Nitrate suppresses internal phosphorus loading in an eutrophic lake

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ABSTRACT

The presence of nitrate in the hypolimnion of the eutrophic, dimictic Upper Mystic Lake has been previously shown to suppress the release of arsenic from lake sediments during seasonal anoxia, in large part by oxidizing iron (II) and producing iron oxyhydroxides that sorb inorganic arsenic. Because of the importance of internal phosphorus loading in the phosphorus budget of many eutrophic lakes, the chemical similarities between phosphate and arsenate, and the need to account for internal phosphorus loading as part of many lake restoration strategies, we carried out measurements to determine if the presence of nitrate also suppressed the release of phosphorus from the sediments of this lake during anoxia. Observations showed that this was the case. Arsenic, phosphorus, and iron (II) concentrations were strongly correlated in the water column, as expected, and the depths below which phosphorus and iron concentrations increased relative to epilimnetic values was predicted by the depth at which nitrate concentration approached zero. The results suggest that knowledge of a lake's nitrogen budget may be a useful tool in the design of lake remediation efforts, even though phosphorus is typically the limiting nutrient.

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1. Introduction

Effecting decreases in nutrient loading is central to the restoration of excessively eutrophied lakes and reservoirs, and the nutrient of most concern is typically phosphorus (P), as was shown for example in split-lake experimental fertilizations of Lake 226 (Schindler, 1974). The key role of phosphorus in the eutrophication of freshwaters is discussed in detail in current texts (e.g. Kalff, 2002; Wetzel, 2001) and is underscored by a variety of management-oriented models (e.g. Jensen et al., 2006; Cooke et al., 1986) that assist in lake restoration by predicting P concentrations in the water column on the basis of total P loading plus lake parameters such as depth or hydraulic residence time. Importantly, total P loading includes internal release of P from sediments as well as input from external point and non-point sources. Although the release of P from sediments can involve several processes (e.g. Bostrom et al., 1988), the release of P accompanying the reductive dissolution of iron is often important in the case of moderately deep lakes with anoxic hypolimnia.

Lake management efforts that result in decreased external P loadings, such as the diversion of wastewater treatment plant effluent or the placement of restrictions on fertilizer applications within a catchment, may incidentally decrease the inputs of other nutrients such as nitrogen. While it might be assumed from a lake management standpoint that any such decreases would be beneficial, nitrogen has roles beyond that of a nutrient. In the form of nitrate, for example, it also contributes to the mineral acidity, photoreactivity and oxidation capacity of water. In Upper Mystic Lake (UML),

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nitrate as an oxidant was observed to exert a controlling influence on the release of iron and arsenic from lake sediments under anoxic conditions (Senn and Hemond, 2002). This observation suggested that the nitrogen budget, as reflected in the presence of nitrate, might affect P cycling in lakes such as UML through the interaction of nitrate with iron cycling. The cycling of P has long been known to be linked to the iron cycle in many lakes (Einsele, 1936; Mortimer, 1941). The classic iron cycling model, in which P is scavenged from the water column and deposited to the sediments by settling iron (III) oxyhydroxides, and then released back to the water column during reductive dissolution of these oxyhydroxides to Fe (II), may be most appropriate when the molar ratio of total iron to total phosphorus in the sediments is at least 15 (Jensen et al., 1992). This model must in some cases be extended to include other reactions, such as the formation of iron (II) phosphate phases in deeper, anoxic sediment, or the binding of iron by sulfides (Gachter and Mueller, 2003).

