

**Bear Creek / Bear Lake (Muskegon County) Watershed  
Implementation (2) Project:  
Internal Phosphorus Loading**

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## Introduction

Bear Lake (Muskegon County, MI) is a small, eutrophic/hypereutrophic (hereafter referred to as eutrophic) lake located within the Muskegon Lake Area of Concern (AOC). Because of elevated total phosphorus (TP) concentrations and excess algal growth, a Total Maximum Daily Load (TMDL) was issued for Bear Lake in 2008. The TMDL estimated an annual phosphorus load to the lake of 3,387 pounds per year, contributed by both external (54%) and internal (46%) sources (MDEQ 2008). The TMDL calls for a total reduction of 56% in annual phosphorus loads, achieved through a 50% reduction in external load and a 79% reduction in internal load, to attain a target total phosphorus (TP) concentration of 30 µg/L in Bear Lake. Phosphorus load reduction is needed in Bear Lake not only to meet water quality standards, but also to remove the eutrophication and undesirable algae beneficial use impairment (BUI) for Bear Lake and ultimately delist the Muskegon Lake AOC.

Management of phosphorus sources is needed in the Bear Lake watershed in order to achieve the phosphorus reductions necessary to meet the TMDL target. Because phosphorus management can be difficult and costly, a critical first step in the management process is to ensure that the information on existing conditions is accurate. Although external load estimates used in the phosphorus TMDL were determined using measured loads, internal load estimates were derived using an indirect modeling approach (MDEQ 2008). Not only is there inherent uncertainty associated with the modeled internal loads, but Bear Lake also has unique characteristics that may result in poor model performance and magnify the uncertainty in the load estimates, including the influence of fluctuating redox conditions, resuspended sediments, and seasonality (temperature).

As a shallow eutrophic lake, Bear Lake has dynamic redox conditions that are not typically found in deeper lakes. Its shallow depth promotes periodic water column mixing due to wind and wave action during the summer months, whereas many deeper lakes experience stratification and hypolimnetic anoxia during that time period. This anoxia can result in diffusion of dissolved phosphorus from the sediments, as phosphorus that is bound to iron oxides and oxyhydroxides ( $\text{Fe}\sim\text{PO}_4$ ) under oxic conditions is released when the iron becomes reduced (i.e.,  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ ) under anoxic or hypoxic conditions (Boström et al. 1982, Steinman et al. 2004). It is unclear if Bear Lake experiences the hypoxic/anoxic conditions necessary to drive redox-mediated release of P from the sediments (otherwise known as internal loading). Although the lake does not typically stratify, shallow eutrophic lakes such as Bear Lake are often subject to diel fluctuations in water column dissolved oxygen (DO) concentrations. High rates of primary production from abundant algal communities can result in elevated daytime DO due to photosynthesis, but then respiration can cause depleted nighttime and early morning DO, especially under calm conditions, which in turn could lead to short-term release of P from the sediments (cf. Premazzi and Provini 1985, Nürnberg 2009, Nürnberg et al. In Press). Hence, the episodic oxygenation of the hypolimnion via water column mixing and diel DO fluctuations has implications for internal phosphorus loading rates in Bear Lake, both in terms of redox-driven and resuspension-driven phosphorus flux.

Resuspended sediments also can serve as a source of P to the water column. If the phosphorus concentrations in the water column are substantially lower than that of the P bound to sediments,

attached phosphorus can desorb from sediment particles due to the concentration gradient (Steinman et al. 2006, Havens et al. 2007, Cyr et al. 2009) and, if in a bioavailable form, stimulate algal blooms. In a shallow lake such as Bear Lake, both wind-generated internal waves and boat propeller action can result in sediment resuspension and possible P release.

Prior studies have shown that internal P loading is influenced by temperature (Kelton and Chow-Fraser 2005, Steinman et al. 2009). As temperatures warm and microbial activity is stimulated, mineralization of organic P in the sediments is enhanced. As a consequence, greater internal phosphorus loading occurs during warmer than colder months. Therefore, an accurate estimate of *annual* P internal loading should include measurements at various times throughout the year.

Given these different sources of uncertainty, and the current TMDL's call for a very substantial reduction in the internal P load to Bear Lake, it is essential that the original estimated load on which the TMDL was based be as accurate as possible. The goal of this project was to empirically determine internal phosphorus loading rates, compare those numbers to the indirectly derived estimates on which the TMDL was based, and provide recommendations for a strategy to reduce phosphorus loads to Bear Lake. In addition to measuring internal phosphorus loading rates from sediment cores, we characterized the diel oxygen dynamics of the lake. To address the uncertainty in redox conditions, we developed 5 different scenarios of potential redox and mixing conditions, ranging from very conservative to very liberal estimates. Combined with our observational data and best professional judgment, this approach allowed us to provide the Michigan Department of Environmental Quality (MDEQ) with a rigorous estimate of internal phosphorous loading in Bear Lake. Because phosphorus management can be costly and difficult to implement, it is critical to base an abatement strategy on accurate source information.

## **Methods**

### *Site Description*

The 29 mi<sup>2</sup> (77 km<sup>2</sup>) Bear Creek/Bear Lake watershed drains into Muskegon Lake and is located in Muskegon County, Michigan. The watershed includes forested areas (44%), urban/residential development (22%), agricultural lands (6%), wetlands (1%), and other land uses (27%) (Cadmus and AWRI 2007). Bear Creek is the major tributary in the watershed and flows into Bear Lake, which feeds into Muskegon Lake and eventually Lake Michigan. Bear Lake is a 410 acre (1.66 km<sup>2</sup>) drowned river mouth lake, with a mean depth of 6.8 ft (2.1 m) and a maximum depth of 11.8 ft (3.6 m) (Wilson et al. 2005). The hydraulic residence time is 30 d (MDEQ 2008). It is a eutrophic lake, characterized by elevated total phosphorus (TP) concentrations and heavy summer blooms of cyanobacteria (Cadmus and AWRI 2007, MDEQ 2008, Xie et al. 2011). Despite the high TP concentrations, soluble reactive phosphorus (SRP) is often below detection in the summer, presumably because of active uptake by cyanobacteria (Xie et al. 2011). Based on N:P molar ratios, the system appears to be P-limited, providing further validation that P control is essential because additional P could result in even more bloom formation (Xie et al. 2011).

### *Water Quality*

Water quality was measured at the 4 primary coring locations (see below) at the time of core collection. Dissolved oxygen, pH, temperature, specific conductance, chlorophyll *a*, and total dissolved solids were measured at the surface, middle, and bottom of the water column using a YSI 6600 sonde. Photosynthetically active radiation (PAR) profiles were measured using a LiCor Li-193SA spherical quantum sensor. Secchi disk depth was measured at each site to estimate water clarity. Water samples for phosphorus analysis were collected at the near-surface and near-bottom with a Niskin bottle. Water for SRP analysis was immediately syringe-filtered through 0.45- $\mu\text{m}$  membrane filters into scintillation vials. Samples were stored on ice until transported to the laboratory, within 5 h of collection. TP samples were stored at 4°C and SRP samples were frozen until analysis. Water quality sampling occurred between 09:00 and 15:00 during each sampling event.

### *Diel Dissolved Oxygen Concentrations*

Measurements of diel DO concentration provided information on the redox status in Bear Lake; we used these data in the annual internal P loading models described below. Water column DO concentrations were measured overnight, from late afternoon until mid-morning, to characterize diel fluctuations in DO. YSI 6600 sondes were suspended from an anchored buoy at the near-surface and near-bottom of the lake at Sites 2 and 5. These sites were chosen because they are the deepest (Site 2, 3.5 m) and shallowest (Site 5, 2.5 m) of the 4 primary coring locations (Figure 1). The sondes were programmed to log data every 10 minutes. Diel DO concentrations were measured 4 times over the study period: 16 August 2011; 14 May 2012; 27 June 2012; and 29 August 2012. Wind speed and direction data for all diel DO events were downloaded from the Muskegon Lake Buoy Observatory (Biddanda and Kendall 2013).

### *Phosphorus Release Rate Determination - Modeled*

Sediment cores were collected (described below) on 4 August 2011 and 11 July 2012, at 15 locations in Bear Lake (Figure 1) for estimation of P release rates using the modeling approach described in Nürnberg (1988). One sediment core was collected at each site and the top 5 cm was removed for analysis of TP in the lab, as described below.

Phosphorus release rate was modeled by applying the regression:

$$P_{\text{rr}} = 0.8 + 0.76 (\log \text{TP})$$

where,  $P_{\text{rr}}$  is the net P release rate (positive values) or retention rate (negative values) per unit surface area of sediments ( $\text{mg}/\text{m}^2/\text{d}$ ) and TP is sediment TP ( $\text{mg}/\text{kg}$ ).

Modeled P release rates were used as a comparison for empirical P release rates. We applied a similar approach to calculate an estimated internal P load in a previous study (Cadmus and AWRI 2007), which was then used by MDEQ in their Bear Lake TMDL. However, our approach differed from the one used in the 2007 report in two ways: 1) we used a different regression based on personal communications with Gertrud Nürnberg and 2) our sediment P sample size was larger in this study ( $n = 15$ ) than in the 2007 ( $n = 9$ ) study, reducing the population variance in our lakewide P estimate.



Figure 1. Sampling locations in Bear Lake. Sites 1, 2, 3, and 5 (red dots) were primary coring locations sampled for empirical determination of internal phosphorous loading. All locations (n=15) were sampled for sediment phosphorus, which was used to model estimates of internal phosphorus loading.

### *Phosphorus Release Rate Determination – Empirical*

Sediment cores were collected from 4 primary locations (Sites 1, 2, 3, and 5) in Bear Lake on 21 April 2011; 4 August 2011; 27 October 2011; and 11 July 2012 (Figure 1). Sediment core sampling and laboratory incubation followed the procedures of Steinman et al. (2004). Six sediment cores were collected from each site using a piston corer (Fisher et al. 1992, Steinman et al. 2004). The corer was constructed of a graduated 0.6-m long polycarbonate core tube (7-cm inner diameter) and a polyvinyl chloride (PVC) attachment assembly for coupling to aluminum drive rods. The piston was advanced 20 to 25 cm prior to deployment to maintain a water layer on top of the core during collection. The corer was positioned vertically at the sediment–water interface and pushed downward with the piston cable remaining stationary. After collection, the core was brought to the surface and the bottom was sealed with a rubber stopper prior to removal from the water, resulting in an intact sediment core that was ~20 cm in length, with a 25-cm overlying water column. The piston was then bolted to the top of the core tube to keep it

stationary during transit. Core tubes were placed in a vertical rack and maintained at ambient temperature during transit. An additional core was collected from each site for sediment chemistry analysis; the top 5 cm was removed for the analysis of TP, major elements (Fe, Al, Mg, and Ca), and ash-free dry mass (AFDM) in the lab (see below).

The 24 sediment cores (6 per site) were placed in a Revco environmental growth chamber, with the temperature maintained to match ambient near-bottom conditions in Bear Lake at the time of collection. The water column in three of the cores from each site was bubbled with N<sub>2</sub> (with 330 ppm CO<sub>2</sub>) to create buffered anoxic conditions, while the remaining three were bubbled with oxygen to create oxic conditions.

Phosphorus release rate estimates were made using the methods outlined in Moore et al. (1998), with minor modifications (Steinman et al. 2004, 2009). Briefly, a 40-mL water sample was removed by syringe through the sampling port of each core tube at 0 h, 12 h, 1 d, 2 d, 4 d, 6 d, 8 d, 12 d, 16 d, 20 d, 24 d, and 27 d (October 2011 samples were collected at 25 d, but not at 24 d and 27 d). Immediately after removal, a 20-mL subsample was refrigerated for analysis of TP, and a 20-mL subsample was filtered through a 0.45- $\mu$ m membrane filter and frozen for analysis of soluble SRP. SRP and TP were analyzed on a SEAL AQ2 discrete automated analyzer (U.S. EPA 1983). P values below detection were calculated as ½ the detection limit (5  $\mu$ g/L). The 40-mL subsample was replaced with filtered water collected from the corresponding site in the lake; this maintained the original volume in the core tubes (at the time of core collection).

Flux (P release rate) calculations were based on the change in water column TP using the following equation (Steinman et al. 2004, 2009):

$$P_{rr} = (C_t - C_0) V/A$$

where,  $P_{rr}$  is the net P release rate (positive values) or retention rate (negative values) per unit surface area of sediments,  $C_t$  is the TP concentration in the water column at time t,  $C_0$  is the TP concentration in the water column at time 0, V is the volume of water in the water column, and A is the planar surface area of the sediment cores. P release rate was calculated over the time period that resulted in the maximum apparent release rate, with the caveat that the initial and final samplings could not be consecutive dates to avoid potential short-term bias.

