal inhibition of diatom growth – transition from mesotrophic to eutrophic community structure. *Science*, **199**, 971–973.

Keeney D., Chen R. & Graetz D. (1971) Importance of denitrification and nitrate reduction in sediments to nitrogen budgets of lakes. *Nature*, **233**, 66.

Klausmeier C.A., Lichtman E., Daufresne T. & Levin S.A. (2004) Optimal nitrogen-to-phosphorus stoichiometry of phytoplankton. *Nature*, **429**, 171–174.

Kleeberg A., Herzog C. & Hupfer M. (2013) Redox sensitivity of iron in phosphorus binding does not impede lake restoration. *Water Research*, **47**, 1491–1502.

Kranzler C., Lis H., Shaked Y. & Keren N. (2011) The role of reduction in iron uptake processes in a unicellular, planktonic cyanobacterium. *Environmental Microbiology*, **13**, 2990–2999.

Kranzler C., Rudolf M., Keren N. & Schleiff E. (2013) Iron in cyanobacteria. *Advances in Botanical Research*, **65**, 57–105.

Kusta A., Sañudo-Wilhemy S.A. & Carpenter E.J. (2003) Iron requirements for dinitrogen- and ammonium-supported growth in cultures of *Trichodesmium* (IMS 101): comparison with nitrogen fixation rates and iron:carbon ratios of field populations. *Limnology and Oceanography*, **48**, 1869–1884.

Lewandowski J., Schauser I. & Hupfer M. (2003) Long term effects of phosphorus precipitations with alum in

hypereutrophic Lake Süsser See (Germany). *Water Research*, **37**, 3194–3204.

Lewis W.M. Jr & Wurtsbaugh W.A. (2008) Control of lacustrine phytoplankton by nutrients: erosion of the phosphorus paradigm. *International Review of Hydrobiology*, **93**, 446–465.

Lewis W.M. Jr, Wurtsbaugh W.A. & Paerl H.W. (2011) Rationale for control of anthropogenic nitrogen and phosphorus to reduce eutrophication of inland waters. *Environmental Science & Technology*, **45**, 10300–10305.

Loewen M.R., Ackerman J.D. & Hamblin F.F. (2007) Environmental implications of stratification and turbulent mixing in a shallow basin. *Canadian Journal of Fisheries and Aquatic Sciences*, **64**, 43–57.

Loh P.S., Molot L.A., Nürnberg G.K., Watson S.B. & Ginn B. (2013) Evaluating relationships between sediment chemistry and anoxic phosphorus and iron release across three different water bodies. *Inland Waters*, **3**, 105–118.

Maldonado M.T. & Price N.M. (1996) Influence of N substrate on Fe requirements of marine centric diatoms. *Marine Ecology Progress Series*, **141**, 161–172.

Maldonado M.T. & Price N.M. (1999) Utilization of iron bound to strong organic ligands by plankton communities in the subarctic Pacific Ocean. *Deep-Sea Research Part II-Topical Studies in Oceanography*, **46**, 2447–2473.

Mann E.L. & Chisholm S.W. (2000) Iron limits the cell division rate of *Prochlorococcus* in the eastern equatorial Pacific. *Limnology and Oceanography*, **45**, 1067–1076.

Manning P.G., Murphy T.P. & Prepas E.E. (1991) Intensive formation of vivianite in the bottom sediments of mesotrophic Narrow Lake, Alberta. *Canadian Mineralogist*, **29**, 77–85.

Maranger R., Bird D.F. & Price N.M. (1998) Iron acquisition by photosynthetic marine phytoplankton from ingested bacteria. *Nature*, **396**, 248–251.

Marino R., Howarth R.W., Shamess J. & Prepas E.E. (1990) Molybdenum and sulfate as controls on the abundance of nitrogen-fixing cyanobacteria in saline lakes in Alberta. *Limnology and Oceanography*, **35**, 245–259.

