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Testing assumptions for nitrogen transformation in a low-gradient agricultural stream

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SUMMARY

Common assumptions of the nitrogen cycle in agricultural streams point to biologic transformation of nitrate being tightly linked to benthic carbon turnover within fine sediments of the streambed. While the nitrogen and carbon linkage has been supported in agricultural streams using multi-week stream injection studies, few studies have tested these assumptions using multi-year time-series of carbon and nutrient species. We made elemental and isotopic measurements from 8 years of weekly suspended sediment samples on the main-stem, 14 months of dissolved nitrate samples on the main-stem and tributaries, and point observations of sediment samples from benthic algae and stream banks in an agricultural stream to test the assumptions. Results from Empirical Mode Decomposition of carbon and nitrogen time series suggest agreement with the prevailing assumption and coupling of benthic carbon dynamics with nitrate from late spring through fall during the 8 year sampling period for the temperate stream. During late spring, summer and fall, autotrophic growth and organic matter decomposition assist with controlling temporary sequestration of nitrate and denitrification in stream sediments, respectively. Contrary to conventional wisdom, our data results suggest decoupling of carbon and nitrogen dynamics from winter through mid-spring for much of the 8 year sampling period. During the winter and spring, nitrate loadings from upland fertilizer application and delivery of upland sediments by storm events are shown to instantaneously increase sediment nitrogen and instantaneously decrease transported nitrate. The result is attributed to abiotic transfer of transient nitrate storage during the winter and early spring due to variably charged sesquioxides within streambed sediments. The results provide the first study, to our knowledge, of the potential importance of nitrate sorption in the stream nitrogen cycle and potential implications are that sorption could retard nitrate loadings from downstream transport and increase the potential for denitrification beyond which would be expected with purely biologic based assumptions.

1. Introduction

Mechanisms controlling source, fate and transport of nitrogen in agricultural and urban disturbed watersheds (<100 km^2) have received increasing attention over the past decade as a result of negative impacts from anthropogenic nitrogen loadings on drinking water quality and eutrophic conditions in receiving water bodies (Alexander et al., 2008; Galloway et al., 2008; Seitzinger, 2008; Xue et al., 2009; French et al., 2012; Trimmer et al., 2012). Despite the environmental significance, studies of nitrogen in human disturbed streams have assumed in-stream dynamics are consistent with the conceptual model developed for small, pristine, forested streams where nutrient loads are small, hill slopes and streambeds have steep gradients and organic matter dynamics are governed by allochthonous sources (Peterson et al., 2001; Bernhardt et al., 2005; Mulholland et al., 2008; Sebestyen et al., 2014). Conversely, agriculturally and urban disturbed streams, dominant throughout the mid-western U.S., are characterized by fine sediment surface soils, mild streambed gradients that promote transient sediment storage, and high background nutrient loadings and low canopy cover that promote autotrophic benthic algae as the dominant organic matter source (Walling et al., 2006;

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Griffiths et al., 2012; Ford and Fox, 2014). The characteristics of mid-western agricultural and urban streams promote formation of a thin, advection dominated, biologically active surface fine-grained laminae (SFGL) layer, a heterogeneous mixture of autotrophic algae, heterotrophic bacteria and fine sediment aggregates, effectively integrating erosion/deposition and biogeochemical sediment processes (Droppo and Stone, 1994; Droppo et al., 2001; Russo and Fox, 2012; Fox et al., 2014; Zahraeifard et al., 2015). The contrasting stream characteristics suggests a need to test current conceptual models for in-stream nitrogen cycling in low-gradient human disturbed systems characterized by surface fine-grained laminae.

The emerging conceptual model of nitrogen dynamics in surface fine-grained laminae dominated, agricultural streams stem from a review by Birgand et al. (2007) and a large scale tracer study of headwater streams by Mulholland et al. (2008), and point to hydrodynamics and benthic mediated biological redox reactions driving dissolved inorganic nitrogen, or DIN (i.e., NH_4^+ and NO_3^-), attenuation and exchange between dissolved and particulate phases *via* assimilation, ammonification, nitrification and denitrification. Hydrodynamics are the physical drivers for transport of dissolved solutes and particulate matter into and out of stream reaches and transient storage zones associated with the surface fine-grained laminae (Battin et al., 2003; Russo and Fox, 2012; Zahraeifard et al., 2015). Assimilationdenotes the biotic fixation of dissolved inorganic nitrogen, into microbial biomass, amino and nucleic acids, and is dominated by primary production in surface fine-grained laminae streams, as opposed to heterotrophic fixation (Birgand et al., 2007; Kendall et al., 2007; Ford and Fox, 2014). Ammonification is the bacterial mineralization of organic nitrogen to ammonium; the fate of which is determined by reassimilation by benthic biota, indirect nitrification, and regeneration via advection into the water column. Nitrification, the oxidation of ammonium to nitrate through a two-step process including oxidation to nitrite, followed by rapid oxidation to nitrate, can occur from advection of the overlying water column into the surface fine-grained laminae, i.e., direct nitrification, or following the mineralization of organic matter, i.e., indirect nitrification. Denitrification, or the dissimalatory reduction of nitrate into gaseous nitrogen, is performed by anaerobic, heterotrophic organisms that can occur in either deep diffusion dominated zones where oxygen is low, or in localized anoxic pockets, e.g., within algal mats, where sharp gradients in dissolved oxygen profiles occur over short distances (Birgand et al., 2007; Gu et al., 2007; Findlay et al., 2011; Harvey et al., 2013).

