Water Research 84 (2015) 181–189

Contents lists available at ScienceDirect

Water Research

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

Characterization of the dissolved phosphorus uptake kinetics for the effluents from advanced nutrient removal processes

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ARTICLE INFO

Article history:
Received 25 March 2015
Received in revised form
11 July 2015
Accepted 15 July 2015
Available online 17 July 2015

Keywords:
Phosphorus uptake model
Bioavailability of phosphorus
TMDL
Nutrient removal

ABSTRACT

Given the importance of the watershed protection plans, direct determination of phosphorus (P) mineralization rates in advanced wastewater treatment facility effluents is crucial for developing the most protective strategies minimiz eutrophication in receiving surface waters. In this study, algal bioassays were used to determine the uptake rate of dissolved P in effluents from a broad range of advanced nutrient removal technologies (e.g., membrane biological reactor, traditional biological, tertiary membrane, Blue PRO™, etc.). Dissolved P uptake kinetics were fit to a gamma model and three first-order decay models. A traditional one-pool model correlated poorly with the experimental data (i.e., $r^2 = 0.73 \pm 0.09$), whereas two-pool model and three-pool models performed much better (i.e., $r^2 > 0.9$). These models also provided strong evidence for the existence of recalcitrant P in the effluents from these tertiary facilities. The Gamma model showed the mineralization of organic P followed a reactive continuum and further suggested the partitioning of P loads with different bioavailability levels should be accounted for the future modeling practices. From a modeling perspective, the Gamma model should be considered to be the theoretically best model as it gave the most parsimonious fit to the data using the fewest terms. Our study suggested that the current Total Maximum Daily Load (TMDL) model could be easily modified with the updated mineralization kinetics, which should lead to both ecological and economic benefits.

1. Introduction

Among the environmental factors acting as drivers of eutrophication, phosphorus (P) is the most widely investigated because of the recognition that it is the most common limiting nutrient which can also be controlled because it does not have a gas phase (Gurkan et al., 2006; Schindler et al., 2008). Extensive efforts have been devoted to developing management schemes for P loading control in impaired water systems. Phosphorus in Wastewater Treatment Plant (WWTP) effluents and natural systems is found in a variety of forms including dissolved inorganic phosphate, dissolved organic compounds, and both organic and inorganic molecules attached to particulate matter (Bradford and Peters, 1987; Dodds, 2003; Li and Brett, 2013b). Several studies have demonstrated that certain organic P forms are highly bioavailable for phytoplankton (Bostrom et al., 1988; Cotner and Wetzel, 1992; Li and Brett, 2013a). Other studies have demonstrated that a majority of the dissolved P in some advanced P removal effluents is recalcitrant and probably undergoes much slower uptake and utilization (Christen, 2007; Effler et al., 2012; Li and Brett, 2012; 2013b). Bioassays with pure P compounds further suggested this recalcitrant fraction may consist of molecules that are too large to be hydrolyzed or are bound in humic Al/Fe complexes that cannot be cleaved free by the enzymes typically used by phytoplankton or bacteria (Gerke, 2010; Li and Brett, 2013a). Assigning the same uptake rate for this recalcitrant pool as for other organic P fractions is problematic and could introduce a substantial prediction error in water quality models. Therefore, it is crucial to understand and characterize the uptake kinetics of P fractions with slower turnover times from a management perspective.

Although several studies have investigated phosphorus mineralization rates in natural waters or sediments, little is known about the biological uptake mechanism for the dissolved organic P in advanced WWTP effluents (Reitzel et al., 2007; Wilson et al., 2010). Nevertheless, the function embedded in most water quality models

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http://dx.doi.org/10.1016/j.watres.2015.07.028
0043-1354/

to represent the mineralization process from organic to inorganic P is generally described by first-order kinetics with a single constant decay coefficient, k. This statement that all organic P compounds decompose at the same rate has long been challenged since numerous studies on natural organic matter have shown considerable heterogeneity for the biodegradation kinetics of different organic species (del Giorgio and Davis, 2003; Guillemette and del Giorgio, 2011; Vahatalo et al., 2010). Ahlgren et al. (2005) distinguished individual components of organic P by ^{31}P NMR technology and found certain forms of organic P in lake systems, such as pyrophosphate, are mineralized to PO_4 with a half-life time of 10 years; whereas mono- and diester-P compounds may persist for several decades in sediments (Ahlgren et al., 2005). To partition the bioavailability gradient that might exist in organic compounds, first-order decay functions with multiple terms (commonly two or three) have been proposed to represent the various pools of organic matter (Harmon et al., 2009). This approach can differentiate the organic compounds into several fractions with specific decay rates designated for each pool.

$C_{tot,t}$ = i,0 = bioavailable fraction in i pool;
k_i = mineralization rate in i pool;
t = mineralization time.

