Nitrogen and Productivity in the Late Devonian Appalachian Basin

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Abstract

The Late Devonian witnessed the emergence of a new relationship between the terrestrial and marine biogeochemical cycles of the limiting nutrients nitrogen and phosphorus. The development of extensive lowland forest ecosystems augmented the flux of fixed N to coastal marine ecosystems while the development of deep soils retarded the flux of P, increasing the relative abundance of N to P in coastal seas. The accumulation of terrestrially-derived NO_3^- would have been particularly pronounced in epicontinental seas such as the Appalachian Basin which enjoyed limited communication with the open ocean. Nitrogen and carbon stable isotope analyses of sediments at or near the Frasnian/Famennian boundary within the Appalachian Basin indicate an underutilization of NO_3^- coupled with high productivity corresponding to the globally correlated Upper and Lower Kellwasser horizons. High C_{org}:P values from similarly-aged sediments reveal that the supply of P necessary to support high productivity was remobilized from organic matter within oxygen-depleted sediments. Sea level rise may have served as the global trigger for high organic matter deposition during the Upper and Lower Kellwasser intervals by increasing the outwelling flux of terrrestrially-derived organic carbon and nitrate from lowland forests.

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Acknowledgements

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Introduction

Terrestrial and marine ecosystems are intimately linked on the modern Earth through the biogeochemical cycles of the essential nutrients carbon, nitrogen, sulfur, phosphorous, and iron. However, life in the sea long predates the advent of significant terrestrial ecosystems and so the nature of those cycles cannot have remained unchanged. The period of transition from essentially no life on the land surface to abundant life would, by necessity, have been a period of profound change in nutrient biogeochemistry on land and in the sea. That period in Earth history is the Devonian. From sparse, diminutive Early Devonian progenitors, terrestrial plants underwent a vast radiation in the Middle Devonian and by the Late Devonian forests dominated large areas of the land surface (Bateman, *et al*. 1998). In the sea, tropical reefs with an areal extent far greater than their modern counterparts (Copper 2002) supported a diverse fauna of invertebrate and early vertebrate life. Marine life, however, experienced a very dramatic reversal of fortune beginning as early as the Givetian and by the Frasnian/Famennian transition, the diversity of marine species had plunged by as much as 80% (McGhee 1996; Bambach 2006).

The global geological record of the Late Devonian is punctuated by episodic deposition of organic-rich black shales and associated positive $\delta^{13}C$ excursions among both inorganic carbonates and sedimentary organic matter (Joachimski, *et al*. 1993; Algeo, *et al*. 1998; Gong, *et al*. 2002; Joachimski, *et al*. 2002; Over 2002; Chen, *et al*. 2003; Sageman, *et al*. 2003; Gong, *et al*. 2005; Saltzman 2005; Buggisch, *et al*. 2006).

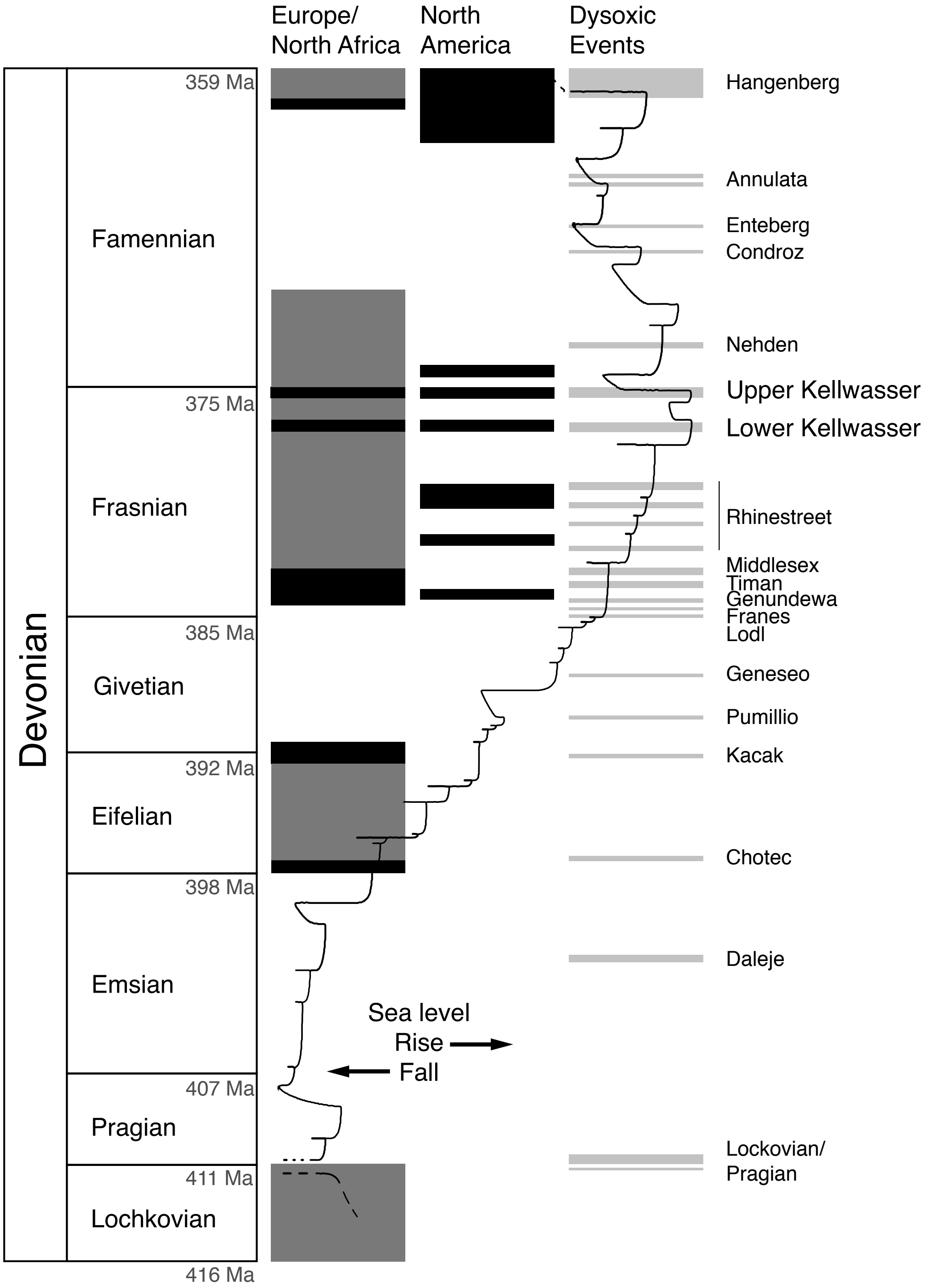


Figure 1. Devonian dysoxic events, periods of extended black and grey shale deposition, and sea level change. Adapted from Buggisch & Joachimski 2004. Events from House 2002. Sea level curve from Johnson, et al. 1985.

Many of these dysoxic episodes can be correlated biostratigraphically and isotopically across several continents and have been identified as marking coeval strata among disparate basins. Figure 1 marks the location in the stratigraphic column of these events as well as showing extended periods of black and gray shale deposition in North America and Europe/North Africa.

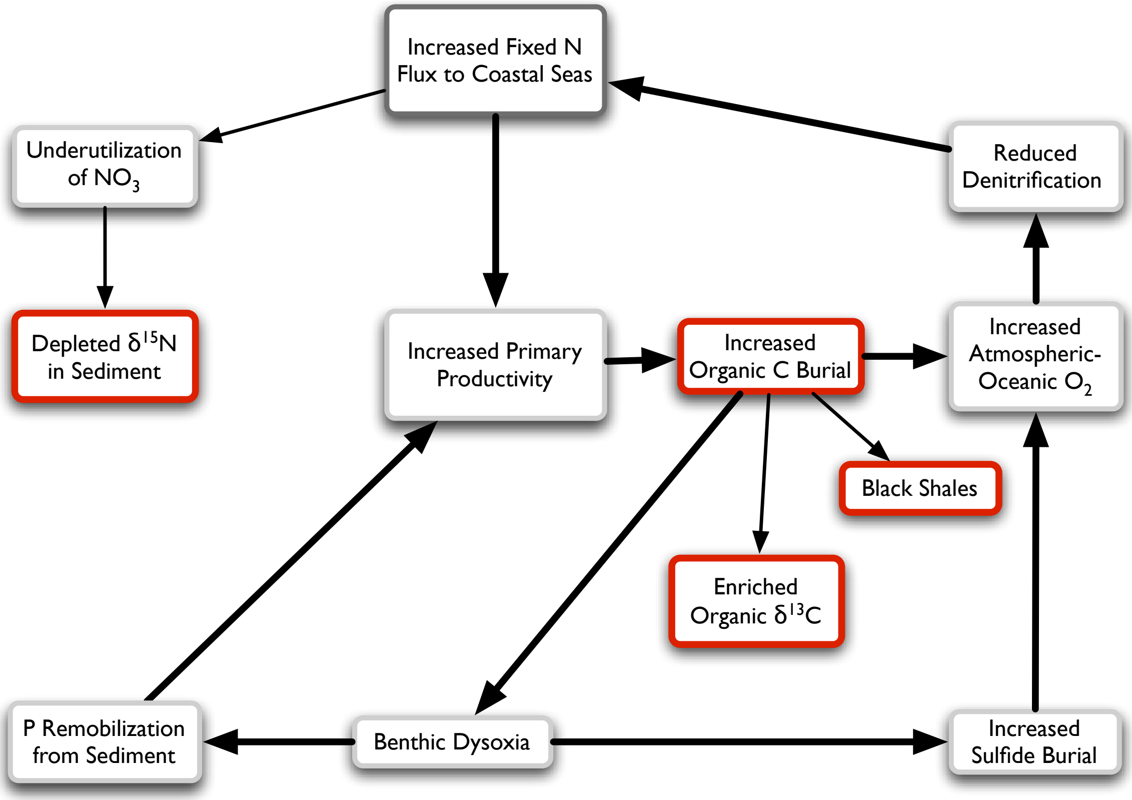


Figure 2. Graphical representation of a model that links the expansion of terrestrial forest ecosystems with the deposition of organic rich sediments in the Late Devonian. Boxes outlined in red represent observations from the fossil and geochemical records. Boxes outlined in gray represent inferred events.

