# KECK GEOLOGY CONSORTIUM

# PROCEEDINGS OF THE TWENTY-FIFTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

April 2012
Amherst College, Amherst, MA

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# GEOCHEMICAL CHARACTERIZATION OF TIDAL COVES OF THE CONNECTICUT RIVER ESTUARY

**HANNAH BLATCHFORD,** Beloit College
Research Advisor: Carl Mendelson

## INTRODUCTION

Estuarine environments are dynamic systems of both local and regional importance. Because estuaries are characterized by the confluence of saline and fresh waters, these brackish locations host a variety of species that tolerate a range of salinities. Anadromous fish (e.g., alewives) are born in freshwater and travel through estuaries to the ocean to breed and mature, whereas catadromous fish (e.g., American eel) mature in estuaries and migrate to the sea to spawn (CRWC, n.d.). Estuarine environments are vital to fish having both migration patterns. Estuaries are susceptible to changes in water content and chemistry, as tidal fluctuations change the distance that salt water intrudes upriver, and rainfall or snowmelt in the watershed dampens the input of saltwater and introduces terrestrial material. While these variations are natural and occur at regular intervals (semi-diurnal tides and spring freshets), their influences are not necessarily felt uniformly throughout an estuary.

Sediment chemistry (C/N and $\delta^{13}$C) is also a variable component of estuaries that can be influenced by location. The C/N ratio is a valuable source of information in discriminating the source of organic matter as terrestrial or aquatic, as the C/N ratio of aquatic algae ranges from 6-9 (Bordovskiy, 1965) and is greater than 20 for land-derived organic material (Meyers and Teranes, 2001). In estuaries mixing occurs between marine and terrestrial inputs, so higher values are interpreted to represent environments dominated by terrestrial inputs, whereas lower C/N values indicate environments dominated by aquatic inputs. The in situ production of algae complicates matters somewhat, as organic material developing in estuaries has a C/N value equal to both marine phytoplankton and lacustrine algae (Kaushal and Binford, 1999; Bordovskiy, 1965), making the sources impossible to differentiate using C/N alone. However, trends have still been observed in C/N and distance from a river's mouth (Matson and Brinson,1990; Thornton and McManus, 1994). Even though fresh and saltwater algae display the same C/N signatures, these trends were observed because of variable input of terrestrial material from site to site, with greater terrestrial input occurring farther form the mouth of the estuary.

The origin of aquatic organic matter as well as the distance that a sample is from freshwater and saline inputs is readily reflected in $\delta^{13}$C values. $\delta^{13}$C values for temperate marine phytoplankton range from -18 to -24‰, whereas river-estuarine phytoplankton, more enriched in $^{12}$C, falls between -24 and -30‰ (Fry and Sherr, 1984). Because each geochemical technique has its advantages, using both C/N and $\delta^{13}$C can provide a more complete characterization of an estuarine environment.

## RESEARCH SETTING

The Connecticut River is the longest river in New England. The river has a watershed of about 29,000 km$^2$ (Gordon, 1980), and flows south from Québec 650 km before emptying into Long Island Sound (LIS) at Old Saybrook, Connecticut (Horne and Patton, 1989). The tidal influence in the river can be observed 100 km north of the mouth to the first dam on the river. However, the part of the river that feels the real impact of the saline, LIS water is only the lower 15 km (Metzler and Damman, 1985).

The lowermost 5 km of the river harbor several tidal coves adjacent to the main river channel. One of these coves, South Cove, is the focus of this study. Two other coves (Lords Cove and Selden Cove) are in the upper 10 km of the 15 km section O'Connell, this volume, fig. 1). Cores were collected in each cove to detect environmental changes as reflected by sources of organic carbon and geochemical trends.

