ARTICLE IN PRESS

Water Research xxx (2018) 1–9

Contents lists available at ScienceDirect

Water Research

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

Spatial-temporal variations of dissolved organic nitrogen molecular composition in agricultural runoff water

Liguang Li [a], Zhenli L. He [a, *], Malak M. Tfaily [b], Patrick Inglett [c], Peter J. Stoffella [a]

[a] University of Florida, Institute of Food and Agricultural Sciences, Indian River Research and Education Center, Fort Pierce, FL, 34945, USA
[b] Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, 99354, USA
[c] Soil and Water Sciences Department, University of Florida, Gainesville, FL, 32608, USA

ARTICLE INFO

Article history:
Received 27 October 2017
Received in revised form
9 January 2018
Accepted 14 January 2018
Available online xxx

Keywords:
Mass spectrometry
Organic nitrogen molecules
Photodegradation
South Florida
Water quality

ABSTRACT

Leaching of dissolved organic nitrogen (DON) has been reported as a pathway of N loss from agriculture, but the molecular composition of DON in agricultural water is poorly understood. Runoff water samples were collected from citrus grove furrows (CGF), ditches (CGD) and pasture ditches (PD) in four seasons. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) was used to investigate molecular composition of DON. Chemodiversity index of DON had spatiotemporal variations, while the molecular composition of total DON showed minimal variations, except for PD in November. Lignin derivatives constituted 61% of the total DON compounds. Relative abundance of aliphatic compounds, char and condensed aromatics of unique DON compounds varied spatiotemporally and had a significant correlation with DON concentration. Aromaticity index decreased from CGF to connected CGD, implying that photodegradation is possibly the dominant process that alters molecular composition of aquatic DON during the transport. Significant differences in unique DON composition between CGD and PD indicates that fertilization and land use affect DON composition. The information on molecular characterization of DON should be useful for tracking DON source and developing technologies to remove DON in the agricultural runoff water.

1. Introduction

Excessive leaching of nitrogen (N) from agricultural production systems has been reported to result in eutrophication of receiving water bodies (Smith et al., 1999). Inorganic N forms are frequently targeted for control in watershed management plans, with less attention to dissolved organic nitrogen (DON). However, organic N accounts for 61–99% of the total N in water, soil, and sediment environments (Pisani et al., 2017; Schulten and Schnitzer, 1997). Recent studies indicated that DON in runoff might represent a significant N loss from agricultural production systems (van Kessel et al., 2009). Our previous studies also indicated that DON accounted for 53% of total dissolved N in runoff water from agricultural production systems (Li et al., 2016a). High DON concentration was reported to inhibit ammonification and nitrification, thus, influencing aquatic N transformations (Xia et al., 2013). It is suggested that in addition to inorganic forms, N control in effluents should also include DON (Lewis et al., 2011).

In freshwater ecosystems, intrinsic properties of organic matter control the stability of organic matter (Kellerman et al., 2015). A significant proportion of DON, including amino acids, urea, and amino sugars, is considered bioavailable to both microorganisms and phytoplankton (Bronk et al., 2007; See et al., 2006; Seitzinger et al., 2002). Recently, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) has been applied to characterize molecular composition of DON in surface and ground water (Lusk and Toor, 2016). The FT-ICR-MS technique determines the mass-to-charge ratio (m/z) of ions based on the cyclotron frequency of ions in a high magnetic field and can identify different types of organic molecules. Therefore, it has advantages over traditional methods such as wet-chemistry, pyrolysis-gas chromatography, X-ray photoelectron spectroscopy, high-performance liquid chromatography, tetramethylammonium hydroxide (Hatcher et al., 1995), ^{15}N-NMR (Kogel-Knabner, 2002) or K-edge XANES spectroscopy (Vairavamurthy and Wang, 2002), which can only identify a specific type of organic N molecules.

Dissolved organic N from agricultural catchments is more

* Corresponding author. University of Florida, Institute of Food and Agricultural Sciences, Indian River Research and Education Center, Fort Pierce, FL, 34945, USA.
E-mail address: zhe@ufl.edu (Z.L. He).

https://doi.org/10.1016/j.watres.2018.01.035
0043-1354/

bioavailable, as compared to natural catchments (Graeber et al., 2015). Agriculture-affected streams were reported to contain more protein-like organic matter (Bida et al., 2015). Dissolved organic N from agricultural production systems is more reactive with large amounts of non-humic high-molecular-weight compounds (Heinz et al., 2015). However, minimal studies have investigated the composition of DON in agricultural runoff water at the molecular level. In south Florida, decomposition of organic materials is rapid due to high temperature and humidity, and leaching of DON is remarkable, particularly in sandy soils during the rainy season (Li et al., 2016a). Concentrations of DON in the agricultural catchment varied spatially and temporally (Li et al., 2016a) and represent a good opportunity to study the dynamic change of DON molecular composition. The objective of this study was to characterize molecular composition of DON in runoff water from the representative citrus grove and pasture land. We hypothesized that: (1) runoff water contains a high percentage of labile DON pools, and (2) molecular composition of DON varies spatiotemporally. To our knowledge, this is the first report on the molecular composition of DON in runoff water from agricultural drainage channels.

