

# **Phosphorus binding dynamics in the aluminum floc layer of Half Moon Lake, Wisconsin**

**William F. James<sup>1\*</sup>**

*<sup>1</sup>University of Wisconsin – Stout, Discovery Center - Sustainability Sciences Institute,  
Department of Biology, Menomonie, WI 54751*

[\\*Corresponding author email: jamesw@uwstout.edu](mailto:jamesw@uwstout.edu)

*Abbreviated title:* Alum floc layer phosphorus binding dynamics

## **Abstract**

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Half Moon Lake is a shallow oxbow located in Eau Claire, Wisconsin. Eutrophic to hypereutrophic conditions and cyanobacteria blooms driven primarily by sediment internal P loading led to a buffered aluminum sulfate treatment in 2011. Aluminum (Al) dosage was based on the redox-sensitive P (redox-P) concentration in the upper-4 cm sediment layer. The west arm was treated with 150 g/m<sup>2</sup> to sequester 1 to 5 mg/g redox-P while the east arm was treated with 75 g/m<sup>2</sup> to bind an order of magnitude lower redox-P concentration (0.15 mg/g). Four years after treatment, the Al floc layer was positioned on top of the original sediment surface due to density differences between sediment and the Al floc. Rather than sinking or mixing into the sediment, P binding has occurred primarily via upward diffusive P flux into the Al floc layer. Changes in vertical P profiles over time suggested that the Al floc in the western arm has bound only ~60% of this upward diffusive P flux while the other portion has become associated with Fe and now potentially contributes to the lake P budget through redox-driven recycling pathways. The east arm Al floc layer has sequestered ~90% of the much lower upward diffusive P flux. Laboratory-derived anaerobic diffusive P fluxes in the west arm have increased from near 0 in 2011 to ~ 3.7 mg/m<sup>2</sup> d in 2015. P binding inefficiency may be attributed to Al polymerization to a more ordered crystalline structure over time in the absence of exposure to sediment P.

**Key words:** alum, aluminum, diffusive P flux, phosphorus, phosphorus fractionation

Aluminum (Al) sulfate or chloride application to bind sediment mobile P has been an effective management tool for reducing and controlling internal P loading in lakes (Cooke et al. 2005).

Recent dosage strategies have focused on estimating the Al required to bind mobile P fractions in sediment connected with internal P loading (i.e., loosely-bound, iron-bound, and labile organic P; Rydin and Welch 1999, Reitzel et al. 2003, 2005, Pilgrim et al. 2007, James 2011, Huser and Pilgrim 2014, Jensen et al. 2015). Although freshly formed  $\text{Al}(\text{OH})_3$  in distilled water can bind  $\text{PO}_4$  near a molar 1:1 ratio (Lijklema 1980), factors such as reaction with other ions and dissolved organic matter (de Vicente et al. 2008a) and competition for binding sites on the Al floc as a function of mobile P concentration (Cheng et al. 2004, Guan et al. 2006, Huser and Pilgrim 2014, James and Bischoff 2015) can result in much higher Al:P binding ratios ranging between 2:1 and > 10:1 (Huser 2017). In addition, relatively rapid aging and polymerization of the Al floc in the absence of P can greatly reduce future binding efficiency for mobile P (Berkowitz et al. 2005, 2006, de Vicente et al. 2008b) and reduce Al treatment longevity.

Researchers have suggested that multiple lower dose applications may be more effective than a single higher dose treatment in stabilizing Al crystallization and enhancing P binding efficiency (Lewandoski et al. 2003, de Vicente et al. 2008a, Huser 2012, Jensen et al. 2015). Indeed, the success and longevity of internal P loading control after Al application have varied tremendously (Huser et al. 2016), complicating standardization of Al dosage and application protocols.

Half Moon Lake, Wisconsin, was treated with a single high Al dose application in 2011 to control diffusive P flux from sediments. Dosage was based on the redox-sensitive P (i.e., redox-P; the sum of the loosely-bound and iron-bound P fractions) concentration in the upper 4 cm sediment layer but constrained by a financial budget. Redox-P concentrations ranged between 1 and 5 mg/g in the west arm and were an order of magnitude lower at ~ 0.15 mg/g in the east arm sediments. Approximately 150 g/m<sup>2</sup> of buffered aluminum sulfate-sodium aluminate, arguably one of the highest Al dosages applied to a lake as of 2015 (Huser et al. 2016), were applied to the west arm while the east arm was treated with 75 g/m<sup>2</sup>. The objectives of this research were to monitor changes in sediment redox-P and Al-bound P fractions, P binding efficiency of the Al floc, and anaerobic diffusive P flux control between 2011 and 2015.

## Site description

Half Moon Lake is a small (area = 0.5 km<sup>2</sup>; volume = 8.9 x 10<sup>5</sup> m<sup>3</sup>), shallow (mean depth = 1.6 m; maximum depth = 4 m) wind-sheltered urban oxbow lake located in Eau Claire, Wisconsin (Fig. 1). Minor watershed P inputs occur primarily via a storm sewer system that drains residential, commercial and industrial land uses from a 2.3 km<sup>2</sup> watershed. Before Al treatment, the summer P budget was dominated by internal loading from sediment (42%), decomposition of *Potamogeton crispus* (20%) and sediment resuspension by motor boat activity (17%, James et al. 2002). The lake was classified as eutrophic to hypereutrophic (Carlson Trophic State Index = 74). Mean summer trophic state indicators were 0.110 mg/L total P, 82 mg/m<sup>3</sup> viable chlorophyll and 1.1 m Secchi transparency. Total alkalinity concentrations were moderate at ~ 50 mg CaCO<sub>3</sub>/L and pH averaged ~ 9.0 std units during the summer.

## **Methods**

### ***Sediment sampling***

Sediment traps (PVC) were deployed on an anchored cable and buoy in the east and west arm one day before the Al application in June, 2011, and retrieved two weeks later for determination of Al and extractable P content (Fig. 1). Trap contents overwhelmingly reflected deposited Al, since the lake is well protected from wind-generated resuspension of bottom sediment. The traps, measuring 4 in diameter by 20 in long (aspect ratio = 5:1) were positioned so that the opening was ~ 0.5 m above the sediment surface at each station. Intact sediment cores (~ 30 cm length) were collected in summer from a station located in the east and west arm of the lake in late June to July between 2010 and 2015 to examine sediment physical-chemical characteristics and diffusive P flux under laboratory-controlled anaerobic conditions (Fig. 1). A gravity coring device (Aquatic Research Instruments; Hope, ID), equipped with an acrylic core liner (6.5 cm ID and 50 cm length), was used to collect sediment. Cores were immediately stoppered, covered to prevent light exposure, and transported vertically to the laboratory for sectioning and processing within 24 h.

### ***Sediment characteristics***

Sediment trap contents were centrifuged at 500 g to concentrate the material and subsampled for determination of moisture content. The equivalent of 0.025 g dry mass was extracted in 1 N NaOH for 24 hr, centrifuged, and filtered through a 0.45  $\mu\text{m}$  syringe filter for measurement of

soluble reactive P (APHA 2005) and Al (microwave-assisted digestion and ICP-AES analysis, EPA method 3051a and 6010c).

Sediment cores collected from a station established in the east and west arms of the lake (Fig. 1) were sectioned at 1 to 2 cm intervals over the upper 10 to 15 cm for analysis of physical-chemical characteristics. A known volume of sediment was dried at 105 C for determination of moisture content and sediment wet and dry bulk density and burned at 550 C for determination of loss-on-ignition organic matter (Avnimelech et al. 2001, Håkanson and Jansson 2002). Sequential P fractionation was conducted according to Psenner and Puckso (1988) for the determination of ammonium-chloride-extractable P (loosely-bound P), bicarbonate-dithionite-extractable P (iron-bound P), and sodium hydroxide-extractable P (aluminum-bound P or Al-bound P). Redox-sensitive P (redox-P) was estimated as the sum of the loosely-bound and iron-bound P fractions. Additional sediment was dried and ground for determination of total Al using methods described above.

### ***Diffusive phosphorus flux***

Five replicate cores were collected at east and west arm stations for determination of rates of diffusive P flux under anaerobic conditions. The upper 10 cm was transferred intact to a smaller acrylic core liner (6.5 cm dia and 20 cm ht) using an extruder. Surface water collected from the lake was filtered through a glass fiber filter (Gelman A-E) and 300 mL was siphoned onto the sediment contained in the small acrylic core liner without causing sediment resuspension.

Sediment incubation systems were placed in the darkened environmental chamber and incubated

at a constant temperature (20 C). The oxidation-reduction environment in the overlying water was controlled by gently bubbling nitrogen (anaerobic) through an air stone placed just above the sediment surface in each system.

