Urban headwaters: Model systems for DOM generation at the aqua-terrestrial interface

Megan Fork[1] and Chris Osburn[2]

1. Umeå University - Department of Ecology, Environment and Geoscience; Umeå, Sweden
2. North Carolina State University - Department of Marine, Earth and Ocean Sciences; Raleigh, North Carolina, USA

While considerable research links changes in DOM composition to abiotic processing by light[1–3], less is known about changes in optical properties of DOM during microbial processing. This is particularly true for DOM in urban streams, where both DOM sources and transport differ from forested streams. Using the engineered headwaters (EH, *sensu* Kaushal and Belt 2012[4]) of an urban stream network (i.e. roof gutters, roadside gutters, stormwater pipes) as models of the aquatic-terrestrial interface, we examined differences in DOC loss and DOM composition change between leachates of potential DOM sources and DOM in stormwater during microbial processing.

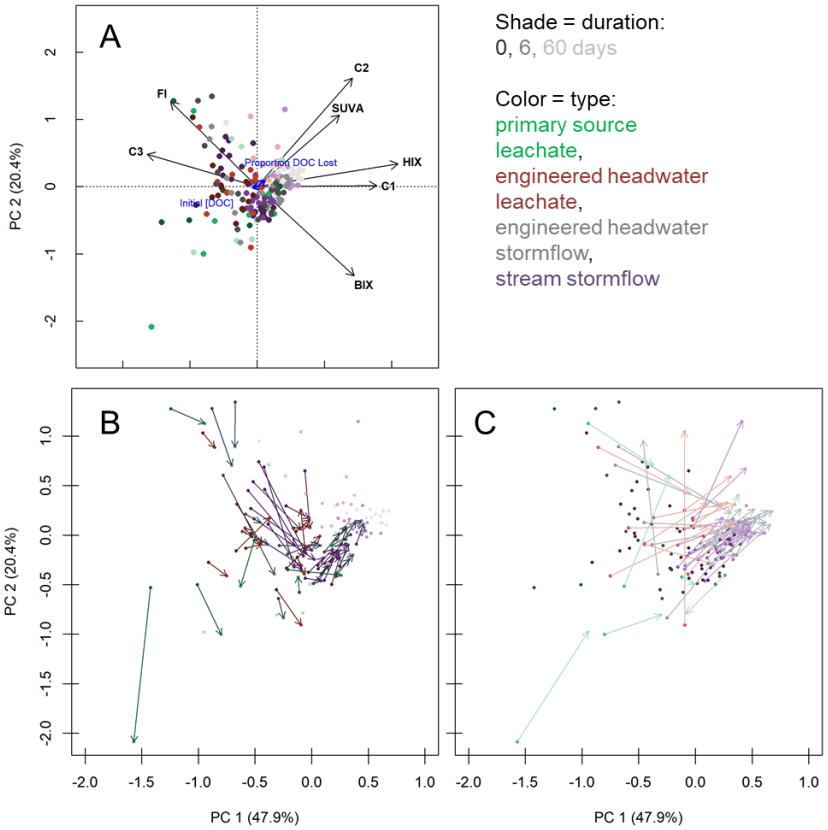
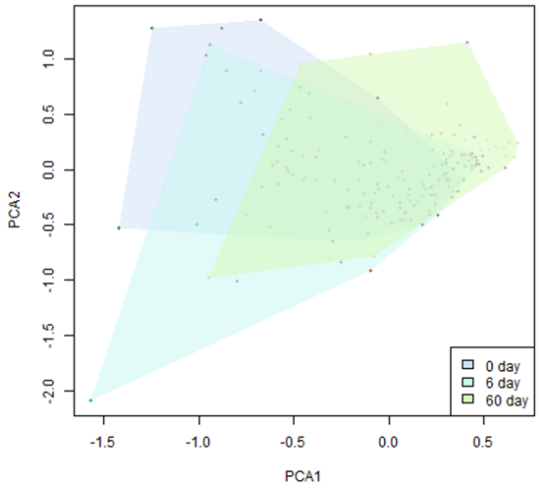


Figure 1. Principle component analysis of DOM composition in urban leachate and stormwater samples over the course microbial incubation using optical indices of DOM composition (SUVA, HIX, FI, BIX) and PARAFAC component intensities (scaled by sample DOC concentration; A). Loadings of optical properties are shown in black and proportional DOC loss and initial DOC concentration are shown in blue. Trajectories of the changes in DOM composition between 0-6 days of incubation (B) show greater variation than changes in composition between 6-60 days (C).