### *Annual Internal Phosphorus Loading*

Using the sediment P release rates from our laboratory incubations, combined with different redox and water mixing scenarios, we generated five different annual internal P load estimates (Table 1). We purposefully included conservative and liberal internal load estimates, to provide the boundaries for plausible low and high annual internal P loads, respectively.

We caveat these loading estimates given the limitations of our data. First, although the diel DO measurements provide an indication of daily redox conditions, much higher-resolution data are needed to characterize the diel changes in DO both spatially and temporally. Second, the hydrodynamics of Bear Lake have not been documented. It is clear that wind- and wave-induced mixing occurs during the summer months, but the spatial and temporal extent of such events is

not known. Third, our estimates do not account for internal loading that may be associated with sediment resuspension, which we could not accurately mimic in our incubations.

Annual internal P load (lbs/yr) was calculated for scenarios 1, 2, 3, and 5 according to the following equation:

$$L_{int} = ([RX_{spring} + RX_{summer} + RX_{fall} + RX_{winter}] \times d \times A_X) + ([RO_{spring} + RO_{summer} + RO_{fall} + RO_{winter}] \times d \times A_O)$$

where  $L_{int}$  is the annual internal P load, RX is the anoxic release rate, RO is the oxic release rate, d is the number of days per season (91.25),  $A_X$  is the anoxic lake area, and  $A_O$  is the oxic lake area. Winter release rates were assumed to be 0. Summer release rates were calculated as the average of rates measured in August 2011 and July 2012.

Scenario 4 was based on the model by Nürnberg et al. (2012) for the active sediment release area and time (AA), which represents the length of time (days/season) that an area similar to the lake surface area is actively releasing P. This model was developed to calculate the number of anoxic days a polymictic lake may experience during a season or year (Nürnberg et al. 2012). Annual internal P load for polymictic lakes was estimated as follows:

1. Active sediment release area and time (AA; Nürnberg 2012)

$$AA = -36.2 + 50.2 \log (P_{season}) + 0.762 z/A^{0.5}$$

where P is the average water column TP concentration during a given season, z is mean depth, and A is lake surface area. AA values (days/season) were used to calculate annual internal P load, according to the equation that follows, which we modified from Nürnberg (2012) to explicitly account for the spring and fall seasons.

2. Annual internal P load ( $L_{int}$ )

$$L_{int} = [(AA_{spring}(RX_{spring}) + \dots + AA_{winter}(RX_{winter})) + (dO_{spring}(RO_{spring}) + \dots + dO_{winter}(RO_{winter}))] A$$

where  $AA_{season}$  is the number of anoxic days per season, RX is the anoxic release rate, dO is the number of oxic days per season ( $91.25 - AA_{season}$ ), RO is the oxic release rate, and A is lake surface area.

Table 1. Scenarios used to calculate a range of annual internal P load estimates for Bear Lake, ordered from most conservative (Scenario 1) to most liberal (Scenario 5) estimates.

<b>Scenario</b>	<b>Hypoxic Surface Area of Lake Bottom</b>	<b>General Explanation</b>	<b>Rationale</b>
1. Aerobic: entire lake	0 km <sup>2</sup>	Assumes entire lake remains oxic throughout year; most conservative internal loading estimate	Lack of thermal stratification restricts anoxia although still possible to get hypoxic zones
2. Anaerobic: depths > 3.0 m; rest of lake aerobic	0.047 km <sup>2</sup>	Assumes lake becomes hypoxic at deepest depths; very conservative estimate	Water column mixing is less likely to introduce oxygenated water at deepest depths, allowing hypoxia to develop during calm periods
3. Anaerobic: depths > 2.7 m; rest of lake aerobic	0.296 km <sup>2</sup>	Assumes lake becomes hypoxic at relatively deep locations; generally conservative estimate	Similar to Scenario 2, but this scenario allows a greater surface area of lake bottom to go hypoxic than Scenario 2, potentially resulting in more sediment P release during calm periods
4. Polymictic lake estimate (Nürnberg et al. 2012)	N/A	Based on a modeled value for the number of anoxic days per year in polymictic lakes; moderate estimate	Water column mixing is a temporal phenomenon in polymictic lakes; this model estimates the number of days a polymictic lake experiences anoxia, which is then used to calculate redox-specific loading.
5. Anaerobic: entire lake	1.518 km <sup>2</sup>	Assumes entire lake becomes anoxic; most liberal estimate	This scenario does not happen under current conditions, but it provides an extreme upper limit for how much internal loading theoretically could occur in Bear Lake



### *Sediment Core Chemistry*

Immediately following the sediment core incubations, the overlying water was drawn off with a peristaltic pump. A subsample of the overlying water was preserved with nitric acid and analyzed for total Fe content. The top 5 cm of sediment was then removed from each core, homogenized, and subsampled for analysis of TP, major elements (Al, Ca, Fe, Mg), and AFDM. Elements were analyzed according to U.S. EPA (2007); AFDM and TP (on ashed material) were analyzed according to APHA (1992). Sediment Fe:P ratios were determined by weight using dry weight TP concentrations.

Another subsample (5 g) of wet sediment was centrifuged to remove excess porewater and sequentially fractionated (Moore and Reddy 1994) to determine the fraction of phosphorus bound to iron and calcium minerals in the sediments. pH of the porewater was measured (summer 2011 and 2012 only) using a micro pH probe (Lazar Research Laboratories) and porewater samples were filtered, frozen, and analyzed for SRP as described previously. Residual sediment was shaken for 17 h with 0.1M NaOH, centrifuged, filtered, frozen, and analyzed for total soluble phosphorus (TSP) with persulfate digestion. This fraction is referred to Al- and Fe-bound phosphorus and represents a mineral association that can become soluble under anoxic conditions. After this extraction, the sediment was extracted for 24 h with 0.5M HCl, centrifuged, filtered, frozen, and analyzed for TSP. This fraction is referred to as Ca- and Mg-bound phosphorus and represents a stable mineral association. The TSP-P analysis was used to remove the color from the extracts and provide a more accurate measure of phosphorus. Values below the detection limit were calculated as  $\frac{1}{2}$  the detection limit.

### *Statistical Analysis*

The effects of site and sampling date on maximum TP concentrations measured during core incubations, maximum apparent TP release rates, sediment TP concentration, and sediment elemental content were evaluated using either a one-way analysis of variance (ANOVA) or Kruskal-Wallis one way ANOVA on ranks, if assumptions of normality and/or equal variance were not met. Multiple comparison tests were performed for all significant contrasts ( $p < 0.05$ ) using the Holm-Sidak method (ANOVA) or Tukey test (Kruskal-Wallis). The effect of redox treatment on sediment TP concentrations, sediment elements, and water column Fe concentrations was tested using a t-test or rank sum test, if assumptions of normality and/or equal variance were not met. Differences between modeled and measured TP release rates were evaluated using either a t-test or rank sum test. NaOH- and HCl-extractable TSP was analyzed using a three-way ANOVA to examine the effects of site, redox condition, and extractant. When necessary, TSP concentrations were transformed (ln, square root, reciprocal) prior to analysis in order to meet normality and equal variance requirements of the ANOVA.

## **Results**

### *Water Quality*

Water depth was shallowest at Site 5 and deepest at Sites 1 and 2 (Table 1). Secchi depth was  $< 1$  m during all sampling events, with the shallowest Secchi depths of  $\leq 0.5$  m measured during the summer months (Table 1). Mean light extinction coefficients ranged from 1.60 in April 2011 to

2.89 in August 2011. Water temperature showed no sign of thermal stratification on the dates and at the times we sampled, with near-bottom temperatures usually within 1°C of the near-surface temperatures (Table 1). Mean dissolved oxygen (DO) concentrations were 11-12 mg/L during the April and October 2011 sampling events. Although DO was lower during the August 2011 and July 2012 events, the lowest near-bottom concentration measured was 6.06 mg/L (Site 2, August 2011; Table 1), well above potentially hypoxic conditions. Mean turbidity was higher during the summer sampling events (August 2011 and July 2012; 16.9-21.9 NTU) than in April and October 2011 (5.6-8.7 NTU; Table 1). Mean chlorophyll *a* concentrations were lowest in April 2011 and highest in October 2011, when they ranged from 19-24 µg/L (Table 1). Sensor malfunction in July 2012 prohibited the collection of chlorophyll data during that sampling event. Water column TP was similar among sites and between near-surface and near-bottom depths. TP was lowest in April and October 2011 (30-40 µg/L) and highest in August 2011 and July 2012 (50-70 µg/L; Table 1).

#### *Diel Dissolved Oxygen Concentrations*

Overnight measurements of dissolved oxygen (DO) concentration revealed diel DO fluctuations at Site 2, the deepest primary coring location. Low DO concentrations were measured near the bottom of Site 2 (2.7-3.0 m sensor depth) during the night and early morning. This was especially pronounced during the mid-summer measurements (August 2011 and 2012), when DO concentrations dipped below 2 mg/L by early morning (Figures 2 and 5). During the late spring diel measurement (May 2012), DO concentrations were <5 mg/L by early morning (Figure 3). In contrast, near-bottom DO at Site 2 during the early summer measurement (June 2012) was >7 mg/L, most likely due to wind-induced mixing (Figure 4). Wind speeds of 15-20 knots were measured at the Muskegon Lake Buoy Observatory beginning at 11:00 on June 27 (data not shown) and continued until 03:00 on June 28 (Figure 4; Biddanda and Kendall 2013). Wind speeds during the other diel measurements were <10 knots (Figures 2, 3, and 5).

Table 1. Selected water quality variables for primary coring locations in Bear Lake. All measurements were taken between 09:00 and 15:00. NA = data not available due to sensor malfunction.

Variable	Date	Site 1		Site 2		Site 3		Site 5		Mean (SD)			
Bottom depth (m)	4/2/2011	2.85		3.15		3.20		2.20		2.85	(0.46)		
	8/4/2011	3.65		3.80		3.30		2.60		3.34	(0.53)		
	10/27/2011	3.60		3.60		3.40		2.70		3.33	(0.43)		
	7/11/2012	3.55		3.40		3.00		2.40		3.09	(0.51)		
Secchi depth (m)	4/2/2011	0.75		0.60		0.75		0.75		0.71	(0.08)		
	8/4/2011	0.50		0.50		0.50		0.50		0.50	(0.00)		
	10/27/2011	0.75		0.90		0.75		0.75		0.79	(0.08)		
	7/11/2012	0.40		0.35		0.40		0.50		0.41	(0.06)		
Light extinction coefficient ( $K_d$ )	4/2/2011	1.72		1.43		1.50		1.75		1.60	(0.16)		
	8/4/2011	2.55		2.81		2.81		3.37		2.89	(0.34)		
	10/27/2011	2.58		2.08		1.90		2.11		2.17	(0.29)		
	7/11/2012	2.62		2.41		2.59		2.85		2.62	(0.18)		
		Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom		
Temp (°C)	4/2/2011	8.23	7.69	7.36	7.33	7.27	7.18	7.85	6.66	7.68	(0.45)	7.22	(0.43)
	8/4/2011	28.14	27.40	27.55	27.07	27.44	26.94	26.67	26.64	27.45	(0.60)	27.01	(0.31)
	10/27/2011	9.91	9.50	9.58	9.63	9.63	9.65	9.60	9.40	9.68	(0.15)	9.55	(0.12)
	7/11/2012	27.76	26.63	27.91	26.66	27.54	26.73	27.23	26.32	27.61	(0.30)	26.59	(0.18)
DO (mg/L)	4/2/2011	11.99	11.99	12.05	11.97	11.91	11.83	11.51	11.82	11.87	(0.24)	11.90	(0.09)
	8/4/2011	9.52	7.26	8.87	6.06	7.67	6.54	6.91	6.53	8.24	(1.17)	6.60	(0.50)
	10/27/2011	11.81	11.17	11.42	10.84	11.07	10.96	11.07	10.69	11.34	(0.35)	10.92	(0.20)
	7/11/2012	9.45	7.06	9.99	7.62	9.87	7.99	9.50	9.34	9.70	(0.27)	8.00	(0.97)
Turbidity (NTU)	4/2/2011	5.7	6.0	5.8	5.9	5.7	5.8	5.2	6.2	5.6	(0.3)	6.0	(0.2)
	8/4/2011	19.6	20.6	19.4	28.1	19.6	21.7	17.3	17.3	19.0	(1.1)	21.9	(4.5)
	10/27/2011	5.5	5.8	5.2	11.7	10.1	6.5	5.6	10.6	6.6	(2.3)	8.7	(2.9)
	7/11/2012	15.6	19.8	22.3	18.3	14.9	17.6	14.9	22.1	16.9	(3.6)	19.5	(2.0)
Chl <i>a</i> (µg/L)	4/2/2011	5.6	10.9	7.9	11.4	2.6	11.5	5.5	12.1	5.4	(2.2)	11.5	(0.5)
	8/4/2011	5.3	13.4	14.2	16.4	11.9	14.4	12.1	11.7	10.9	(3.9)	14.0	(2.0)
	10/27/2011	18.8	22.5	24.0	22.1	24.3	22.3	23.5	18.1	22.7	(2.6)	21.3	(2.1)
	7/11/2012	NA		NA		NA		NA		NA		NA	
TP (µg/L)	4/2/2011	30	30	30	30	30	30	30	40	30	(0)	33	(5)
	8/4/2011	60	70	60	60	60	70	50	60	58	(5)	65	(6)
	10/27/2011	30	30	30	30	30	30	30	40	30	(0)	33	(5)
	7/11/2012	70	70	60	70	70	70	60	40	65	(6)	63	(15)