The bulk of the limnological literature focuses on the presence or absence of molecular oxygen as the primary factor controlling the redox status of iron. For this reason, hypolimnetic aeration is sometimes proposed as a tool for the restoration of eutrophic lakes and reservoirs, primarily acting by inhibiting internal P loading from the sediments (Cooke et al., 1986), although this technique may not be successful when processes other than the iron cycle control P release (Gachter and Mueller, 2003). There is evidence, however, that nitrate can serve as effectively as oxygen at controlling the iron redox cycle. Ripl (1976) proposed the addition of nitrate, together with iron and lime, to a polluted lake as a means of lake restoration; the nitrate was intended to oxidize organic material and thereby lessen sediment oxygen demand, thus inhibiting P release. Andersen (1982), in a study of eutrophic Danish lakes, reported that a concentration of oxidized nitrogen species in excess of about 1 mg/L was statistically associated with lower rates of release of phosphate from the sediment into anoxic waters. Sondergaard et al. (1999) point to both oxygen and nitrate as a oxidants that can contribute to P retention by sediments, and Hansen et al. (2003) experimentally show inhibition of P release from cores of softwater lake sediments by amendment of the overlying water with nitrate.

While nitrate could act to lessen oxygen demand by supporting the oxidation of organic material in a lake (i.e. denitrification), nitrate reduction can also be coupled directly to the oxidation of iron (II) (Straub et al., 1996; Hauck et al., 2001). In the role of an oxidant of Fe (II), nitrate was observed to seasonally become the principal control on arsenic release from the sediments of eutrophic Upper Mystic Lake (UML), a dimictic urban lake near Boston, MA (Senn and Hemond, 2002). As nitrate became depleted in the anoxic hypolimnion, both Fe (II) and total As concentrations increased; at the same time, arsenic (V) began to be replaced by As (III).

Arsenic in the +V oxidation state has similar chemical characteristics to phosphorus in the +V state, the oxidation state in which the latter is almost always found in lakes. Thus, we expected that many of the conclusions previously drawn regarding the relationship of nitrate to arsenic release from sediments in the UML would also apply to phosphorus. If this proved to be the case, such a relationship might also apply to other iron-rich lakes having seasonally anoxic hypolimnia.

Although it was not be expected that the oxidation state of P would affected, the formation of sorptive and settleable solid-phase iron species via the oxidation of Fe (II) by nitrate was expected to inhibit the net release of P by scavenging phosphorus and retaining it in or returning it to the sediments. This could be consequential for lake management, inasmuch as many of the watershed management techniques employed to limit phosphorus loading also decrease nitrogen loading.

We therefore observed the spatiotemporal patterns of nitrate, arsenic, iron and P concentrations in UML during the summer and fall, when strong seasonal hypolimnetic anoxia develops. Phosphorus, arsenic, and iron (II) were expected to be spatiotemporally correlated in the anoxic hypolimnion during summer stratification, and release of P from the sediments was expected to be enhanced, not by oxygen depletion of the bottom waters, but by the later-occurring depletion of nitrate from water overlying the sediments.

2. Methods

Upper Mystic Lake is located north of Boston MA in the towns of Winchester, Arlington, and Medford. It has a maximum depth of 24 m, area of 50 ha, and volume of 7×10^6 m³. Historically the lake received heavy inputs of metals from industrial operations, notably chemical manufacture and leather processing, during the late 19th and early 20th centuries (Durant et al., 1990; Spliethoff and Hemond, 1996). Although the deep sediments retain a strong-layered structure within which annual cycles of net deposition can be resolved (e.g. Rauch et al., 2006), the lake also exhibits pronounced seasonal release of metals and nutrients from the sediments (Aurilio et al., 1994).

The water column was sampled at intervals of from 2 to 4 weeks during the summer and fall of 2003 and 2004, corresponding to the seasons of strong thermal stratification. Measurements were made at depths of 3 m, 10 or 12 m, and several depths at or below 20 m where the highest concentrations and gradients of As, P and Fe were found. Water samples were collected in 125 ml plastic Nalgene bottles by means of a peristaltic pump, with Tygon® tubing attached to the probe of a Hydrolab Mini-sonde whose depth sensor served to indicate sampling depth; three volumes were allowed to overflow and the bottles were immediately capped and stored on ice for transport back to the lab. In general, analytical methods followed those of Senn and Hemond (2002). Oxygen was measured in-situ using the Mini-sonde. To account for possible artifacts in anoxic waters resulting from small electrical leakage currents, we considered that oxygen measurements were indistinguishable from zero when probe readings of less than 1 ppm were observed and nearly identical readings were observed at all greater depths. Total arsenic was measured by reduction to the hydride followed by atomic fluorescence photometry using a Questron Excalibur hydride analyzer. Fe (II) was measured by the ferrozine method (Stookey, 1970); to initiate the release of loosely bound, particle associated Fe^{2+} as well as to inhibit oxidation, water samples were transferred immediately after collection to 1.5 ml plastic centrifuge tubes containing 63 µl of

concentrated hydrochloric acid. Acidified samples were stored and transported in a dark box to minimize possible photooxidation.