McKay R., Wilhelm S., Hall J., Hutchins D., Al-Rshaidat M., Mioni C. *et al.* (2005) Impact of phytoplankton on the biogeochemical cycling of iron in subantarctic waters southeast of New Zealand during FeCycle. *Global Biogeochemical Cycles*, **19**, GB4S24.

McQueen D.J. & Lean D.R.S. (1987) Influence of water temperature and nitrogen to phosphorus ratios on the dominance of blue-green algae in Lake St-George, Ontario. *Canadian Journal of Fisheries and Aquatic Sciences*, **44**, 598–604.

Michalak A.M., Anderson E.J., Beletsky D., Boland S., Bosch N.S., Bridgeman T.B. *et al.* (2013) Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions. *Proceedings of the National academy of Sciences of the United States of America*, **110**, 6448–6452.

Millie D.F., Fahnenstiel G.L., Bressie J.D., Pigg R.J., Rediske R.R., Klarer D.M. *et al.* (2009) Late-summer phytoplankton in western Lake Erie (Laurentian Great Lakes): bloom distributions, toxicity, and environmental influences. *Aquatic Ecology*, **43**, 915–934.

Molot L.A. & Brown E.J. (1986) Method for determining the temporal response of microbial phosphate-transport affinity. *Applied and Environmental Microbiology*, **51**, 524–531.

Molot L.A. & Dillon P.J. (2003) Variation in iron, aluminum and dissolved organic carbon mass transfer coefficients in lakes. *Water Research*, **37**, 1759–1768.

Molot L.A., Heintsch L. & Nicholls K.H. (1990) Responses of phytoplankton in acidic lakes in Ontario to whole-lake neutralization. *Canadian Journal of Fisheries and Aquatic Sciences*, **47**, 422–431.

Molot L.A., Li G., Findlay D.L. & Watson S.B. (2010) Iron-mediated suppression of bloom-forming cyanobacteria by oxine in a eutrophic lake. *Freshwater Biology*, **55**, 1102–1117.

Morgan B. & Lahav O. (2007) The effect of pH on the kinetics of spontaneous Fe(II) oxidation by O_2 in aqueous solution – basic principles and a simple heuristic description. *Chemosphere*, **68**, 2080–2084.

Murphy T., Lean D.R.S. & Nalewajko C. (1976) Blue-green algae – their excretion of iron-selective chelators enables them to dominate other algae. *Science*, **192**, 900–902.

Neilands J. (1995) Siderophores – structure and function of microbial iron transport compounds. *Journal of Biological Chemistry*, **270**, 26723–26726.

Nixon S.W., Ammerman J.W., Atkinson L.P., Berounsky V.M., Billen G., Boicourt W.C. *et al.* (1996) The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. *Biogeochemistry*, **35**, 141–180.

Nürnberg G.K. (2004) Quantified hypoxia and anoxia in lakes and reservoirs. *The Scientific World Journal*, **4**, 42–54.

Nürnberg G.K. (2007) Low-Nitrate-Days (LND), a potential indicator of cyanobacteria blooms in a eutrophic hard-water reservoir. *Water Quality Research Journal of Canada*, **42**, 269–283.

Ontario Ministry of Environment and Energy (1994) *Water Management Policies Guidelines and Provincial Water Quality Objectives*, Toronto, ON, Canada.

Paerl H.W. (1988) Nuisance phytoplankton blooms in coastal, estuarine and inland waters. *Limnology and Oceanography*, **33**(4, part 2), 823–847.

Paerl H.W., Hall N.S. & Calandrino E.S. (2011a) Controlling harmful cyanobacterial blooms in a world experiencing anthropogenic and climatic-induced change. *Science of the Total Environment*, **409**, 1739–1745.

Paerl H.W. & Paul V.J. (2012) Climate change: links to global expansion of harmful cyanobacteria. *Water Research*, **46**, 1349–1363.