Water samples for soluble reactive P were collected from the center of each system using an acid-washed syringe and filtered through a 0.45  $\mu\text{m}$  membrane syringe filter. The water volume removed from each system during sampling was replaced by addition of filtered lake water preadjusted to the proper oxidation-reduction condition. These volumes were accurately measured for determination of dilution effects. Soluble reactive P was measured colorimetrically using the ascorbic acid method (APHA 2005). Rates of P release from the sediment ( $\text{mg}/\text{m}^2 \text{ d}$ ) were calculated as the linear change in mass in the overlying water divided by time (days) and the area ( $\text{m}^2$ ) of the incubation core liner. Regression analysis was used to estimate rates over the linear portion of the data.

## Results

Sediment traps placed above the sediment in Half Moon Lake during the Al treatment in 2011 captured 86 and 143  $\text{g Al}/\text{m}^2$  in the east and west arm, respectively, close to target application concentrations. The Al-bound P concentration was 0.39  $\text{g}/\text{m}^2$  in east arm and 0.45  $\text{g}/\text{m}^2$  in west arm trapped material, suggesting some P sequestration during Al floc formation and settling. Al concentrations measured in sediment cores collected one month after Al application were higher than target concentrations at 125  $\text{g}/\text{m}^2$  in east arm sediments and 298  $\text{g}/\text{m}^2$  in west arm sediments. In 2014, ~ 103 and 146  $\text{g}/\text{m}^2$  of the applied Al were recovered from east and west arm

sediment cores, respectively. These differences suggested variability in Al floc distribution over the original sediment surface.

In conjunction with surface peaks in Al concentration one month after Al application in 2011 (Fig. 2), solids content and sediment bulk densities were very low while moisture content was high in the upper 2 and 3 cm layer of the east and west arm sediments (Fig. 3), respectively. Below the surface Al floc layer, sediment physical characteristics were like those measured in sediment cores collected in both arms in 2010, prior to Al application (Fig. 3). Moisture content declined while solids content and sediment bulk densities increased sharply below the surface Al floc layer, nearly matching vertical sediment physical patterns in both arms prior to Al application in 2010 (Fig. 3).

In 2014, three years after Al application, the Al floc layer continued to reside on top of the original sediment surface and was ~ 2 cm in thickness in the east arm and ~ 3 cm thick in west arm sediments (Fig. 2). This layer continued to exhibit a higher moisture content, lower solids content, and lower sediment bulk densities in 2014 compared to the original sediment surface layer (Fig. 4). Physical sediment characteristics below the original sediment surface in 2014 were nearly identical to those prior to Al treatment in 2010 (Fig. 4).

Time series variations in the upper 2 and 3 cm layer of east and west arm sediment indicated that the deposited Al floc was initially much less dense than the pretreatment sediment surface (Fig. 5). For instance, moisture content of the sediment surface layer prior to Al treatment was < 92%



in both arms of the lake. One month after Al application in 2011, surface layer moisture content was very high at 98% in the west arm and 96% in the east arm sediments. In contrast, sediment wet and dry bulk densities and solids content declined substantially after Al application in 2011, relative to pretreatment sediment surface characteristics. Surface layer moisture content steadily declined while solids content and sediment bulk densities increased between 2011 and 2015 at both stations, suggesting some consolidation of the Al floc layer and potential deposition of new sediment. However, an Al floc layer with distinctly lower bulk densities, lower solids content, and higher moisture content residing on top of the original sediment surface was apparent in both arms as of 2015. Differences in Al floc layer physical characteristics may be attributed to Al dosage differences between arms. West arm sediments exhibited a thicker Al floc layer with higher moisture content and lower bulk densities and solids content relative to east arm sediments in 2015, coinciding with a 2X higher Al dosage to the west arm.

One month after Al treatment in 2011, redox-P concentrations in west arm sediments were relatively low in the Al floc layer and increased to a maximum ~ -1 to -4 cm below the original sediment surface, coinciding with the pretreatment redox-P surface maxima observed in 2010 (Fig. 6). Thus, a strong vertical redox-P concentration gradient was established between the sediment and Al floc layer in west arm sediments shortly after Al treatment. Al-bound P concentrations peaked at 2.1 mg/g in the Al floc layer in the 2011 sediment core, suggesting some binding of P by Al most likely from the water column during deposition. Below the original sediment surface in the west arm, Al-bound P concentrations were lower but exhibited a secondary peak at the -4-cm depth in 2011 that aligned with a similar Al-bound P peak observed in 2010 before the Al treatment. East arm sediments exhibited a similar pattern of low redox-P

and higher Al-bound P in the Al floc layer located above the original sediment surface. However, redox-P concentrations below the original sediment surface were much lower versus west arm sediments, resulting in a lower vertical redox-P gradient between the sediment and overlying Al floc layer.

The prominent redox-P concentration maximum was again detected below the original sediment-water interface in west arm sediment in 2014 (Fig. 7). However, concentrations of redox-P were now elevated in the west arm Al floc layer (i.e., 0 to 3 cm above the original sediment surface) in 2014 compared to 2011, increasing from near zero to ~ 0.45 mg/g, respectively. In addition, Al-bound P concentrations also increased in the Al floc layer of the west arm from ~ 1.4 mg/g in 2011 to 2.37 mg/g in 2014. By contrast, redox-P concentrations remained relatively low at 0.11 mg/g in the Al floc layer of east arm sediments in 2014, while Al-bound P increased from ~ 0.70 mg/g in 2011 to 0.97 mg/g in 2014. The Al:Al-bound P ratios in the Al floc layer were relatively high in 2014 at 62:1 and 31:1 for the east and west arm, respectively.

Area-weighted concentrations of redox-P and Al-bound P increased approximately linearly in the Al floc layer of the west arm sediment between 2011 and 2015 (Fig. 8). This pattern suggested that P has largely diffused into the west arm Al floc layer from the deeper sediment over time. A portion of this upward diffusive P flux was sequestered by the Al floc as Al-bound P while another portion became readsorbed back onto Fe oxyhydroxides (i.e., Fe-(OOH)) as redox-P and is now available for internal P loading. For instance, redox-P concentrations increased in west arm sediments from only 0.04 mg/g in 2011 to 0.68 mg/g 2015 (Fig. 9). Similarly, Al-bound P

concentrations also increased from 1.41 mg/g in 2011 to 2.09 mg/g in 2015. Thus, although P binding onto  $\text{Al}(\text{OH})_3$  continued through 2015, efficiency has declined in west arm sediments, resulting in the accumulation of redox-P in the Al floc.

Unlike west arm sediments, redox-P concentrations have remained relatively low in the east arm Al floc layer and only increased slightly over time (Fig. 9). The redox-P concentration was only 0.11 mg/g in 2015. However, Al-bound P concentrations increased in the Al floc layer of east arm sediments between 2011 and 2015 (Fig. 9). Thus, most of the P diffusing into the Al floc layer of east arm sediment has been sequestered as Al-bound P versus entering recycling pathways as redox-P.

To estimate the P sorption onto the Al floc layer, I assumed that P inputs were primarily derived from upward diffusive P fluxes originating from the sediment located below the AL floc layer. Since Half Moon Lake receives very low watershed P loads, downward diffusive P flux into Al floc layer from newly deposited sediment is probably minor. I also assumed that the sum of the redox-P and Al-bound P in the Al floc layer approximated diffusive P flux (Fig. 8). Thus, ~ 0.35 and 1.1 g P/m<sup>2</sup> y have diffused into the east and west arm Al floc layer, respectively, between 2011 and 2015. Higher apparent P diffusion into the west arm versus east arm Al floc layer coincided with differences in the redox-P concentration of the sediment below the Al floc layer. Al floc binding efficiency was calculated as the percentage of the combined P diffusing into the Al floc that became Al-bound P (Fig. 10). P binding efficiency in 2015 declined to 65% in west arm sediments while it has remained high at 97% for east arm sediments.

Before Al treatment, mean laboratory-derived anaerobic diffusive P flux in 2010 was 8.5 and 11.8 mg/m<sup>2</sup> d for east and west arm sediments, respectively (Fig. 11). Anaerobic diffusive P flux was not detected in replicate sediment incubation systems collected from east and west arm stations during the post-treatment years of 2011 through 2013. However, mean anaerobic diffusive P flux in the west arm increased to 1.0 and 3.3 mg/m<sup>2</sup> d in 2014 and 2015, respectively, in conjunction with the buildup of redox-P in the Al floc layer. While relatively high, the 2015 west arm mean represented a 72% reduction over the pretreatment 2010 mean diffusive P flux. For east arm sediments, mean anaerobic diffusive P flux increased slightly to 1.2 mg/m<sup>2</sup> d in 2015, respectively, suggesting 90% control over the pretreatment mean. Overall, there was a strong linear relationship between redox-P concentration in the Al floc layer and the laboratory-derived anaerobic diffusive P flux (Fig. 12.)