Total phosphorus was determined according to Murphy and Riley (1962) using a predigestion with potassium peroxodisulfate followed by colorimetric determination. Reactive P was measured by the same colorimetric method but without prior digestion. Data on oxygen and Fe for 2004, and nitrate data, are from Peterson (2005), who used the same methods as above for oxygen and iron, and measured nitrate by ion chromatography on a Dionex model 10 retrofitted with an electrically self-regenerating ASRS-1 suppressor and a Beckman 507 autosampler, and using a Dionex AS4A-SC column with 1.8 mM Na_2CO_3 + 1.7 mM $NaHCO_3$ eluent at ̄1.3 ml min^{-1}.

3. Results

3.1. Correlation of P and As concentrations in the water column

Arsenic and both reactive P and total P were strongly correlated in the water column of UML (Fig. 1). In profiles from four dates between 6/26/03 and 8/13/03, Pearson product–moment correlations (r) between total P and As ranged from 0.82 (on 6/26) to 0.99 (on 7/30). Between reactive P and As the corresponding values ranged from 0.85 (on 6/26) to 0.99 (on 7/30). When all data were analyzed together, r between total P and As was 0.90; between reactive P and As it was 0.93. For two profiles in which Fe (II) was also measured, Fe (II) was strongly correlated with both As and P (r = 0.99 between As and Fe (II)). The above correlations are all significant at $p < 0.001$ (Downie and Heath, 1965) and vary little if the single epilimnetic datum is omitted from each profile. Correlations between As and P increase slightly, to 0.93 and 0.91 for reactive and total P, respectively, if reactive P and total P data for 7/30 are interchanged; on this one
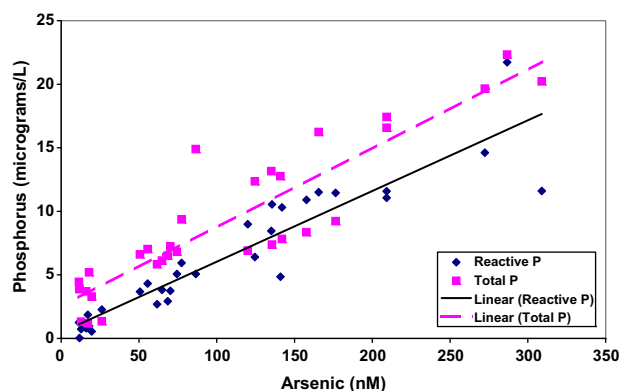

Fig. 1 – As concentration vs. concentrations of total P and reactive P in Upper Mystic Lake. The lowest concentrations (where As < 30 nM) are from oxic, epilimnetic water at 3 m depth; all other data are from anoxic, hypolimnetic water from 10 m depth or greater. The correlation between As and reactive P is consistent with a common mechanism, believed to be the release of As and P from sediments during the reductive dissolution of iron, beginning at the time of nitrate depletion.

date all reported reactive P values exceed corresponding total P values, suggesting a possible mislabeling of data pairs which we can neither confirm nor refute, but which have no effect on the overall results.

Total P and reactive P themselves are correlated (r = 0.82, $p < 0.001$) and the slopes of the regressions of each quantity against As are essentially equal (0.60 μg P nmol^{-1} As). However, ANCOVA (Miller, 2008) showed that the reactive P and total P profiles are significantly offset from each other (F = 76.9, p = 0.000), the means differing by 2.8 ug/L; the corresponding intercepts were 0.096 ug/L and 2.9 ug/L, respectively. The above results are consistent with As and reactive P being sorbed and released from lake sediments by a common mechanism. The small but significant and nearly constant difference between reactive P and total P leads us to speculate that an additional source of P other than release from sediments by reductive dissolution (perhaps a refractory organic or particulate fraction) could be contributing more or less independently to total P values. The key result, however, is that the data lend indirect support to the idea that nitrate, previously shown to seasonally control As in the hypolimnetic waters of UML, may also be seasonally controlling P release.

