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Bioavailability and characterization of dissolved organic nitrogen and dissolved organic phosphorus in wastewater effluents

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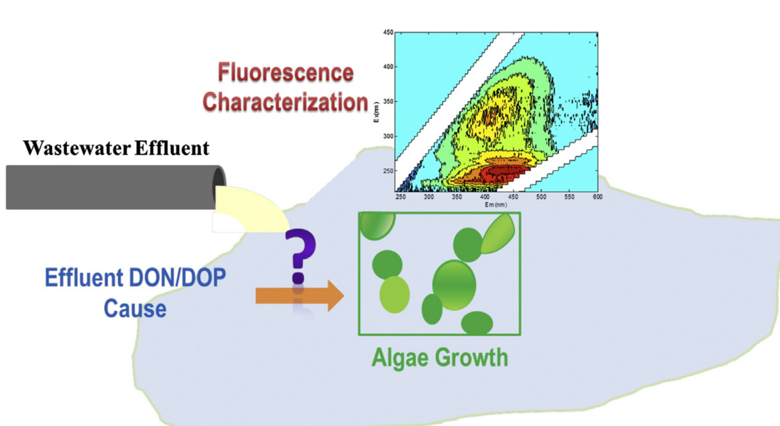
HIGHLIGHTS

- The bioavailability of DON/DOP in wastewater effluents were examined.
- The majority of DON was hydrophilic while more DOP existed in hydrophobic forms.
- Hydrophobic fraction of effluent DOP was more likely to be bioavailable for algae.
- Hydrophilic fraction of effluent DON seemed to exhibit higher bioavailability.
- Fluorescence spectroscopy analysis provided insights of DOM in wastewater effluents.

GRAPHICAL ABSTRACT



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ABSTRACT

There is still a great knowledge gap in the understanding of characteristics and bioavailability of dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) in wastewater effluents, which surmise implications related to both discharge regulation and treatment practice. In this study, we simultaneously investigated the characteristics and bioavailability of both DON and DOP, with separated hydrophilic versus hydrophobic fractions, in highly-treated wastewater effluents for the first time. The tertiary effluents from two wastewater treatment plants were separated into two fractions by XAD-8 resin coupled with anion exchange resin based on the hydrophobicity. Results showed that the majority of DON was present in hydrophilic forms while more DOP existed in hydrophobic forms. Hydrophilic DON contributed to 64.0%–72.2% of whole DON, while hydrophobic DOP accounted for 61.4%–80.7% of total DOP for the two plants evaluated. The effluents and their fractions were then subject to bioavailability assay based on 14-day algae growth. The results indicated that majority (~73–75%) of the effluent DOP, particularly the hydrophobic fraction with lower C/P ratio was more likely to be bioavailable for algal growth. The bioavailable fraction of DON varied widely (28%–61%) for the two plants studied and the hydrophilic fraction with lower C/N ratio seemed to exhibit higher bioavailability than the hydrophobic portion. The differences in bioavailable DON and DOP distributions of effluents from those two plants could be attributed to different receiving effluent compositions and wastewater treatment processes. In addition, fluorescence excitation–emission matrices (EEMs) combined with parallel factor analysis (PARAFAC) were used

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Hydrophilic
Hydrophobic fractionation

to characterize the dissolved organic matter (DOM) in wastewater effluent, which provided insights into the nature of organic matter in wastewater samples with different characteristics and originating sources.

1. Introduction

The effluent discharged from wastewater treatment plants (WWTPs) can be an important source of nutrient loading to aquatic environments and thus contributes to eutrophication. More stringent nitrogen and phosphorus discharge limits have been implemented on wastewater treatment plants in environmentally sensitive areas (Clark et al., 2010). For example, in Chesapeake Bay, more stringent permit limits have been required for plants to achieve effluent quality of 3 mg/L total nitrogen (TN) and 0.3 mg/L total phosphorus (TP). In advanced WWTPs that apply enhanced nutrient removal technologies to meet very low nutrient levels, most of the dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) in wastewater can be removed, then dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) could account for substantial fractions (40–85% of TN, 26–81% of TP) of the remaining TN and TP in effluents (Pagilla et al., 2006; Ragsdale, 2007; Gu et al., 2011, 2014; Liu et al., 2012). Watershed protection plans may therefore have to differentiate the bioavailability of different forms of nitrogen and phosphorus to balance the costs and benefits of removing DON/DOP versus controlling the remaining inorganic nutrient sources (Pehlivanoglu and Sedlak, 2004; Mulholland et al., 2007; Filippino et al., 2011; Simsek et al., 2013).

However, standardized or consented methods to measure the bioavailability of DON and DOP from wastewater effluent are currently not available. And discounting wastewater-effluent DON/DOP from total discharge regulations could substantially reduce construction costs of WWTPs and associated upgrades for advanced nutrient removal (Bronk et al., 2010). For these reasons, it is important to evaluate the potential bioavailability of DON and DOP to effluent receiving water and provide evidence to assist regulatory agencies for determining the necessity in excluding DON/DOP from the nutrient discharge allowance and, whether plants are required to upgrade current nutrient reduction technology for further removal of those organic nutrients in the effluents.

