PROCEEDINGS OF THE TWENTY-EIGHTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

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Keck Geology Consortium: Project 2014-2015
Short Contributions— Aquatic Biogeochemistry *Sophomore* Project

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AQUATIC BIOGEOCHEMISTRY: TRACKING POLLUTION IN FLUVIAL SYSTEMS

ANOUK VERHEYDEN-GILLIKIN, Union College, project director
Students: Anny Sainvil (Smith College), Larenz Storey (Union College), Celina Brieva (Mount Holyoke College), Alesia Hunter (Beloit College), Sara Marcela Gutierrez Diaz (University of California, Berkeley) and Angel Xavier Tate (Oberlin College).

INTRODUCTION

Eutrophication is causing major damages to freshwater, estuarine and marine systems. Monitoring water quality and nutrient loading is an important first step in determining the sources of pollution in watersheds, drafting management plans to reduce pollution in aquatic systems and, in the long term, evaluate the success of the actions taken. Nitrogen and carbon isotopic composition of primary producers (e.g., algae) and consumers have been used as an indicator of nutrient loading (Cabana and Rasmussen, 1996, McKinney et al., 2001, Wayland and Hobson, 2001, Cole et al., 2004) and as a way to evaluate the effectiveness of sewage upgrades (Costanzo et al., 2005).

Filamentous algae of the genus *Cladophora* are non-rooted algae that take up their nutrients directly from the water column (see Duarte, 1995). The isotopic composition of the algae, therefore, reflects those of the nutrients in the water during the growing season. Algae take up dissolved inorganic nitrogen (DIN), in the form of ammonia or nitrate. Moving up the food chain, nitrogen isotopic values increase due to trophic enrichment. At each increase in trophic level, the $\delta^{15}N$ value of the tissues increases with about 3 to 4 ‰ (see Cabana and Rasmussen, 1996). Trophic enrichment is caused by the metabolic breakdown of molecules with lighter isotopes, resulting in tissues incorporating the heavier isotopes. The isotopic composition of animal waste then contains high ammonia, with a low $\delta^{15}N$ value. After microbial breakdown (nitrification) this waste is then enriched in ^{15}N due to the bacterial preference of lighter isotopes (Fry, 2008). Therefore, streams that have a high input of sewage, which can be caused by leaking sewage systems or agricultural runoff, are expected to have primary producers with high $\delta^{15}N$ values. In addition, a further ^{15}N enrichment of this organic pollution can occur during volatilization of ammonia, which is typically ^{15}N depleted (Frank et al, 2004). Several studies have successfully used $\delta^{15}N$ values of primary producers and/or consumers to identify sources of anthropogenic nutrient inputs (Aravena et al., 1993; McClelland and Valiela, 2001; McKinney et al., 2002; Cole et al., 2004; Cole et al., 2005). Costanzo et al. (2005) used a threshold level of 5‰ to be indicative of anthropogenic nutrient loading.

While terrestrial plants use CO_2 as their carbon source during photosynthesis, aquatic plants obtain their carbon from the dissolved inorganic carbon (DIC, the sum of CO_2, HCO_3^- and CO_3^{2-}). The relative abundance of each of those carbon species is pH dependent. *Cladophora* probably has a preference for CO_2, but is also able to use HCO_3^-, or a combination of both (Raven et al., 1994). During photosynthesis, an overall discrimination of about -20‰ occurs compared to their carbon source (Fry, 2008). While dissolved CO_2 has an isotopic value close to atmospheric CO_2, the conversion to HCO_3^- results in a temperature-dependent discrimination (-10‰ at 15C, see Mook, 2000), causing lower $\delta^{13}C_{DIC}$ values. Since, *Cladophora* is able to use both dissolved CO_2 and HCO_3^-, its $\delta^{13}C$ value of the algal tissues will depend on the availability of the carbon species (and therefore of pH) and of the $\delta^{13}C_{DIC}$ value. In streams

Figure 1. Our Keck group in the field (from left to right: Anny Sainvil (Smith College), Larenz Storey (Union College), Celina Brieva (Mount Holyoke College), Michelle Berube (Union College), Anouk Verheyden-Gillikin (Union College), Alesia Hunter (Beloit College), Sara Marcela Gutierrez Diaz (University of California, Berkeley) and Angel Xavier Tate (Oberlin College).