3.2. Spatiotemporal pattern of P, O_2, Fe, and NO_3^- concentrations

Nitrate concentration as a function of depth in the water column was compared directly with corresponding depth profiles of O_2, reactive P, and Fe (II) concentrations in data sets from six 6 dates between 09/15/04 and 11/22/04, during a continuous period of hypolimnetic anoxia (Fig. 2). The depth of oxygen depletion was defined as the depth at and below which oxygen concentration was not distinguishable from zero by the oxygen probe. The depth of nitrate depletion was defined in an analogous manner. The depths of phosphorus increase and of iron (II) increase were defined as the shallowest depths at which concentrations were observed to increase relative to relatively low and uniform concentrations at all shallower depths. These definitions are essentially visually-determined inflection points in the plots of concentration vs. depth. Below the depths of P and Fe increase so defined, concentrations of Fe and P in almost all cases increased monotonically with depth.

On all dates, the depth of oxygen depletion was shallower than the depth of nitrate depletion. Although the depth of oxygen depletion was poorly defined on 15 Sept., when readings decreased only gradually with depth below 6 m, in no case was the depth of oxygen depletion a predictor of the depths of Fe or P increase. By contrast, the depths of nitrate depletion were clear predictors of the depths of Fe (II) increase (Fig. 2). The depth of P increase coincided with that of Fe (II) increase in three profiles, and was at the next deepest sampling station in the other three profiles.