## **Discussion**

Shortly after application in 2011, the Al floc layer was very low in solids content and bulk density, and high in moisture content, relative to most natural lake sediments, suggesting deposition on top rather than mixing or sinking into denser Half Moon Lake sediments. Unless mixing into sediments can be achieved rapidly by resuspension or bioturbation (Huser et al. 2016, Huser 2017), P sequestration by the Al floc is likely to proceed via much slower upward P diffusion from deeper sediments rather than more direct exposure to redox-P, as was the case for the Half Moon Lake Al treatment. Current Al dosage approaches based on sediment mobile P concentration do not consider that vertical separation between the Al floc layer and sediment P pools could lead to a long time lag until eventual contact. Findings from this present study also

suggested that the location of peaks in Al concentration several cm below the sediment interface years after treatment may be largely attributed to new deposition on top of the Al floc layer over time rather than incorporation or sinking into the sediment.

Others have shown that  $\text{Al}(\text{OH})_3$  binding efficiency for P declines substantially (i.e., by as much as 75%; de Vicente et al. 2008a) over time if it has not sequestered P within 30 d of application, due to polymerization into a more ordered crystalline structure in the absence of adsorbed P. This scenario was relevant to the Half Moon Lake alum treatment because the Al floc initially adsorbed only a small amount of P during initial deposition and layered over the top rather than becoming exposed and incorporated into the high redox-P concentration bulge of the original sediment, particularly in the west arm. Although the Al dosage was very high for west arm sediments, upward P diffusion into the Al floc has also been high owing to substantial subsurface redox-P concentrations that led to steep diffusive P gradients between these deeper sediments and the Al floc layer. Although the west arm Al floc layer efficiently sequestered P from this source shortly after treatment, P binding efficiency has steadily declined as of 2015 and a significant portion of the upward diffusive P flux into the Al floc layer has now become adsorbed to Fe-(OOH), leading to internal P loading into the water column under anaerobic conditions. Thus, although the Al floc continues to bind P, high upward diffusive P flux has overwhelmed P binding efficiency in west arm sediments resulting in a rebounding of anaerobic diffusive P flux to the overlying water column. Future Al applications will be needed to offset current  $\text{Al}(\text{OH})_3$  polymerization and P binding inefficiency.

In contrast, Al binding efficiency for P has been much higher in east arm sediments four years after Al application. Although the Al dosage was lower at 75 g/m<sup>2</sup>, redox-P concentrations in the original surface sediment layer were an order of magnitude lower compared to the west arm, resulting in a much lower diffusive P concentration gradient into the Al floc layer. Despite probable Al(OH)<sub>3</sub> polymerization and crystallization in the east arm Al floc layer, Al binding efficiency has remained high relative to this much lower upward diffusive P flux. Thus, this relatively high single application to east arm sediment has been sufficient to bind most of the upward diffusive P flux over a 4 y period.

Findings from this research have implications for future Al dosage and application strategies in lakes. Most recently, Al dosage estimation has been based on redox-P and labile organic P concentrations in the sediment and a molar Al:P ratio ranging between 2:1 and > 10:1 (Rydin et al. 2000, Huser 2017). However, the rate of diffusive P flux into the Al floc coupled with a rate of Al(OH)<sub>3</sub> polymerization and resulting P binding inefficiency need to be considered in Al dosage estimation as well. Because Al floc density is initially very low relative to most lake sediments, it may layer over the original sediment rather than be incorporated by resuspension or bioturbation. Under the former scenario, P sequestration will ultimately be limited by much slower upward diffusive P flux from these mobile P pools and decreased binding efficiency over time as a function of Al(OH)<sub>3</sub> polymerization. However, more quantitative information is needed on P binding efficiency of the Al floc and the long-term Al:Al-bound P ratio end point to better understand and quantify Al dosage and application strategies for future situations.

For Half Moon Lake, Al dosage was based on the redox-P concentration in the sediment and a single application strategy (James 2012) that was designed approximately 6 years before the actual application in 2011. More recent findings have suggested 1) inclusion of labile organic P as well as redox-P in Al dosage estimation (Jensen et al. 2015), 2) an adaptive management approach of applying lower Al concentrations spread out over a period of years (i.e., 2-5 year intervals) and monitoring lake response for future Al maintenance applications, and 3) exposure of the Al floc to hypolimnetic soluble P during initial deposition (de Vicente et al. 2008a and b). The goal of these approaches is to increase overall P binding efficiency and internal P loading control longevity by stabilizing  $\text{Al}(\text{OH})_3$  polymerization and enhancing P saturation of binding sites. Thus, the success and longevity of a single application appears to depend on adding enough Al to sequester and control internal P loading while compensating for Al polymerization and P binding inefficiency. This management scenario will be less efficient and require more Al. While more information is needed, application of multiple lower Al concentrations spread out over a period of years may be more effective in saturating binding sites, lowering the Al:P binding ratio, and stabilizing polymerization for longer internal P loading control. Dose splitting can also be used as an adaptive management approach to address slower degradation of labile organic P into mobile forms (Reitzel et al. 2007) as well as increasing P binding efficiency onto the Al floc. Alternatively, direct injection of Al into the sediment would promote rapid exposure of  $\text{Al}(\text{OH})_3$  to sediment mobile P for more efficient sequestration (Schütz et al. 2017).

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## References

- Avnimelech Y, Ritvo G, Meijer LE, Kochba M. 2001. Water content, organic carbon and dry bulk density in flooded sediments. *Aquat Eng* 25:25-33.
- APHA (American Public Health Association). 2005. Standard methods for the examination of water and wastewater. 21st ed. Washington (DC).
- Berkowitz J, Anderson MA, Graham R. 2005. Laboratory investigation of aluminum solubility and solid-phase properties following alum treatment of lake waters. *Wat Res* 39:3918-3928.
- Berkowitz J, Anderson MA, Amrhein C. 2006. Influence of aging on phosphorus sorption to alum floc in lake water. *Wat Res* 40:911-916.
- Cheng WP, Chi FH, Yu RF. 2004. Effect of phosphate on removal of humic substances by aluminum sulfate coagulant. *J Colloid Interf Sci* 272:153-157.



- Cooke GD, Welch EB, Peterson SA, Nichols SA. 2005. Restoration and management of lakes and reservoirs. 3<sup>rd</sup> ed. Boca Raton (FL): CRC Press.
- de Vicente I, Huang P, Andersen FØ, Jensen HS. 2008a. Phosphate adsorption by fresh and aged aluminum hydroxide. Consequences for lake restoration. *Environ Sci Technol* 42:6650-6655.
- de Vicente I, Jensen HS, Andersen FØ. 2008b. Factors affecting phosphate adsorption to aluminum in lake water: Implications for lake restoration. *Sci Total Environ* 389:29-36.
- Håkanson L, Jansson, M. 2002. Principles of lake sedimentology. Caldwell (NJ). The Blackburn Press.
- Huser BJ. 2012. Variability in phosphorus binding by aluminum in alum treated lakes explained by lake morphology and aluminum dose. *Wat Res* 46:4697-4704.
- Huser BJ. 2017. Aluminum application to restore water quality in eutrophic lakes: maximizing binding efficiency between aluminum and phosphorus. *Lake Reserv Manage* (In Press).
- Huser BJ, Pilgrim KM. 2014. A simple model for predicting aluminum bound phosphorus formation and internal loading reduction in lakes after aluminum addition to lake sediment. *Wat Res* 53:378-385.
- Huser BJ, Egemose S, Harper H, Hupfer M, Jensen H, Pilgrim KM, Reitzel K, Rydin E, Futter M. 2016a. Longevity and effectiveness of aluminum addition to reduce sediment phosphorus release and restore lake water quality. *Wat Res* 97:122-132.

- Huser BJ, Bajer PG, Chizinski CJ, Sorensen PW. 2016b. Effects of common carp (*Cyprinus carpio*) on sediment mixing depth and mobile phosphorus mass in the active sediment layer of a shallow lake. *Hydrobiologia* 763:23-33.
- James WF. 2011. Variations in the aluminum:phosphorus binding ratio and alum dosage considerations for Half Moon Lake, Wisconsin. *Lake Reserv Manage* 27:128-137.
- James WF, Bischoff JM. 2015. Relationships between redox-sensitive phosphorus concentration in sediment and the aluminum:phosphorus binding ratio. *Lake Reserv Manage* 31:339-346.
- James WF, Barko JW, Eakin HL, Sorge PW. 2002. Phosphorus budget and management strategies for an urban Wisconsin lake. *Lake Reserv Manage* 18:149-163.
- Jensen HS, Reitzel K, Egemose S. 2015. Evaluation of aluminum treatment efficiency on water quality and internal phosphorus cycling in six Danish lakes. *Hydrobiologia* 751:189-199.
- Lewandowski J, Schauser I, Hupfer M. 2003. Long term effects of phosphorus precipitations with alum in hypereutrophic Lake Süsser See (Germany). *Wat Res* 37:3194-3204.
- Lijklema L. 1980. Interaction of orthophosphate with iron (III) and aluminum hydroxides. *Environ Sci Technol* 14:537-541.
- Pilgrim KM, Huser BJ, Brezonik PL. 2007. A method for comparative evaluation of whole-lake and inflow alum treatment. *Wat Res* 41:1215-1224.
- Psenner R, Puckso R. 1988. Phosphorus fractionation: Advantages and limits of the method for the study of sediment P origins and interactions. *Arch Hydrobiol Biel Erg Limnol* 30:43-59.