### August 16-17 2011

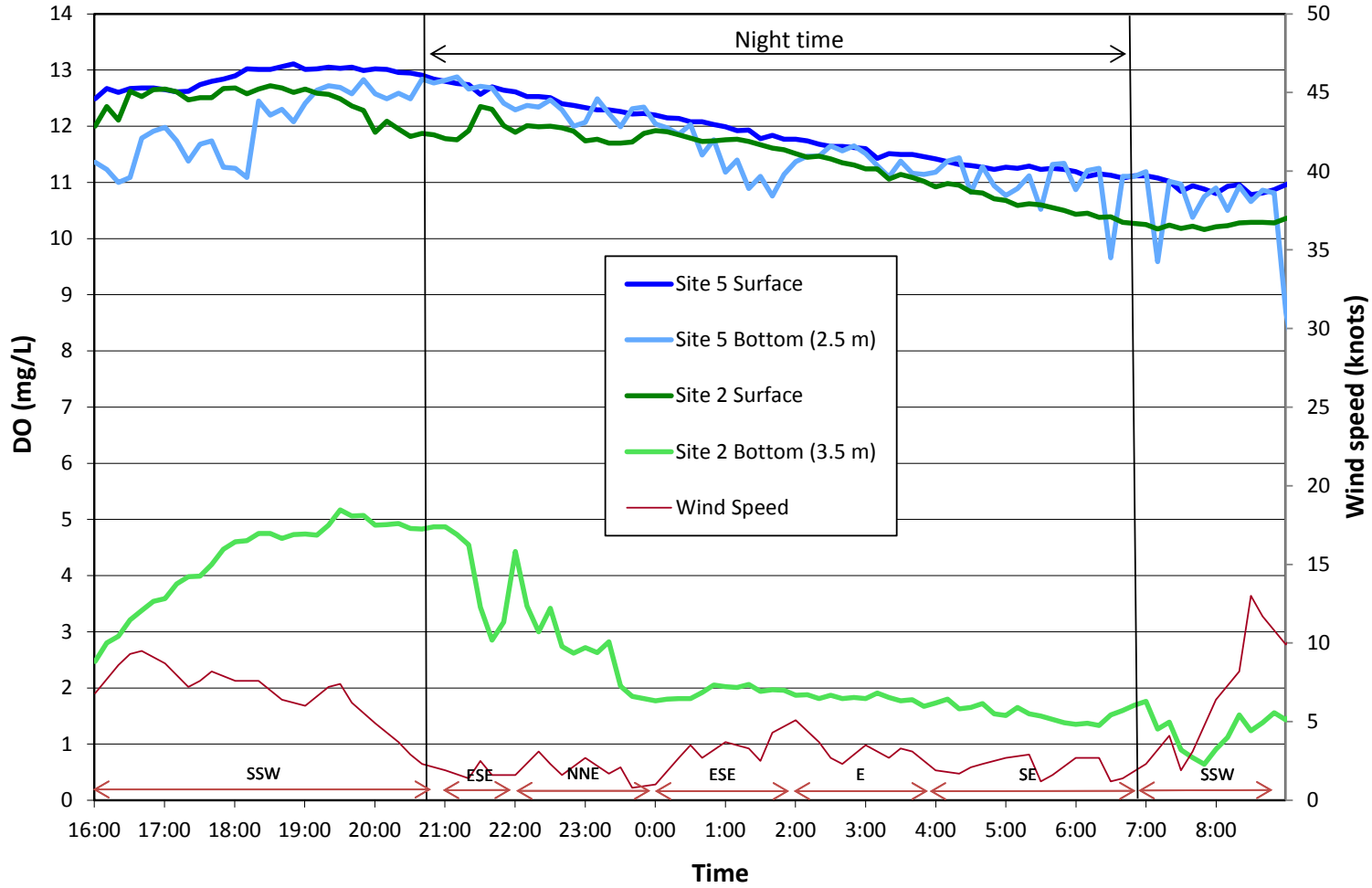


Figure 2. Diel dissolved oxygen (DO) data measured August 16-17, 2011 at the shallowest (Site 5) and deepest (Site 2) primary coring locations in Bear Lake. Wind speed (red line) and cardinal direction, shown at the bottom of the figure, are from Biddanda and Kendall (2013).

### May 14-15 2012

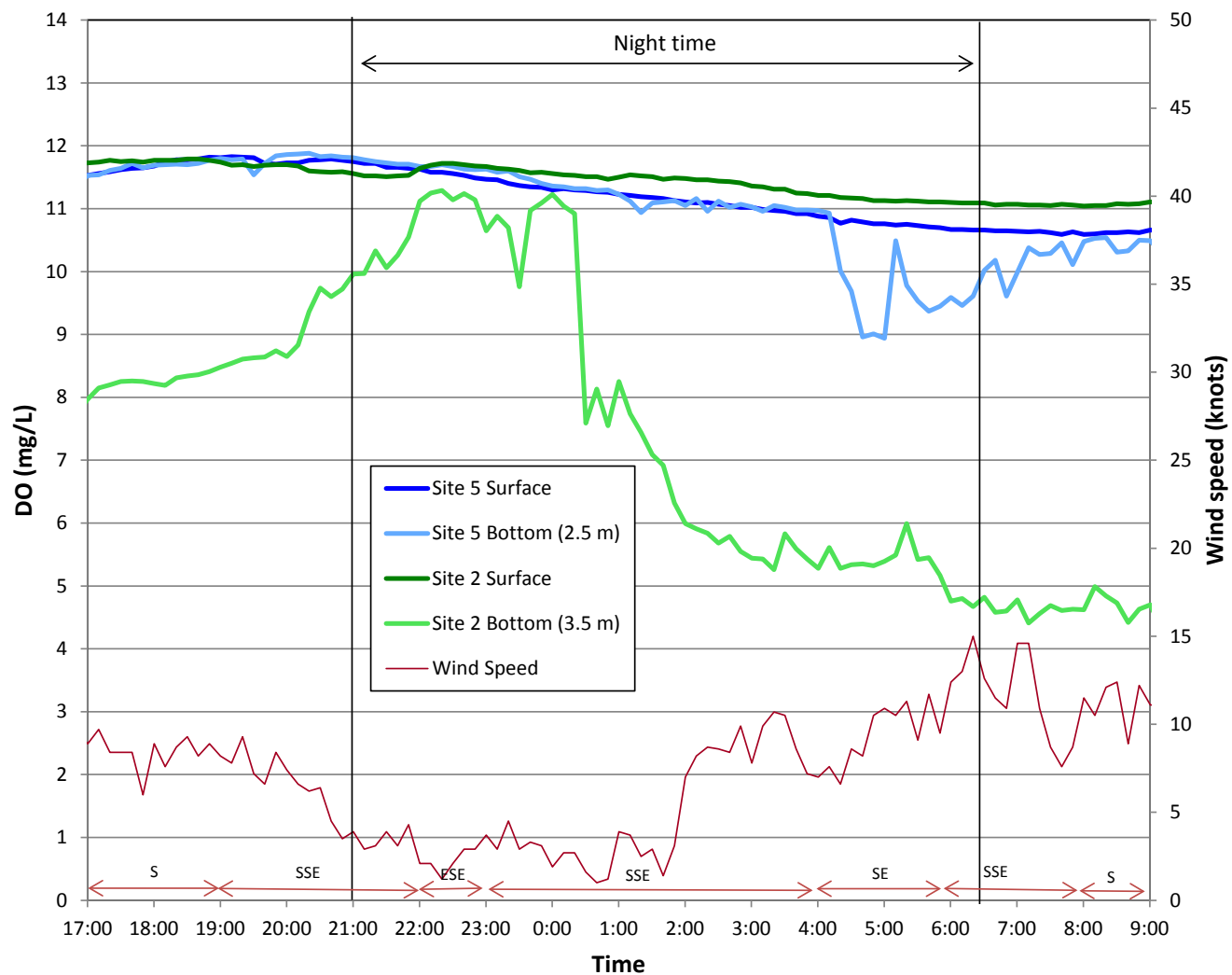


Figure 3. Diel dissolved oxygen (DO) data measured May 14-15, 2012 at the shallowest (Site 5) and deepest (Site 2) primary coring locations in Bear Lake. Wind speed (red line) and cardinal direction, shown at the bottom of the figure, are from Biddanda and Kendall (2013).

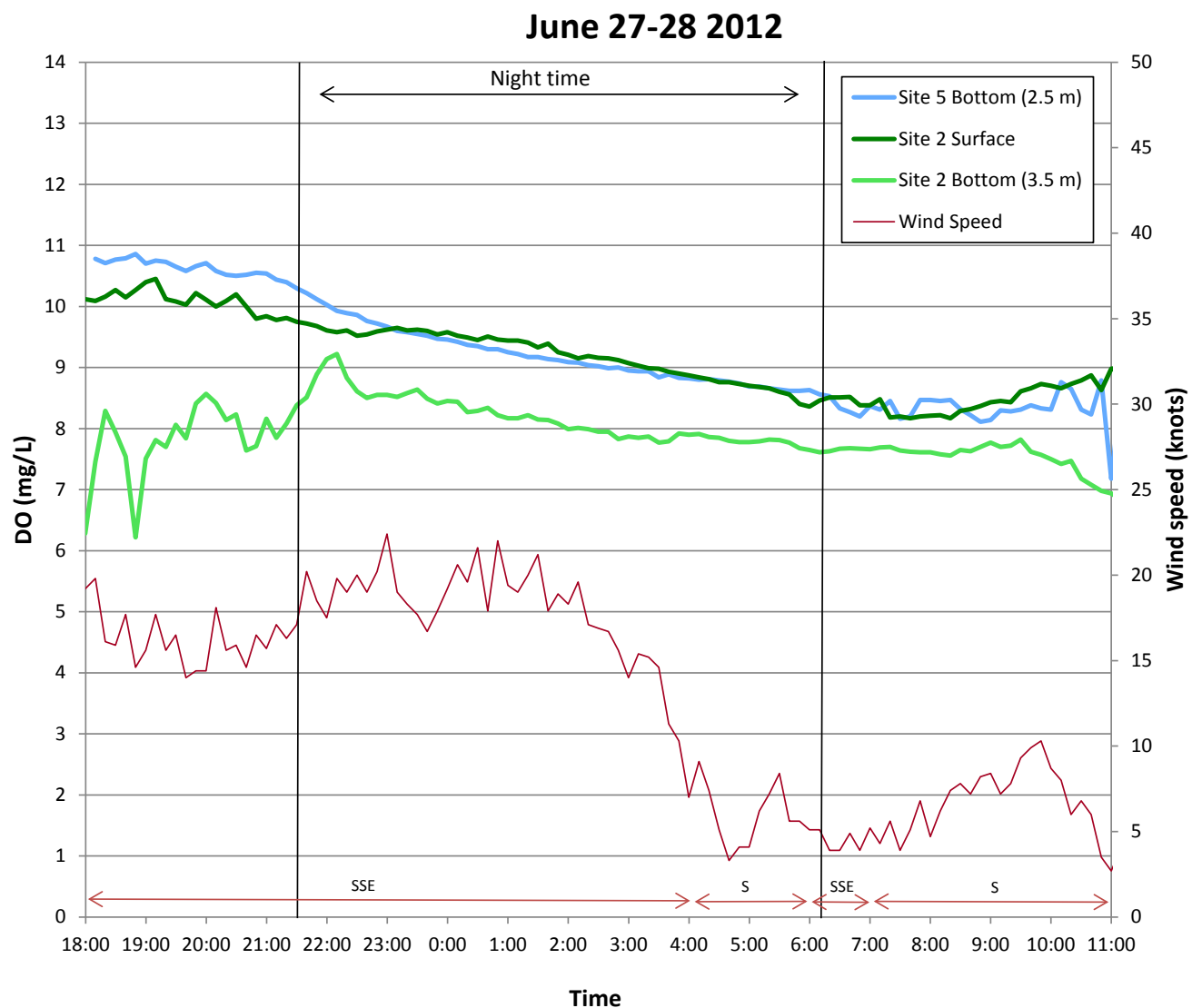


Figure 4. Diel dissolved oxygen (DO) data measured June 27-28, 2012 at the shallowest (Site 5) and deepest (Site 2) primary coring locations in Bear Lake. Due to sensor malfunction, no data were logged at Site 5 surface. Wind speed (red line) and cardinal direction, shown at the bottom of the figure, are from Biddanda and Kendall (2013).