Our 60 ha study catchment was located in Durham, NC, USA with 39.4% impervious cover[5] (primarily roads and single family homes) and approximately 60% canopy cover[6]. Within this small urban catchment, we collected particulate organic for leachates as well as stormflow (one storm in each of spring and fall) in EH and in the natural bed stream draining the catchment. We incubated samples from leachates (primary sources: biofilms, leaves of dominant tree species, grass clippings, soil, etc. and from the particulate OM that collected in EH between storms) and samples of stormflow (through EH and the natural bed stream) with a common inoculum. We measured DOC concentration, absorbance spectra, and EEMs at 0, 6, and 60 days. We fit a three component PARAFAC model to 225 EEMs (75 samples at each of 3 time points). We then conducted PCA with the intensities of PARAFAC components (after scaling to sample DOC concentration) combined with common optical indices of DOM composition (FI, SUVA, HIX, and BIX). We characterized changes in the DOM composition of samples over time by tracing their trajectories in this ordination space over the course of incubation (Figure 1). We also characterized changes in the chemodiversity of bulk DOM during the incubation experiment as the area of the convex hull polygon in ordination space (Figure 2).

Over the first six days of incubation, leachate samples did not show significant DOC loss, while the total area occupied in ordination space increased (Figure 2). In contrast, DOM from stormflow exhibited decreases in DOC concentration concurrent with decreases in convex hull area in ordination space over the first six days of the experiment. By 60 days, samples lost an average of more than 50% of their initial DOC and the total DOC loss between leachates and stormflow was not significantly different. The area of the convex hull (apparent chemodiversity) was smaller at 60 days than at 0 days for all sample types and for the pooled population of samples.

We propose two different mechanisms drive changes in DOM composition during this incubation experiment: In the first, leachate DOM derived from urban particulate OM is "conditioned," increasing the apparent chemodiversity of the DOM pool concurrent with little change in the DOC concentration. Biotic processing generates DOM of microbial origin that is generally considered to be labile to biodegradation[7] and is mineralized later in the experiment. This conditioning of DOM is not observed in samples of aquatic DOM. The second mechanism by which processing changes DOM composition is preferential removal of some compounds, leaving behind more humic and aromatic DOM[8]. This mechanism is consistent with the changes observed in samples of DOM from the urban aquatic environment throughout our experiment, but in leachate samples only after an initial conditioning phase.



Scaled Convex Hull Areas	0 days	6 days	60 days
Primary source leachates	1.98	2.21	1.17
EH leachates	0.75	0.94	0.31
EH flow	1.20	0.97	0.38
Stream flow	0.65	0.27	0.47
Whole data set	2.56	3.07	2.12

Figure 2. Convex hulls of the pooled samples at 0, 6, and 60 days. At the right, the table shows convex hull areas for each sample type as well as the pooled population of samples.

References

1. Bertilsson, S. & Tranvik, L. J. Photochemical transformation of dissolved organic matter in lakes. *Limnol. Oceanogr.* **45,** 753–762 (2000).
2. Cory, R. M., McKnight, D. M., Chin, Y.-P., Miller, P. & Jaros, C. L. Chemical characteristics of fulvic acids from Arctic surface waters: Microbial contributions and photochemical transformations. *J. Geophys. Res.* **112,** G04S51 (2007).
3. Moran, M. & Zepp, R. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnol. Oceanogr.* **42,** 1307–1316 (1997).
4. Kaushal, S. S. & Belt, K. T. The urban watershed continuum: Evolving spatial and temporal dimensions. *Urban Ecosyst.* **15,** 409–435 (2012).
5. City of Durham Stormwater and GIS Services. Durham Storm Water GIS Layers. (2010).
6. i-Tree Cooperative & USDA Forest Service. i-Tree Landscape v2.1.2. (2016). Available at: www.itreetools.org/landscape/index.php. (Accessed: 23rd February 2017)
7. Cory, R. M. & Kaplan, L. a. Biological lability of streamwater fluorescent dissolved organic matter. *Limnol. Oceanogr.* **57,** 1347–1360 (2012).
8. Vannote, R. L., Minshall, G. W., Cummins, K. W., Sedell, J. R. & Cushing, C. E. The River Continuum Concept. *Can. J. Fish. Aquat. Sci.* **37,** 130–137 (1980).