4. Discussion

The above observations support the idea that nitrate is responsible for suppression of the release of P from the UML sediments. At any given hypolimnetic depth in UML, nitrate
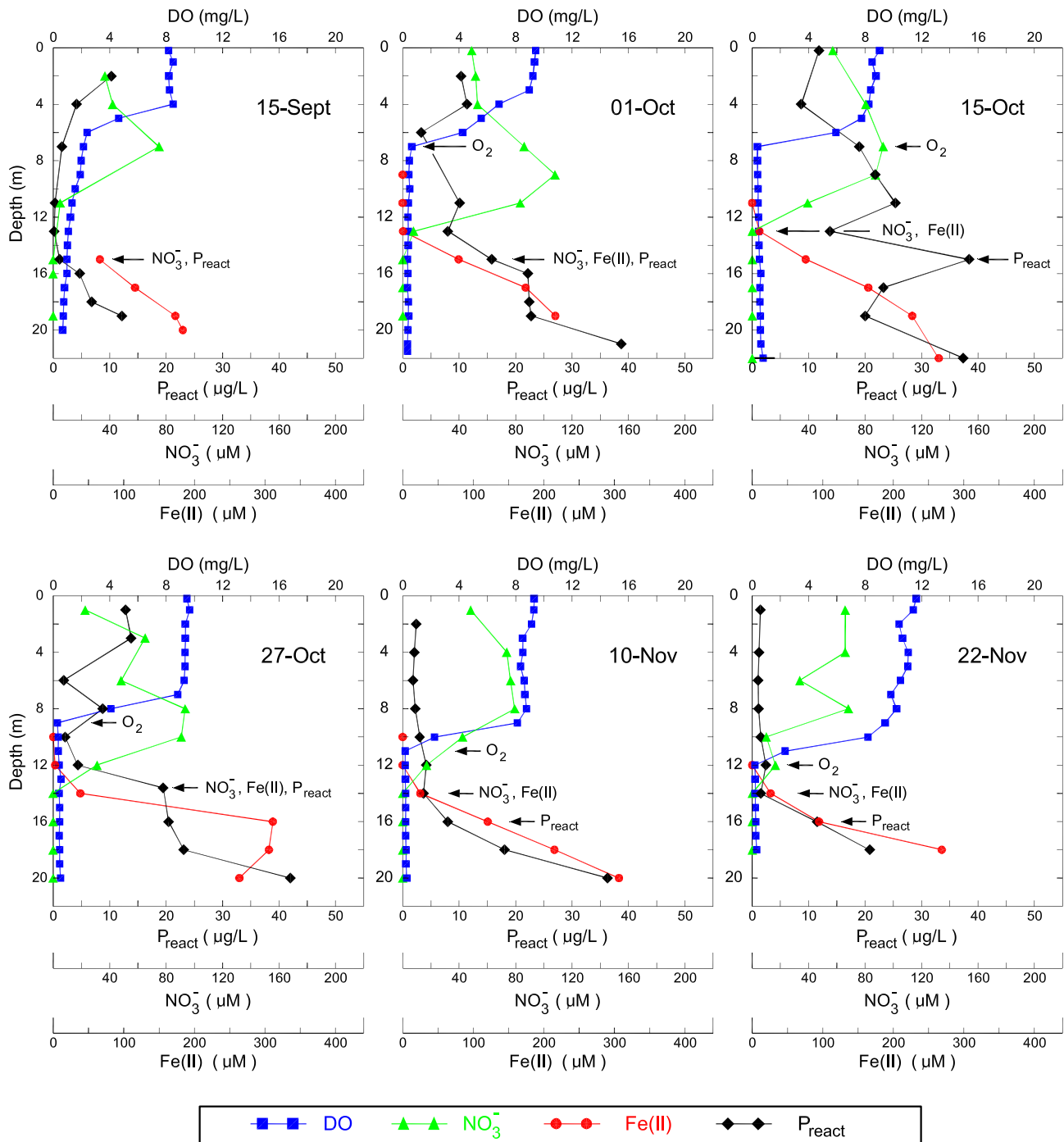
Fig. 2 – Depth profiles of O_2, Fe(II), NO_3^-, and reactive P concentrations in Upper Mystic Lake on six dates in 2004. Data show that the *depth of nitrate depletion*, rather than the *depth of oxygen depletion*, predicts the *depth of increase* of both Fe (II) and P. Below their *depths of increase*, concentrations of both P and Fe (II) increase rapidly with increasing depth, an indication that release from sediments is occurring.

becomes depleted at a later date than oxygen, and it is thus the onset of nitrate depletion rather than oxygen depletion that triggers P release and initiates a period of increasing hypolimnetic concentrations of P and Fe (as well as As) in UML.

The data do not distinguish whether, in the presence of nitrate, the P and Fe are prevented from diffusing out of the sediments by upper layers of more oxidized sediment containing iron oxyhydroxides, or are rapidly scavenged from the water column and returned to the sediments by settling particulate iron oxyhydroxides. Both phenomena may occur, and both could in principle contribute to the suppression of internal P loading to the lake.

Of practical concern is whether the relationship between N and P cycling that is observed in UML occurs generally in

eutrophic lakes, and whether it is a strong enough relationship to warrant consideration in the design and implementation of lake management measures. Indeed, there are conditions under which adding to hypolimnetic oxidation capacity does not suppress P release (Gachter and Mueller, 2003); such conditions would presumably be similar whether the oxidizing capacity was from oxygen or nitrate. A practical suggestion would be to consult the criterion of Jensen et al. (1992); specifically, they suggest that a sedimentary Fe to P ratio of the order of 15 or greater is an indication that iron cycling (and, by extension, N cycling) may well exert controls on internal P loading.