- Reitzel K, Hansen J, Jensen HS, Andersen FØ, Hansen KS. 2003. Testing aluminum addition as a tool for lake restoration in shallow eutrophic Lake Sønderby, Denmark. *Hydrobiologia* 506-509:781-787.
- Reitzel K, Hansen J, Andersen FØ, Hansen KS, Jensen HS. 2005. Lake restoration by dosing aluminum relative to mobile phosphorus in the sediment. *Environ Sci Tech* 39:4134-4140.
- Reitzel K, Ahlgren J, DeBradandere H, Waldebäck M, Gogoll A, Tranvik L, Rydin E. 2007. Degradation rates of organic phosphorus in lake sediment. *Biogeochemistry* 82:15-28.
- Rydin E, Welch EB. 1999. Dosing alum to Wisconsin lake sediments based on *in vitro* formation of aluminum bound phosphate. *Lake Reserv Manage* 15:324-331.
- Rydin E, Huser B, Welch EB. 2000. Amount of phosphorus inactivated by alum treatments in Washington Lakes. *Limnol Oceanogr* 45:226-230.
- Schütze J, et al. 2017. A newly developed injection method for aluminum treatment in eutrophic lakes: effects on water quality and phosphorus binding efficiency. *Lake Reserv Manage* (in press).

Figure 1. A map of Half Moon Lake, Wisconsin, showing 2011 buffered aluminum treatment areas, dosages, and sediment sampling locations.

Figure 2. Vertical variations in west and east arm sediment Al in 2011 (left panels) and 2014 (right panels) versus the Al concentration in 2010, before alum application. The gray horizontal lines denote the original sediment interface before Al application. The original sediment interface was assigned a depth of zero (Y-axis) with increasing negative depths below the interface. Positive depths denote the location of the deposited Al floc on top of the original sediment interface. Circles represent Al concentrations after application. Error bars for means collected in 2014 (n=3) represent 1 standard error.

Figure 3. Vertical variations in west and east arm sediment moisture content, solids content, wet bulk density, and dry bulk density in 2010, before Al application and in 2011, one month after Al application. The gray horizontal lines denote the location of the original sediment interface before Al application. The original sediment interface was assigned a depth of zero (Y-axis) with increasing negative depths below the interface. Positive depths denote the location of the deposited Al floc on top of the original sediment interface.

Figure 4. Vertical variations in west and east arm sediment moisture content, solids content, wet bulk density, and dry bulk density in 2010, before Al application and in 2014, three years after Al application. The gray horizontal lines denote the location of the original sediment interface before Al application. The original sediment interface was assigned a depth of zero (Y-axis) with

increasing negative depths below the interface. Positive depths denote the location of the deposited Al floc on top of the original sediment interface. Error bars for means collected in 2014 (n=3) represent 1 standard error.

Figure 5. Annual variations in moisture content, solids content, wet bulk density, and dry bulk density in the Al floc layer of west and east arm sediments. The Al floc layer thickness was estimated as ~ 3 cm and 2 cm in west and east arm sediments, respectively, based on vertical profile Al and physical characteristics (Fig. 2, 3, and 4). The black column represents pretreatment conditions of the upper 2 or 3-cm surface sediment layer while the gray columns denote post-treatment conditions in the Al floc layer.

Figure 6. Vertical variations in west and east arm sediment redox-sensitive P (redox-P) and Al-bound P in 2010, before Al application and in 2011, one month after Al application. The gray horizontal lines denote the location of the original sediment interface before Al application. The original sediment interface was assigned a depth of zero (Y-axis) with increasing negative depths below the interface. Positive depths denote the location of the deposited Al floc on top of the original sediment interface.

Figure 7. Vertical variations in west and east arm sediment redox-sensitive P (redox-P) and Al-bound P in 2010, before Al application and in 2014, three years after Al application. The gray horizontal lines denote the location of the original sediment interface before Al application. The original sediment interface was assigned a depth of zero (Y-axis) with increasing negative depths below the interface. Positive depths denote the location of the deposited Al floc on top of the original sediment interface.

Figure 8. Annual variations in the area-weighted concentration of redox-sensitive P (redox-P), Al-bound P, and the combined P (i.e., redox-P plus Al-bound P) in the Al floc layer of west and east arm sediments.

Figure 9. Annual variations in redox-sensitive P (redox-P) and Al-bound P in the Al floc layer of west and east arm sediments. The Al floc layer thickness was estimated as ~ 3 cm and 2 cm in west and east arm sediments, respectively, based on vertical profile Al and physical characteristics (Fig. 2, 3, and 4). The black column represents pretreatment conditions of the upper 2- or 3-cm surface sediment layer while the gray columns denote post-treatment conditions in the Al floc layer.

Figure 10. Estimated P binding efficiency in the Al floc layer between 2011 (one month after Al treatment) and 2013, 2014, or 2015 for the west and east arm. P binding efficiency was calculated as the percent change in Al-bound P mass (i.e.,  $\text{g/m}^2$ ) divided by the change in combined P mass.

Figure 11. Annual variations in the laboratory-derived mean ( $n=5$ ,  $\pm$  SE) anaerobic diffusive phosphorus (P) flux from sediments collected in the east and west arms. The black column represents pretreatment conditions while the gray columns denote post-treatment conditions.

Figure 12. Post-treatment anaerobic diffusive phosphorus (P) flux versus the redox-P concentration in the Al floc layer.

Fig. 1.

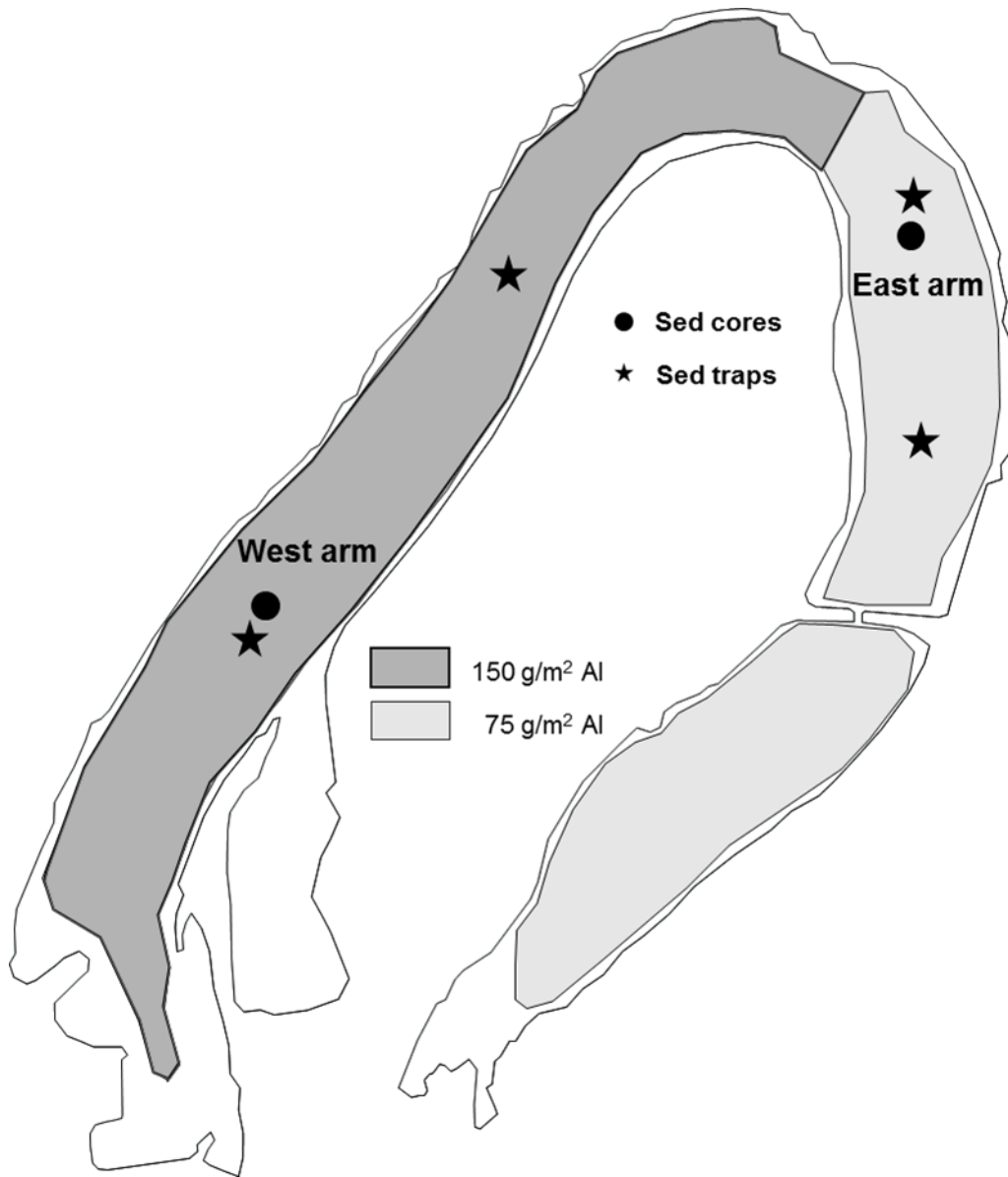




Fig. 2.