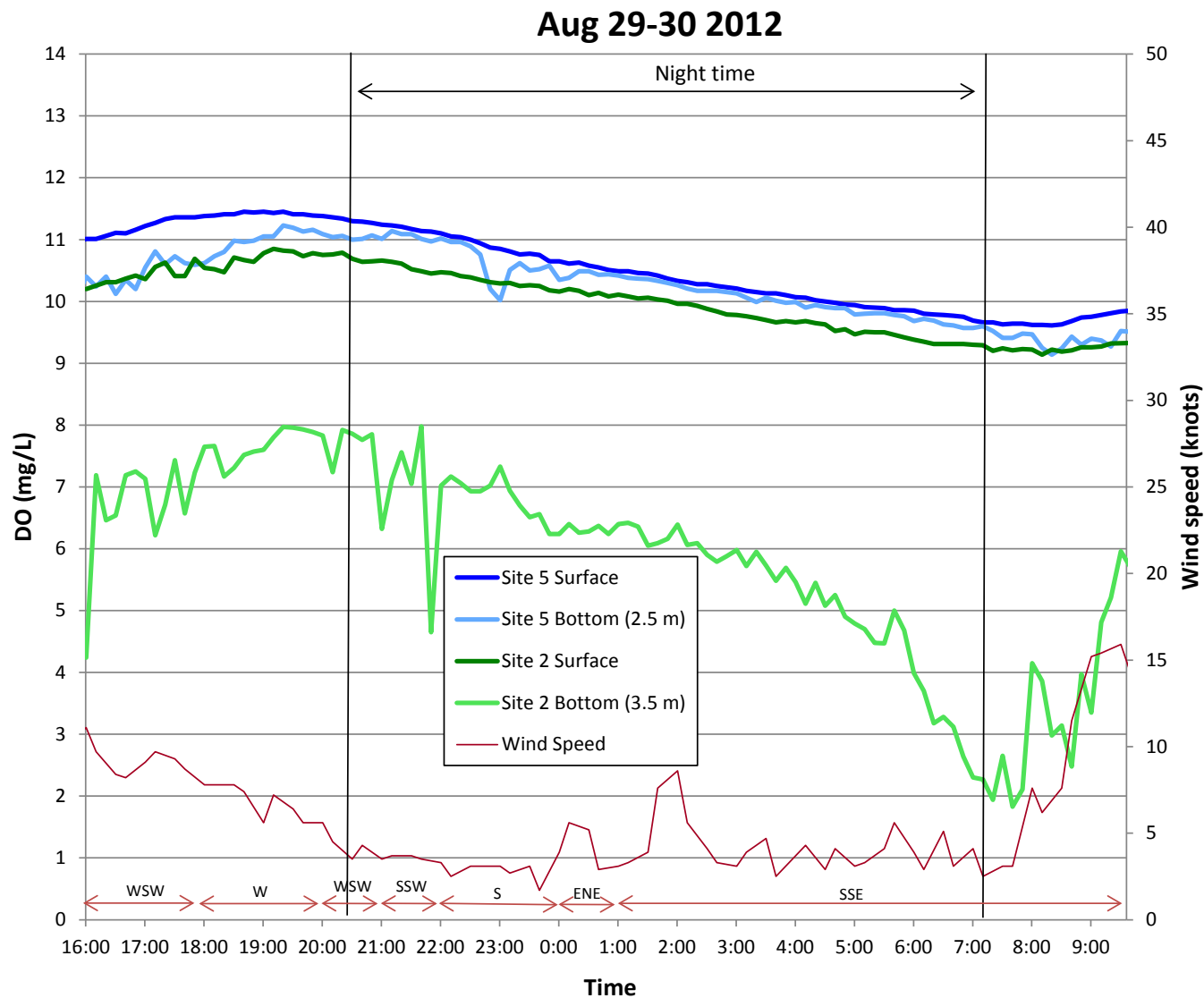


Figure 5. Diel dissolved oxygen (DO) data measured August 29-30, 2012 at the shallowest (Site 5) and deepest (Site 2) primary coring locations in Bear Lake. Wind speed (red line) and cardinal direction, shown at the bottom of the figure, are from Biddanda and Kendall (2013).

### *Phosphorus Release Rates*

SRP concentrations in the water column overlying sediment cores were below detection (April 2011 and October 2011) and/or very low (August 2011 and July 2012); therefore all P release analyses were performed using TP concentrations. TP concentrations generally followed the same pattern within each incubation period, with an initial decline in TP followed by 1) some degree of increase in TP in the anoxic treatments or 2) a stabilization or slowing of the TP decline in the oxic treatments (Figure 6). Maximum TP concentrations were highest during the summer incubations, with mean values of 146-192  $\mu\text{g/L}$  in August 2011 and 103-147  $\mu\text{g/L}$  in July 2012 ( $p < 0.001$ ; Figure 7). Site was not a factor in P release, as maximum TP concentrations were not statistically different among sites within each season (Figure 7).

Maximum apparent TP release rates under anoxic conditions were greatest during the summer incubations, with grand means of 6.69  $\text{mg/m}^2/\text{day}$  in August 2011 and 3.92  $\text{mg/m}^2/\text{day}$  in July 2012 ( $p < 0.001$ ; Table 2); the difference in summer release rates not statistically significant ( $p > 0.05$ ) because of high variance. Similar to maximum TP concentrations, there were no statistically significant differences in anoxic TP release rates among sites. Oxic TP release rates were very low, ranging from grand means of 0  $\text{mg/m}^2/\text{day}$  in April 2011 to 0.77  $\text{mg/m}^2/\text{day}$  in August 2011 (Table 2).

Summer release rates in Bear Lake were comparable to those measured in White Lake (Muskegon County), where internal loading was determined to be of relatively low importance to the overall P budget of the lake (Steinman et al. 2008), and Spring Lake (Ottawa County) 5 years after an alum treatment that effectively curbed internal P loading (Table 3; Steinman and Ogdahl 2012). Mona Lake (Muskegon County) and pre-alum Spring Lake, area lakes where internal loading has been implicated as a major P source, had considerably higher anoxic release rates during summer (Table 3; Steinman et al. 2004, 2009).

Anoxic TP release rates modeled according to Nürnberg (1988) compared reasonably well with measured rates and were not statistically different (Table 3). Modeled anoxic TP release rates ranged from 0.51  $\text{mg/m}^2/\text{day}$  to 8.36  $\text{mg/m}^2/\text{day}$  in 2011 and 0.45  $\text{mg/m}^2/\text{day}$  to 8.09  $\text{mg/m}^2/\text{day}$  in 2012 (Table 4).



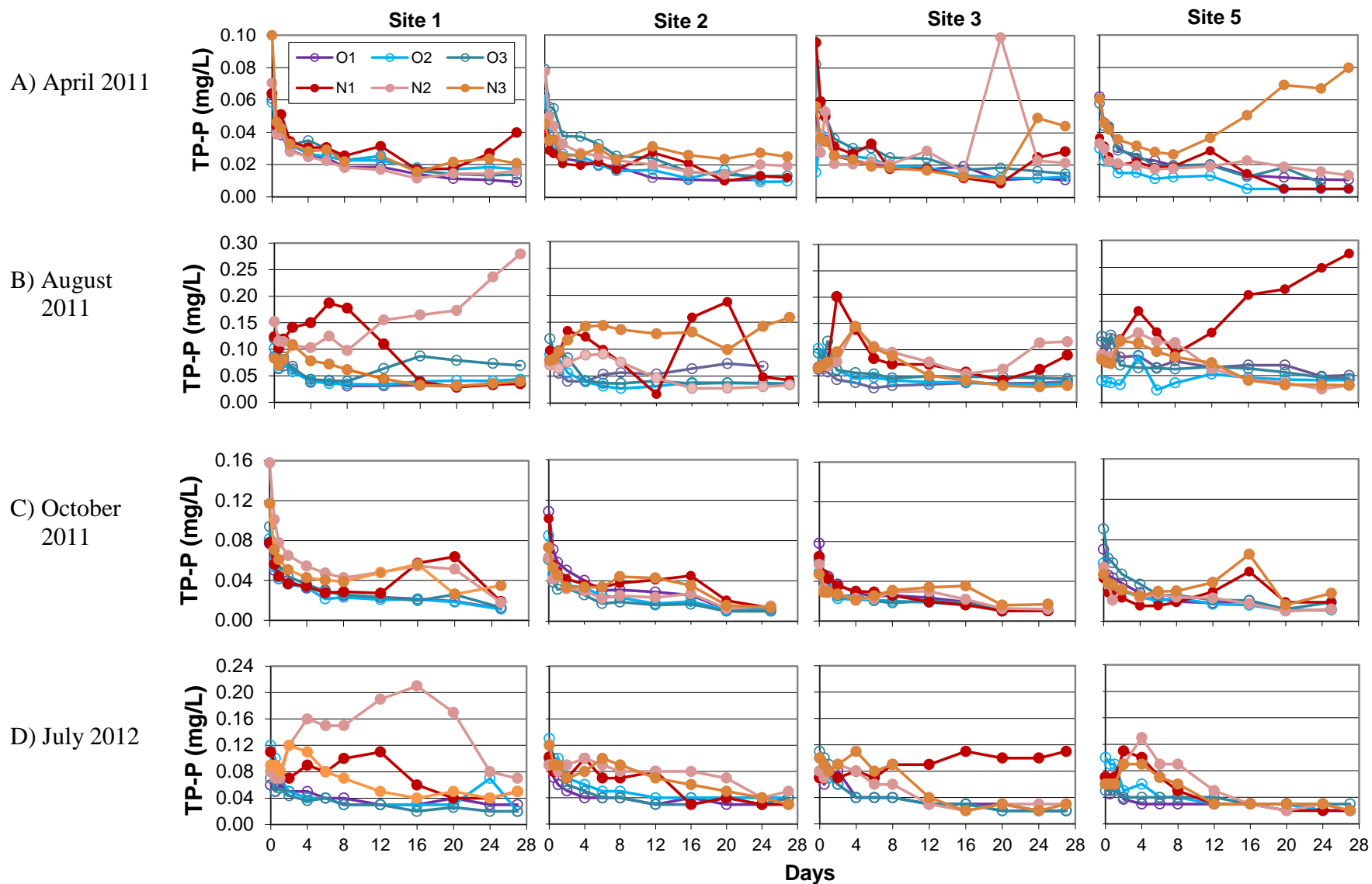


Figure 6. Total phosphorus (TP) concentrations in the water overlying sediment cores from 4 Bear Lake sites sampled in 2011 and 2012. The letter in the legend refers to redox state (N = nitrogen, anoxic treatment; O = oxygen, oxic treatment); the number refers to replicate number (1-3).

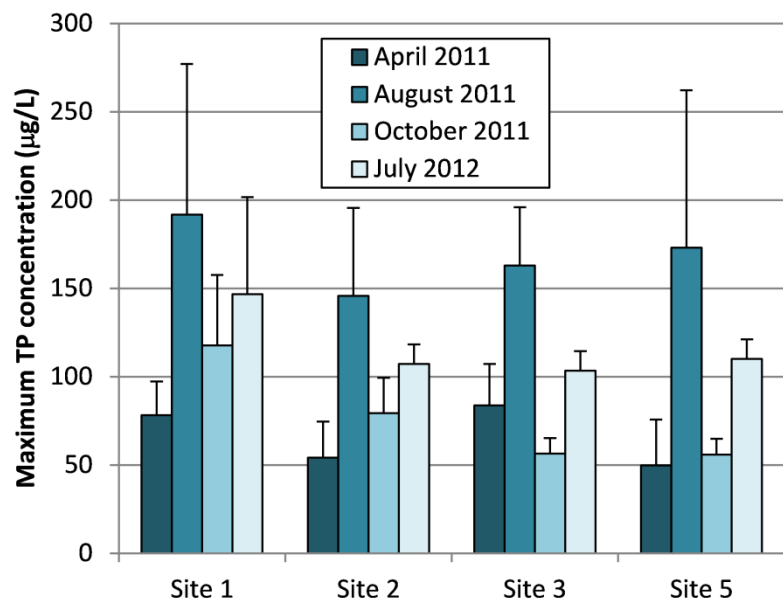


Figure 7. Mean ( $\pm$ SD) maximum TP concentrations ( $n=3$ ) in water overlying sediment cores incubated under anoxic conditions.