From both a lake and a watershed management perspective, it matters whether inorganic N in the water column is in the form of nitrate or a more reduced form of nitrogen such as ammonium. Although N released to a watershed as nitrate (e.g. from nitrate-based agricultural fertilizers or atmospheric deposition) may be attenuated by uptake or denitrification before reaching a lake, any nitrate that enters a lake will directly add to its oxidizing capacity. Ammonium sources to a watershed, on the other hand, may be more difficult to assess for their redox effects on a receiving lake. Although ammonium N tends to create oxygen demand in a receiving water, transformation of ammonium to nitrate via nitrification during riverine transport to a lake or within a lake prior to stratification results in a net input of nitrate to the lake. This would correspond to a net addition of oxidizing capacity to the hypolimnion, assuming that the oxygen that is necessarily consumed by nitrification is substantially replaced from the atmosphere (or possibly from photosynthetic oxygen evolution) prior to stratification of the lake. In the case of the Upper Mystic Lake, the major source of N actually does originate as ammonium (Cutrofello and Durant, 2007) and becomes nitrified during transport within the Aberjona River and within the UML itself prior to summer stratification (Orosz, 2003).

For N–P interactions within a lake to be important from a lake management point of view, the nitrate input must be large enough that it conveys oxidizing capacity to the hypolimnion amounting to a significant fraction of that conveyed by DO. A typical surface water dissolved oxygen (DO) concentration of 10 mg/L (312 uM O_2) corresponds in oxidizing capacity to 240 uM NO_3^-, or 3.3 mg/l of nitrate-N (4 electrons being accepted per oxygen molecule reduced, and 5 electrons being accepted in the net reduction of a nitrate molecule to elemental nitrogen). Levels of N high enough to be significant to the oxidation capacity of natural fresh waters are not infrequently encountered. For example, of the fresh surface water samples collected in Massachusetts, USA, between 1959 and 2009 for which USGS has published complete major ion composition (U.S.G.S., 2009), 120 out of 625 measurements, or almost 20%, exceeded 100 μM NO_3^- (A. Mueller, personal communication), a level that in UML would contribute significantly to the suppression of P regeneration from the sediments.

5.   Conclusions

These results suggest that it may be important, in situations where control of phosphorus loading is key to the mitigation of eutrophication, to simultaneously assess the nitrogen status of a lake and its watershed. Maintaining or increasing levels of oxidation capacity in a lake may be important to prevent increased release of phosphorus from sediments (internal P loading) as external sources are mitigated. Similarly, it may be worthwhile to determine if selective P mitigation is feasible, given that the N to P ratio of various nutrient sources varies considerably.

These results also lead to speculation that mitigating the loading of nitrate without counterbalancing measures to maintain or increase the oxidation capacity of a lake's hypolimnion could in some cases enhance the release from sediments of lead or other substances that tend to be sequestered by oxidized iron and thus subject to release via reductive dissolution (e.g. Benoit and Hemond, 1990).

These results do not imply a recommendation for the deliberate addition of nitrate to any natural waters where eutrophication is a management concern, although there may be case-specific situations where nitrate addition could be considered as a useful tool in concert with other measures. We do, however, argue that it may be beneficial to anticipate and account for possible effects on redox chemistry and thus, potentially, on processes such as internal P loading, when management efforts are undertaken in nitrogen-rich waters.

REFERENCES

Andersen, J.M., 1982. Effect of nitrate concentration in lake water on phosphate release from the sediment. Water Research 16, 1119–1126.

Aurilio, A.C., Mason, R.P., Hemond, H.F., 1994. Speciation and fate of arsenic in three lakes of the Aberjona watershed. Environmental Science and Technology 28 (4), 577–585.

Benoit, G., Hemond, H.F., 1990. [210]Po and ^{210}Pb remobilization from lake sediments in relation to iron and manganese cycling. Environmental Science and Technology 24 (8), 1224–1234.

Bostrom, B., Andersen, J.M., Fleischer, S., Jansson, M., 1988. Exchange of phosphorus across the sediment–water interface. Hydrobiologia 170, 229–244.

Cooke, G.D., Welch, E.B., Peterson, S.A., Newroth, P.R., 1986. Lake and Reservoir Restoration. Butterworth Publishers, Stoneham, MA, ISBN 0-250-40643-8, 392 pp.

Cutrofello, M., Durant, J.L., 2007. Fate of high loads of ammonia in a pond and wetland downstream from a hazardous waste disposal site. Chemosphere 68, 1365–1376.

Downie, N.M., Heath, R.W., 1965. Basic Statistical Methods, second ed. Harper and Row, New York, 325 pp.