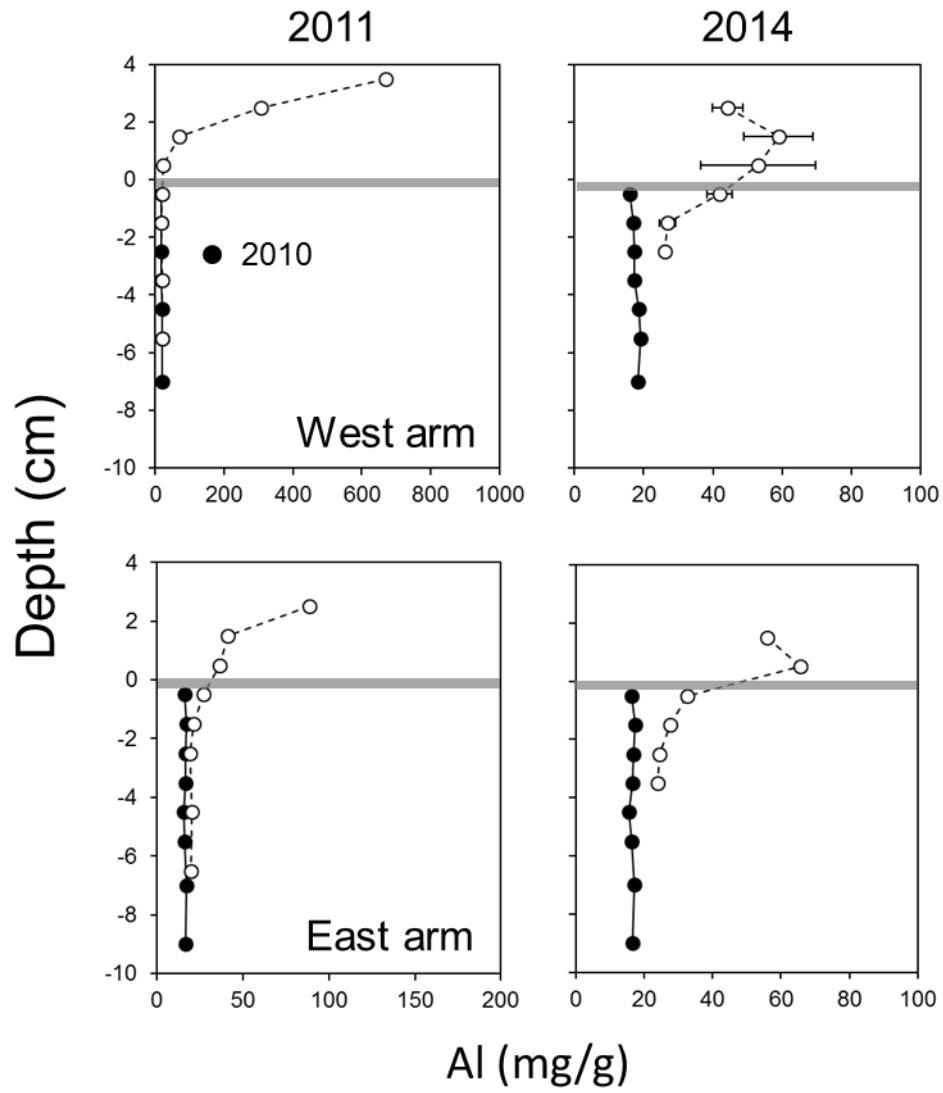


Fig. 3.

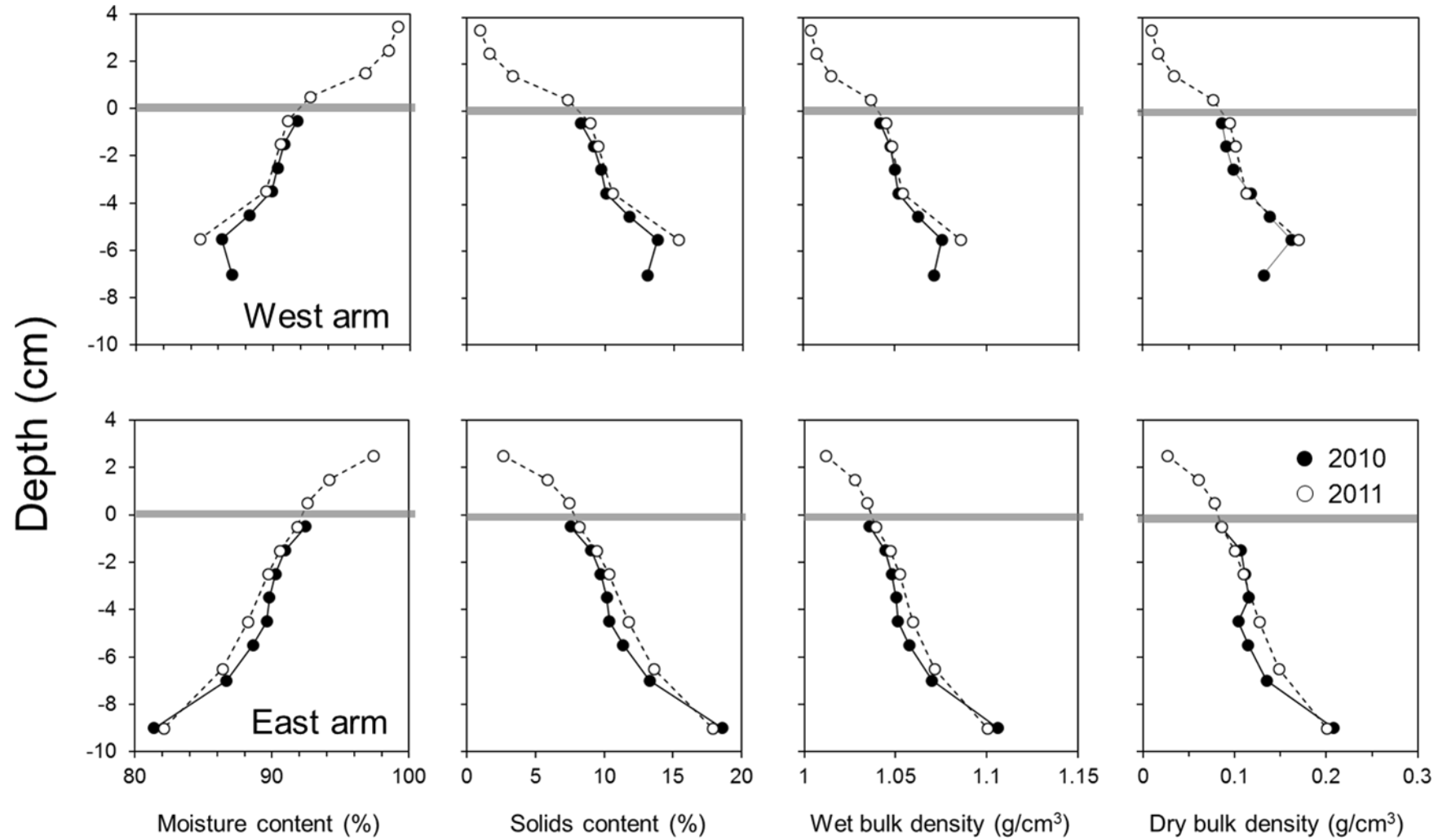


Fig. 4.