Before the emergence of significant forest ecosystems in the late Middle Devonian, the flux of reactive nitrogen (both organic and inorganic forms) from the land surface via riverine and atmospheric transport to coastal seas was minimal. In modern coastal seas, terrrigenously-derived fixed nitrogen accounts for a significant proportion of nitrogen available for primary productivity in regions that are not subject to regular upwelling (Falkowski, *et al.* 1998; Jickells 1998; Galloway, *et al.* 2004). A direct result of the increased reactive nitrogen flux in the Late Devonian may have been an increase in marine primary productivity and the transition from a nitrogen-limited ocean to a phosphorous-limited ocean (Saltzman 2005). Figure 2 represents a simplified box model of the consequences of an increased flux of fixed N into Late Devonian coastal and epeiric seas.

The elevated rate of primary productivity augmented the rate of organic carbon burial in sediments. Late Devonian black shales are the direct result. On a geological timescale, the increased deposition of unoxidized organic carbon caused the $p\mathrm{CO}_2$ of the atmosphere and the oceans to fall and the $p\mathrm{O}_2$ to rise from much lower early Paleozoic levels (Berner 2004). Denitrification, an obligately anaerobic microbial activity, was diminished in an increasingly aerobic ocean, contributing to the pool of fixed nitrogen available for primary productivity.

Nitrate (NO_3) is the most common form of reactive nitrogen in sea water. While nitrate levels in Late Devonian seas increased dramatically as a consequence of both terrestrial N fixation and a diminished rate of denitrification, primary productivity could not increase proportionately because phosphorous and iron became limiting nutrients (Saltzman 2005). As a consequence, nitrate in surface waters was increasingly underutilized; so, as organisms assimilated nitrate they enjoyed an energy savings by preferentially assimilating isotopically lighter nitrate. Because nitrate utilization in surface waters is reliably recorded in the nitrogen isotope composition of organic matter preserved in underlying sediments (Altabet, *et al.* 1994), the increasing concentration of nitrate during episodes of increased carbon burial should be characterized by $\delta^{15}N$ values that are more depleted than are recent sediments.

The maximum rate of productivity may have been raised by increasing the availability of the limiting nutrient phosphorous. The elevated organic carbon burial rate created an anoxic zone at the sediment surface as heterotrophic microbes depleted the available oxygen. Under those dysoxic conditions, inorganic phosphorous was preferentially released from the sediment and made available to primary producers in the water column (Vancappellen, *et al.* 1994; Algeo, *et al.* 2007). Benthic dysoxia may also have had the effect of contributing to extinction rates by hypercapnia or suffocation of benthic fauna.

Another feedback mechanism illustrated in Figure 2 may also be a direct consequence of benthic anoxia. Where oxygen is scarce, sulfate reducing bacteria oxidize organic matter using sulfate, depositing reduced, isotopically depleted sulfides and increasing atmospheric O_2 on geological timescales (Berner, *et al.* 1983). Enriched $\delta^{34}S$ in Late Devonian sulfate deposits offers positive evidence of enhanced sulfide deposition and increasing pO_2 throughout the period (Claypool, *et al.* 1980).

Multiple reinforcing feedbacks ratcheted marine primary productivity and biomass upward through the Late Devonian as the input flux of reactive nitrogen from terrestrial ecosystems grew. One observable consequence of the expanding biomass at the base of food webs was an increase in the energetics of marine fauna (Bambach 1993, 1999). For instance, active predators with high metabolic requirements, including jawed fishes and ammonoid cephalopods, replaced more sluggish Early Devonian predecessors at the top of food chains. The expansion of food resources had an overall negative impact, however, on marine diversity. The abundance of nutrients in what had long been a dominantly oligotrophic environment diminished selection pressure for trophic specialization, especially among benthic invertebrates, thereby diminishing rates of origination. Two-thirds of the diversity loss in the Late Devonian was a function of diminished rates of origination (Bambach, *et al.* 2004). The remaining third is attributable to higher extinction rates.

The Emergence of Forest Ecosystems

Terrestrial plants are a monophyletic group whose ancestors successfully gained a foothold on the land surface in the Middle Ordovician (Bateman, *et al.* 1998). As would be the case with vertebrate animals nearly 100 million years later, the transition from an aqueous to a gaseous medium would entail a long period of evolutionary innovation. Through the Early and into the Middle Devonian, most terrestrial vegetation was diminutive (20 cm in height or less) and still dependent upon proximity to water for reproduction. A rapid adaptive radiation of plant forms in the Middle Devonian, however, resulted in a proliferation of plant species and ecosystems (Stein, *et al.* 2007). By the end of the Givetian, stratified forests had emerged as a dominant terrestrial ecosystem supporting a wide variety of plant types (Kenrick, *et al.* 1997).

Archaeopteris was the dominant genus of tree-like progymnospores in Late Devonian forests, reaching heights of as much as 30 meters (Meyer-Berthaud, *et al.* 1999). Extending its range throughout the Late Devonian, *Archaeopteris*-dominated forests extended from seasonally wet coastal interfluves to more arid upland areas (Algeo, *et al.* 1998). Anatomical fossil evidence indicates that *Archaeopteris* was deciduous, shedding entire branches and creating a thick blanket of organic-rich forest litter (Kenrick, *et al.* 1997). As is the case in modern terrestrial ecosystems, some fraction of the reactive nitrogen in that organic material found its way, through atmospheric deposition and riverine transport, into coastal seas.

The development of arborescence, the above-ground stature of woody plants, necessitated the simultaneous development of below-ground root systems. The co-evolution of deep roots and soils is a distinctive feature of Middle to Late Devonian terrestrial ecosystem evolution. Paleosols from Middle to Late Devonian forests resemble their modern counterparts in composition and structure (Retallack 1997).

Soils play a central role in the biogeochemical cycling of elements through the environment and mediate processes with significant long-term consequences. The weathering of rock in soil formation entails the consumption of CO_2 and on geological timescales increasing rates of soil formation can result in lowered levels of atmospheric CO_2 (Berner 1997, 2004). Coupled with growing O_2 production from terrestrial primary productivity and the sequestration of organic carbon on the land and in the sea, the Late Devonian was a period of falling pCO_2 and rising pO_2 both in the atmosphere and in the sea (Berner 1997, 2004; van Geldern, *et al.* 2006; Simon, *et al.* 2007). A consequence of elevated ocean O_2 levels would have been a diminished rate of denitrification and a corresponding increase in the bioavailability of reactive nitrogen in the sea.

The Reactive Nitrogen Flux to Coastal Seas

Biological nitrogen fixation (BNF) is the dominant source of reactive nitrogen both in the oceans and on the land (excluding anthropogenic sources). Annual total BNF on the land and in the sea are roughly equivalent (~120 Tg/yr) (Galloway, *et al.* 2004). The estimated annual pre-industrial flux of terrestrially-fixed reactive nitrogen to oceans via rivers and atmospheric deposition is the sum of these values:

Atmospheric deposition of NO_x	6.2 Tg N/yr
Atmospheric depsition of NH_x	8 Tg N/yr
Riverine flux of N_r	27 Tr N/yr

This flux, totaling 41.2 Tg N/yr, is equivalent to 34% of the total annual BNF for all the world's oceans. The overwhelming majority of this total, however, is deposited in coastal seas which comprise less than 10% of total ocean area but account for the majority of ocean productivity and biodiversity. In some modern coastal seas, the terrestrial flux is augmented by nitrate-rich upwelling waters; however, in the extensive epicontinental seas of the Devonian, such as the Appalachian Basin, upwelling from deep ocean basins would not have been as important.

Prior to the rapid diversification and expanding areal extent of land plants in the Middle Devonian, the flux of reactive nitrogen to coastal seas was likely quite modest by modern standards. Modern deposition of nitrogen fixed by lightening over the entire Earth amounts to 5.4 Tg N/yr (Galloway, *et al.* 2004) and there is no reason to assume a higher rate during the Devonian. Nitrogen is not a common element among minerals in the Earth's crust, so the weathering flux of reactive nitrogen is now and likely then was very small. Because of the vicissitudes of fossilization, especially on the land surface, we are unlikely to ever know the true geographic extent of forest ecosystems through the Devonian. Therefore, we cannot with certainty estimate the flux of plant-derived reactive nitrogen from the land surface to the sea. Nevertheless, based upon an improving knowledge of modern nitrogen budgets and growing fossil evidence of extensive and complex Late Devonian forest ecosystems, I believe that it is reasonable to infer that the flux of reactive nitrogen from the land to coastal seas grew substantially during the Devonian.