Table 2. Maximum apparent TP release rates ( $\text{mg}/\text{m}^2/\text{day}$ ) from sediment cores collected in Bear Lake and incubated under anoxic and oxic conditions.

Date	Site	Anoxic	Oxic
		Mean $\pm$ SD	Mean $\pm$ SD
April 2011	1	0.38 $\pm$ 0.38	0.00 $\pm$ 0.00
	2	0.34 $\pm$ 0.07	0.00 $\pm$ 0.00
	3	0.69 $\pm$ 0.66	0.00 $\pm$ 0.00
	5	0.23 $\pm$ 0.41	0.00 $\pm$ 0.00
	Grand Mean	0.41 $\pm$ 0.20	0.00 $\pm$ 0.00
August 2011	1	5.15 $\pm$ 1.62	0.78 $\pm$ 0.75
	2	3.49 $\pm$ 1.83	0.33 $\pm$ 0.33
	3	11.40 $\pm$ 9.88	0.23 $\pm$ 0.20
	5	6.72 $\pm$ 1.34	1.75 $\pm$ 2.28
	Grand Mean	6.69 $\pm$ 3.41	0.77 $\pm$ 0.70
October/ November 2011	1	0.66 $\pm$ 0.33	0.11 $\pm$ 0.19
	2	0.48 $\pm$ 0.17	0.00 $\pm$ 0.00
	3	0.37 $\pm$ 0.34	0.00 $\pm$ 0.00
	5	0.94 $\pm$ 0.40	0.00 $\pm$ 0.00
	Grand Mean	0.61 $\pm$ 0.25	0.03 $\pm$ 0.05
July 2012	1	3.95 $\pm$ 3.48	0.55 $\pm$ 0.69
	2	1.79 $\pm$ 0.16	0.24 $\pm$ 0.21
	3	3.22 $\pm$ 0.51	0.35 $\pm$ 0.61
	5	6.72 $\pm$ 1.83	0.00 $\pm$ 0.00
	Grand Mean	3.92 $\pm$ 2.07	0.28 $\pm$ 0.51

Table 3. Maximum apparent TP release rates ( $\text{mg}/\text{m}^2/\text{day}$ ) measured during summer from sediment cores collected from Bear Lake and three other west Michigan lakes: Mona Lake, Spring Lake, and White Lake.

Lake	Anoxic	Oxic	Source
	Mean $\pm$ SD	Mean $\pm$ SD	
Bear Lake (2011)	6.69 $\pm$ 3.41	0.77 $\pm$ 0.70	This study
Bear Lake (2012)	3.92 $\pm$ 2.20	0.28 $\pm$ 0.51	This study
Mona Lake	11.38 $\pm$ 3.90	0.83 $\pm$ 0.40	Steinman et al. 2009
Spring Lake (pre-alum)	17.97 $\pm$ 8.07	0.03 $\pm$ 0.44	Steinman et al. 2004
Spring Lake (1 yr post-alum)	0.41 $\pm$ 0.38	0.20 $\pm$ 0.08	Steinman and Ogdahl 2008
Spring Lake (5 yr post-alum)	2.27 $\pm$ 0.46	1.14 $\pm$ 1.24	Steinman and Ogdahl 2012
White Lake	3.75 $\pm$ 2.77	0.02 $\pm$ 0.14	Steinman et al. 2008

Table 4. TP release rates ( $\text{mg}/\text{m}^2/\text{day}$ ) under anoxic conditions, modeled based on sediment TP concentration (Nürnberg 1988) and measured during laboratory incubations during August 2011 and July 2012. See Figure 1 for site locations in Bear Lake.

Site	August 2011		July 2012	
	Modeled	Measured	Modeled	Measured
1N	7.26		5.34	
1	7.72	5.15 $\pm$ 1.62	5.40	3.95 $\pm$ 3.48
1S	7.71		0.45	
2N	6.81		5.26	
2	7.50	3.49 $\pm$ 1.83	3.73	1.79 $\pm$ 0.16
2S	7.01		5.57	
3N	8.36		6.50	
3	8.31	11.40 $\pm$ 9.88	4.75	3.22 $\pm$ 0.51
3S	0.49		0.47	
4N	0.51		0.77	
4	6.92		6.33	
4S	7.60		8.09	
5N	6.77		6.26	
5	6.94	6.72 $\pm$ 1.34	4.55	6.72 $\pm$ 1.83
5S	6.18		0.47	
Mean	6.41 $\pm$ 2.47	6.69 $\pm$ 3.41	4.26 $\pm$ 2.52	3.92 $\pm$ 2.07

### *Annual Internal Phosphorus Loading*

Estimates of annual internal P loading ranged from the most conservative value of 169 lbs/yr to the most liberal value of 1,931 lbs/yr (Table 5). The lower bound of 169 lbs/yr is likely overly conservative given that our DO measurements indicated occasional periods of hypoxic conditions. Conversely, the highest estimate is an implausible scenario given that our DO data clearly indicate aerobic conditions through much of the lake. The annual internal P loading estimate from the Bear Lake TMDL (MDEQ 2008) is 3-7× greater than our estimates that appear to be most accurately reflect actual conditions in Bear Lake (Scenarios 2 and 3; Table 5).

Table 5. Annual internal TP load estimates (lbs/yr) for Bear Lake under 5 different redox and mixing scenarios.

<b>Scenario</b>	<b>Annual Internal TP Load</b>
1. Aerobic: entire lake	169
2. Anaerobic: depths > 3.0 m; rest of lake aerobic	224
3. Anaerobic: depths > 2.7 m; rest of lake aerobic	513
4. Polymictic lake estimate (Nürnberg et al. 2012)	1,166
5. Anaerobic: entire lake*	1,931
TMDL estimate (MDEQ 2008)	1,548

\*Highly unlikely scenario

### *Sediment Chemistry*

Porewater SRP was below the detection limit (5 µg/L) in all cores following the April and August 2011 incubations, with the exception of one core in August (Table 6). Measureable concentrations of SRP were prevalent in porewater following the October 2011 and July 2012 incubations, but concentrations were generally low (Table 6). Two cores from Site 5 (October 2011) and one core from Site 1 (July 2012) had elevated porewater SRP concentrations, resulting in high mean concentrations, but with considerable variation among replicates (Table 6).

Porewater pH was circumneutral at the end of the two summer incubations, with values ranging from 6.8 to 7.6 for all sites and treatments.

Table 6. Porewater soluble reactive phosphorus (SRP) measured in sediment cores at the end of the incubation period. BDL = below detection limit (<5 µg/L).

Site	Treatment	Porewater SRP (µg/L)			
		April 2011	August 2011	October 2011	July 2012
		Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
1	Oxic	BDL	BDL	9 ± 7	10 ± 2
	Anoxic	BDL	BDL	9 ± 3	85 ± 126
2	Oxic	BDL	BDL	12 ± 13	9 ± 1
	Anoxic	BDL	BDL	11 ± 2	10 ± 1
3	Oxic	BDL	5 ± 4	10 ± 13	10 ± 4
	Anoxic	BDL	BDL	17 ± 10	8 ± 2
5	Oxic	BDL	BDL	9 ± 4	24 ± 3
	Anoxic	BDL	BDL	56 ± 42	13 ± 8

Sediment TP was not significantly affected by redox treatment, therefore data analysis was performed on grand means from each site for each sampling date (n=6 cores per site). Post-incubation sediment TP varied both among sites and sampling dates (Figure 8). Site 5 had the lowest sediment TP (as a function of dry weight) during all sampling events; in April 2011 Site 5 was significantly lower than Sites 2 and 3 (p=0.005), in August 2011 and July 2012 Site 5 was significantly lower than Site 1 (p=0.04), and in October 2011 Site 5 was significantly lower than Sites 1 and 2 (p=0.003). Sediment TP was significantly lower in July 2012 than any other sampling event, and was also significantly lower in October 2011 than in April 2011 (p<0.001; Figure 8); the reason for the lower sediment TP in July 2012 at all sites is unknown.

Mean sediment TP (pooled across all sites, dates, and treatments) was similar to average concentrations reported for White Lake (Steinman et al. 2008) and Spring Lake (1 yr post-alum; Steinman et al. 2004, Steinman and Ogdahl 2012), but lower than those reported for Mona Lake (Steinman et al. 2009; Figure 9).

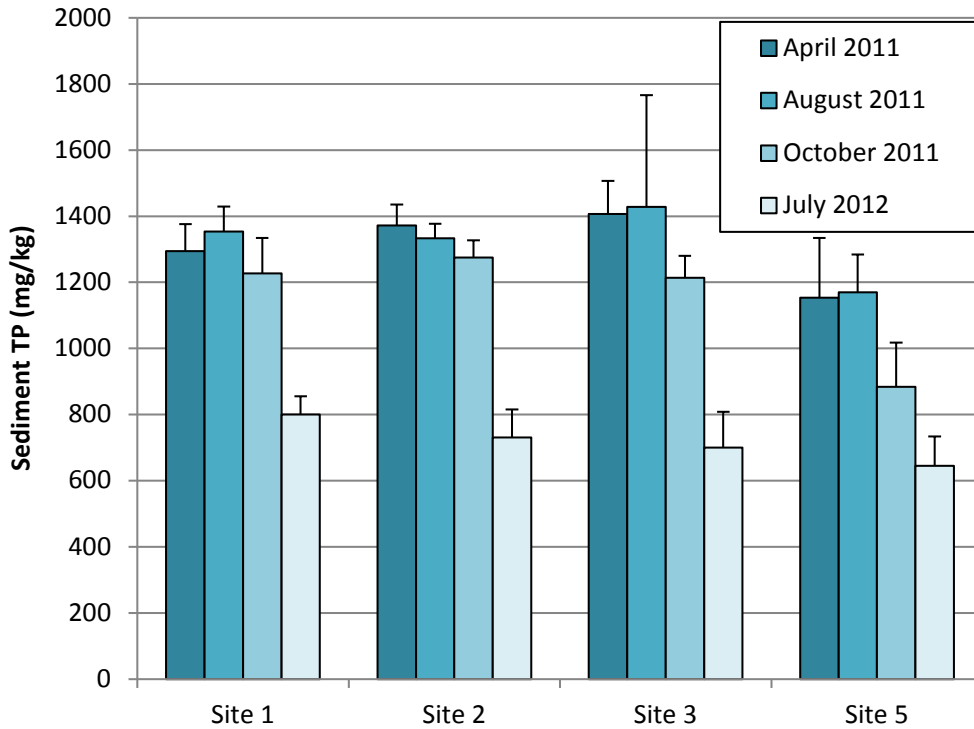


Figure 8. Mean ( $\pm$ SD) total phosphorus (TP) content of dry sediment in sediment cores collected in 2011 and 2012. Mean values include oxic and anoxic treatments (n=6).

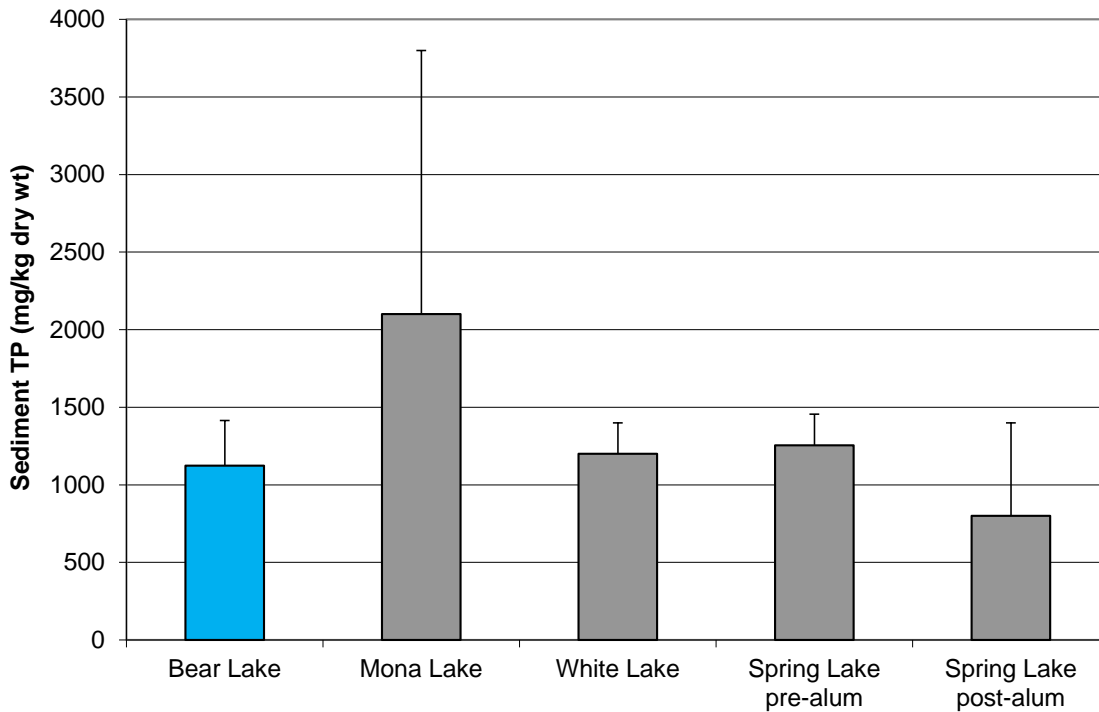


Figure 9. Mean ( $\pm$ SD) sediment TP concentrations measured in Bear Lake and three other west Michigan lakes. Sources: Mona Lake, Steinman et al. 2009; White Lake, Steinman et al. 2008; Spring Lake pre-alum, Steinman et al. 2004; Spring Lake post-alum, Steinman and Ogdahl 2008.