Durant, J.L., Zemach, J.J., Hemond, H.F., 1990. The history of leather industry waste contamination in the Aberjona watershed: a mass balance approach. Civil Engineering Practice 5, 44–69.

Einsele, W., 1936. Uber die beziehung des eisenkreislaufs zum phosphorkreislauf in eutrophen seen. Archiv Fur Hydrobiologie 29, 664–686.

Gachter, R., Mueller, B., 2003. Why the phosphorus retention of lakes does not necessarily depend on the oxygen supply to their sediment surface? Limnology and Oceanography 48 (2), 929–933.

Hansen, J., Reitzel, K., Jensen, H.S., Andersen, F.O., 2003. Effects of aluminum, iron, oxygen and nitrate additions on phosphorus release from the sediment of a Danish softwater lake. Hydrobiologia 492, 139–149.

Hauck, S., Benz, M., Brune, A., Schink, B., 2001. Ferrous iron oxidation by denitrifying bacteria in profundal sediments of a deep lake (Lake Constance). FEMS Microbial Ecology 37, 127–134.

Jensen, H.S., Kristensen, P., Jeppesen, E., Skytthe, A., 1992. Iron: phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes. Hydrobiologia 235/236, 731–743.

Jensen, J.P., Pedersen, A.R., Jeppesen, E., Sondergaard, M., 2006. An empirical model describing the seasonal dynamics of phosphorus in 16 shallow eutrophic lakes after external loading reduction. Limnology and Oceanography 51, 791–800.

Kalff, J., 2002. Limnology. Prentice Hall, Upper Saddle River, NJ, ISBN 0-13-033775-7, 592 pp.

Miller, B., 2008. OpenStat version 11.9.08. http://openstat.en.softonic.com downloaded January 2010.

Mortimer, C.H., 1941. The exchange of dissolved substances between mud and water in lakes. Journal of Ecology 29, 280–329.

Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27, 31–36.

Orosz, M.S., 2003 Total and Dissolved Organic Nitrogen Analysis in an Urban Watershed. M. Eng thesis, Massachusetts Institute of Technology, Cambridge, MA, USA.

Peterson, Eliza J.R., 2005. Carbon and Electron Flow via Methanogenesis, SO_4^{2-}, NO_3^-, and Fe^{3+} Reduction in the Anoxic Hypolimnia of Upper Mystic Lake. MS thesis, Massachusetts Institute of Technology, Cambridge, MA, USA.

Rauch, S., Hemond, H.F., Brabander, D.J., 2006. High spatial resolution analysis of lake sediment cores by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Limnology and Oceanography Methods 4, 268–274.

Ripl, W., 1976. Biochemical oxidation of polluted lake sediment with nitrate- a new lake restoration method. Ambio 5 (3), 132–135.

Schindler, D.W., 1974. Eutrophication and recovery in experimental lake 226: implications for lake management. Science 184 (4139), 897–899.

Senn, D.S., Hemond, H.F., 2002. Nitrate controls on iron and arsenic in an urban lake. Science 296, 2373–2376.

Sondergaard, M., Jensen, J.P., Jeppesen, E., 1999. Internal phosphorus loading in shallow Danish lakes. Hydrobiologia 408/409, 145–152.

Spliethoff, H.M., Hemond, H.F., 1996. History of toxic metal discharge to surface waters of the Aberjona watershed. Environmental Science and Technology 30 (1), 121–128.

Stookey, L.L., 1970. Ferrozine – a new spectrophotometric reagent for iron. Analytical Chemistry 42 (7), 779–781.

Straub, K.L., Benz, M., Schink, B., Widdel, F., 1996. Anaerobic, nitrate-dependent microbial oxidation of ferrous iron. Applied and Environmental Microbiology 62, 1458–1460.

U.S.G.S., 2009. National water information system: web interface. http://nwis.waterdata.usgs.gov/nwis/qwdata.

Wetzel, R.G., 2001. Limnology: Lake and River Ecosystems, third ed. Academic Press, San Diego, ISBN-13:978-0-12-744790-5; 1006 pp.