Many authors have proposed a connection between terrestrially-derived nutrients, the deposition of organic-rich facies and diversity loss among Late Devonian marine life (Bambach 1993; Caplan, *et al*. 1996; Martin 1996; Algeo, *et al*. 1998; Martin 1998;

Bambach 1999; Gong, *et al*. 2002; Chen, *et al*. 2003; Martin 2003; Gong, *et al*. 2005; Saltzman 2005) without, however, specifying how the changing biogeochemical cycling of specific elements created the evidence found in the geological record. The fundamental hypothesis that this study seeks to address is that the link between the biogeochemical cycle of nitrogen on the land and in the sea is a key to explicating the deposition of organic-rich sediments and consequent changes in the oceans, atmosphere, and biosphere during the Late Devonian. More explicitly, I intend to test these hypotheses: there is a clear distinction in the C and N isotopic composition of high and low organic matter sediments; those isotope values reflect dominantly terrestrial values during intervals of high organic matter deposition; and, there will be a trend of increasing $\delta^{15}N$ enrichment with distance from shore.

Methods

Figure 3. Site locations within the Appalachian Basin

Six study locations at or near the Frasnian/Famennian boundary within the Appalachian Basin were chosen based upon identification of the boundary by conodont biostratigraphy (Over 2002) (Figure 3). All six locations feature organic-rich shales with varying amounts of intercalated gray shales. Three sections from western New York - Perry Farm, Irish Gulf, and Walnut Creek - represent a roughly 70 km transect of increasingly distal depositional environments perpendicular to the basin axis spanning the black shale interval of the terminal Frasnian Upper Kellwasser (UKW) horizon. At the northern end of the Appalachian Basin the Frasnian/Famennian boundary marks the top of the Hanover member of the Java formation (Figure 4). The three boundary sections, each less than one meter in height, were sampled in detail at each change in lithology. The nearby Pipe Creek section spans the earlier Lower Kellwasser (LKW) horizon and was sampled at similar intervals.

At the basin's southern end, the Frasnian/Famennian boundary lies at the top of the Java formation equivalent within the Chattanooga Shale. At the section near Big Stone Gap, Virginia approximately 20 meters of uppermost Java formation and overlying Lower Huron strata are accessible. At this location, samples were collected every meter on a 40° slope. Stratigraphic height of each sample was determined trigonometrically. The base of the Chattanooga Shale section at Hurricane Creek near Smithville, Tennessee sits at the Frasnian/Famennian boundary.

All samples were ground to no greater than 200 mesh with an agate mortar and pestle, acidified with a 30% HCl solution to remove carbonates, washed to neutrality, and dried at 50° C. The carbonate-free residues were weighed (sample weights ranged from approximately 5 mg to 45 mg, depending upon the organic matter content of the sample) into tin capsules and converted to CO_2 and N_2 for isotope analysis using a Carlo Erba elemental analyzer (EA) which is coupled to an OPTIMA stable isotope ratio mass spectrometer (Micromass, Manchester, UK). Carbon and nitrogen isotopes were determined with a single combustion using a dual furnace system composed of an oxidation furnace at $1020^{o}C$ and a reduction furnace at $650^{o}C$. The resulting gases are

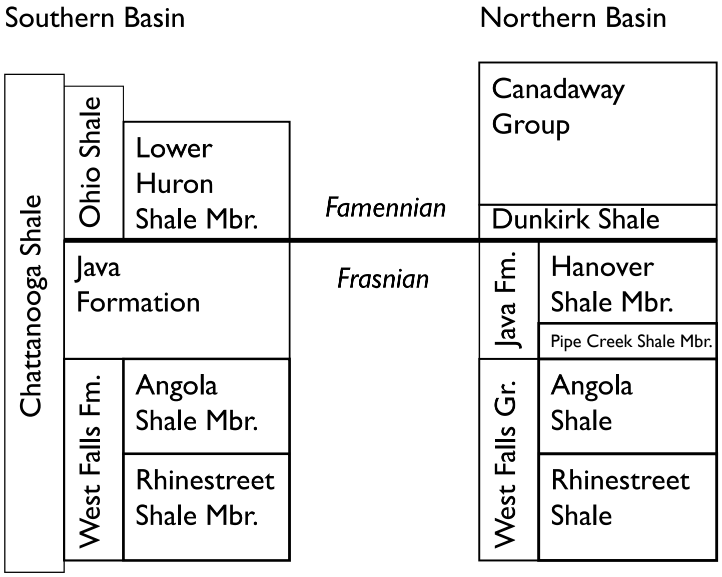


Figure 4. Stratigraphic nomenclature of the Late Devonian Appalachian Basin

chemically dried and directly injected into the source of the mass spectrometer. The stable isotopic ratio is reported as follows:

$$^{N}E = [R_{sample}/R_{standard} - 1]\ 10^{3}\ (‰)$$

where N is the heavy isotope of the element E and R is the abundance ratio of the heavy to light isotopes ($^{13}C/^{12}C$ or $^{15}N/^{14}N$) of that element. The standard for carbon is the Peedee Belemnite limestone (PDB), for nitrogen the standard is atmospheric N_2 (Air) which are assigned ^{N}E values of 0.0‰. For carbon the value is corrected for the mass overlap with the isotopes of oxygen. In the laboratory, the samples are commonly measured against tanks of carbon dioxide and nitrogen gases which have been calibrated against NBS 22 and atmospheric N_2 respectively.

At the beginning and end of every set of five or fewer samples, calibrated standards were run to ensure reproducibility of results. A script written in the AppleScript language and embedded in Microsoft Excel (see Appendix) allowed isotope values to be normalized to the laboratory's internal standards which are calibrated in turn to the international standards PDB for $\delta^{13}C$ and Air for $\delta^{15}N$. Reproducibility between duplicate standards for $\delta^{13}C$ averaged ±0.28‰ and for $\delta^{15}N$ averaged ±0.17‰. Reproducibility between duplicate standards for both $\%C_{org}$ and $\%N_{total}$ averaged less than 2%.

Results

The summary of mean composition and isotope values presented in Table 1 indicates similarities and differences among sites and an apparent trend along the three site transect. Data from Hurricane Bridge reveal an exceptional level of organic matter preservation. $\delta^{13}C_{org}$ values appear to have a significant regional component. Along the transect, there appears to be an increasing $\delta^{15}N_{total}$ enrichment with distance from shore.

Compositional and isotopic values for each study site are presented in Figures 5 through 10 below. When comparing values across sites, note that chart axis values differ. Samples that contain less than one percent organic carbon are marked by gray circles; those with more are in black. In each section, with the exception of Pipe Creek, the approximate location of the Frasnian/Famennian boundary is marked with a dotted line. The sections at Perry Farm, Irish Gulf, Walnut Creek, and Pipe Creek all share the same vertical scale. The Big Stone Gap and Hurricane Bridge sections are scaled alike.

Table 1. Mean composition and isotope values from study sites

Site	**%C_{org}**	**%N_{total}**	**C_{org}/N_{total}**	**δ^{13} C_{org}**	**$\delta^{15}N_{total}$**
Perry Farm	2.31	0.12	18.29	-27.3	0.0
Irish Gulf	1.83	0.12	13.32	-27.7	0.2
Walnut Creek	1.76	0.14	10.28	-27.1	0.5
Pipe Creek	2.43	0.15	14.69	-27.2	0.1
Hurricane Bridge	13.48	0.48	29.95	-29.7	0.5
Big Stone Gap	4.25	0.23	17.63	-29.2	-0.4