Paerl H.W. & Scott J.T. (2010) Throwing fuel on the fire: synergistic effects of excessive nitrogen inputs and global warming on harmful algal blooms. *Environmental Science & Technology*, **44**, 7756–7758.

Paerl H.W., Xu H., McCarthy M.J., Zhu G., Qin B., Li Y. *et al.* (2011b) Controlling harmful cyanobacterial blooms in a hyper-eutrophic lake (Lake Taihu, China): the need for a dual nutrient (N & P) management strategy. *Water Research*, **45**, 1973–1983.

Paterson M.J., Schindler D.W., Hecky R.E., Findlay D.L. & Rondeau K.J. (2011) Comment: lake 227 shows clearly that controlling inputs of nitrogen will not reduce or prevent eutrophication of lakes. *Limnology and Oceanography*, **56**, 1545–1547.

Powe C., Verschoor M., Molot L., Loh P.S., Watson S.B. & Howell T. (2013) Assessment of cyanobacteria dominance in embayments long the Georgian Bay coastline. Final report to Georgian Bay Forever, Caledon, ON, Canada (www.georgianbayforever.org). June 10, 2013.

Prepas E.E., Field K.M., Murphy T.P., Johnson W.L., Burke J.M. & Tonn W.M. (1997) Introduction to the Amisk Lake Project: oxygenation of a dee, eutrophic lake. *Candian Journal of Fisheries and Aquatic Sciences*, **54**, 2105–2110.

Price N. (2005) The elemental stoichiometry and composition of an iron-limited diatom. *Limnology and Oceanography*, **50**, 1159–1171.

Ramm K. & Scheps V. (1997) Phosphorus balance of a polytrophic shallow lake with the consideration of phosphorus release. *Hydrobiologia*, **342**, 43–53.

Rautio M., Dufresne F., Laurion I., Bonilla S., Vincent W.F. & Christoffersen K.S. (2011) Shallow freshwater ecosystems of the circumpolar Arctic. *Ecoscience*, **18**, 204–222.

Raven J.A. (1988) The iron and molybdenum use efficiencies of plant growth with different energy, carbon and nitrogen sources. *New Phytologist*, **109**, 279–287.

Redfield A.C., Ketchum B.H. & Richards F.A. (1963) The influence of organisms on the composition of sea-water. In: *The Sea* (Ed M.N. Hill), pp. 26–77, Vol. **2**, Interscience, New York, NY.

Scavia D., Lang G.A. & Kitchell J.F. (1988) Dynamics of Lake Michigan plankton: a model evaluation of nutrient loading, competition and predation. *Canadian Journal of Fisheries and Aquatic Sciences*, **45**, 165–177.

Schindler D.W. & Hecky R.E. (2009) Eutrophication: more nitrogen data needed. *Science*, **324**, 721–722.

Schindler D.W., Hecky R.E., Findlay D.L., Stainton M.P., Parker B.R., Paterson M.J. *et al.* (2008) Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. *Proceedings of the National academy of Sciences of the United States of America*, **105**, 11254–11258.

Singleton V.L. & Little J.C. (2006) Designing hypolimnetic aeration and oxygenation systems – a review. *Environmental Science & Technology*, **40**, 7512–7520.

Smith J.L., Boyer G.L. & Zimba P.V. (2008) A review of cyanobacterial odorous and bioactive metabolites: impacts and management alternatives in aquaculture. *Aquaculture*, **280**, 5–20.

Smith R. & Kalff J. (1983) Competition for Phosphorus among co-occurring freshwater phytoplankton. *Limnology and Oceanography*, **28**, 448–464.

Smith V. (1983) Low nitrogen to phosphorus ratios favor dominance by blue-green algae in Lake phytoplankton. *Science*, **221**, 669–671.

Sommer U. (1993) Phytoplankton competition in Plußsee – a field test of the resource-ratio hypothesis. *Limnology and Oceanography*, **38**, 838–845.

