Dissolved organic nitrogen in runoff/storm water from Agricultural Fields

Liguang Li[1], Zhenli He[1], Patrick Inglett [2], Malak M. Tfaily[3] and Peter J. Stoffella[1]

[1]University of Florida, IFAS, Indian River Research and Education Center, Fort Pierce, FL 34945

[2]Soil and Water Sciences Department, University of Florida, Gainesville, FL 32608

[3] Environmental Molecular Sciences Laboratory and Biological Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99354

Introduction

Our previous studies indicate that dissolved organic N (DON), rather than NO_3-N, is the dominant N form in the agriculture runoff and stormwater, which needs to be considered to develop TMDLs and BMAP in the Indian River Lagoon watershed (Li et al. 2016). Limited research has been conducted on DON speciation and bioavailability. We seasonally collected water samples from representative agricultural field furrows in 2014 and determined DON speciation by **Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS)**.

Objectives

To determine dynamic change of molecular composition of DON in the runoff or storm water from agricultural fields, as affected by land use.

Materials and Methods

- Sampling sites: CGF=citrus grove furrow, CGD=citrus grove ditch, PD=Pasture Ditch
- DON (Li et al. 2016), DON molecular composition in water samples was determined by FT-ICR MS (Tfaily et al. 2015).
- DBE (double bond equivalents parameter), DBE-O (C=C unsaturation) and AI (aromaticity index) (Koch and Dittmar 2006) of elemental composition ***CcHhNnOoSsPp*** is calculated as:

$$\mathrm{DBE} = 1/2 * 2c + n + p - h + 2) \quad (1)$$

$$\mathrm{DBE} - O = 1/2 * (2c + n + p - h + 2) - o \quad (2)$$

$$\mathrm{AI} = \frac{1 + c - 0.5o - s - 0.5h}{c - 0.5o - s - n - p} \quad (3)$$

Results

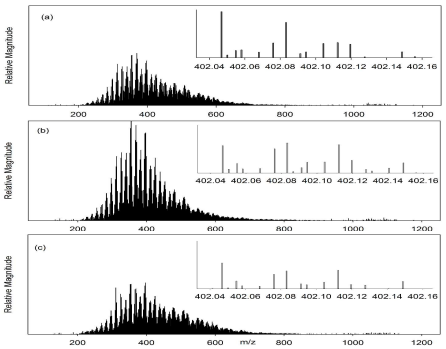

Fig. 1. Mass spectra of the water samples from (a) CGF, (b) CGD and (c) PD in July.

Results and Discussion

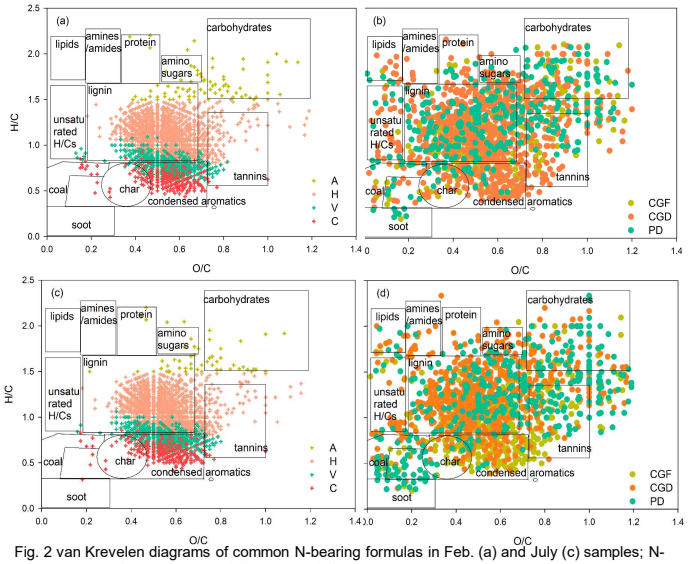

Fig. 2 van Krevelen diagrams of common N-bearing formulas in Feb. (a) and July (c) samples; N-bearing unique formulas in Feb (b), and July (d) samples across sites (A= Aliphatic compounds, 2.0 ≥ H/C >1.5; H = Highly unsaturated and phenolic compounds, AI ≤ 0.50 and H/C < 1.5; V= Vascular plant–derived polyphenols, 0.66 ≥ AI > 0.50; C = Combustion-derived polycyclic aromatics, AI > 0.66)

