Effects of Agricultural Land Use on the Molecular Composition of Streamwater Dissolved Organic Matter and Microbial Community Structure

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Amount Requested: $32,000; Project Duration: two years (02/15/14-02/15/16)

1. Motivation and Significance

Dissolved organic matter/organic carbon (DOM/DOC) plays a pivotal role in a variety of environmental and ecosystem processes within aquatic systems (DOC and DOM are often used interchangeably because DOC is the primary component of DOM). DOM protects aquatic biota by attenuating ultraviolet-B penetration [*Williamson and Zagarese* 1994], affects the physical states and transport of ecotoxins and trace metal pollutants [*Driscoll et al*. 1988; *Worrall et al.* 1997; *Yamashita and Jaffé* 2008], and serves as the basal substrate and energy sources for heterotrophic food webs [*Benner* 2003; *Kirchman* 2003].

Agricultural land use has been recognized as a global change that has fundamentally altered terrestrial landscapes and soil environments [*Foley et al.* 2005]. Land use may directly alter the quantity and characteristics of allochthonous DOM, i.e., DOM exported from watersheds to receiving waters. By changing physical landscapes and through the effects of nutrients and organics transferred from land to water, agricultural land use can also indirectly modify autochthonous DOM, i.e., DOM from the algae and bacteria living in water. Recent studies have shown that agricultural land use in watersheds may change the quantity, sources, ages, composition and reactivity of DOM in receiving waters [e.g., *Warner et al.* 2009; *Wilson and Xenopoulos* 2009; *Aitkenhead-Peterson et al.* 2009; *Sickman et al.* 2010; *Williams et al.* 2010], which may have substantial environmental and ecological ramifications for downstream rivers and coastal oceans.

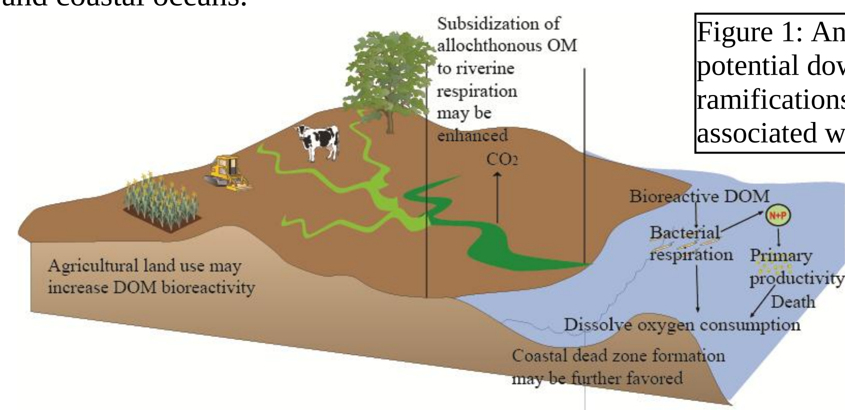

Figure 1: An example of the potential downstream ramifications of changes in DOM associated with agricultural land

An example of the potential downstream ramifications is that agricultural land use may favor hypoxia (Fig.1). Hypoxia, defined as dissolved oxygen concentrations less than 2mg/L and also referred to as ‘dead zones’, has plagued coastal ecosystems worldwide despite many costly management practices and restoration efforts [*Bianchi et al.* 2010]. Although the conventional understanding of the underlying mechanisms primarily identifies the importance of elevated nutrients in creating hypoxic events, organic matter exported from the land to coastal waters has gained much attention for its significant role in oxygen consumption [e.g., *Eldridge and Morse* 2008; *Bianchi et al.* 2010]. This role may be further enhanced by the possibility of agricultural land use increasing the proportions of bioreactive DOM (i.e., DOM can be readily remineralized or assimilated by heterotrophic bacteria) [*Williams et al.* 2010]. Bioreactive DOM has a greater potential than biorefractory DOM to contribute to hypoxia, either directly through bacterial respiration—the consumption of oxygen to convert DOM to CO_2—or indirectly through supplying organic and inorganic nutrients, which stimulates algal blooms that eventually decompose and consume oxygen (Fig. 1).

Compared with coastal oceans, riverine metabolism may be more susceptible to land use-induced changes in the properties of DOM [*Aufdenkampe et al.* 2011]. Allochthonous OM acts as a substrate source for riverine food webs [*Roach* 2013] and heavily subsidizes riverine respiration, as shown by the prevalence of net heterotrophic rivers (i.e., respiration > autochthonous primary productivity) [*Raymond et al.* 1997; *Jassby and Cloern* 2000; *Griffith and Raymond* 2011]. The changes in DOM due to agricultural land use can alter how DOM is processed, and therefore, the relative importance of allochthonous *vs.* autochthonous OM in supporting riverine metabolism. For example, agricultural land use may reduce the structural complexity and molecular weights of DOM [*Wilson and Xenopoulos* 2009], providing easier access to bacterial remineralization and thereby increasing the subsidies of allochthonous OM to riverine respiration (Fig. 1). Using high-resolution molecular analysis, Lu and students found a similar pattern demonstrating that agricultural watershed exported DOM with lower amounts of condensed and aromatic structures [*Li et al.*, in prep].