Sorichetti R.J., Creed I.F. & Trick C.G. (2014a) Evidence for iron-regulated cyanobacterial predominance in oligotrophic lakes. *Freshwater Biology*, **59**, 679–691.

Sorichetti R.J., McLaughlin J.T., Creed I.F. & Trick C.G. (2014b) Suitability of a cytotoxicity assay for detection of potentially harmful compounds produced by freshwater bloom-forming algae. *Harmful Algae*, **31**, 177–187.

Stainsby E.A., Winter J.G., Jarjanazi H., Paterson A.M., Evans D.O. & Young J.D. (2011) Changes in the thermal stability of Lake Simcoe from 1980 to 2008. *Journal of Great Lakes Research*, **37**, 63–71.

Stal L., Staal M. & Villbrandt M. (1999) Nutrient control of cyanobacterial blooms in the Baltic Sea. *Aquatic Microbial Ecology*, **18**, 165–173.

Steffensen D.A. (2008) Economic cost of cyanobacterial blooms. *Advances in Experimental Medicine and Biology*, **619**, 855–865.

Sunda W.G. & Huntsman S.A. (1995) Iron uptake and growth limitation in oceanic and coastal phytoplankton. *Marine Chemistry*, **50**, 189–206.

Sunda W.G., Swift D.G. & Huntsman S.A. (1991) Low iron requirement for growth in oceanic phytoplankton. *Nature*, **351**, 55–57.

Tang D. & Morel F.M.M. (2006) Distinguishing between cellular and Fe-oxide-associated trace elements in phytoplankton. *Marine Chemistry*, **98**, 18–30.

Taylor P. & Williams P. (1975) Theoretical studies on coexistence of competing species under continuous-flow conditions. *Canadian Journal of Microbiology*, **21**, 90–98.

Tilman D., Kiesling R., Sterner R., Kilham S. & Johnson F. (1986) Green, bluegreen and diatom algae – taxonomic differences in competitive ability for phosphorus, silicon and nitrogen. *Archiv für Hydrobiologie*, **106**, 473–485.

Titman D. (1976) Ecological competition between algae – experimental confirmation of resource-based competition theory. *Science*, **192**, 463–465.

Tortell P.D., Maldonado M.T., Granger J. & Price N.M. (1999) Marine bacteria and biogeochemical cycling of iron in the oceans. *FEMS Microbiology Ecology*, **29**, 1–11.

Tortell P.D., Maldonado M.T. & Price N.M. (1996) The role of heterotrophic bacteria in iron-limited ocean ecosystems. *Nature*, **383**, 330–332.

Tovar-Sanchez A., Sañudo-Wilhemy S.A., Garcia-Vargas M., Weaver R.S., Popels L.C. & Hutchins D.A. (2003) A trace metal clean reagent to remove surface-bound iron

from marine phytoplankton. *Marine Chemistry*, **82**, 91–99.

Trimbee A. & Prepas E.E. (1988) Dependence of lake oxygen depletion rates on maximum oxygen storage in a partially meromictic lake in Alberta. *Canadian Journal of Fisheries and Aquatic Sciences*, **45**, 571–576.

Tuit C., Waterbury J. & Ravizza G. (2004) Diel variation of molybdenum and iron in marine diazotrophic cyanobacteria. *Limnology and Oceanography*, **49**, 978–990.

Twiss M., Auclair J. & Charlton M. (2000) An investigation into iron-stimulated phytoplankton productivity in epipelagic Lake Erie during thermal stratification using trace metal clean techniques. *Canadian Journal of Fisheries and Aquatic Sciences*, **57**, 86–95.

Verschoor M.J. & Molot L.A. (2013) A comparison of three colorimetric methods of ferrous and total reactive iron measurement in freshwaters. *Limnology and Oceanography: Methods*, **11**, 113–125.