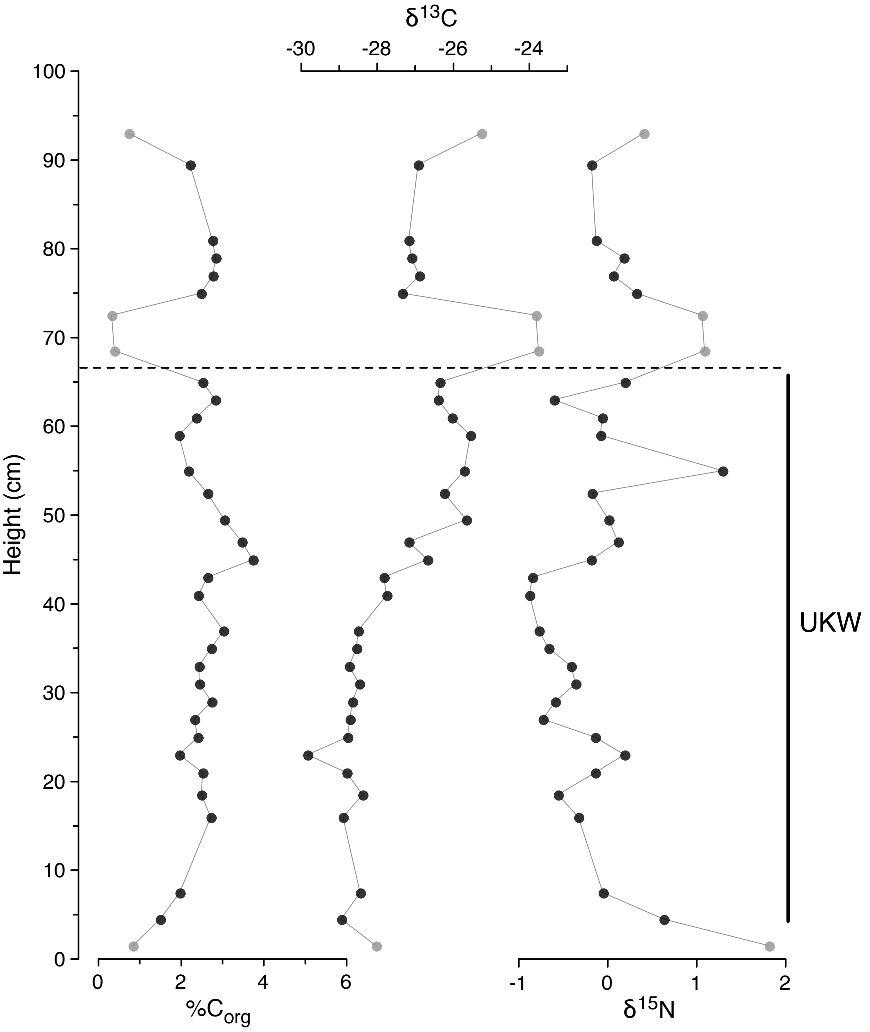


Figure 5. %C_{org}, $\delta^{13}C$, and $\delta^{15}N$ data from Perry Farm plotted by stratigraphic height

The Perry Farm section encompasses the UKW interval of high organic matter deposition that terminates the Frasnian. The UKW interval at Perry Farm is ~60 cm in height, The top of the Frasnian in this detailed section lies at a height of about 70 cm, at the base of a low %C_{org} interval of ~10 cm. A positive $\delta^{13}C$ excursion of ~5‰ begins gradually at 35 cm and turns more dramatically positive at the boundary, mirroring the drop in %C_{org}. The corresponding $\delta^{15}N$ positive excursion of ~1‰ has not been previously reported in any Frasian/Famennian boundary section.

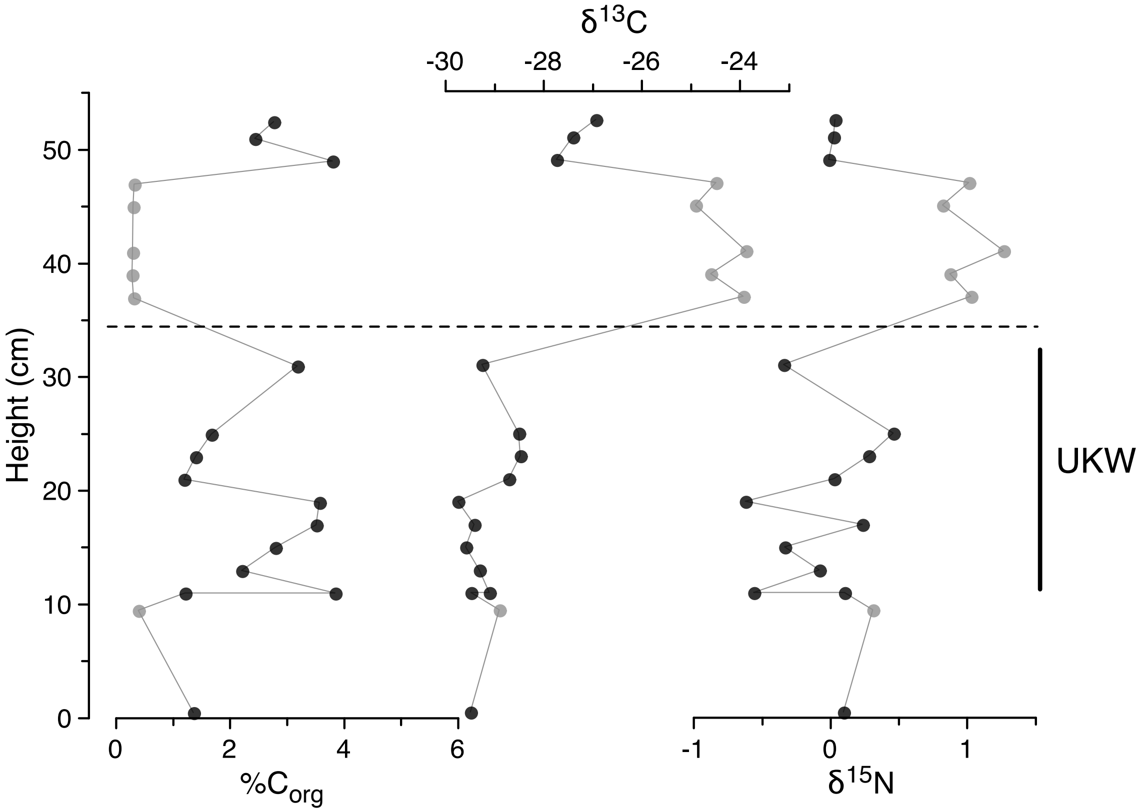


Figure 6. %C_{org}, $\delta^{13}C$, and $\delta^{15}N$ data from Irish Gulf plotted by stratigraphic height

At Irish Gulf the Upper Kellwasser interval extends ~20 cm. Unlike at Perry Farm, the $\delta^{13}C$ excursion of ~5‰ is precipitous and extends ~20 cm above the Frasnian/ Famennian boundary. As at Perry Farm, a positive $\delta^{15}N$ excursion of ~1‰ parallels the $\delta^{13}C$ excursion in the low %C_{org} interval above the boundary.

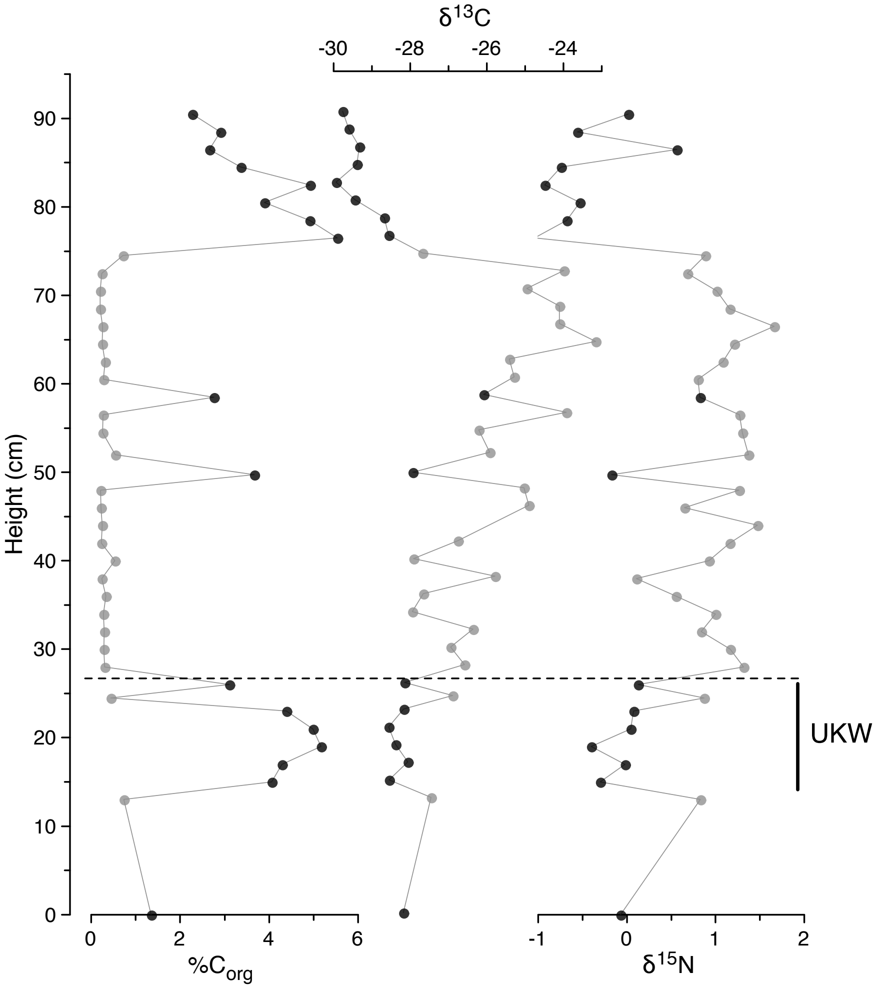


Figure 7. %C_{org}, $\delta^{13}C$, and $\delta^{15}N$ data from Walnut Creek plotted by stratigraphic height

The site at Walnut Creek represents a depositional environment 38 km further from shore than Irish Gulf. The UKW interval is ~12 cm deep. Although sedimentation rates were lowest at this most distal site, the positive isotope excursion of ~5‰ observed at the two previous locations, while more diffuse at Walnut Creek, extends over 40 cm, twice the height at Irish Gulf and four times the height at Perry Farm. This long low %C_{org} interval is interrupted twice by episodes of high organic matter deposition, each represented by a single sample. The $\delta^{15}N$ excursion spans ~1.5‰.

