Science of the Total Environment 643 (2018) 1091–1097

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Improving phosphorus removal in a surface flow wetland and land application system by geochemical augmentation with alum

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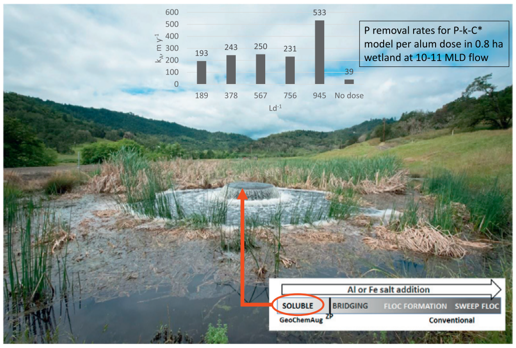
## HIGHLIGHTS

- High PO4-P removal rate in surface flow wetland with soluble alum dose
- P removal rate improvement about an order of magnitude of literature values
- Improved TP removal in land application system with soluble alum dose
- Soluble dose defined as non-flocculating, about 10 mg $L^{-1}$ alum or less

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 3 March 2018
Received in revised form 23 May 2018
Accepted 4 June 2018
Available online xxxx

*Keywords:*
Phosphorus
Aluminum
Geochemistry
Wetland

## ABSTRACT

Constructed surface flow (SF) wetlands are commonly used for phosphorus (P) removal. Geochemistry of wetlands provides explicit mechanisms for permanent P-sequestration in sediments. This study had two goals: (1) Find P removal performance and rate at the highest alum doses that do not produce floc in an SF wetland; and (2) Determine potential improvements to P removal performance with low alum doses in a 140-ha land application system downstream from the wetland. The study started with a small fraction of a conventional, flocculation/sedimentation alum dose, then progressively increased the dose to observe initiation of floc formation and removal of P. For flows near 10 megaliters per day in an 0.8 ha SF wetland, doses started 189 L $d^{-1}$ for two weeks, then increasing by 189 L $d^{-1}$ every two weeks until the final two weeks at 946 L $d^{-1}$. At an alum dosing rate of 189 L $d^{-1}$ (alum concentration of 9.5 mg $L^{-1}$), there was an order of magnitude improvement in P removal rates over literature values. Floc formation in the wetland was observed at 567 L $d^{-1}$, but no significant improvement in P removal rates were observed until a conventional alum dose of 946 L $d^{-1}$ was applied.

Alum addition improved P removal performance in the land application system. In 2014, during which there was no alum dosing, the median effluent total P (TP) during the July–September dry season (groundwater dominated outflow) was 0.43 mg $L^{-1}$. In 2015, (alum dosing August–October) median dry weather TP of 0.18 mg $L^{-1}$ was significantly lower ($p < 0.0001$). Alum dosing in 2016 at 189 L $d^{-1}$ produced a dry weather median of 0.28 mg $L^{-1}$, which was significantly lower ($p = 0.015$) than in the 2014 median. Mean daily dry weather TP loads to the land application system were 44 kg $d^{-1}$ in 2014, 45 kg $d^{-1}$ in 2015, and 41 kg $d^{-1}$ in 2016.

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https://doi.org/10.1016/j.scitotenv.2018.06.044
0048-9697/

## 1. Introduction

Phosphorus (P) removal is a common design goal for constructed surface flow (SF) wetlands (Kadlec and Wallace, 2009). Long-term removal of total phosphorus (TP) is a process of accretion in which biogeochemical cycles entomb a fraction of inflow P in organic residuals or minerals in wetland soils (Kadlec, 2006; Kadlec, 2005).

In SF wetlands, much, if not most, of inflow P flows out in soluble forms on an annual average basis. Surface flow treatment wetlands are shallow, lacustrine environments that are typically eutrophic or hypereutrophic, characterized by high sediment oxygen demand (Kadlec and Wallace, 2009). Sediments are anoxic, readily solubilizing settled particulate P (Palmer-Felgate et al., 2011). When high P-loading saturates available sorption sites of soil or organic detritus there is negligible net P removal (Kovacic et al., 2000). Mobilization of P from wetland soils due to sulfate reduction is the fate of a large fraction of inflow P (D'Angelo and Reddy, 1994), as is well-known in aquatic sediments in general (Mortimer, 1942). Because plant roots take up P from sediments, a substantial fraction of sediment P ends up in plants and then into the water column when plants decompose (Kadlec and Wallace, 2009). Observed annual P removal rates likely represent a transient state in which P-adsorption capacity is exhausted near the inlet, but downstream adsorption capacity remains (M. Bostic et al., 2010; White et al., 1999). Long-term P removal rates will degrade if adsorption is the dominant P-removal mechanism.

Net removal rates of P in SF wetlands are low, forcing large design treatment areas. Kadlec and Wallace (2009) report a global median first-order P areal removal rate coefficient of 10 m $y^{-1}$. The 10th and 90th percentiles are 1.4 and 60 m $y^{-1}$. Thus, for practical purposes a substantial percentage of designs fail at P removal. At the median rate, a flow of 10,000 $m^3\ d^{-1}$ in an SF wetland that polishes wastewater TP from 1.0 mg $L^{-1}$ to 0.05 mg $L^{-1}$ would require approximately 200 ha of wetted surface as calculated using the P-k-C* model with P (reactors in series) of 7 and an irreducible background concentration (C*) of 0.002 mg $L^{-1}$. Safety factors, wetland hydraulics and hydrology, local climate, and site-specific geochemistry entail variability in the design treatment area. Nevertheless, the land take tends to be impractically large to meet permit TP discharge concentration limits for wastewater applications.