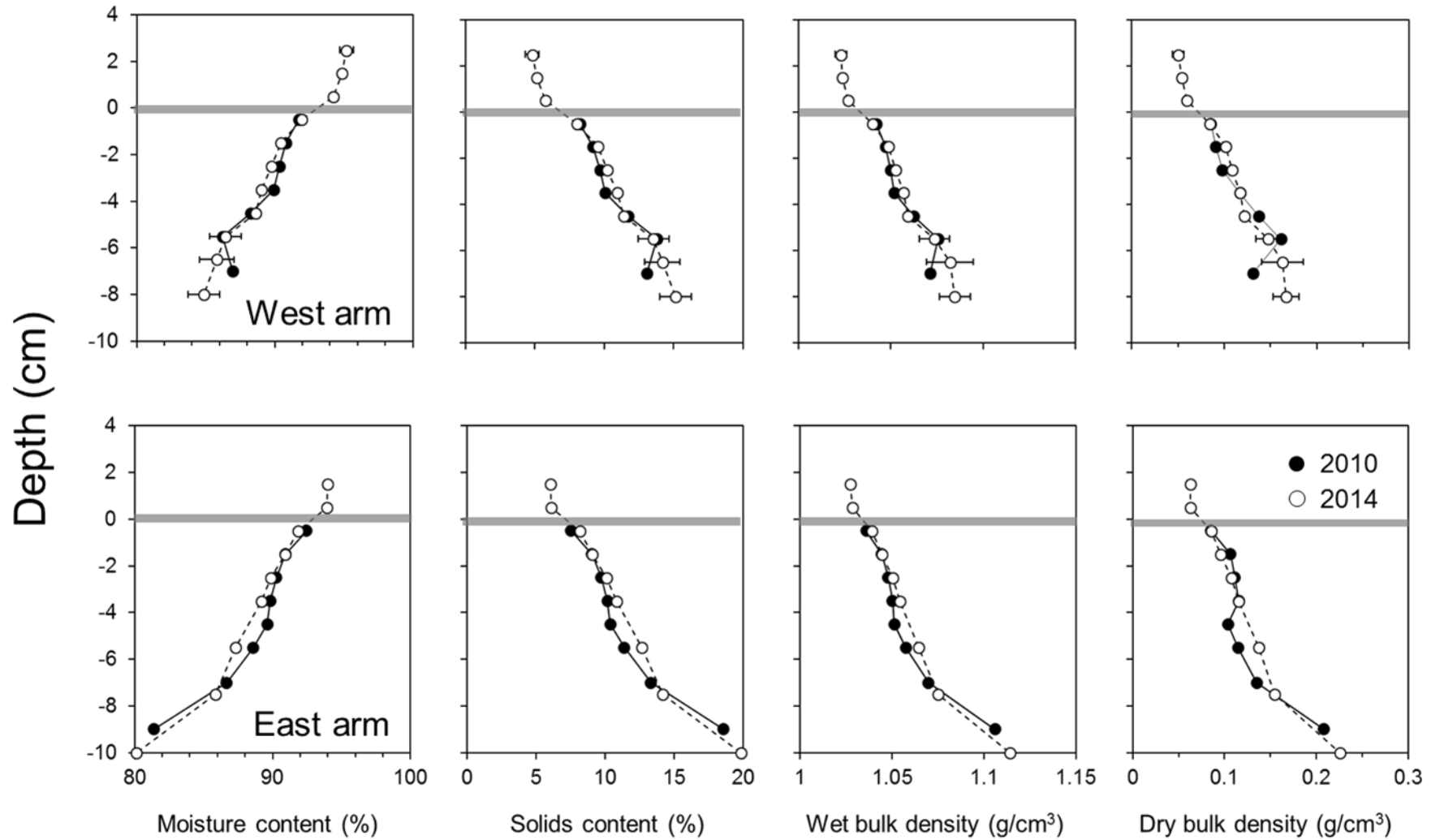


Fig. 5.

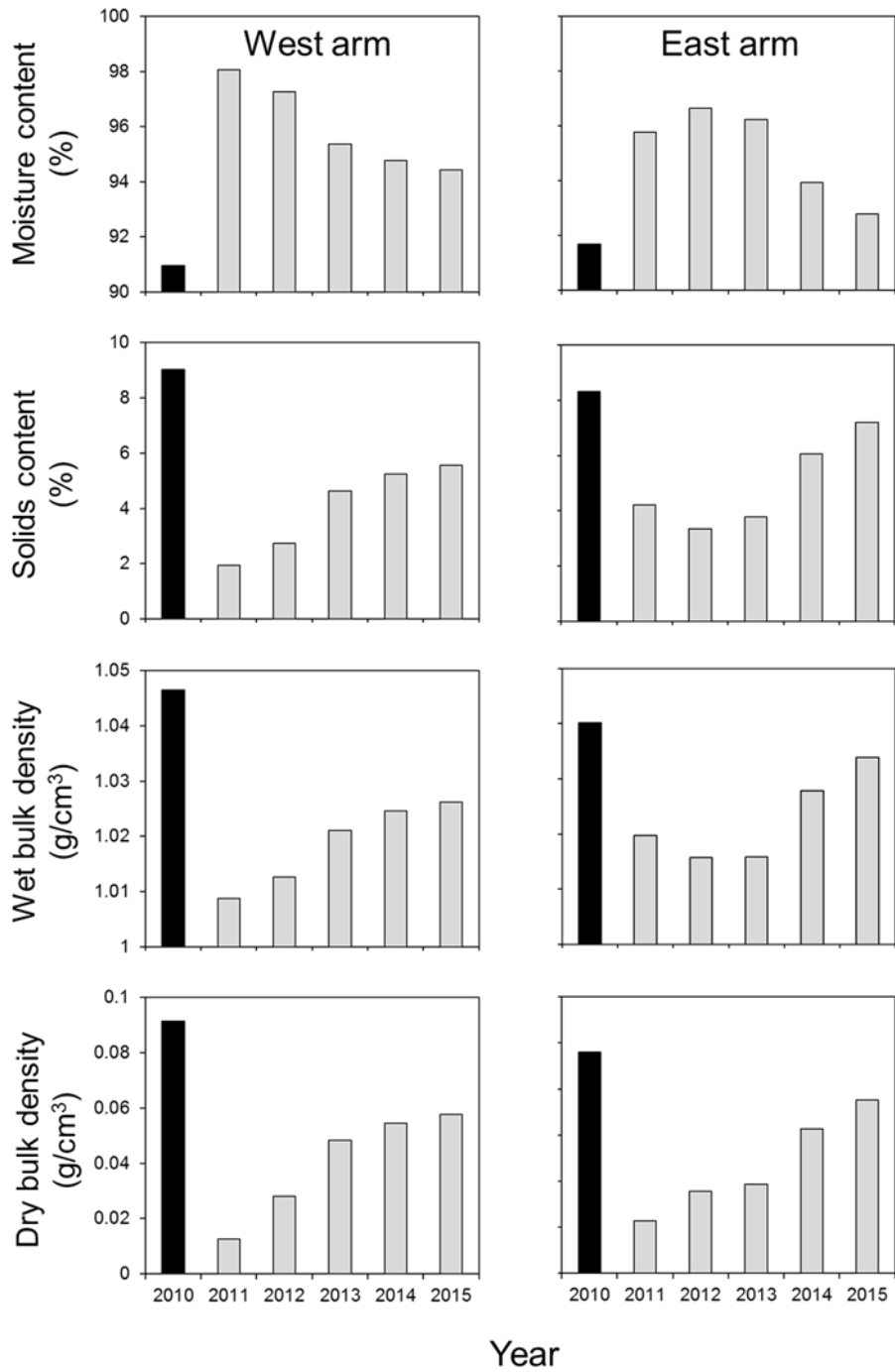


Fig. 6.