Vincent W.F. & Quesada A. (2012) Cyanobacteria in high latitude lakes, rivers and seas. In: *Ecology of Cyanobacteria II: Their Diversity in Space and Time* (Ed. B.A. Whitton), pp. 371–385. DOI: 10.1007/978-94-007-3855-3_13. Springer Science+Business Media B.V., Dordrecht.

Voelker B., Morel F.M.M. & Sulzberger B. (1997) Iron redox cycling in surface waters: effects of humic substances and light. *Environmental Science & Technology*, **31**, 1004–1011.

Vörös L., Callieri C., Balogh K. & Bertoni R. (1998) Freshwater picocyanobacteria along a trophic gradient and light quality range. *Hydrobiologia*, **370**, 117–125.

Wagner F., Falkner R. & Falkner G. (1995) Information about previous phosphate fluctuations is stored via an adaptive response of the high-affinity phosphate-uptake system of the cyanobacterium *Anacystis nidulans*. *Planta*, **197**, 147–155.

Walsby A.E. & McAllister G.K. (1987) Buoyancy regulation by *Microcystis* in Lake Okaro. *New Zealand Journal of marine and Freshwater Research*, **21**, 521–524.

Walsby A.E., Utkilen H.C. & Johnsen I.J. (1983) Buoyancy changes of a red coloured *Oscillatoria agardhii* in Lake Gjersjoen, Norway. *Archiv fur Hydrobiologie*, **97**, 18–38.

Walve J. & Larsson U. (2007) Blooms of Baltic Sea *Aphanizomenon* sp. (Cyanobacteria) collapse after internal phosphorus depletion. *Aquatic Microbial Ecology*, **49**, 57–69.

Watson S.B., McCauley E. & Downing J.A. (1997) Patterns in phytoplankton taxonomic composition across temperate lakes of differing nutrient status. *Limnology and Oceanography*, **42**, 487–495.

Welch E.B. & Schrieve G.D. (1994) Alum treatment effectiveness and longevity in shallow lakes. *Hydrobiologia*, **275**, 423–431.

Wersin P., Höhner P., Giovani R. & Stumm W. (1991) Early diagenetic processes on iron transformations in a freshwater lake sediment. *Chemical Geology*, **90**, 233–252.

Wilhelm S.W. (1995) Ecology of iron-limited cyanobacteria: a review of physiological responses and implications for aquatic systems. *Aquatic Microbial Ecology*, **9**, 295–303.

Wilhelm S.W., Bullerjahn G.S., Eldridge M.L., Rinta-Kanto J.M., Poorvin L. & Bourbonniere R.A. (2006) Seasonal hypoxia and the genetic diversity of prokaryote populations in the central basin hypolimnion of Lake Erie: evidence for abundant cyanobacteria and photosynthesis. *Journal of Great Lakes Research*, **32**, 657–671.

Wilhelm S.W. & Trick C.G. (1994) Iron-limited growth of cyanobacteria – multiple siderophore production is a common response. *Limnology and Oceanography*, **39**, 1979–1984.

Winter J.G., DeSellas A.M., Fletcher R., Heintsch L., Morley A., Nakamoto L. *et al.* (2011) Algal blooms in Ontario, Canada: increases in reports since 1994. *Lake and Reservoir Management*, **27**, 107–114.

Wisniewski R. (1999) Phosphate inactivation with iron chloride during sediment resuspension. *Lakes & Reservoirs: Research and Management*, **4**, 65–73.

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

Zepp R., Faust B. & Hoigne J. (1992) Hydroxyl radical formation in aqueous reactions (pH 3-8) of iron(II) with hydrogen peroxide – the photo-Fenton reaction. *Environmental Science & Technology*, **26**, 313–319.

Zhang Y. & Prepas E.E. (1996) Regulation of the dominance of planktonic diatoms and cyanobacteria in four eutrophic hardwater lakes by nutrients, water column stability, and temperature. *Canadian Journal of Fisheries and Aquatic Sciences*, **53**, 621–633.

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