## METHODS

### Field Methods

Three days during June and July of 2012 were spent collecting core samples in tidal coves of the lower Connecticut River. Four of the cores were used in this project: (one from Selden Cove (SDC 5), farthest from LIS, one from Lord Cove (LDC 1), and two from South Cove (SCC 2 and SCC 3), closest to LIS). All coring locations were accessed by boat. Water depth and location were noted at all coring sites using a handheld depth sounder and a GPS unit. Cores were gathered using a push-piston coring device, and each drive was removed with the aid of a farmers jack. Extracted cores were plugged with floral foam to prevent water from disturbing the sediment column. Multiple drives were taken to produce a longer core and sedimentary record.

### Laboratory Methods

Cores were split down the middle and half was archived at Wesleyan University. The other half was photographed and described, focusing on distinct transitions in water content, color, and grain size. Depths of distinct layers were noted and color was assigned with a Munsell soil color chart. Preliminary samples were taken from visually distinct layers, and smear slides were made to aid in description. Density was determined as follows: samples were weighed and centrifuged, combined volume of sediment and water was recorded; then, the samples were dried at low temperature to determine the weight of the dried sediment.

After sampling for density and smear slides, geochemical samples were taken at approximately 5-cm intervals. Thesis-related studies include analysis of mercury, C/N, C and N isotopes, diatom assemblages, and XRF. Sediment in contact with the core barrel was not sampled, so as to prevent possible mixing and contamination.

Samples not immediately processed were shipped to Beloit where they were processed in September, 2012. Processing protocols for C/N and $\delta^{13}C$ at Beloit College and Wesleyan University were identical and were completed as follows: samples were emptied into 30- or 50-mL beakers, dried at 40°C overnight, ground to a flour-like consistency, and stored at room temperature in 8-mL glass vials until they were analyzed at Wesleyan University in July or October, 2012.

### C/N Analysis

Samples were analyzed using a CE Instruments Flash 1112 Series EA at Wesleyan University in July and October. The elemental analyzer (EA) converts the sediment samples into $N_2$ and $CO_2$ gases by combustion, and then measures concentrations by gas chromatography. Initially, C is observed as $CO_2$, but N is detected as $N_2$ in addition to N-oxides ($NO_x$). To transform all N-bearing molecules to $N_2$, the gases pass through a reduction column filled with Cu wire chips, allowing the N-oxides to exit as $N_2$. Magnesium perchlorate is used to “dry” the gas before gas chromatography is performed. $N_2$ elutes from the GC column before $CO_2$, so the gases can be differentiated and their concentrations measured.

The typical EA run consists of 60 samples contained by tin capsules (8 x 5 mm). The first sample in each run was an empty tin capsule, followed by five standard samples of aspartic acid (wt% N=10.52%, wt% C=36.09%) at masses between 0.5 and 5.0 mg, and two L-cystine samples (wt% N=11.613%, wt % C=29.949%) in the same mass range. An aspartic acid sample was run after every 10 sediment samples. Sediment samples were run in random order to improve statistical reliability and had masses of 30-40 mg.

### Stable Carbon Isotope Analysis

Twenty-three samples from South Cove and Selden Cove were sent to the University of California Davis Stable Isotope Facility, where they were analyzed using a PDZ Europa ANCA-GSL elemental analyzer connected to a PDZ Europa 20-20 isotope ratio mass spectrometer. Samples were analyzed between standards similar in composition to the sediment. The sample’s isotope ratio was initially referenced to the standards run with the sample, then corrected for the values of the entire batch using the known values of the standards. Ultimately, delta values were reported relative to PDB (Stable Isotope Facility, n.d.).

### Statistical Analysis

Microsoft Excel was used to carry out a single factor analysis of variance test (ANOVA) on C/N and $\delta^{13}$C. ANOVA displays the average C/N and $\delta^{13}$C of each core. Coupled with a calculation of standard error, ANOVA makes it possible to discern if the differences in the average C/N and$\delta^{13}$C values between cores are statistically significant.