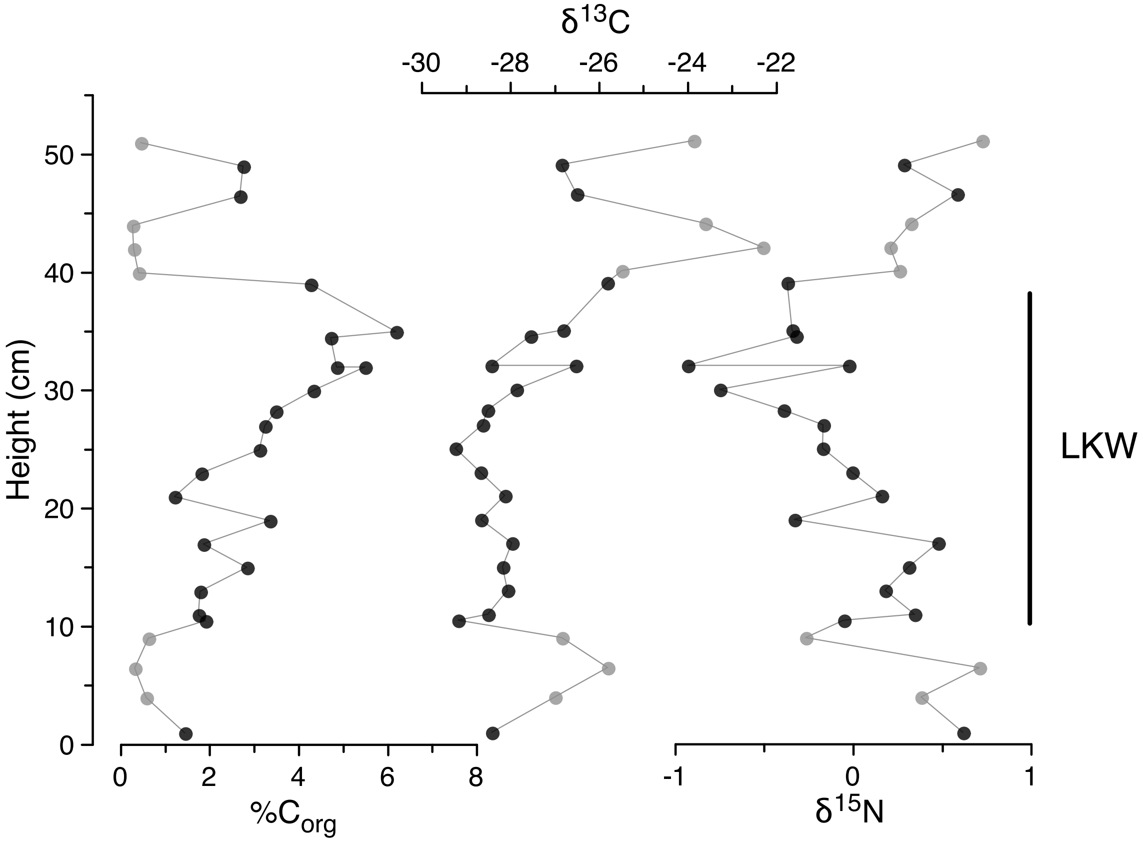


Figure 8. %C_{org}, $\delta^{13}C$, and $\delta^{15}N$ data from Pipe Creek plotted by stratigraphic height

The Lower Kellwasser (LKW) interval at Pipe Creek extends ~30 cm and exhibits many of the characteristics of the three Upper Kellwasser intervals described above. There is an apparent trend of both increasing %C_{org} and decreasing $\delta^{15}N$ upward through the LKW interval. A positive $\delta^{13}C$ excursion of ~6‰ corresponds to an 8 cm interval of low %C_{org} deposition above the LKW interval. The $\delta^{15}N$ excursion in the low %C_{org} interval extends only ~0.5‰ and becomes even more positive above the interval.

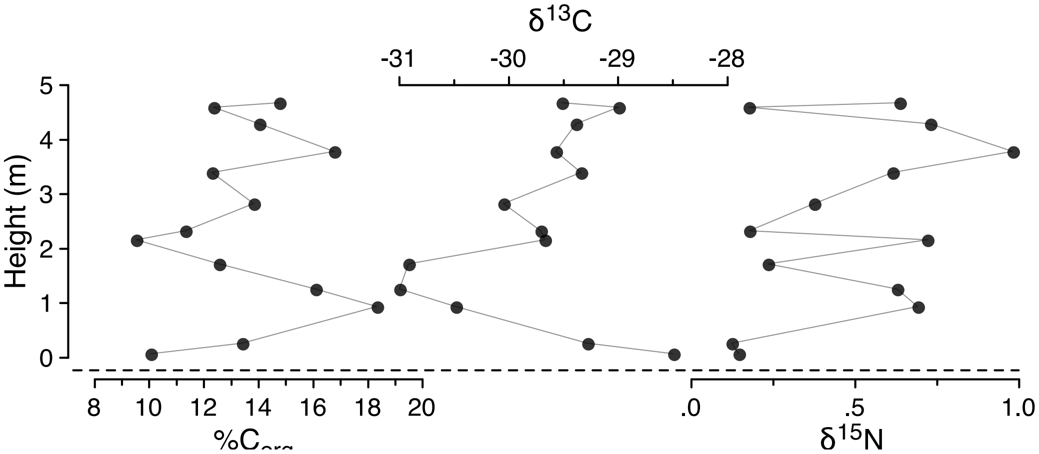


Figure 9. %C_{org}*,* $\delta^{13}C$*, and* $\delta^{15}N$ *data from Hurricane Bridge plotted by stratigraphic height*

The section at Hurricane Bridge represents a 5 meter interval of exceptionally high organic matter content at the base of the Famennian within the Chattanooga Shale of central Tennessee. The strong correlation (r = 0.9) between %C_{org} and %N_{total} (see Figure 11) indicates that organic matter is overwhelmingly the primary source of sediment N at this location. The site also exhibits the most depleted mean $\delta^{13}C_{org}$ value (-29.7‰) among all the sites examined.