2. Materials and methods

2.1. Study sites

Sampling sites were located along Canal C-24 in St. Lucie Watershed, Fort Pierce, Florida (Fig. 1), characterized as flat landscape (<1% slope), sandy soils, and shallow water table (<3 m) with an extensive network of artificial drainage channels (Li et al., 2016a). Mean monthly precipitation varied from 53 mm in December to 195 mm in September in 2014. A rainy season occurs between June and November with a mean temperature of 30.8 °C, and a drier season starts from December through May with a mean temperature of 24.4 °C. Approximately 70% of land use in this area is citrus grove and pasture. A total of 34 samples from nine sites and four seasons were analyzed. Runoff water samples were collected from two citrus grove furrows (CGF, 27°19′N, 80°30′W), four citrus grove ditches (CGD, 27°19′N, 80°30′W) and three pasture ditches (PD, 27°21′N, 80°32′W). Samples were collected during the storm events in February (Feb, 48 mm rainfall), May (7.6 mm rainfall), July (83 mm rainfall), and November (Nov, 24 mm rainfall) of 2014, representing winter, spring, summer, and fall. No CGF runoff water samples were collected in May due to lack of rainfall. Water from CGF entered CGD, and CGD and PD were disconnected (Fig. 1). Soil orders in citrus grove and pasture are Alfisol and Spodosol, respectively. Only the citrus groves were fertilized with approximately 134–224 kg N ha^{-1}yr^{-1} and over 134 kg P_2O_5 ha^{-1}yr^{-1} (Li et al., 2017). For citrus grove, blended inorganic fertilizers (N8-P2-K8) [$(NH_4)_2PO_4$ + KNO_3] were mostly applied. Pastureland was managed via cow-calf operation as cattle ranch. Density of cattle is 1–2 heads/ha in this area. Groundwater in this area was ~30 m deep and used for irrigation in the citrus grove. Groundwater and ditch water were not connected.

2.2. Sample collection and preparation

Water samples were collected into pre-cleaned 1-L HDPE bottles

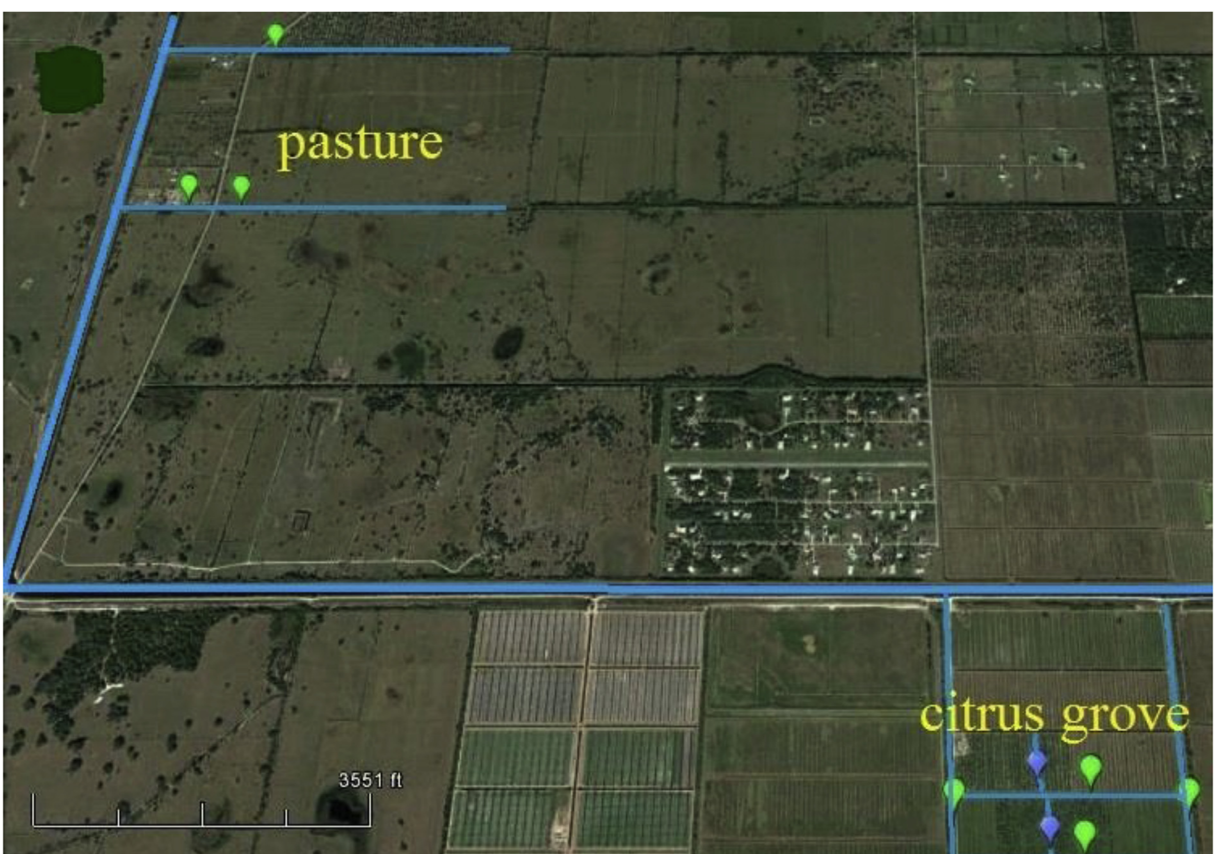

Fig. 1. The map of sampling sites: blueline is the waterway, green pin is the ditch sampling sites, and purple pin is the furrow sampling site. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Please cite this article in press as: Li, L., et al., Spatial-temporal variations of dissolved organic nitrogen molecular composition in agricultural runoff water, Water Research (2018), https://doi.org/10.1016/j.watres.2018.01.035