## RESULTS

### Sediment Description

Sediments in each core were approximately 90% silt to clay, with mm to cm scale layers of fine sand and condensed plant material. Only slight color variation was observed. Most frequently described colors were 5y 2.5/1 (black) and 5y 3/1 (black). Material at tops of drives had significantly higher water content.
C/N Variation

The C/N values measured by elemental analysis were plotted against depth to show C/N variation within each core (fig. 1). All cores occupy a similar range of C/N values. The mean values and their standard errors were recorded for each core (Table 1, Fig. 2). These values reveal that there is no statistically significant difference between SDC 5, SCC 2, and LDC 1. SCC 3 has a mean C/N value statistically lower than the other cores. The highest C/N value in any core is 19.21 in LDC 1, at 107.5 cm. The lowest C/N value found is 10.53 from SCC 2 at 42.25 cm. These values fall within the two end-member values outlined earlier (C/N < 9 for aquatic material, C/N > 20 for terrestrial material).

### $\delta^{13}$C Variation

Three cores were analyzed for $\delta^{13}$C (Table 1 and Figure 3). The standard error shows that there is no statistical difference between the mean $\delta^{13}$C of SCC 2 and SCC 3, and that SDC 5 contains sediment that is statistically more enriched in$^{12}$C.

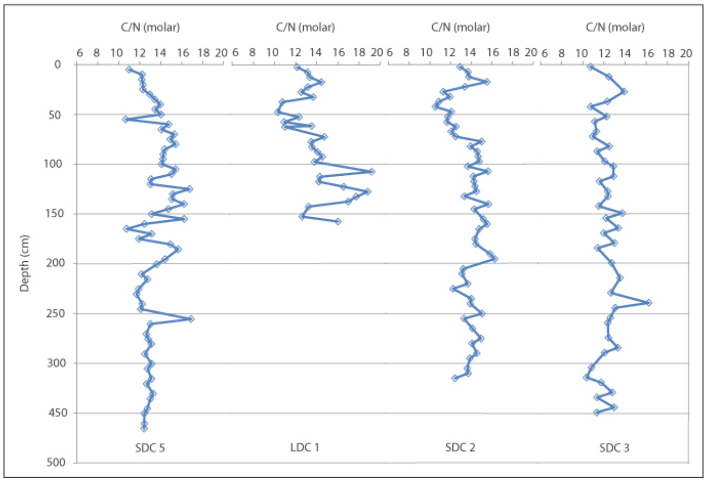

*Figure 1. C/N variation with depth in four cores from three coves in the Conniecticut River estuary.*

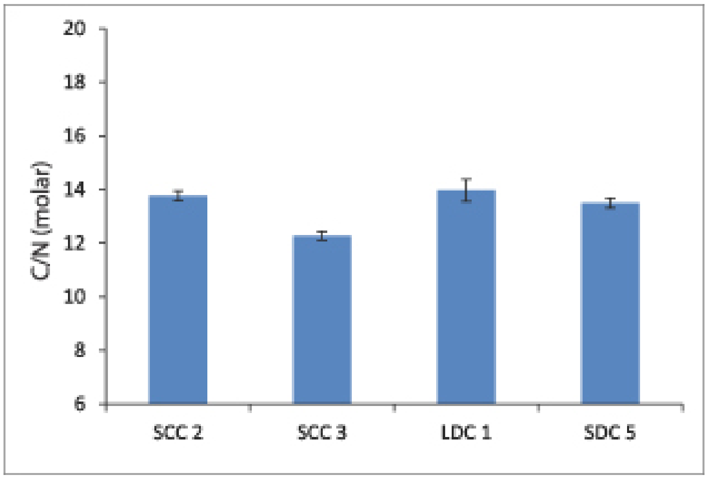

*Figure 2. Mean C/N for each examined core. Bars indicate standard error.*

| | C/N (molar) | | $\delta^{13}$C (‰) | |
|---|---|---|---|---|
| | Mean | Standard error | Mean | Standard error |
| SDC 5 | 13.49 | 0.18 | -26.56 | 0.20 |
| LDC 1 | 13.97 | 0.42 | — | — |
| SCC 2 | 13.77 | 0.18 | -23.12 | 0.35 |
| SCC 3 | 12.27 | 0.17 | -22.67 | 0.19 |