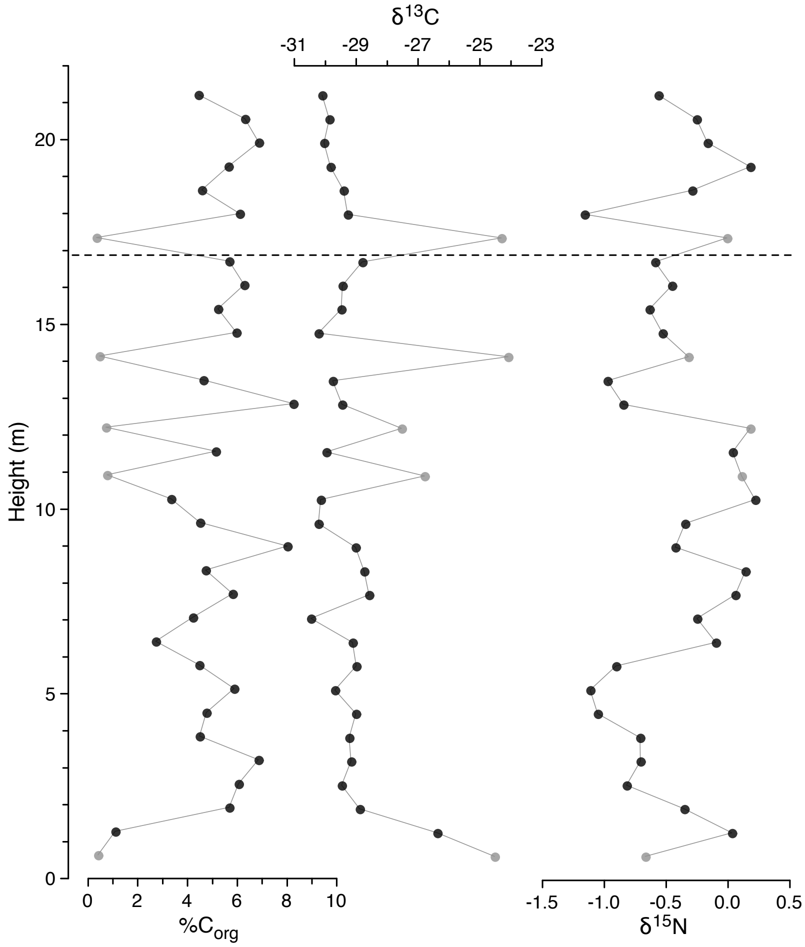
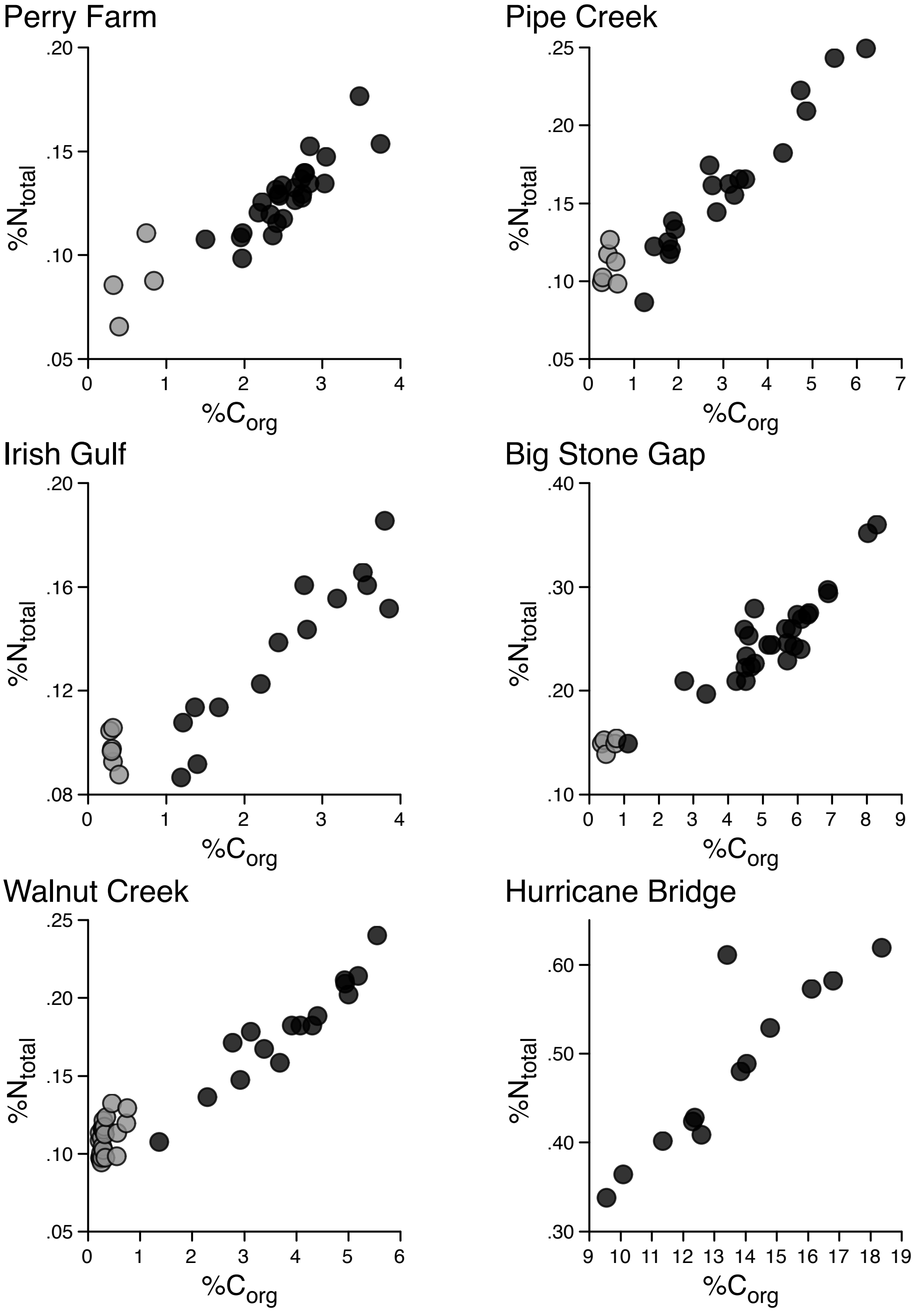


Figure 10. %C_{org}, $\delta^{13}C$, and $\delta^{15}N$ data from Big Stone Gap plotted by stratigraphic height

The section at Big Stone Gap measures more than 20 meters but it was sampled at a lower resolution than the other sites. The Frasnian/Famennian boundary, having been located via conodont biostratigraphy (Over 2002), lies between 16m and 18m and is marked by a positive 5‰ $\delta^{13}C$ excursion and a corresponding 0.5‰ increase in $\delta^{15}N$. There are four other isotope excursions in the section of similar magnitude to those at the Frasnian/Famennian boundary. The LKW horizon lies a few meters below the base of this section.



Perry Farm

Pipe Creek

Irish Gulf

Big Stone Gap

Walnut Creek

Hurricane Bridge

Figure 11. *Cross plots of %C_{org} and %N_{total} for all sites. Linear regressions for high organic matter samples (black dots) are highly significant at each site: Perry Farm (r=0.87), Irish Gulf (r=0.93), Walnut Creek (r=0.95), Pipe Creek (r=0.97), Big Stone Gap (r=0.90), Hurricane Bridge (r=0.90).*

High and low organic matter content differences

Both the stratigraphic graphs and Figure 11 suggest significant differences between high and low organic matter content (%C_{org}) samples. To test the statistical significance of this observation, an unpaired samples, two-tailed T test was conducted to evaluate the statistical significance of the %C_{org}, $\delta^{13}C_{org}$, and $\delta^{15}N_{total}$ differences between high (>1%) and low (<1%) organic content samples at each site (Table 2). All differences were significant with the exception of the $\delta^{15}N_{total}$ at Pipe Creek and Big Stone Gap. While the Pipe Creek p value falls very close to the 95% threshold, the failure to reject the null hypothesis at Big Stone Gap may be an artifact of the lower sampling resolution.

Table 2. Results of unpaired samples, two-tailed T test conducted to evaluate the statistical significance of the %C_{org}*,* $\delta^{13}C_{org}$*, and* $\delta^{15}N_{total}$ *differences between high (>1%) and low (<1%) organic content samples*

Site	n_{high}	n_{low}	**%**C_{org}	$\delta^{13}C_{org}$	$\delta^{15}N_{total}$
Perry Farm	29	4	$p < 0.001$	$p = 0.002$	$p < 0.001$
Irish Gulf	14	6	$p < 0.001$	$p < 0.001$	$p < 0.001$
Walnut Creek	17	24	$p < 0.001$	$p < 0.001$	$p < 0.001$
Pipe Creek	20	7	$p < 0.001$	$p < 0.001$	$p = 0.054$
Big Stone Gap	28	6	$p < 0.001$	$p < 0.001$	$p = 0.211$

Having established the significance of the differences between high and low %C_{org} samples, Table 3 shows that where %C_{org} is less than 1%, $\delta^{13}C$ values are very consistent and ~2-4‰ more enriched than the higher %C_{org} samples from the same section. $\delta^{15}N$ values are also markedly more enriched in the low %C_{org} samples. Among the three transect sites, $\delta^{15}N_{total}$ of high and low $\%C_{org}$ samples differ by less than the analytical error.

Table 3. Mean isotope values for low and high $\%C_{org}$ *samples*

	$\%C_{org} < 1$		**$\%C_{org} > 1$**	
Site	**$\delta^{13}C_{org}$**	**$\delta^{15}N_{total}$**	**$\delta^{13}C_{org}$**	**$\delta^{15}N_{total}$**
Perry Farm	-25.2	1.1	-27.6	-0.2
Irish Gulf	-25.1	0.9	-28.8	-0.1
Walnut Creek	-25.8	1.0	-28.6	-0.2
Pipe Creek	-25.0	0.3	-27.9	-0.1
Hurricane Bridge			-29.7	0.5
Big Stone Gap	-25.1	-0.2	-29.4	-0.5

While acidification removed inorganic carbonate from the samples leaving only organic C for bulk isotope analysis, all samples likely contain both organic and inorganic N. If all of the N in the analyzed samples were bound up in sedimentary organic matter, the y-intercept in each cross plot of $\%C_{org}$ vs. $\%N_{total}$ would be at 0 because the absence of organic C necessitates the absence of organic N. Inorganic N in marine sediments exists primarily as bound NH_4 within clay mineral matrices, retaining the isotopic signature of the soil ammonium with which the clays formed (Schubert, *et al.* 2001). The y-intercept values in Table 4 ($\%N_{bound}$) show the inorganic sediment N percent composition based upon regression lines for all samples where $\%C_{org} > 1\%$ in each section. Percentage N_{org} was calculated as the difference between $\%N_{total}$ and $\%N_{bound}$.

Table 4. %N composition of total, bound, and organic N and the ratio of N_{org} *to* N_{total} *in samples where %Corg > 1%*

Site	**%N_{total}**	**%N_{bound}**	**%N_{org}**	**N_{org}:N_{total}**
Perry Farm (n=29)	0.13	0.05	0.08	0.62
Irish Gulf (n=14)	0.14	0.07	0.07	0.50
Walnut Creek (n=17)	0.18	0.08	0.10	0.55
Pipe Creek (n=20)	0.16	0.07	0.09	0.56
Hurricane Bridge (n=13)	0.48	0.03	0.45	0.94
Big Stone Gap (n=28)	0.25	0.11	0.14	0.56

Having determined a value for the percent N_{org} in high %C_{org} samples, it is now possible to calculate the ratio of organic C to organic N at each site. This ratio offers a more accurate determination of organic matter source than the ratio given in Table 1 because that ratio includes inorganic N bound within the clay mineral matrix of the sediment.