Assumptions surrounding the nitrogen cycle in agricultural streams include coupled carbon and nitrogen processes and the significance of biotic processes in hyporheic zones. Three primary avenues in which carbon and nitrogen are assumed to be coupled are during nitrification, denitrification and assimilation and immobilization of algal biomass. Coupled assimilation of carbon and nitrogen occurs during photoautotrophic algal growth, and has been suggested to have significant implications for downstream delivery and in-stream retention through degradation of detrital algae (Birgand et al., 2007; Godwin et al., 2009). Nitrification rates of chemoautotrophic bacteria are dependent upon ammonium mineralization of labile carbon and will be inversely related to carbon content in nitrogen limited systems since labile carbon stimulates competition from heterotrophic bacteria. However for agricultural systems where nitrogen is typically non rate-limiting, nitrification is assumed to increase with labile carbon content due to enhanced mineralization rates (Butturini et al., 2000; Arango and Tank, 2008). Denitrification rates are assumed to increase with labile carbon availability and high nitrate concentrations characteristic of agriculturally disturbed streams (Arango et al., 2007; Arango and Tank, 2008; Findlay et al., 2011; Newcomer et al., 2012). Recent advancements made in agricultural streams regarding the role of the hyporheic zone suggest uncertainty in the conceptual model is still pronounced (Gu et al., 2007; Zarnetske et al., 2011, 2012; Baker et al., 2012; Harvey et al., 2013). While abiotic processes have been included for cationic ammonium, biological transformations have generally been assumed to be the primary mechanisms impacting in-stream fate of the nitrate anion thus neglecting processes such as sorption as a potential mechanism for transient storage (Hantush, 2007).

While the prevailing assumptions regarding biologically mediated redox reactions of nitrogen in agriculturally disturbed streams have gained general acceptance and prompted inclusion into widely accepted numerical model decision making tools (Wool et al., 2006; Chapra et al., 2008; Park and Clough, 2012), the assumptions remain untested using long-term, comprehensive, ambient datasets that can be used to infer stream nitrogen dynamics. Rather, methods to measure biotic fluxes and transformations have relied on laboratory or field analyses of ambient samples and stream augmentation approaches. Bench-scale laboratory sediment core experiments and *in situ* mesocosms have been used extensively to estimate nitrogen transformation rates, however they have been shown to bias results as they do not adequately simulate vertical advective fluxes into substrates, hence underestimating delivery of solutes to biota, and only providing a point sample of processes (Birgand et al., 2007; Turlan et al., 2007). Reach-scale *in situ* studies have utilized conservative and non-conservative tracer injections (e.g., dye tracing, bromide, ^{15}N of nitrate) to characterize solute storage potential and in-stream fate, however the expense and labor intensive nature of the approaches limit temporal domain to a few weeks (Mulholland et al., 2008; Baker et al., 2012). Ambient point measurements of upstream and downstream reaches have been coupled with mass-balance calculations to estimate uptake, however these processes do not account for regeneration from the pore water, thus over-estimating rates (Seitzinger et al., 2006; Trimmer et al., 2012). Finally, ambient point measurements of sediment nitrogen have provided little fruitful insight as a result of the added complexity of sediment source variability (Kendall et al., 2001; Akamatsu et al., 2011). Collectively, studies have placed heavy emphasis on sampling during presumed periods when biological processes are most pronounced including late spring through fall and less when autotrophic and heterotrophic pools are temperature limited in winter through mid-spring (Birgand et al., 2007; Sebestyen et al., 2014). In addition to methodological limitations from measurements, time-series analysis of hydrologic and water quality data have primarily utilized Fourier-based approaches that assume parametric, linear and stationary characteristics of constituent datasets, despite recent findings that contradict those assumptions for transported constituents in agricultural streams (Machiwal and Jha, 2012; Ford and Fox, 2014).

The nitrogen cycling measurement methods above have been critical in substantiating the existence and importance of nutrient spiraling and its connectivity to organic matter processes in streams. However, the current assumptions of coupled biological processes as controlling the nitrogen cycle in agricultural streams has been untested using long-term, ambient datasets to infer stream nutrient dynamics. The objective of the present study was to test existing assumptions in the conceptual model of stream nitrogen dynamics in a low-gradient agricultural system controlled by surface fine-grained laminae. To complete our goal, we collected approximately weekly samples for an 8 year time period of carbon and nitrogen elemental and isotopic signatures of particulates that integrate streambed benthic and nutrient processes; applied the data driven Empirical Mode Decomposition of the 8 year time series to quantify seasonal coupling, or de-coupling, of carbon and nitrogen signatures; and collected and analyzed 14 months