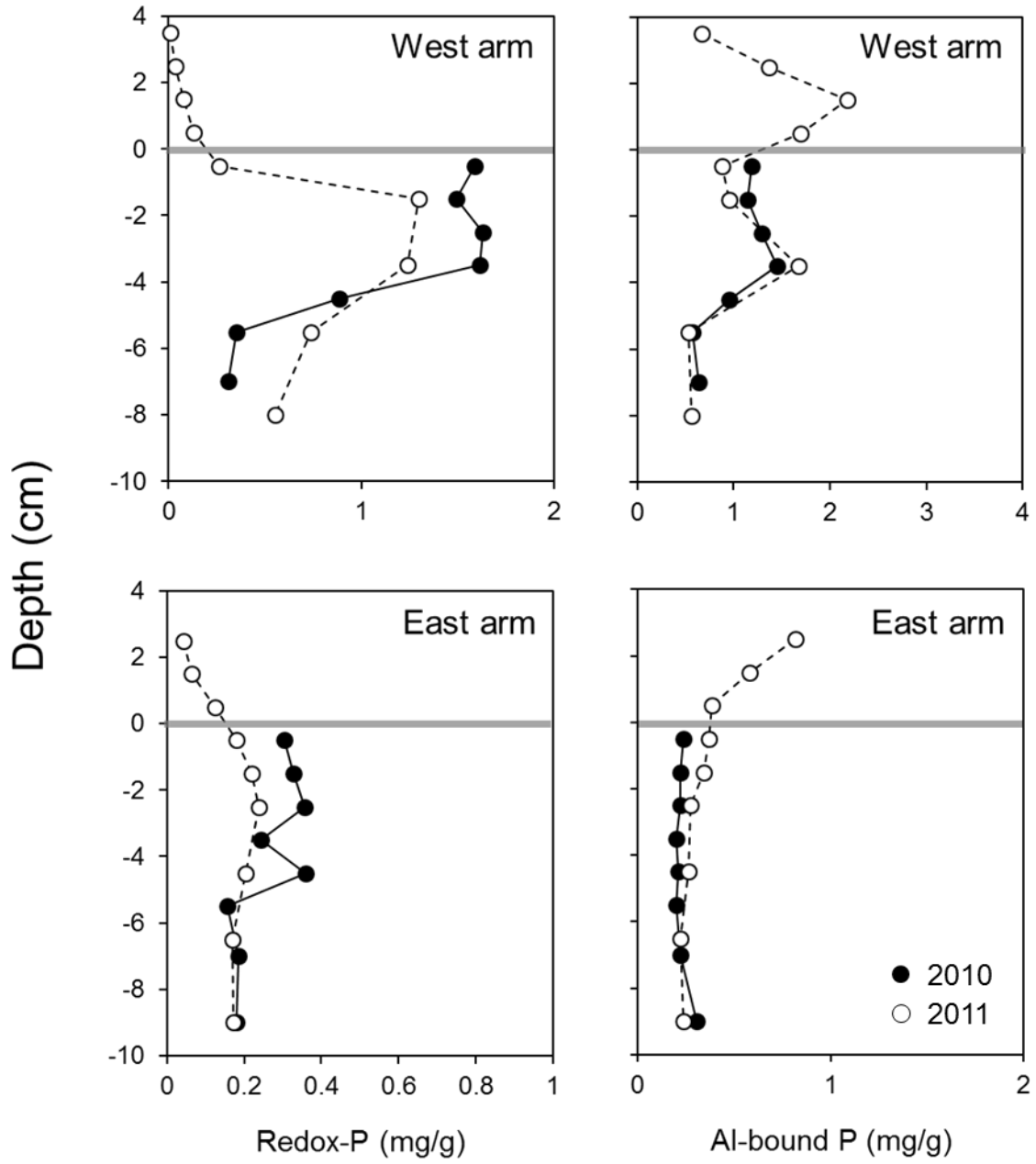


Fig. 7.

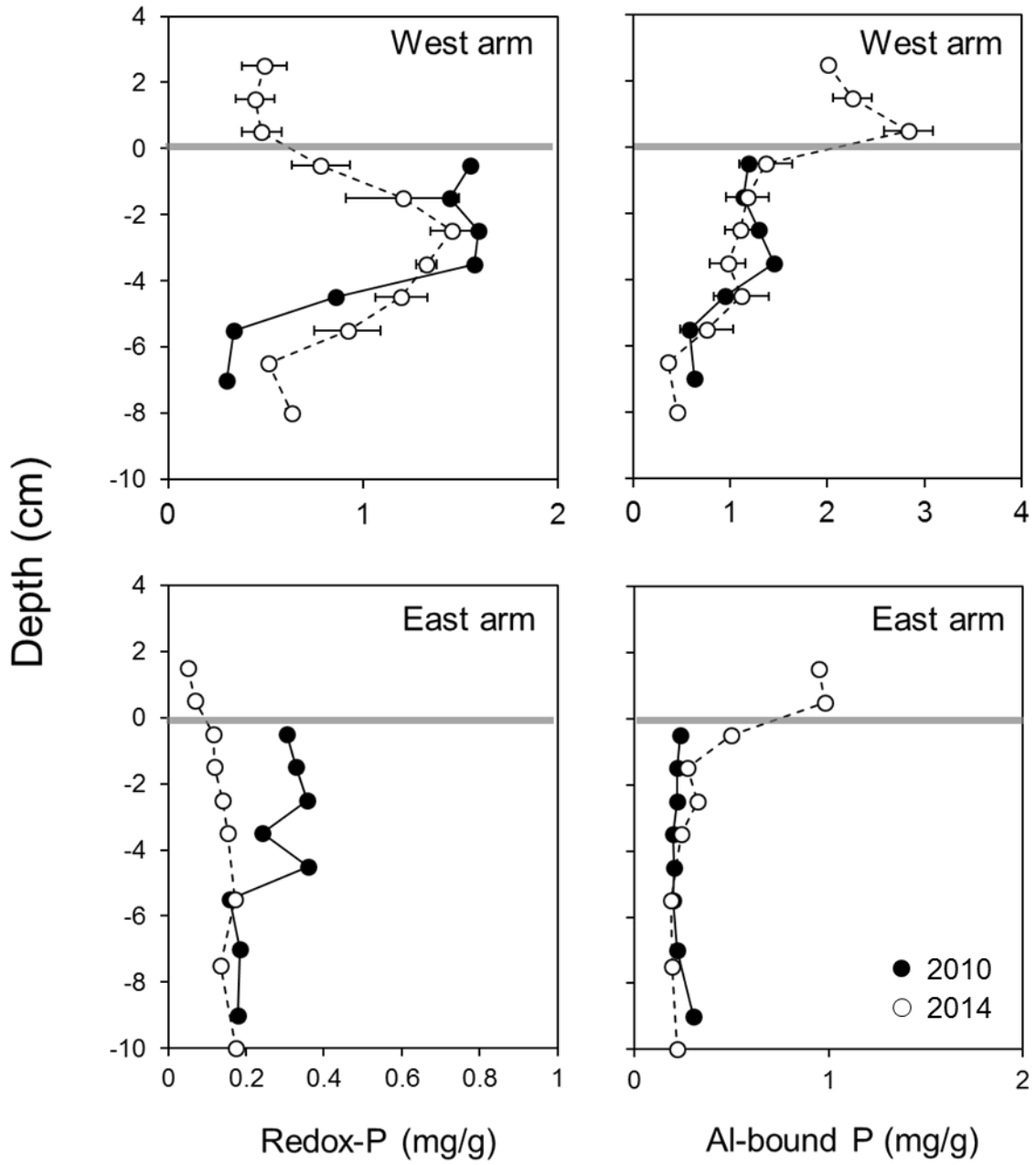


Fig. 8.

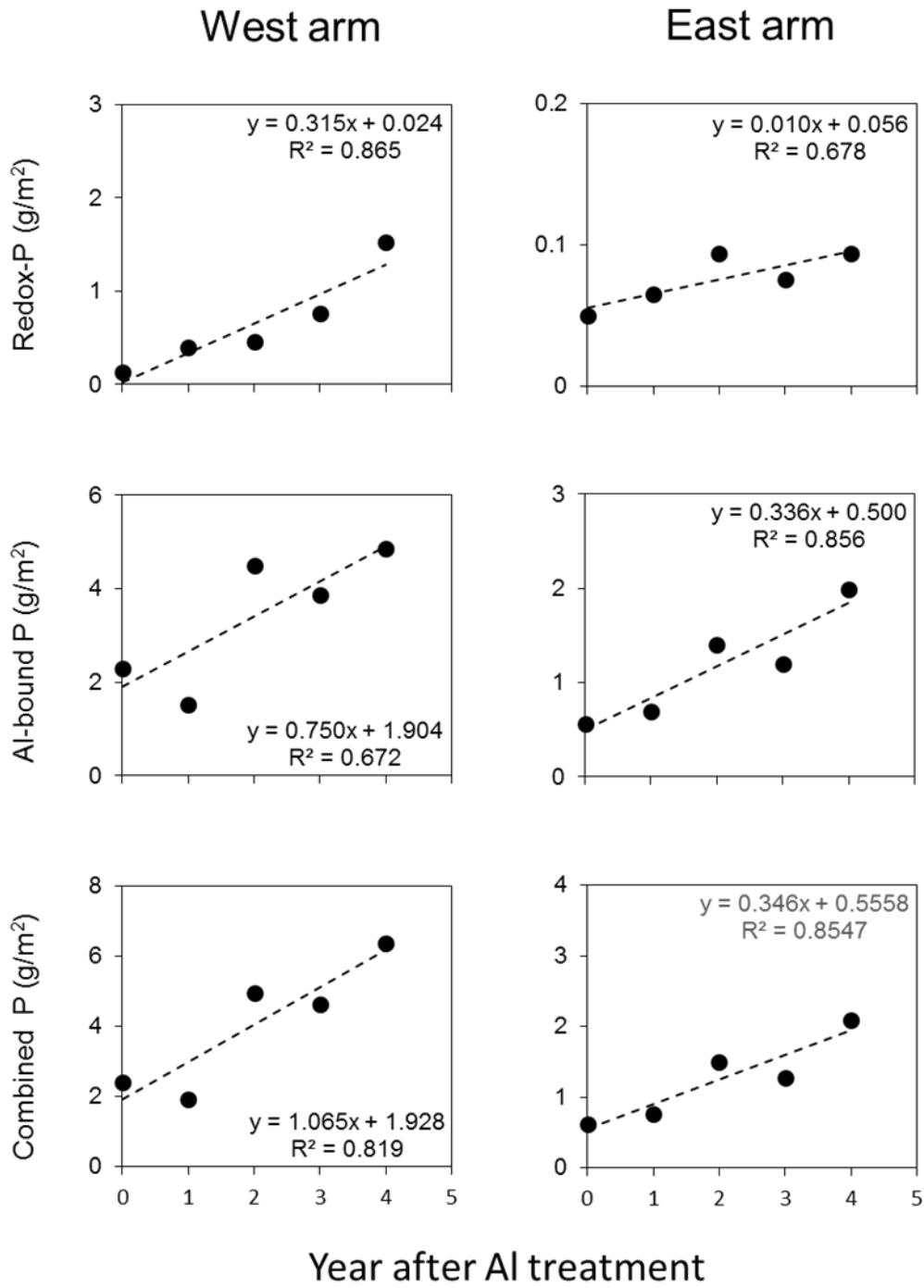


Fig. 9.