Table 5. Calculation of mean C_{org}*:*N_{org} *in samples where %*C_{org} *> 1%*

Site	**%C_{org}**	**%N_{org}**	**C_{org}:N_{org}**
Perry Farm	2.55	0.08	31.9
Irish Gulf	2.49	0.07	35.6
Walnut Creek	3.78	0.10	37.8
Pipe Creek	3.14	0.09	34.9
Hurricane Bridge	13.39	0.45	27.9
Big Stone Gap	5.27	0.14	37.6

Discussion

There are significant isotopic and compositional differences between the high and low $\%C_{org}$ samples in every section except Hurricane Bridge, where there are no low $\%C_{org}$ samples. The differences suggest that two distinct processes may be the cause of episodes of high and low organic matter deposition. The mean ratios of C_{org} to N_{org} in samples where $\%C_{org} > 1\%$ at each site except Hurricane Bridge exceed 30:1, well above the Redfield ratio of 106:16 for marine plankton biomass and more typical of terrestrial organic matter. The C_{org}:N_{org} values and the reported abundance of plant materials in Appalachian Basin sediments (Over 2002) provide evidence for the significant role of terrestrially-derived dissolved organic carbon (DOC) and particulate organic matter (POM) in basin productivity. The $\delta^{13}C_{org}$ data also support this interpretation. Low $\%C_{org}$ $\delta^{13}C_{org}$ values vary little about the mean -25.4‰ while mean $\delta^{13}C_{org}$ values in high $\%C_{org}$ samples are depleted by an average of ~3‰. This finding suggests that the flux of depleted terrestrially-derived organic carbon was coincident with periods of high productivity.

The mean $\delta^{15}N_{bound}$ value of 1.0‰ along the three-site transect preserves the nitrogen isotope signature of the soil ammonium present during pedogenesis and clay mineral formation. Assuming that the $\delta^{15}N_{bound}$ value remains constant, the relatively depleted $\%N_{total}$ values at the three sites represent a mixing of the $\delta^{15}N_{bound}$ signal with a more depleted $\delta^{15}N_{org}$ signal. The isotope mixing equation will yield an estimate of the value of $\delta^{15}N_{org}$ at the three sites,

$$\delta^{15}N_{total} = f\,N_{org} \bullet \delta^{15}N_{org} + f\,N_{bound} \bullet \delta^{15}N_{bound}$$

Using a value of -0.2‰ for $\delta^{15}N_{total}$, 1.0‰ for $\delta^{15}N_{bound}$, and a mean ratio of 56:44 for the organic:bound fraction, the result is -1.2‰, a value consistent with a terrestrial organic source.

All comparisons among the three transect sites are complicated by the diminishing rate of sedimentation with distance from shore. The height of the UKW interval at Walnut Creek is less than a quarter of the height of the interval at Perry Farm yet it has a mean $\%C_{org}$ that is 33% greater. This would seem to indicate that the burial ratio of organic matter to inorganic sediment was higher in the more distal site and that the higher $\%C_{org}$ within the UKW interval at Walnut Creek is a function of diminished dilution of organic matter by inorganic sediment.

Although sampling of the LKW is limited to one site, Pipe Creek, the compositional and isotopic pattern is sufficient to argue that the LKW represents an event of similar origins as the UKW. The multiple excursions below the UKW observed in the Big Stone Gap section suggest that the phenomenon was not restricted to the LKW and UKW intervals.

Data from the Hurricane Bridge site are distinctly different from the basal Famennian at any of the other sites and argue strongly that this was an environment unlike any of the others examined.. Schieber (1994) offered evidence that the extensive Chattanooga shale was formed in relatively shallow (tens of meters) waters and suggested that that organic matter may have been a product of floating mats of macroalgae or aquatic plants. Although further evidence would be necessary to confirm this hypothesis, it is not inconsistent with the unusually high productivity and a C_{org}:N_{org} ratio that is lower than other basin values.

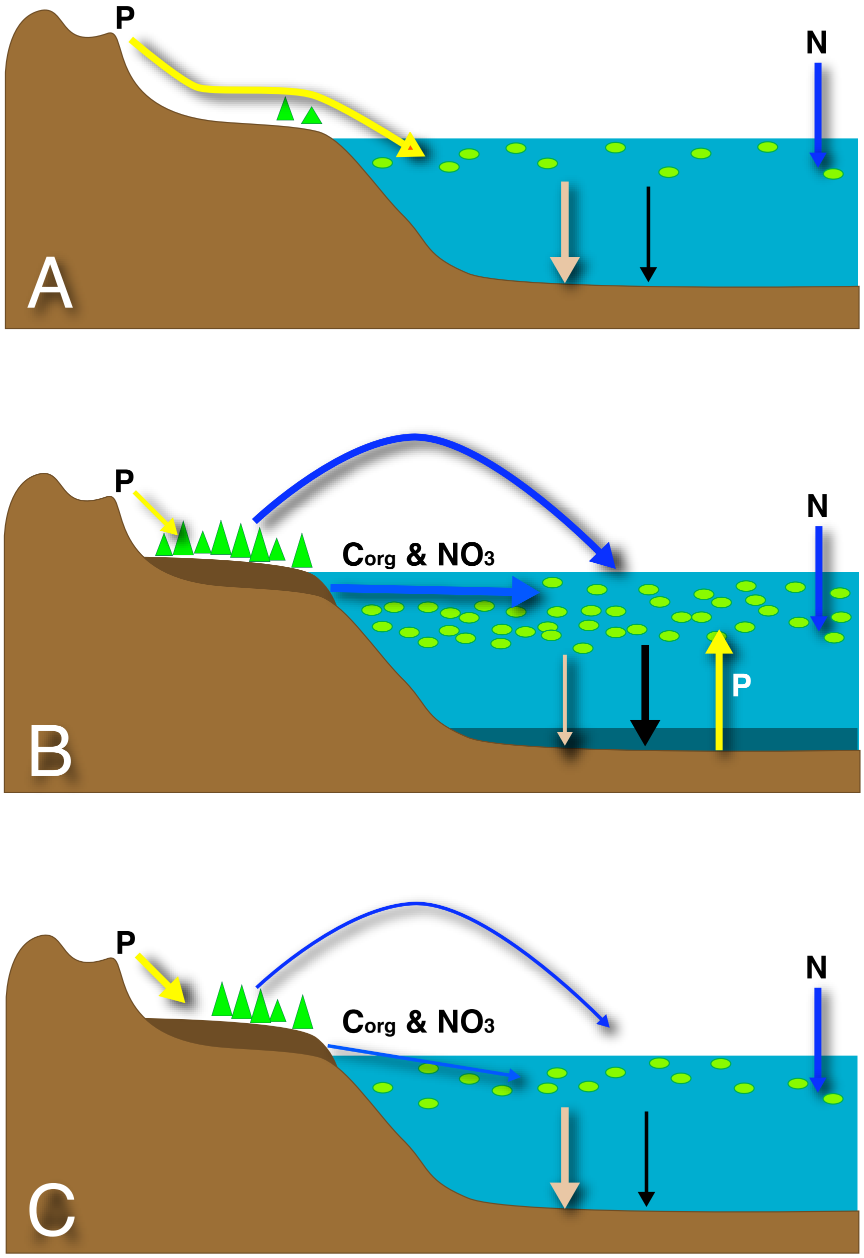


Figure 12. Proposed model for Late Devonian nitrogen biogeochemistry. Blue arrows represent fixed N and organic C fluxes, Yellow arrows represent P flux. Beige arrow represent inorganic sediment deposition and black arrows represent organic matter deposition.

Late Devonian Biogeochemistry

Modern coastal seas are roughly twice as productive as the open ocean because of their proximity to terrestrially-derived organic and inorganic nutrients that are delivered via rivers and estuaries (Schlesinger 1997). Prior to the Middle to Late Devonian, riverine and estuarine delivery of nutrients was limited largely to inorganic mineral weathering products such as P, Fe, and Si (Figure 12, A). Following the emergence of extensive Late Devonian forests, the delivery of organic matter to coastal seas introduced an entirely new source of nutrients into coastal seas.

Archaeopteris-dominated Late Devonian forests were common in coastal areas and on poorly drained flood plains at tropical and temperate latitudes, including the shores of the Appalachian Basin (Figure 12, B) (Algeo, *et al*. 1998; Bateman, *et al*. 1998; Greb, *et al*. 2006). Analagous modern lowland tropical forests are not N limited (Martinelli, *et al*. 1999). Instead, they are characterized by low C:N and high N:P. ratios Nitrogen loading from these ecosystems to aquatic systems is much higher than is P loading (Vitousek, *et al*. 1991). The differences between N and P cycling in terrestrial ecosystems are determined by chemical properties and microbial processes that are likely unchanged since the Devonian.

Modern developing forests are net consumers of P, while mature forest soils retard the weathering of P (Vitousek, *et al*. 1991; Schlesinger 1997). By analogy, as the areal extent of Middle to Late Devonian forests expanded, the seaward flux of weathered P was increasingly consumed and recycled by terrestrial ecosystems, diminishing the overall weathering flux, the sole source of new P for marine primary producers. The impact of increasing plant biomass and pedogenesis on the flux of fixed N from the land to the sea was likely much different. Atmospheric nitrogen is fixed by microbial symbionts in the roots of some plants and by asymbiotic diazotrophic soil microbes. Nitrifying microbes oxidize NH_4 to NO_3. Nitrate that is not taken up by plant roots is mobile, especially in moist soils, and is readily carried off into riverine systems from which it is delivered to coastal seas (Schlesinger 1997). Nitrogen is also fixed by diazotrophic marine microbes but primarily in the open ocean; so, the fixed N necessary to sustain the high productivity of most coastal seas derives from terrestrial sources (Galloway, *et al.* 2004). The net effect of terrestrial ecosystem development in the Late Devonian was to diminish the flux of P to the sea while increasing the flux of fixed N, resulting in a direct impact on marine primary productivity and organic matter deposition.