Another alternative is the Gamma model, which was first used to characterize the decay of recalcitrant organic matter by Boudreau and Ruddick (Boudreau and Ruddick, 1991). These authors hypothesized that organic matter bioavailability should vary along a continuum of highly available to very low availability according to the following function:

$$C(k,0) = C_0 \Gamma(\nu)^{-1}\, k^{\nu-1}\, \exp(-a*k)$$

Where, C = total bioavailable fraction;

C_0 = initial concentration;
k = mineralization rate;
a = the average life-time of the more reactive components of the organic pool;
ν = the shape of the distribution near k = 0.

This reactivity continuum approach is featured with a time-variable function for the decomposition rate, k, and a spectrum of reactive forms that is a continuous definition of an infinite distribution (Boudreau and Ruddick, 1991). In studies on natural organic matter (NOM), the Gamma model has been shown to characterize the biodegradation continuum in a realistic manner (Vahatalo et al., 2010). However, those models primarily characterized the biodegradation of NOM, while the kinetics associated with the transformation of dissolved P remain unexplored.

In Total Maximum Daily Loading (TMDL) analyses, the non-point and point source pollution control actions that are needed to attain water quality goals are assessed with aquatic biogeochemistry models (Chapra, 1997; EPA, 2013). To meet the increasing needs of addressing a broad range of watershed pollution issues, various modeling approaches have been used, such as the Stream Water Quality Model (QUAL2K), Water Quality Analysis Simulation Program (WASP), CE-QUAL-W2, etc. (EPA, 2013). The majority of TMDL models used for regulating nutrient discharge permits estimate the P fraction in Wastewater Treatment Plant (WWTP) discharges that can be utilized by phytoplankton in natural systems using an effective mineralization rate for total P (TP) concentrations to soluble reactive P, regardless of the P composition (Berger et al., 2009; Water Quality Research Group, 2010). This assumption that a single rate can represent all potential mineralization processes over-simplifies the complex phosphorus cycle. While some models like HydroQual include phosphorus forms with different levels of reactivity (e.g., labile-P or recalcitrant-P), the uptake rates of these forms are still assumed to follow first-order kinetics. To improve evidence-based decision-making to minimize eutrophication potential from WWTP effluent discharges, there is a need for more sophisticated TMDL modeling approaches. Thus, direct determination of the dissolved P mineralization rate is critical in the TMDL assessment process and could influence management decisions.

In our study, algal nutrient uptake bioassay experiments were used to determine the loss rate of dissolved P from advanced WWTP effluents. It is assumed that the loss of P in this experimental system approximately corresponds to the mineralization of organic P to phosphate. We used conventional statistical tools to identify which P uptake kinetic model gave the most parsimonious fit to the data in order to obtain a conservative measure of dissolved P mineralization rates. Ultrafiltration was used to size-fractionate P in the effluents to enhance our understanding of recalcitrant P. The bioavailability continuum of dissolved P in nature was discussed relative to the Gamma model. The potential consequences of replacing a two-pool P kinetic model with a more comprehensive Gamma model were discussed from a management perspective. The findings presented in this study could be used to guide future TMDL analyses and eutrophication modeling in lakes and reservoirs.

2. Materials and methods

2.1. Sampling

A total of 22 effluent samples from the five main Spokane Region WWTPs were analyzed: Spokane County Regional Water Reclamation Facility (SCRWRF), City of Post Falls Water Reclamation Facility (PFWRF), Hayden Wastewater Research Facility (HWRF), Coeur d'Alene Advanced Wastewater Treatment Plant (CDA) and Inland Empire Paper (IEP). The facility information is listed in Table 1. All of the samples were collected in one-liter acid washed (HCl) polyethylene bottles from as near to the final outfall as practical from May 2013 to Dec 2013. Samples were stored at 4 °C immediately after collection and shipped to our laboratory on ice and in the dark within 24 h.

2.2. Chemical analyses

Chemical analyses for each sample determined whether the phosphorus pool was reactive and/or dissolved according to the acid-molybdate method described in Standard Methods 4500-P. Absorbance was measured using a Shimadzu spectrophotometer, Model UV-1601 and a 10 cm cuvette which gave a 2 μg/L detection limit. Four classic operational categories, total P (TP), total reactive P (TRP), dissolved P (DP), and dissolved reactive P (DRP) in the effluents could be directly determined. TP was determined after 45 min of autoclave-mediated digestion (120 °C, 100 kPa, with 0.012 M $K_2S_2O_8$ and 0.45 M H_2SO_4) of an unfiltered sample. TRP was determined using the same reaction on unfiltered samples without persulfate digestion. Samples for DP and DRP analyses (120 mL) were first filtered through a 0.45 μm polycarbonate membrane filter (Millipore®). DP was measured after persulfate digestion while DRP was measured without persulfate digestion. Dissolved organic P (DOP) was calculated as the difference between DP and DRP. Values for particulate phosphorus (PP) were estimated by subtracting DP from TP to represent the particulate phase.