If long-term P removal rates were higher, SF wetlands for P-removal would be smaller. Mechanistically, increasing sequestration of P in organic matter or insoluble minerals are the only means to realize higher P-removal rates.

Photosynthetic carbon fixation rates fundamentally limit incorporation of P into the recalcitrant fraction of autochthonous organic carbon (C). Only a small fraction of fixed C becomes peat in treatment wetlands because mineralization of plant litter increases in proportion to P loading at neutral pH values (Qualls and Richardson, 2000). The peat fraction remaining will be P-enriched, but P-mobilization from wetland sediments, as previously noted, renders much of sediment P a temporary storage.

Saturation extinguishes adsorption as a design basis to sequester P except in the near to intermediate-term after wetland commissioning. For adsorption to be a significant long-term P-removal process, supplemental adsorption sites would need to be injected to inflow or into the wetland, perhaps as suspensions of biochar (Chintala et al., 2014) or drinking water treatment residuals from flocculation/sedimentation basins (Gersten, 2017). Such a strategy to improve P-removal rates merits further investigation.

Geochemistry provides explicit mechanisms for permanent P-sequestration in sediments that entail mineral formation, such as calcium phosphates (Dodds, 2003), vivianite [$Fe_3(PO_4)_2 \cdot 8(H_2O)$] (Rothe et al., 2016), or precipitation with gibbsite [$Al(OH)_3$] (van Riemsdijk and Lyklema, 1980). Ann et al. (1999) determined that mineral amendment of wetland soils immobilizes soil P in order of mass removal per unit mass of amendment as $Fe^{3+} > Al^{3+} > Ca^{2+}$.

Geochemically explicit process designs are emerging in treatment wetlands and shallow ponds to improve P-removal:

- Inflow enriched with $FeCl_3$ immobilizes P in sediments (Sherwood and Qualls, 2001).
- Coprecipitation of P with calcium carbonates ($CaCO_3$) at high pH on calcareous periphyton mats is a dominant treatment mechanism in the periphyton stormwater treatment areas (PSTA) in South Florida (Gu and Dreschel, 2008). PSTA systems have higher removal rates for soluble reactive P than do stormwater treatment areas dominated by emergent macrophytes in the same geographic location and inflow conditions (Gu and Dreschel, 2008; Zamorano et al., 2018).
- Heterogeneous precipitation of P onto surfaces of apatite gravel has been demonstrated to be effective in subsurface flow wetland pilot studies (Harouiya et al., 2011). After an initial higher P removal rates due to adsorption, rates fall to a sustainable steady state dominated by calcium phosphate mineral deposition on apatite surfaces. Observed removal rate coefficients at steady state are one to two orders of magnitude over 10 m $y^{-1}$. Similar results and P-removal mechanisms have been observed in steel slag filters (Claveau-Mallet et al., 2013).
- Sub-flocculant (soluble) dispersion of alum into a stormwater pond in Minnesota, USA since 1997 has consistently achieved discharge TP near 50 μg $L^{-1}$ (Osgood, 2012) without apparent accumulation of floc (Austin, personal observation). Prior to alum addition, TP was 170 μg $L^{-1}$, which is near a median value for soluble P in stormwater ponds and would be expected to be the approximate discharge TP concentration per US EPA criteria (Athayde et al., 1983). A recent project closely following Osgood's methods achieved similar TP treatment in a small Kansas, USA lake (Austin et al., 2017).

Effectiveness for mineral P sequestration under various methods described above depends on site geochemistry, natural or induced. For example, PSTA technology depends on calcareous surficial geology. Either the shallow muck needs to be scrapped off native calcareous bedrock or crushed calcareous gravel needs to be lain on top of muck so that there is sufficient $Ca^{2+}$ in solution to drive P sequestration at high pH over periphyton mats. PSTAs are not "natural" in the sense that physical alternation to the site is essential to provide the driving geochemistry of P removal (Gu and Dreschel, 2008). Moreover, periodic herbicide application is needed to prevent growth of emergent macrophytes that would shade water, lower pH and degrade P removal performance. Thus, amendments in the form of herbicides indirectly, but decisively, drive design geochemical P-removal processes in PSTA systems.

The examples above entail "designer" geochemistry to drive mineral P sequestration. We call this family of methods *geochemical augmentation* when there is injection of sub-flocculent doses of $Fe^{2+}$ or $Al^{3+}$ into an SF wetland (Fig. 1). Metal salts common to water and wastewater are not coagulants at doses below a charge neutralization concentration threshold. Rather, they are in solution as mineral species set by eH, pH, or reaction with other solutes. If the TP concentration is low, then dosing to meet stochiometric mass ratios of Al:P = 0.87:1 and Fe:P = 1.8:1 will be far below a flocculating dose (Mac Berthouex and Brown, 2017). Thus, geochemical augmentation has potential to increase rates of P-removal through mineral accretion to wetland sediments without turning

**Fig. 1.** Schematic dosing definition of geochemical augmentation. Dosing is always less than particle's neutral zeta potential (ZP), which is the charge neutralization threshold for floc formation.