Both the Upper and Lower Kellwasser intervals of high organic content deposition are associated with episodes of rising sea level followed by relative sea level fall (Hallam, *et al.* 1999; Over 2002; Godderis, *et al.* 2004). As sea levels rose, flooded drainages likely increased the area of estuaries and embayments, increasing the areal extent and biomass of coastal forests, mires, marshes, and swamps. Rising sea levels may thus have triggered the episodic deposition of high organic content sediments by diminishing the seaward flux of weathered sediment, increasing the outwelling of organic matter and NO_3 from flooded coastal estuaries and embayments (Odum 1980), stimulating high photic zone productivity and creating dysoxic conditions at the sediment-water interface due to the increased oxygen demand. Subsequent regressive periods (Figure 12, C) would have diminished the outwelling flux of organic matter while increasing the flux of weathered sediment. Therefore, the positive $\delta^{13}C$ excursions in the low organic matter strata that lie immediately above the Upper and Lower Kellwasser intervals in the sections examined may be a consequence of the curtailment of the flux of depleted terrestrial organic matter. The corresponding positive $\delta^{15}N$ excursions record the unmasking of the isotopic signature of inorganic ammonium bound in clay matrices by more depleted terrestrially-derived organic N.

As compared to modern marine $\delta^{15}N$ sediment values which average 4-8‰ (Brandes 2004), the consistently more depleted $\delta^{15}N_{total}$ values for all six Appalachian Basin sites indicates that NO_3 utilization in the photic zone was very low (Altabet, *et al.* 1994; Holmes, *et al.* 1997). Episodes of high productivity such as the LKW and UKW interval require sources of C, N, and P. The isotope evidence reveals that the fluxes of both C_{org} and NO_3 from terrestrial ecosystems were plentiful. But if terrestrial ecosystem development served to retard the weathering flux of P to coastal seas, what was the source of the P necessary to sustain the high productivity during the LKW and UKW intervals? Inorganic P is readily remobilized from dysoxic sediments and made available for productivity in the overlying water column (Vancappellen, *et al.* 1994; Algeo, *et al.* 2007). Figure 13 shows a running average of C_{org}:P values in sediments over the last 500 Ma (data from Algeo and Ingall 2007). The uniquely high C_{org}:P values of the Middle to Late Devonian suggest that large amounts of P were drawn from dysoxic sediments.

Together, $\delta^{13}C$ and $\delta^{15}N$ values as well as the C_{org}:P record suggest that LKW and UKW interval productivity was initiated by a rising sea level driven flux of terrestrial organic matter and sustained by that flux plus a "eutrophication pump" (Sageman, *et al.*

2003) that recycled P from organic rich dysoxic sediments. The productivity was self-sustaining until falling sea levels diminished the outwelling flux below the threshold necessary to prime the eutrophication pump.

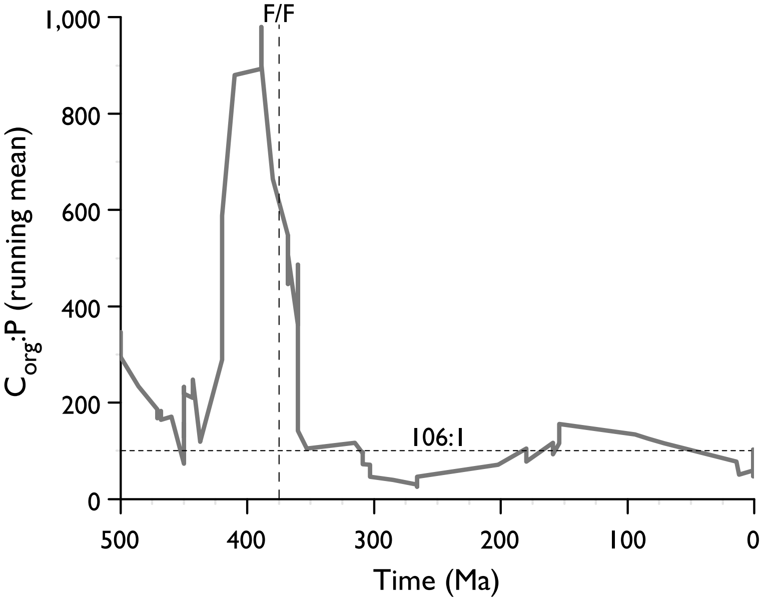


Figure 13. Running mean of C_{org}:P from marine sediments from past 500 Ma (data from Algeo & Ingall 2007). Frasnian/Famennian boundary is marked as F/F. Redfield C:P ratio is marked with line at 106:1.

Conclusion

The Late Devonian is a singular period of transition in the relationship between terrestrial and marine ecosystems. In earlier periods, productivity was limited by the diffuse pool of reactive N that is fixed within the oceans. From the Late Devonian onward, an additional source of reactive N fueled higher levels of marine productivity, while the flux of P from the land surface was diminished. The evolution of the relatively long mean residence time of P relative to N in the oceans (~25,000 versus ~2000 years) (Schlesinger 1997; Brandes, *et al*. 2002) may reflect a large scale evolutionary and ecological response to higher relative reactive N availability since the Late Devonian. Regardless, the data presented in this study offer evidence that terrestrially-derived organic matter provided the raw material for episodic elevated organic matter deposition and that fixed nitrogen, in particular, was the nutrient that facilitated the expansion of marine biomass in the Late Devonian. With respect to the specific hypotheses laid out in the introduction, there is a clear compositional and isotopic distinction between intervals of high and low organic matter deposition; C and N isotope values do indicate terrestrial sources during the high organic matter intervals; but, there was no evidence of a trend of increasing $\delta^{15}N$ enrichment with distance from shore.

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Appendix

The script that follows was written in the AppleScript language and was embedded in a Microsoft Excel spreadsheet in order to automate the process of normalizing reported isotope values to internal laboratory standards which are, in turn, calibrated to international standards. The script requires that the user select at least three cells in a column, the first and last of which are assumed to be standards. The user may choose one of three (carbon, nitrogen, or sulfur) standards to which the data will be normalized.

```
--choose which standard - C, N, or S
display dialog "Pick a standard" buttons  (***"Carbon", "Nitrogen", "Sulfur"***)
set the button_pressed to the button returned of the result
if the button_pressed is "Carbon" then set theStd to "-27.07"
if the button_pressed is "Nitrogen" then set theStd to "4.77"
if the button_pressed is "Sulfur" then set theStd to "-11"

tell application "Microsoft Excel"
	activate
	
	-- check that 3 rows were selected
	set theContent to value of selection --this works
	set itemCount to count theContent
	
	-- if itemCount < 3 then try again with dialog
	if itemCount < 3 then
		display dialog "You need to select at least three cells" buttons
					(***"OK"***) default button 1
	end if
	
	set theSelection to (get address selection) as text
	set theColumn to word 2 of theSelection
	set firstRow to word 4 of theSelection
	set lastRow to word 8 of theSelection
	set firstCell to first item of theContent
	set lastCell to last item of theContent
	
	-- find the adjustment value
	set firstDiff to (theStd - firstCell)
	set lastDiff to (theStd - lastCell)
	set theAdjustment to ((firstDiff - lastDiff) / (itemCount - 3))
```

```
		-- three conditions + > <
		if firstDiff = lastDiff then
			set theCounter to 1
			set theRow to firstRow
			repeat itemCount times
				set theAdjustment to firstDiff
				select cell ("$" & theColumn & "$" & theRow)
				set oldValue to (get value of selection)
				set value of selection to (oldValue + theAdjustment)
				set theCounter to (theCounter + 1)
				set theRow to (theRow + 1)
			end repeat
		end if
		
		if firstDiff < lastDiff then
			set baseLineShift to lastDiff
			set theAdjustment to ((firstDiff - baseLineShift) / (itemCount - 1))
			set theCounter to 1
			set theRow to (firstRow)
			
			--fix rows from top down
			repeat (itemCount) times
				select cell ("$" & theColumn & "$" & theRow)
				set oldValue to (get value of selection)
				set value of selection to (oldValue + baseLineShift + ((itemCount -
							theCounter) * theAdjustment))
				set theCounter to (theCounter + 1)
				set theRow to (theRow + 1)
			end repeat
		end if
		
		if firstDiff > lastDiff then
			set baseLineShift to firstDiff
			set theAdjustment to ((lastDiff - baseLineShift) / (itemCount - 1))
			set theCounter to 1
			set theRow to (lastRow)
			
			--fix rows from bottom up
			repeat (itemCount) times
				select cell ("$" & theColumn & "$" & theRow)
				set oldValue to (get value of selection)
				set value of selection to (oldValue + baseLineShift + ((itemCount -
							theCounter) * theAdjustment))
				set theCounter to (theCounter + 1)
				set theRow to (theRow - 1)
			end repeat
		end if
	end tell
```