Figure 2. Larenz, Sara and Angel collecting water samples.

with high nutrient loading, we expect high respiration rates will lead to the use of respired (and therefore ^{13}C depleted) CO_2. Therefore, very low $\delta^{13}C$ values could be indicative of nutrient loading.

In this study, a total of 32 streams were sampled in both urban and rural settings and located in one of three geographic regions: Schenectady area, Schoharie valley, or the Catskill region. This study focusses on identifying areas of high anthropogenic nutrient loading, investigating the difference in water quality between urban and rural areas, and the difference between the three geologically different areas. Nitrogen isotopic values of primary producers were used as a measure of anthropogenic nutrient loading. The possibility of using carbon isotopic composition of the algae for eutrophication as well as the potential of several ions as tracers of urbanization was also investigated.

PROJECT OVERVIEW

Unlike other Keck projects, this project was aimed at attracting sophomore students of underrepresented groups to the field of Geology. During the four week stay at Union College, students were exposed to every aspect of higher level research, including site selection, data and sample collection in the field, sample preparation, sample analysis, data interpretation, literature research, and data presentation.

During the first week of the project, field methods were tested on a stream that runs through Union's campus, short lectures about isotopes and the goal of the project were given and students were actively involved in selecting sampling sites. Our team mostly relied on the satellite view of google maps to find appropriate sites. Sites needed to be easily accessible without having to cross private property. Another resource that was used during site selection was the Department of Environmental Conservation (DEC) website, which provided boat launch locations and fishing locations. The three regions mentioned above were chosen for their different geology, geomorphology, as well as the different levels of urbanization. All potential sites were mapped and a route was created.

During the second and third week of the project, samples were collected at the field sites. A total of 32 streams were sampled by the end of week 3. At each site, stream characteristics were described using a qualitative assessment (stream size, flow rate, surrounding area, grain size, and abundance of algae). Physicochemical parameters of the water that were measured on-site included conductivity, temperature, pH, and dissolved oxygen. Water samples were collected for ion analysis as well as for alkalinity. Where present, filamentous algae of the *Cladophora*

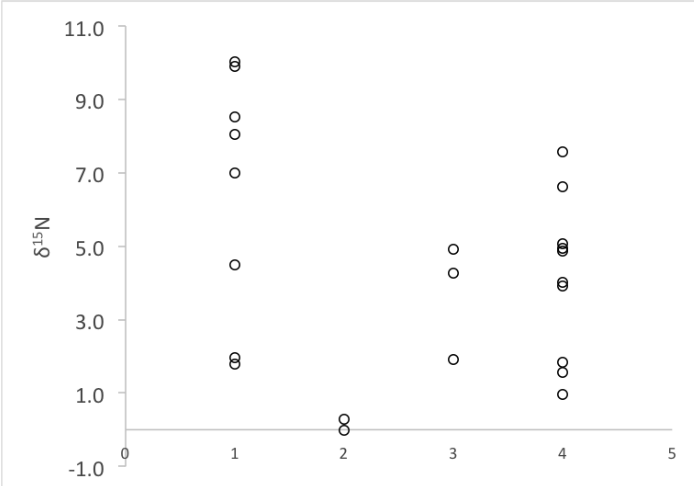

Figure 3. $\delta^{15}N$ values (‰) of Cladophora algae from the streams collected in urban and rural areas of Schenectady, Schoharie and Catskill regions. The dashed line represents the $\delta^{15}N$ threshold value used to identify anthropogenic nutrient loading (Costanzo et al., 2005)

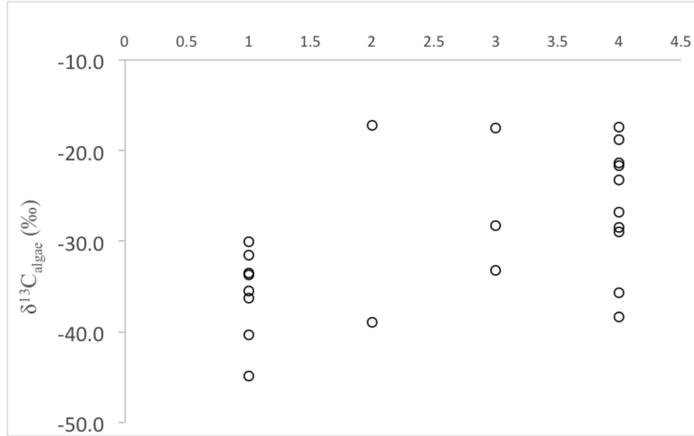

Figure 4. $\delta^{13}C$ values (‰) of Cladophora algae from the streams collected in urban and rural areas of Schenectady, Schoharie and Catskill regions. The shaded area represents the expected $\delta^{13}C$ values of the algae based on published data.