NaOH-extractable total soluble phosphorus (TSP) was greater than HCl-extractable TSP at the end of all incubation periods, except at Site 5 in October 2011 when the extractant did not have a statistically significant effect (Figure 10). Redox condition had a significant effect on extractable TSP except during October 2011; oxic treatments had greater TSP concentrations than anoxic treatments for both NaOH and HCl fractions in April 2011 and for the HCl fraction only in August 2011 and July 2012 (Figure 10). Site had a significant effect on extractable TSP only during August and October 2011, when TSP concentrations were significantly lower at Site 5 than any other site (Figure 10). Significant interaction terms included site  $\times$  extractant (October 2011), site  $\times$  redox condition (August 2011), and redox condition  $\times$  extractant (August 2011 and July 2012). The site  $\times$  extractant  $\times$  redox condition interaction term was not statistically significant for any sampling event.

Elemental composition of sediments was not significantly affected by redox treatment, therefore data analysis was performed on grand means from each site for each sampling date (n=6 cores per site). Iron concentration was greatest among the elements analyzed on all sampling dates ( $p < 0.001$ ), except for April 2011 when iron and calcium concentrations were not significantly different (Figure 11). Calcium was the second most abundant element during all other sampling events (Figure 11).

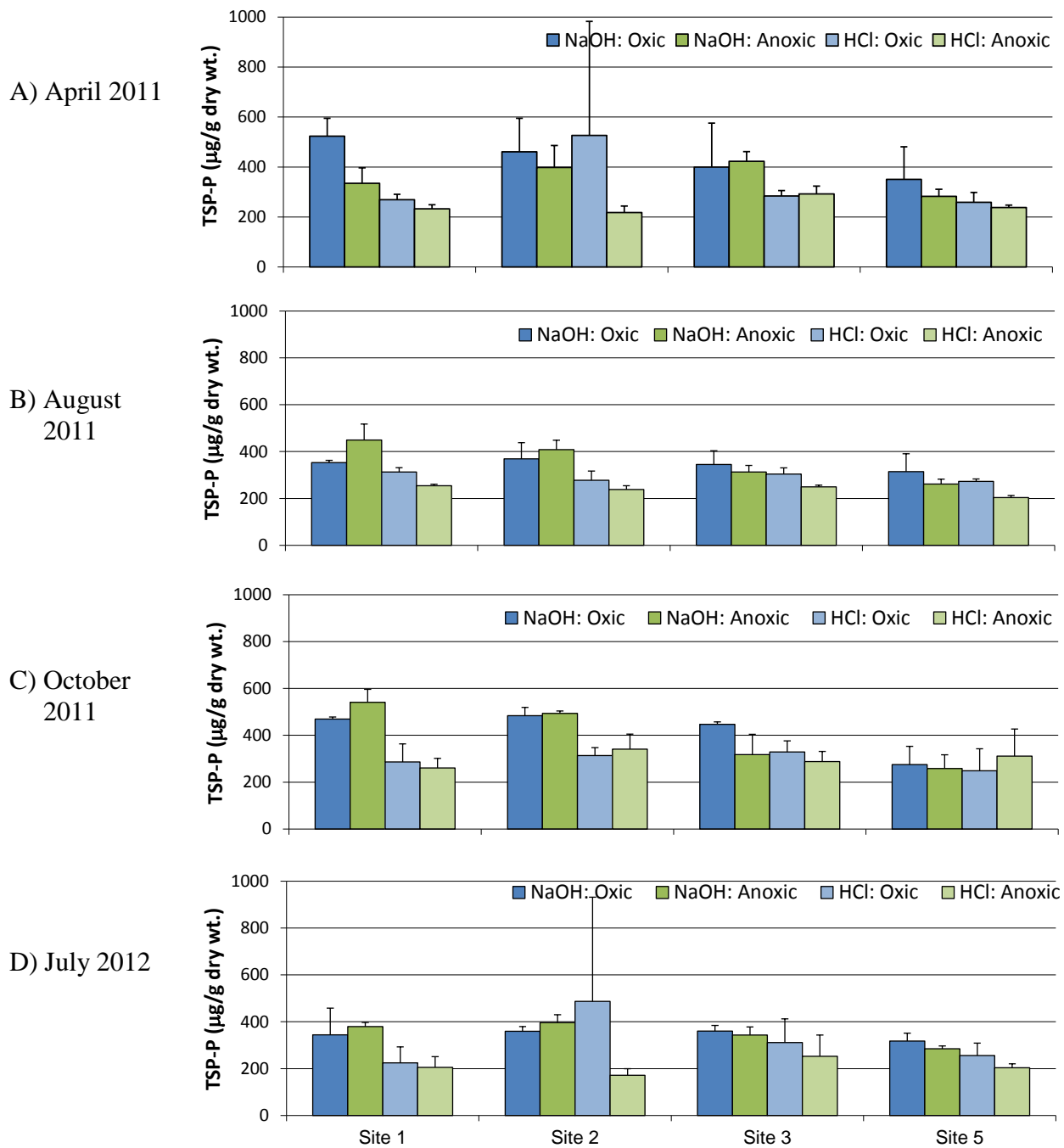


Figure 10. NaOH and HCl-extractable TSP concentrations in sediment cores, measured at the end of the incubation period.



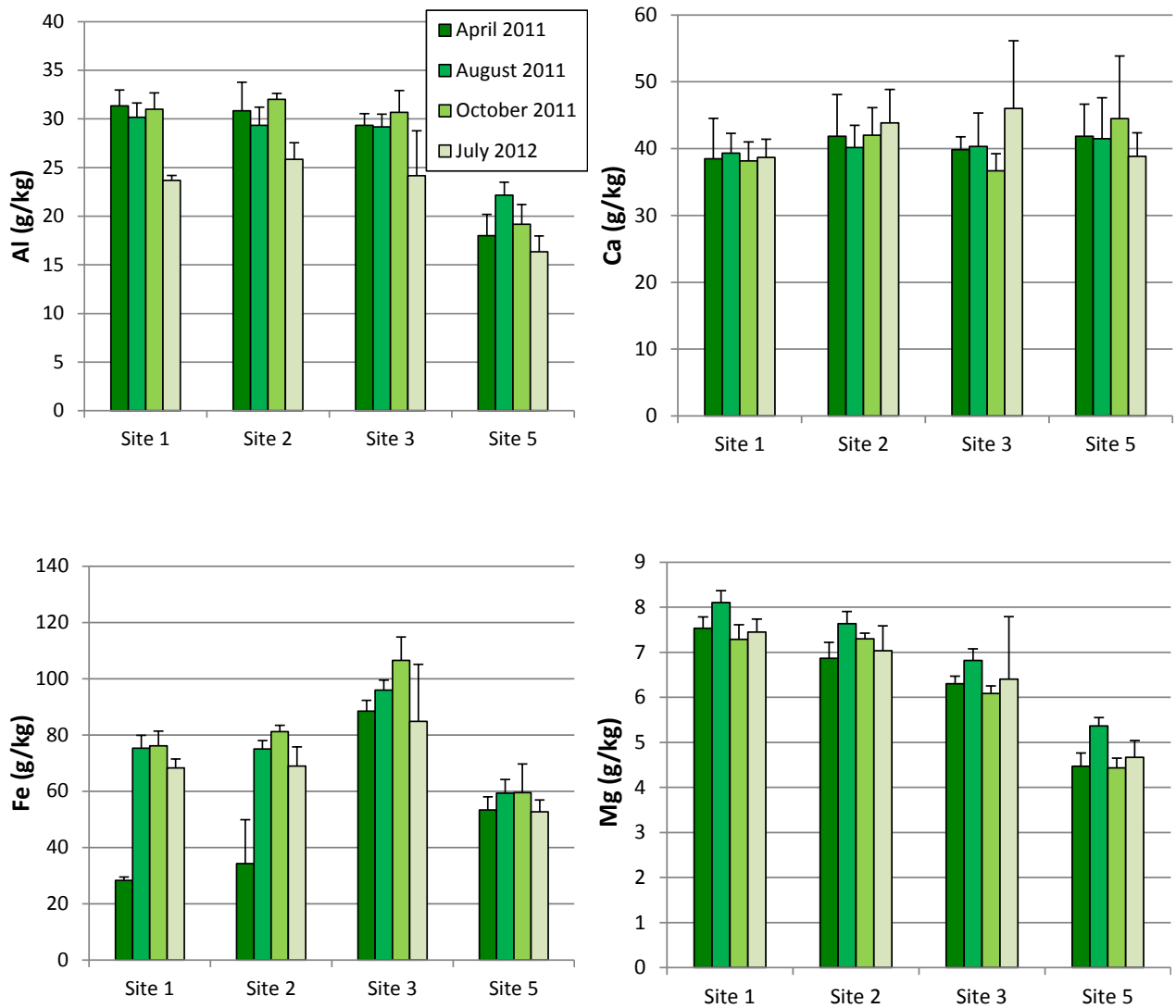


Figure 11. Mean ( $\pm$ SD) aluminum (Al), calcium (Ca), iron (Fe), and magnesium (Mg) in sediment cores collected from Bear Lake in 2011 and 2012. Mean values include oxic and anoxic treatments (n=6). Note that y-axis scales differ among panels.

Analysis of sediment total iron:phosphorus (Fe:P) mass ratios was performed on grand means from each site (n=6), since redox treatment did not have an effect on sediment Fe or P. Mean sediment Fe:P ratios ranged from 45 to 80, except at Sites 1 and 2 in April 2011, which had average Fe:P ratios of 22 and 25, respectively (Figure 12).

Total iron concentrations measured in the water column overlying sediment cores were significantly greater in anoxic treatments than in oxic treatments at the end of all incubations ( $p < 0.001$ ; Figure 13). Water column iron concentrations in anoxic treatments were significantly greater in April and October 2011 than in August 2011 and July 2012 ( $p < 0.001$ ; Figure 13). In oxic treatments, water column iron was often below the detection limit (0.1 mg/L), particularly following the summer incubations (August 2011 and July 2012; Figure 13).

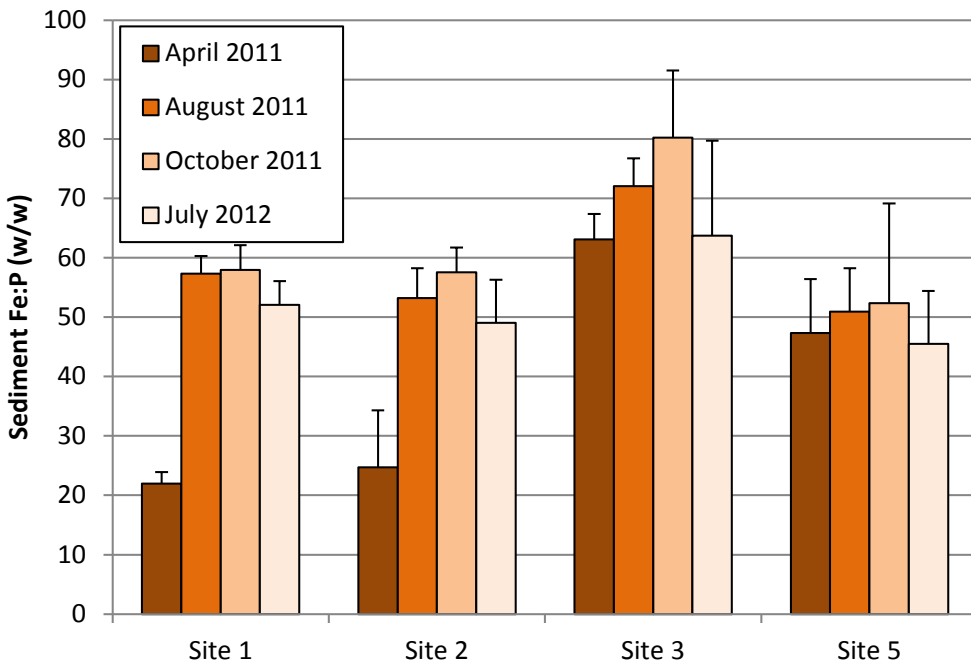


Figure 12. Mean ( $\pm$ SD) Fe:P mass ratios in sediment cores collected from Bear Lake, measured at the end of incubation. Mean values include oxic and anoxic treatments (n=6).