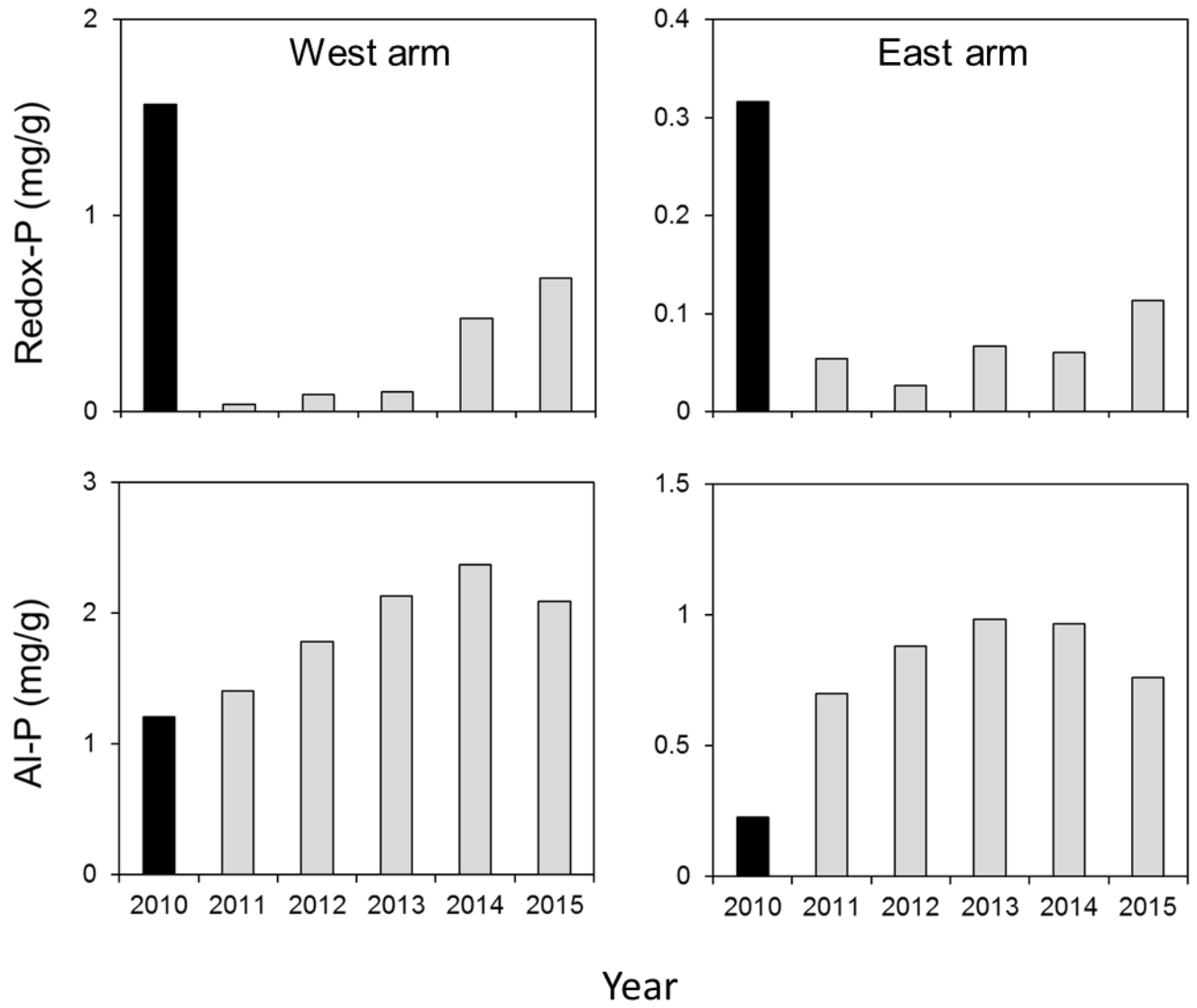




Fig. 10.

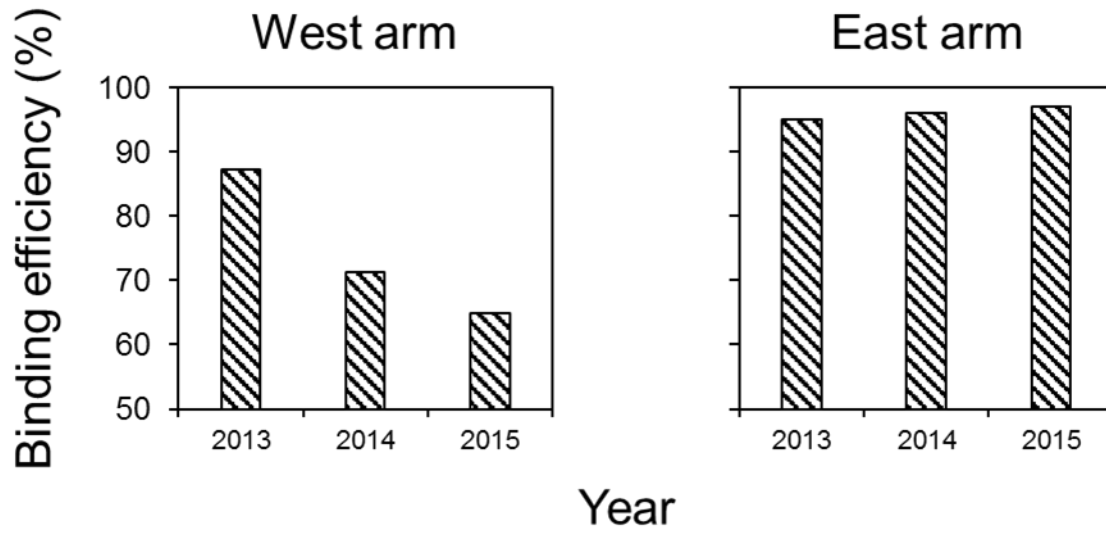


Fig. 11.

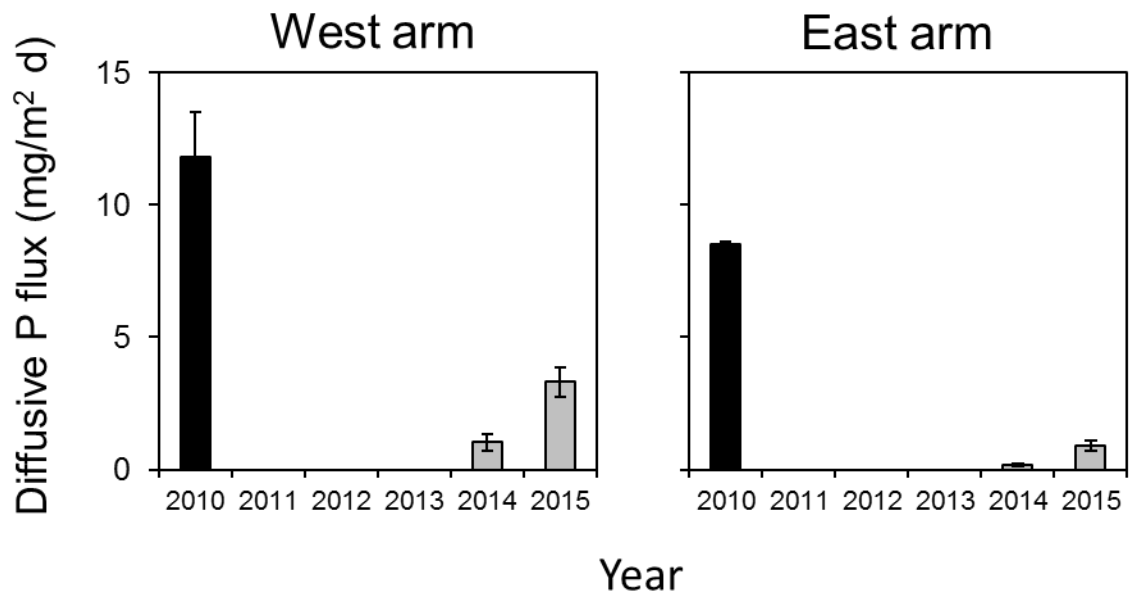


Fig. 12.