*Table 1. Summary of all mean values and standard errors in C/N and $\delta^{13}$C measurements. Note that the portion of SCC 2 sampled does not correspond to the other cores. therefore, meaningful comparisons cannot be made.*

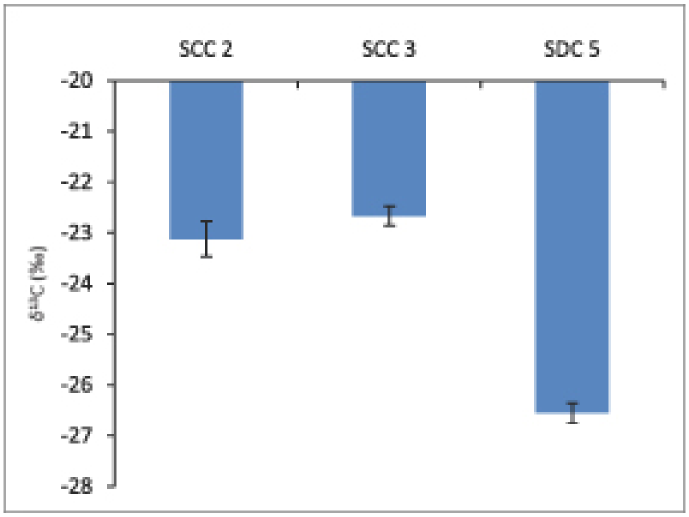

*Figure 3. Mean $\delta^{13}C$ for each examined core. Bars indicate standard error. Note that the portion of SCC 2 sampled does not correspond to the other cores. therefore, meaningful comparisons cannot be made.*

## DISCUSSION

### Inferences from C/N

The objective of this study was to characterize the organic carbon inputs of three tidal coves in the Connecticut River estuary. C/N values indicate that there is mixing of terrestrial and aquatic inputs in all coves, and that the mean C/N values for three of the cores are not statistically distinct. SCC 3 was an exception, with a statistically different C/N value. However, all means fall within the values for a mixed system (between 9 and 20). Production of algae within coves and diagenesis of sediments are two possible explanations for the C/N values observed.

The *in situ* production of algae creates a C/N signature that cannot be differentiated from other aquatic sources of organic carbon. Therefore, high productivity of algae could drown any terrestrial signature that might be more variable between each cove. Sampei and Matsumoto (2001) found that if the ratio of planktonic to terrestrial organic matter is large, the sensitivity of the C/N ratio to more subtle changes in terrestrial-marine influence is reduced. This scenario is possible because the coves are set away from the main channel, so that they may not be nearly as well flushed as the channel itself.

Diagenesis is also a concern. Thornton and McManus (1994) found that C/N values are subject to variable alteration, depending on the original source material. Terrestrial organic matter that is initially nitrogen deficient tends to experience a decreasing C/N ratio that results from bacterial nitrogen production as the terrestrial material undergoes decomposition. Interestingly, nitrogen-rich aquatic matter tends to display an increasing C/N value over time, as efflux of nitrogen from the phytoplankton mass surpasses the influx due to production. This variable diagenesis results in the convergence of aquatic and terrestrial C/N values. Thornton and McManus (1994) found these processes to be relevant in collecting surface samples, implying that it is pertinent when considering older organic matter within a sediment core.

### Inferences from Stable C Isotopes

While C/N provided insight into the degree of mixing between terrestrial and aquatic inputs (barring in situ production and terrestrial inputs), $\delta^{13}C$ values help to differentiate the source of organic material of aquatic origin. Fry and Sherr (1984) found that river-estuarine phytoplankton have $\delta^{13}C$ values of -24‰ to -30‰ and temperate marine phytoplankton have $\delta^{13}C$ values of -18‰ to -24‰. Based on values reported here (Table 1), it is clear that SDC 5 is more enriched in $^{12}C$, indicating that the majority of the phytoplankton present is of a river-estuarine origin and that the less $^{12}C$-enriched South Cove hosts phytoplankton of a marine (saltwater) origin. This is consistent with the location of SDC 5, farthest from LIS.