There are a limited number of studies on wastewater effluent DON bioavailability. In those studies, bioavailability of DON is determined by cultivating defined cultures or microbial communities from natural receiving waters in wastewater final effluent, where monitored net DON decrease was defined as bioavailable DON (Pehlivanoglu and Sedlak, 2004; Urgun-Demirtas et al., 2008; Bronk et al., 2010; Filippino et al., 2011; Liu et al., 2012; Simsek et al., 2013). These studies showed a wide range (18–96%) of the initial DON in low-total-nitrogen wastewater effluents that was bioavailable to algae and/or bacteria. However, the determination of true bioavailable DON only from the net changes of DON might not be accurate as the algae would both consume and release organic nutrients during the bioassay. Most studies mentioned above recognized that the increased DON caused by production from microbial community would mask the true utilization of effluent DON. Using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) analysis, Mesfioui et al. (2012) showed that 79% to 100% of the organic nitrogen compounds present at the start of the incubation were removed during the incubation with new nitrogen-containing compounds produced, which indicated that the effluent DON pool is much more dynamic than the net DON changes could reveal.

The characteristics and bioavailability of wastewater-derived DOP have rarely been studied (Gu et al., 2011, 2014; Li and Brett, 2012, 2013) and less reported than that of DON. These few studies evaluated the bioavailability of soluble reactive phosphorus (SRP) fraction and DOP, and showed that the classic assumption that SRP approximately equals bioavailable P (BAP) was not true for most of the cases (Li and Brett, 2013). They suggested that most organic forms of dissolved phosphorus (P) seemed highly bioavailable and could be utilized as a supplemental P source in the absence of inorganic P. The P fractions in the humic substances did not support algal growth, indicating that the organic P in these humic–Al–Fe complexes had very low bioavailability to algae.

In this study, we simultaneously investigated the bioavailability of both DON and DOP, with separated hydrophilic versus hydrophobic fractions, in highly-treated wastewater effluents for the first time. The bioavailable DON and DOP were determined by algae growth yield since previous studies have shown that using algae growth to assess organic nutrient bioavailability is feasible (Pehlivanoglu and Sedlak, 2004; Li and Brett, 2012). Due to the dynamic changes of the DON and DOP pool in the bioassay as mentioned earlier, we believe that bioavailability determined based on algal growth is more accurate than simply tracking the net changes in the total amount of DON or DOP. Effluents from two wastewater treatment plants were obtained and separated into two fractions based on the hydrophobicity, so as to examine the bioavailability of hydrophobic versus hydrophilic DON and DOP. Moreover, fluorescence excitation–emission matrices (EEMs) combined with parallel factor analysis (PARAFAC) were also applied here to characterize the dissolved organic matter (DOM) in wastewater effluent and monitor the changes in the composition or nature of the complex and dynamic DON and DOP pool during the bioassay.

2. Materials and methods

2.1. Effluent sampling

The wastewater treatment effluents from two enhanced nutrient removal plants were chosen in this study because their final effluents contained higher fraction of DON and DOP in relation to the dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP). The Broad Run Water Reclamation Facility in Loudoun County of Virginia (Loudoun Plant) consists of primary clarifier, fine screen, BNR-Membrane Biological Reactor (MBR) (5-stage Bardenpho process with membrane filtration) and a Granular Activated Carbon (GAC) adsorption process. The Pinery Wastewater Reclamation Facility (Pinery Plant) treats domestic wastewater from a service area located south of Parker Colorado, and the treatment processes include primary treatment, BNR secondary process (5-stage Bardenpho), followed by a multi-stage tertiary filtration process. The two effluents (grab samples taken at one time) were designated as Loudoun and Pinery effluent samples in this paper, respectively. All the effluent samples in this study were collected prior to UV disinfection. The wastewater effluent samples were filtered through a polycarbonate membrane filter (Millipore, 47 mm, 0.45 μm) immediately once shipped to the lab in coolers and then stored at 4 °C prior to use.

2.2. Separation of hydrophobic and hydrophilic fraction in wastewater effluent

The scheme of resin separation for effluent fractionation was shown in Fig. S1 and more details of the separation protocol were given by Liu et al. (2012). All the wastewater effluent samples were first acidified to pH of 2.0 with HCl and then pumped through Amberlite XAD-8 resin (now Supelite XAD-8 resin, Sigma-Aldrich) with flow rate of 1 mL/min. The eluents were collected as hydrophilic fractions that contained hydrophilic DON, DOP, inorganic nitrogen species (NH_4^+, NO_2^-, NO_3^-) and phosphates. The hydrophobic fraction retained on XAD-8 resin was later eluted by 0.1 M NaOH at flow rate of 1 mL/min in reverse direction. To