It is thus clear that agricultural land use may change the bioreactivity and molecules of DOM and that these changes could have far-reaching impacts on downstream environments and ecosystems. However, our understanding of how agricultural land use alters the molecular composition and reactivity of DOM remains incoherent and thus not well integrated in modeling and management efforts [Stanley et al., 2013]. In this proposal, we request funding to conduct a focused investigation on variation in DOM and associated microbial responses from streams draining a gradient of agricultural land use. This project will yield preliminary data and demonstrate the effectiveness of our research strategy in order to lead to a successful large-scale proposal.

2. Work Plan and Hypotheses

Study Area: Five streams along a gradient of watershed land use within the Bear Creek Watershed (BCW), Northwestern Alabama are be chosen for this study. The BCW watershed was selected for the following reasons. (1) *Contrasting co-existance of both agricultural and forest land use*: based on the 2006 NLCD BCW comprises ~16% agricultural land, 57% forestland, 5.5% urban land, and 22% of other land use (open water, wetland, shrub, grassland, and barren land). The delineated subwatersheds show a gradient of % agricultural land use ranging between ~2% and 32%. (2) *Availability of of data on sediment and water quality from long-term monitoring*: sediment/water qualities and organism health are monitored by the Geological Survey of Alabama (GSA) and the Tennessee Valley Authority (TVA) and the USGS monitors the stream discharges. (3) *Easy access and availability of laboratory facilities*: the site is close to the University of Alabama (UA) campus (ca. 80miles away). Sampling efforts may be coordinated with the GSA sediment survey trips of the; thus, the sampling cost and resolution may be further improved.

Plan 1: Quantitatively assessing the importance of agricultural land use in determining streamwater DOM molecular composition, reactivity and associated microbial responses (microbial abundance and community composition) at base flow

The five streams will be sampled three times at base flow. In addition to the characterization of DOM and microbes, a series of watershed, hydrology and inorganic water chemistry variables DOM properties will be determined (Table 1). We hypothesize that watershed land use is the primary factor determining DOM properties during baseflow conditions.

Table 1: Proposed analyses and the associated methods and PI

Variables	Method	PI
Land use (e.g., % forest; %cropland; % urban land)[1]	ArcGIS watershed delineation	Lu
Watershed physical parameters (e.g., stream length, width, depth, drainage area, topography)	ArcGIS analysis and field measurements	Lu
Water chemistry parameters (inorganic nutrients, Chlorophyll-a, *in situ* parameters)	Field sampling and laboratory measurements	Lu
%Groundwater input to streamflow	Radon^{222} in streamwater	Dimova
Stream/river Discharge evaluations	Flow rate measurements	Dimova
DOM biodegradability	Laboratory incubations	Lu
DOM sources	C:N ratios; δ^{13}C-DOC; DOM optical properties	Lu
DOM molecular composition	FT-ICRMS analysis	Lu
Microbial community	Phospholipid fatty acids (PLFA)	Findlay

Plan 2: Quantitatively assessing the importance of agricultural land use *vs.* hydrological variation in determining streamwater DOM reactivity, molecular composition and associated microbial responses.

The five streams will be sampled twice after storm events. Hydrological variations may change the sources, ages and compositions of DOM by shifting hydrologic flowpaths and altering in-stream production and processing of DOM [*Taylor et al.* 2003;*Vidon et al.* 2008; *Fellman et al.* 2009b; *Wiegner et al.* 2009; *Hong et al.* 2012]. Differentiating the influences of hydrological variation *vs.* land use on DOM will be achieved through comparing the DOM in streams during baseflow conditions *vs.* storm events. We hypothesize that high discharges/storm events will reduce the relative importance of watershed land use in determining DOM properties and associated microbial responses.

3. Project Timeline

	Spring 2014	Summer 2014	Fall 2014	Spring 2015	Summer 2015	Fall 2015
Watershed characterization						
Objective 1 data collection						
Objective 2 data collection						
Proposal submission						
Manuscript preparation						

4. Budget and Budget Justification

$6,000 for a Radon instrument; $6,000 for the high-resolution molecular analysis of DOM at the COSMIC lab at Old Dominion University; $3,750 for the PLFA analysis; $ 3,000 for additional DOM and water chemistry parameters such as C:N ratios, optical properties and nutrients; $1,200 for the field sampling ($100/trip *12 trips=$1200); $12,050 for supporting a MS student for spring 2014 (tuition $4750+ stipend $6700+ health insurance $600).

5. External Funding Opportunities Strengthened

a. A proposal to understand the influences of flow paths on DOM and heterotrophic bacteria will be submitted to Hydrological Sciences for co-review by NSF DEB program in December, 2014. Full proposal will be submitted in July, 2015.

b. Lu recently submitted her CAREER proposal to NSF DEB ($~750K) in July 2013. She expects the proposal will be criticized primarily on the lack of the preliminary data to demonstrate the potency of the proposed research strategy. This CFS fund will allow her to collect preliminary data that lead to a more compelling CAREER proposal.

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