It is important to note that terrestrial inputs have varying $\delta^{13}C$ values. Terrestrial $C_4$ plants yield heavier isotopic signatures (-10‰ to -14‰) than $C_3$ plants (-23‰ to -30‰). The same trend exists in $C_4$ and $C_3$ marsh grasses and plants (-12‰ to -14‰ compared to -23‰ to -26‰) (Fry and Sherr, 1984). In Connecticut, freshwater marshes are generally dominated by $C_3$ plants, whereas saltwater marshes tend to contain more $C_4$ plants (Chmura and Aharon, 1995), meaning that the trend of increasing enrichment in $^{12}C$ with increasing distance from marine phytoplankton source is paralleled by the transition from $C_4$ plants to $C_3$ plants. It is no surprise that these trends have also been observed to parallel the salinity gradient of an estuary, as salinity is the control for the presence of $C_4$

over $C_3$ plants as well as marine phytoplankton over river-estuarine phytoplankton (Chmura and Aharon, 1995).

## CONCLUSION

C/N values show that between coves, there is no statistical difference in the relative inputs of terrestrial and aquatic organic matter. However, there are many variables impacting the geochemistry of tidal coves in the Connecticut River estuary. Similar C/N values do not necessarily mean that the relative inputs of organic matter are identical. The two cores from South Cove reveal that C/N can vary as much within coves as between them. In the case of the three coves studied here, the C/N values reveal that the in situ production of photosynthetic organisms appears to be overwhelming any variation that may be present between coves based on differing terrestrial inputs.

Stable carbon isotope analysis confirms that there is an upriver transition from a marine phytoplankton-dominated environment to one dominated by river-estuarine phytoplankton. This is not evident with the use of C/N alone, and the two methods produce a more complete picture of the estuarine environment. C/N and $\delta^{13}C$ reveal that the coves are productive environments for photosynthetic organisms, and that the types of photosynthetic organisms present in the two end-member coves vary (fig. 4).

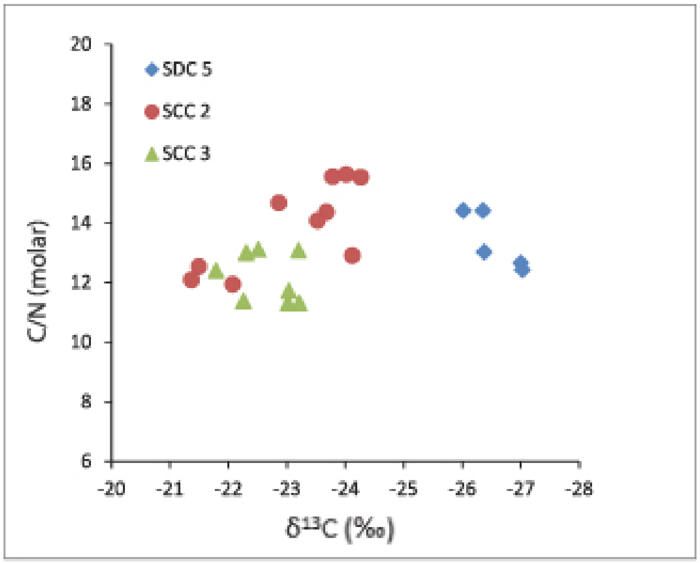

*Figure 4. $\delta^{13}C$ in relation to C/N. C/N shows mixing of terrestrial and aquatic inputs in all cores. $\delta^{13}C$ shows that SDC 5 is more enriched in $^{12}C$ than either of the cores from South Cove.*

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