genus were collected. Samples were kept refrigerated until sample preparation. Days of sampling were alternated with days of sample preparation. Algae were cleaned, dried and homogenized prior to analysis. Students measured algae $\delta^{13}C$ and $\delta^{15}N$ using a Costech elemental analyzer coupled to a Thermo Delta Advantage isotope ratio mass spectrometer via a Conflo III. Alkalinity was analyzed using a Metrohm 888 Titrando potentiometric titrator, and ion concentrations were obtained using a Dionex ion chromatograph.

The final week of the project was spent interpreting the data and preparing posters to be presented at Union College's Summer Research Symposium. For their posters, the students worked in teams of two.

Alesia Hunter (Beloit College) and Angel Xavier Tate (Oberlin College) focused on the algal $\delta^{15}N$ values as an indicator of anthropogenic nutrient loading (Fig. 3). A threshold level of 5‰ (Costanzo et al., 2005) was used to identify streams with high anthropogenic nutrient input. The highest $\delta^{15}N$ values were found in urban areas. All values above 5‰ were from algae collected in either urban or small town settings (only the Schenectady data were separated in urban and rural sample sites on the graph). In the Catskill region, two towns had higher values than 5‰: Grand Gorge and the ski town of Hunter. The third highest value ($\delta^{15}N$ = 7.6 ‰) was from the Hudson River at the confluence of the Esopus. Despite the abundance of agricultural land, the Schoharie region did not show much evidence of anthropogenic nutrient loading. However, it is important to note that the use of $\delta^{15}N$ to trace fertilizer run off from fields is limited to manure and would not allow detection of synthetic fertilizers.

Anny Sainvil (Smith College) and Larenz Storey (Union College) focused their research on Alkalinity and algal $\delta^{13}C$ values (Fig. 4). Lowest $\delta^{13}C$ values were observed in the Schenectady region, however, the relationship between low values and urbanization were not exclusive. Low $\delta^{13}C$ values were also observed in some rural areas. While highest alkalinity were expected from the Schoharie valley due to the presence of limestone bedrock, the highest values were observed in Schenectady (data not shown). This high alkalinity together with the elevated Ca ion concentrations (see below) in the Schenectady area is possibly a result of the weathering of concrete sidewalks and culverts (see for example Tippler et al., 2012 and Ramirez et al., 2014). However, the possibility exists that these data are indicative of the weathering of carbonate present in the glacial till around Schenectady (Hollocher, pers. Comm.).

Celina Brieva (Mount Holyoke College) and Sara Marcela Gutierrez Diaz (University of California,

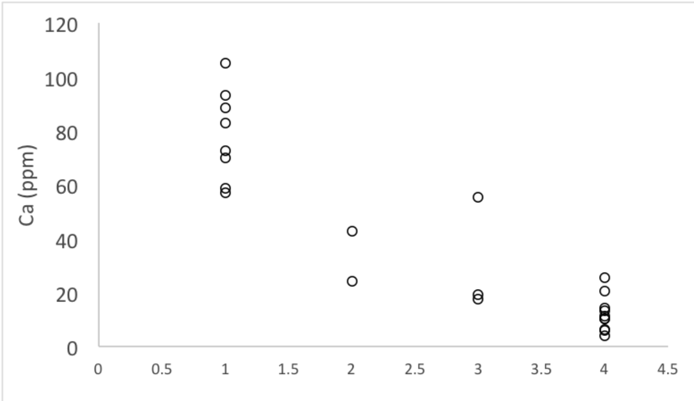

Figure 5. Ca ion (ppm) concentrations from the streams collected in urban and rural areas of Schenectady, Schoharie and Catskill regions.

Berkeley) focused on ion concentrations. Urban Schenectady streams had the highest anion and cation concentrations. The elevated Ca (Fig. 5), Mg and K cation concentrations have been linked to weathering of concrete culverts and walkways in urban environments (Tippler et al., 2012 and Ramirez et al., 2014). High sodium and chloride concentrations were attributed to road salt run off and high fluoride concentrations are most likely related to leaking water and/or waste water pipes or run off caused from watering lawns.

In conclusion, this study found that urban streams had a very different chemical signature from non-urban streams, indicating the effect of urbanization on stream water quality and very likely aquatic life.

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