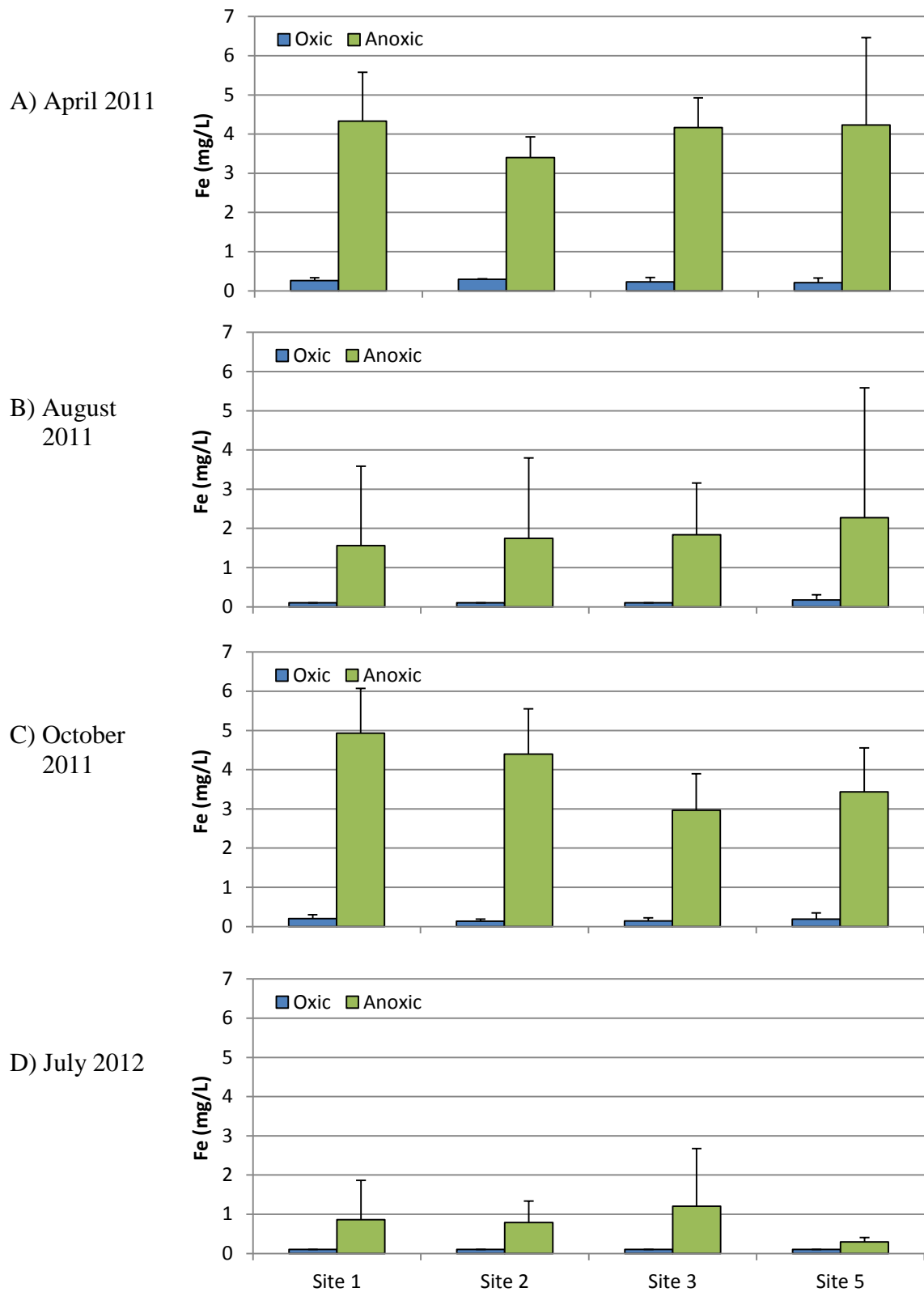


Figure 13. Mean ( $\pm$  SD) total iron (Fe) concentrations measured in the overlying water column of sediment cores at the end of the incubation period.

## Discussion

### *Rationale for this Study*

The 2008 Total Maximum Daily Load for phosphorus for Bear Lake (Muskegon County) states that its overall objective “is to reduce total phosphorus (TP) loads to Bear Lake to levels that are expected to result in the attainment of WQS; specifically, to reduce excessive algal growth and increase water transparency” (MDEQ 2008). The TMDL estimates that on an annual basis, internal phosphorus loads account for 46% of the entire TP load to Bear Lake (i.e., 1,548 out of 3,387 lbs/yr). To reduce the water column TP concentration (from an average of 41 µg/L) to the goal of 30 µg/L called for in the TMDL, internal phosphorus loading would need to be reduced by 79%, from 1,548 to 322 lb/yr. There are numerous lake management strategies that can be employed to reduce internal loading (see below), but given their cost and potential ecological disruption, it is critical to ensure the internal loading estimates used in the TMDL are accurate.

The TMDL discusses three approaches used by Cadmus and AWRI (2007) to estimate the internal phosphorus loading potential in Bear Lake. However, the TMDL calculation is based solely on the Nürnberg regression equation. The TMDL assumes that internal loading occurs from May through August at the rate of 0.0034 g/m<sup>2</sup>/day (derived from Nürnberg 1988), because this time period has the greatest potential for sediment phosphorus release due to increased boat traffic on Bear Lake and warmer water temperatures, which can stimulate internal loading (Holdren and Armstrong 1980, Steinman et al. 2009). The TMDL also acknowledges that the Bear Lake sediment/water interface appears to remain oxic throughout the summer based on limited sampling conducted during daylight hours but that “*a diel dissolved oxygen study of Bear Lake would need to be completed*” to confirm this observation. The TMDL notes that sediments in shallow Bear Lake are susceptible to resuspension to the overlying water column via recreational activities (boat propellers) or wind-induced mixing, which also can contribute to internal loading.

The TMDL does not explicitly address the caveats included in the Cadmus and AWRI report (2007), which noted the limitations of these approaches; indeed, the summary of the internal loading section of this report states:

*“Based on the available data collected from the Bear Lake sediments, and employing multiple lines of evidence, it appears that internal loading likely is not a significant source of P to the Bear Lake water column. Because our analyses are based on indirect lines of evidence and not based on direct measurements of P flux from the sediments, it is impossible to state with confidence how significant internal loading is in Bear Lake. However, based on our analyses from other west Michigan lakes, where internal loading can represent up to 65% of the total load to the lake (Steinman et al. 2004), it seems prudent to reduce external P loading to Bear Lake as quickly as possible to avoid the possibility of internal loading becoming a major source of P to this system.”*

The TMDL notes that more accurate estimates of internal loading could be obtained by conducting internal loading analysis on sediment cores incubated under both aerobic and anaerobic conditions, and comparing these results to estimated rates using Nürnberg’s regression equation. The above observation was the impetus for the current study; the significance of our

findings, as well as what strategies may be adopted to reduce phosphorus loads to Bear Lake so it attains water quality standards, are discussed in detail below.

### *Brief Background on Internal Phosphorus Loading*

Phosphorus release from sediments can occur via at least two different mechanisms: 1) release at the sediment-water interface during periods of anoxia or hypoxia, and the subsequent diffusion of dissolved phosphate into the water column, as reducing conditions can result in the desorption of phosphate from iron oxyhydroxides (Mortimer 1941, Marsden 1989); and 2) wind-induced resuspension and bioturbation at the sediment surface, whereby either the sediment pore water P is released into the water column or the P adsorbed to sediment particles desorbs and enters into the water column (Selig 2003, Steinman et al. 2006). In eutrophic lakes, internal loading can account for a substantial amount of the total P load (Moore et al. 1998). Indeed, many studies have shown that reductions in external loading, to levels where water quality improvement should be detected, do not have the desired effect because of the counteracting release of P from sediments (Björk 1985, Graneli 1999, Steinman et al. 1999).

Because internal phosphorus loading can be a significant source of nutrients in shallow, eutrophic lakes, it can have both ecological and societal implications. Even when external phosphorus loading rates are relatively low, high internal loading rates can help trigger or sustain algal blooms. Hence, costly attempts to reduce external loading (via best management practices in the watershed) may not improve water quality, at least in the short-term, although improvements should occur eventually, assuming internal loading is suppressed. Of course the converse is true as well; it makes no economic or ecological sense to manage internal loading if it is not a major contributing factor to impaired water quality.

### *Comparison of Current Study Results to TMDL*

Our experimental incubations indicated that Bear Lake sediments have the *potential* to diffuse phosphorus at a moderate rate (Table 3). However, anoxic conditions are necessary for this release to occur. Under these reducing conditions, Fe oxides and oxyhydroxides (Fe~PO<sub>4</sub>) are subject to dissolution, releasing phosphate. If Bear Lake was entirely anoxic throughout the year, we estimate the annual internal phosphorus load would exceed the TMDL-derived internal load by ~20% (1,931 vs. 1,548 lbs/yr). However, both our daytime and diel measurements clearly indicate that Bear Lake is mostly oxic throughout the water column, at least to the near-bottom, which is as close to the sediment-water interface that our probes could be deployed without disturbing the sediment layer. Hence, we view the annual internal phosphorus load estimate under Scenario 5 (entirely anaerobic) as being implausible; however, this estimate provides an upper boundary of what theoretically is possible in Bear Lake.

At the other end of the spectrum is the most conservative annual internal P loading estimate (Scenario 1), whereby Bear Lake remains entirely oxic throughout the year. In this case, oxidizing conditions favor phosphate remaining bound to Fe (or Al) oxides or oxyhydroxides. This scenario results in an annual internal P loading estimate of only 169 lbs/yr, or about 89% less than the TMDL estimate (Table 5). While this scenario is more plausible than Scenario 5, it too is unlikely, as other studies have found that even under oxygenated water column conditions,

hypoxia often develops at the sediment-water interface or within the sediments themselves (Holdren and Armstrong 1980, Nürnberg 2009; see below).

Rather, Scenarios 2 and 3, which account for a combination of oxic and anoxic zones in Bear Lake, appear to reflect the most realistic conditions based on our field observations. Scenario 2 assumes only 3% of Bear Lake goes anoxic, whereas Scenario 3 assumes almost 20% of Bear Lake goes anoxic. These zones of potential anoxia (> 3.0 m and > 2.7 m, respectively) are depicted in Figure 14.

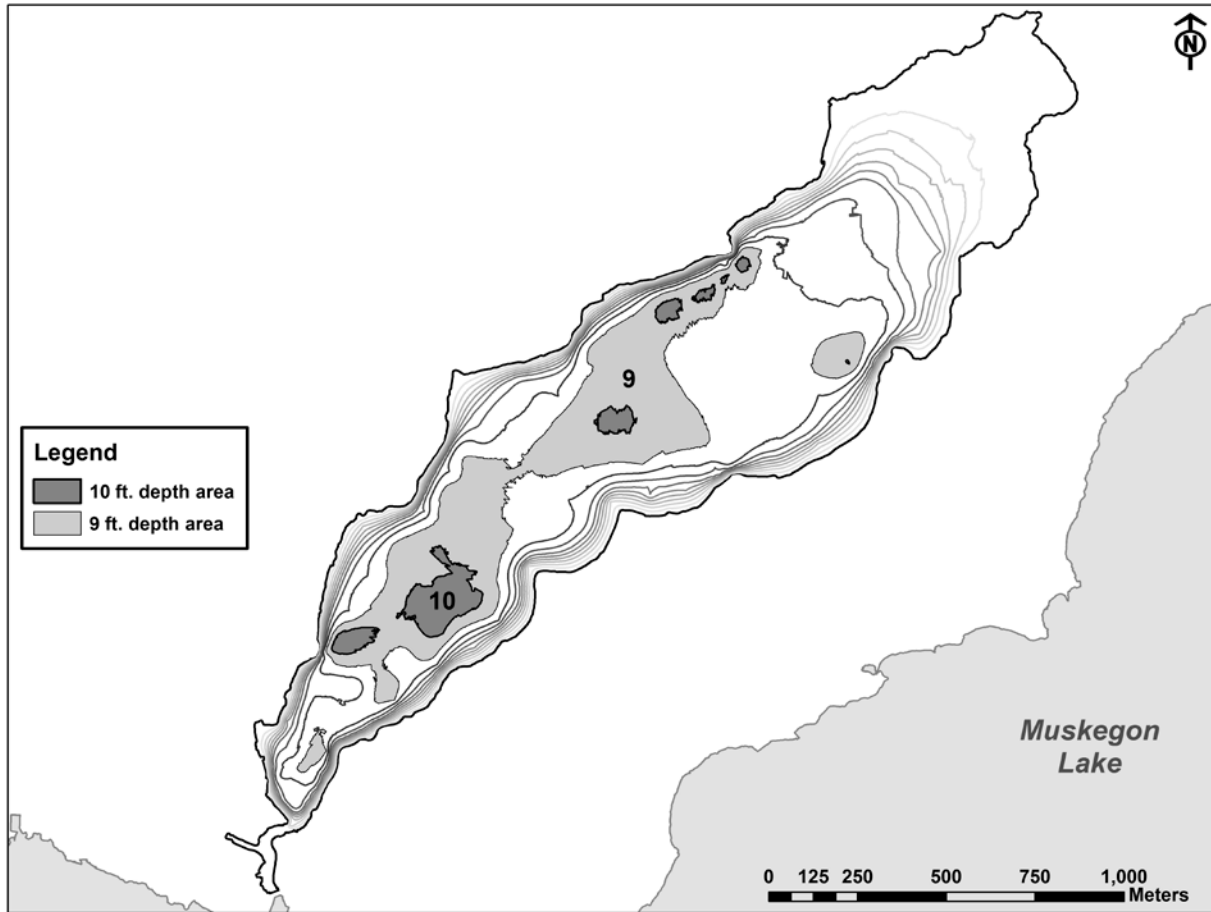


Figure 14. Bathymetry of Bear Lake. Light and dark gray shading show depths greater than 9 and 10 ft, respectively.