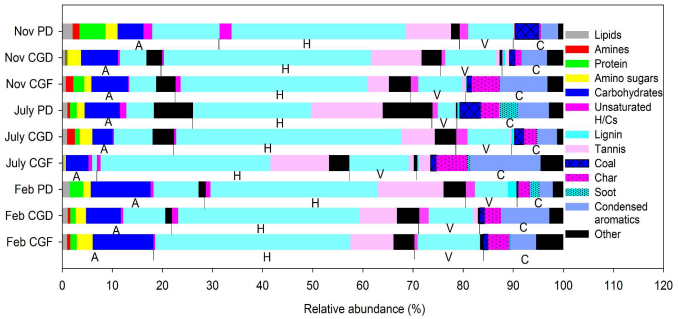

Fig.3 The relative abundance of different compound class regions in various groups across collection sites in Feb, July and Nov.

Table 1 Mean value of number of N peaks, mass, DBE/C, DBE, of DON molecules and DON concentration across the sites

	No.	Mass	DBE	DBE/C	DON(μM)
CGF	2265	481	12	0.58	135
CGD	2216	487	12	0.57	70.9
PD	2058	485	11	0.56	42.1

Table 2 Chemical-physical properties of unique molecular N across the sites

Time	Sites	No.	Mass(Da)	DBE-O	AI	DBE/C
Feb.	**CGF**	313	612b	0.0a	0.323a	0.532a
	CGD	822	546a	0.0a	0.300a	0.516a
	PD	335	684a	-3.0b	0.112b	0.429b
July	**CGF**	419	576b	1.0c	0.441a	0.612a
	CGD	717	582b	0.0b	0.271b	0.484b
	PD	383	670a	-4.0c	0.133b	0.500b
Nov.	**CGF**	411	590b	1.0a	0.341a	0.517a
	CGD	828	634a	-0.75b	0.273b	0.500a
	PD	290	602ab	0.50a	0.225b	0.431b

Table 3 Correlation between DON in water samples and AI, DBE/C, % of aliphatic lipids (ALD) and lignin (ALG), char and condensed aromatics (CA) of unique molecular N across sites.

	AI	DBE/C	%ALP	%ALG	%Char	%CA
DON	0.715*	0.759*	-0.735*	-0.684*	0.878**	0.733*

DON decreased significantly from CGF to PD, but No. of N peaks, median mass, DBE and DBE/C changed slightly (Table 1), suggesting that DON speciation is **similar** across the sites with variant DON concentration. Approximately 1400 common peaks were identified across the sites. Percentages of combustion-derived polycyclic aromatics, ***vascular plant-derived polyphenols***, highly unsaturated and phenolic compounds, and aliphatic compounds were 6, 61, 22 and 11%, respectively. The composition of common peaks changed slightly with seasons (Figs. 1a and c). Unique peaks were most in CGD (Table 2). Mass was highest in PD in Feb and July, but highest in CGD in Nov. DBE decreased significantly from CGF to PD in July. DBE-O was significantly different across the sites. This indicated that ***DBE-O*** was a better indicator than DBE to differentiate oxidation rate of all peaks across the sites. AI and DBE/C was highest in CGF and lowest in PD, suggesting that aromatic and refractory compounds were abundant in CGF and more biodegradable aliphatic compounds were in PD. Hence, the concentration of DON concentration decreased from CGF to PD, the proportion of *bioavailable* DON increased. The most abundant form in DON unique peaks was ***lignin*** (51%), followed by highly unsaturated and phenolic compounds-tannins (9.5%), carbohydrates (7.4%) and condensed aromatics (6.6%). DON was correlated positively with AI, DEC, percent of char, or condensed aromatics of unique molecules but negatively correlated with percent of aliphatic lipids or lignin (Table 3).

Conclusions

- ✓ Molecular composition of DON was similar across the sites, though DON concentration varied significantly.
- ✓ Dominant organic peaks in common peaks were vascular plant-derived polyphenols (61%), which changed little with seasons
- ✓ From Feb. to July, unique peaks were mostly in CGD (Table 2), with the dominant form as lignin (51%).
- ✓ DON concentration decreased with increasing proportion of bioavailable DON from CGF to PD.

References: Li, L., He, Z., Li, Z., Zhang, S., Li, S., Wan, Y. and Stoffella, P.J. Spatial and temporal variation of nitrogen concentration and speciation in runoff and storm water in the Indian River watershed, South Florida. Environmental Science and Pollution Research, **2016**, 1-9.

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Koch, B. P.; Dittmar, T., From mass to structure: an aromaticity index for high-resolution mass data of natural organic matter. *Rapid Commun Mass Sp* **2006,** *20*, (5), 926-932.

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