The annual internal P loading estimate from Scenarios 2 and 3 underestimate the Bear Lake TMDL by  $\sim 7\times$  and  $3\times$ , respectively. Even adjusting these estimates upwards by including the MOS used in the TMDL (i.e., 10%), they still reflect significantly lower internal P loads than presented in the TMDL.

Finally, we also included an annual internal load estimate based on an approach developed by Nürnberg et al. (2012) for a lake in Finland. This lake was shallow and polymictic, similar to Bear Lake, but much larger in size and with lower water column phosphorus concentrations. Nürnberg et al. (2012) reasoned that even though a lake may be well-mixed, there will still be

times when the sediment water interface approaches hypoxic conditions, despite oxic conditions in the overlying water column (Holdren and Armstrong 1980, Nürnberg 2009). This approach uses lake morphometry as a proxy for estimating the lake area that is actively releasing phosphorus from the sediment. As a consequence, the approach has considerable uncertainty and should be used to complement and validate other approaches, as opposed to a stand-alone approach to estimate internal loading (Nürnberg et al. 2012). As shown in Scenario 4, this approach also underestimated the TMDL annual internal load estimate, by ~25%.

Given that 4 of our 5 scenarios (Table 5) underestimated the annual internal phosphorus load estimate presented in the TMDL, and the one scenario that exceeded the TMDL is not realistic, **we conclude the TMDL estimate for annual internal phosphorus load in Bear Lake is too high.** A more reasonable estimate for the annual internal phosphorus load in Bear Lake is between 224 and 513 lbs/yr. This range addresses uncertainty in an ecologically meaningful way (hypoxic conditions based on water depth).

#### *Why are Internal Phosphorus Loads Low?*

Although the anoxic phosphorus release rates in summer from Bear Lake sediments were within the range of release rates measured in other west Michigan lakes, the annual internal phosphorus (based on Scenarios 2 and 3) was low. For example, the internal load in nearby Mona Lake based on just two summer months was ~1500 lbs/yr (Steinman et al. 2009); this value, which represents only a portion of the annual internal phosphorus load, is already 3-7× greater than our annual internal load estimates in Bear Lake. There are several reasons why internal phosphorus loading in Bear Lake may be lower than anticipated, given its relatively high sediment phosphorus concentrations, high water column phosphorus concentrations, and high chlorophyll concentrations.

First, the well-mixed water column appears to keep the lake relatively free of hypoxic conditions. As noted above, this redox status maintains phosphate bound to iron and aluminum oxides and oxyhydroxides. It is unknown how much of the mixing is attributable to wind-wave action or boat traffic.

Second, Bear Lake sediments are iron-rich, which can help keep phosphate bound in the sediment. The release of soluble reactive phosphorus from aerobic sediments, like those found in Bear Lake, is low in lakes with Fe:TP ratios (by weight) greater than 15 (Jensen 1992). Rydin et al. (2000) cautioned to apply this ratio with care because total Fe and TP includes forms of each that may not be available for adsorption. Nonetheless, the mean total Fe:TP ratios in Bear Lake ranged from 22 to 80, easily exceeding the 15 threshold; these data were very consistent with the ratios reported in Cadmus and AWRI (2007) from an earlier study. The relatively high ratios found in Bear Lake suggest that there is sufficient Fe in Bear Lake sediments to deter the release of phosphorus from the sediments. Our results did indicate that the sites in the eastern part of the lake (i.e., 3 and 5), with lower sediment Fe:TP ratios, may be more vulnerable than other areas within the lake to internal loading if phosphorus from external sources continues to enter Bear Lake. These sites are closest to Bear Creek, the major tributary and external source of phosphorus to Bear Lake. The high iron concentrations also may account for the low dissolved phosphorus concentrations in the sediment porewater in Bear Lake.

### *Caveats*

Our diel oxygen and phosphorus release analyses are based on relatively few sites and dates. Although we sampled different seasons and over multiple years, it would be far better to have continuous DO data, as is generated in Muskegon Lake with our monitoring observatory, or to use voltammetric electrodes (cf. Smith et al. 2011) to provide detailed redox chemistry at highly resolved time periods and depths at the sediment-water interface.

Our phosphorus release rate measurements do not account for sediment resuspension, as the sediment cores remain intact during the incubations. It is unlikely that porewater would be a major source of phosphorus given the low SRP concentrations in the Bear Lake porewater (Table 6). However, it is possible that phosphate ions desorbing from sediment, once in suspension, could be a significant source of phosphorus (cf. Istvánovics et al. 2004, Steinman et al. 2006) although prior studies have shown that the effect of sediment resuspension is extremely variable in space and time (Cyr et al. 2009, Niemistö et al. 2012).

### *Management Strategies*

Based on the results of the internal phosphorus loading study, we proposed to complete a desktop study to assess the feasibility of three common mitigation strategies for internal P loading: 1) dredging; 2) chemical inactivation (e.g. alum); and 3) oxygenation/aeration. Given our findings that internal loading is a relatively minor source of phosphorus to Bear Lake, an analysis of these management strategies is somewhat moot. Nonetheless, in case there is a desire to address this source, we discuss these strategies below:

**Dredging (sediment removal)** – Dredging is a highly effective, but expensive, option for sediment P mitigation (Cooke et al. 2005). It is a long-term solution provided that external nutrient loads are controlled. However, for many projects the benefits are not substantially greater than those provided by chemical inactivation, making it difficult to justify the additional cost.

There is wide variability in the estimated costs for dredging. Cooke et al. (2005) report a range from \$2.88/m<sup>3</sup> to \$7.23/m<sup>3</sup>. If a continuous 50-cm depth of sediment was removed from the entire area of Bear Lake, the cost could range from \$2.4 - \$6 million; of course, it could be possible to identify the areas with the highest contributing sediments and dredge those targeted regions, thereby reducing overall cost. Sediments that contain toxic contaminants are significantly more costly to remove, possibly exceeding \$52/m<sup>3</sup> (Cooke et al. 2005).

Several factors should be considered before undertaking dredging:

- A disposal area would have to be identified and associated costs figured into the costs of dredging. If a 50-cm depth of sediment was removed from the entire lake, the disposal area would need to accommodate ~830,000 m<sup>3</sup> of sediment.



- Nutrient-rich sediment can have productive uses, such as soil amendments or potting soil. The sale of dredged sediment can significantly help to offset the overall costs of a dredging project (Cooke et al. 2005). Such options could be explored.
- Preliminary studies are necessary to determine whether Bear Lake sediment is contaminated beyond nutrients. Such a condition would likely make dredging a cost-prohibitive option.
- Additional studies are needed to ensure that dredging does not expose sediment that contains high P concentrations, which could be released into the water column, negating at least in part the benefits of dredging. Presumably, a low-P sand layer exists beneath the organic sediment; it would be necessary to determine the depth to reach that layer, and based on that information, calculate the appropriate depth to dredge, sediment volume involved in dredging, and the associated costs.

**Chemical inactivation** – Chemical treatment with aluminum sulfate (alum), lime, or iron is one of the most common management techniques used to address sediment P release (Cooke et al. 2005). Alum is particularly effective due to its dual mode of action for P removal. Alum reacts with soluble P to form an insoluble precipitate (Stumm and Morgan 1996) and also forms an insoluble aluminum hydroxide floc at pH 6 to 8, which has a high capacity to adsorb large amounts of inorganic P (Kennedy and Cooke 1982). By these two mechanisms, an alum application can irreversibly bind P and inhibit diffusive flux from sediments. Costs of alum application generally range from \$500-700 per acre (Holdren et al. 2001, Cooke et al. 2005), which translates to \$205,000-\$287,000 for the 410-acre (1.66 km<sup>2</sup>) Bear Lake.

Longevity of alum treatment is dependent on several factors, including the degree to which external loading is controlled and presence of macrophytes. Welch and Cooke (1999) evaluated the effectiveness and longevity of alum applications in 21 lakes across the United States. Their analysis revealed that in polymictic (unstratified) lakes, such as Bear Lake, internal loading rate was reduced in 6 out of 9 cases, with average reduction of about 67%, which lasted for 5-11 years. In dimictic (stratified) lakes, internal loading rate was reduced in 7 out of 7 cases, with average reduction of about 80%, and which lasted for 4 to 21 years. The major constraint in polymictic lake application was interference by macrophytes. They concluded that a reasonable expectation of longevity for alum treatments is 10 years in polymictic and 15 years in dimictic lakes. An alum application in Spring Lake (MI) has continued to perform well in reducing internal loading five years after application (Steinman and Ogdahl 2012).

Several factors should be considered before implementing a chemical inactivation plan in the muck fields:

- Disturbance of the floc layer can limit the effectiveness of chemical treatments (Cooke et al. 2005). Significant boat traffic or bioturbation from fish could create problems, and would need further investigation before engaging in chemical treatment.
- Because they may experience an increase in the dissolved and toxic aluminate ion during application, systems with high pH (> 9-10) are considered poor candidates for

alum treatment (Cooke et al. 2005). pH values in Bear Lake ranged from ~8 to 9.2 (data not shown). Lime and/or alum buffered with lime is an alternative option for treatment to avoid Al toxicity (Cooke et al. 2005), but there are drawbacks to using lime because it is generally not as effective as alum, usually requires multiple applications, and less is known about dose and application techniques than for alum (Cooke et al. 2005). Clearly, studies would be needed to better characterize the pH throughout Bear Lake, the appropriate chemical to apply, and dosage amount before a chemical inactivation plan could be implemented in the muck fields.

**Aeration** – This can involve either full-lake mixing or hypolimnetic aeration without mixing (Klapper 2003). Aeration is a short-term management strategy that can regulate both N and P concentrations in the water column, and also limit surface scum formation by cyanobacteria blooms due to the resulting water column turbulence (Hickey and Gibbs 2009).

Artificial mixing uses a compressor to blow air through a perforated tube along the lake bed; rising bubbles result in bottom water being upwelled, thereby disrupting any thermal stratification. Hypolimnetic oxygenation involves the injection of pure oxygen as fine bubbles into a confined column of hypolimnetic water, where oxygen dissolves, resulting in no free gas bubbles and no disruption of the thermocline; this approach is used when there is a high concentration of accumulated toxic contaminants in the hypolimnion. It requires more expensive and specialized equipment than whole lake aeration.

Both aeration approaches appear unnecessary in Bear Lake, as the lake rarely stratifies and remains well-oxygenated most of the time. Regardless, aeration as a management strategy suffers from a major flaw: once stopped, the lake will rapidly revert to its prior condition (Hickey and Gibbs 2009).

**Conclusion**—Given the relatively small contribution of internal loading to the overall phosphorus loads to Bear Lake, we conclude that no management strategies to control internal loading are justified at this time. The cost:benefit ratio simply is too large. **Rather, we recommend that management efforts be directed to controlling the external phosphorus load.** Indeed, even if internal phosphorus load reduction strategies were justified, treatment effectiveness is critically linked to concurrent reductions in external loading, as external loads are the original source of the accumulated phosphorus in the lake sediments contributing to internal loading.

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