**Introduction**

Rivers: The intersection of Earth's two carbon cycles

On timescales ranging from decades to millions of years, Earth's climate and habitability are governed by a delicate balance between the production and consumption of atmospheric carbon dioxide (CO2). Geologic processes such as metamorphic outgassing (Baker et al., 2010), volcanism (Marty and Tolstikhin, 1998), rock weathering (Walker et al., 1981), and subduction of marine sediments (Kelemen and Manning, 2015) act as a net source or sink of CO2 to Earth's surface, thus regulating the size and redox state of the surface carbon reservoir (Hayes and Waldbauer, 2006). On shorter timescales, the mass of carbon contained in the atmosphere as CO2 (reported in partial pressure, or *p*CO2) is largely determined by an intricate network of sources and sinks that shuttle carbon between terrestrial reservoirs such as vegetation and soils, the ocean, and marine sediments (collectively termed the “biosphere”; Sarmiento and Gruber, 2006). By integrating multiple carbon sources on terrestrial landscapes and transferring this material to coastal margins, rivers offer a direct link between the geologic and biospheric carbon cycles (Figure 1.1). Furthermore, the ability of rivers to transfer carbon between these reservoirs is governed by a combination of climatic (*e.g.* precipitation) and tectonic (*e.g.* mountain uplift) controlling mechanisms (Molnar and England, 1990). Fluvial processes act as both a driver of and a response to global carbon cycle perturbations, and therefore uniquely describe the dynamic intersection between Earth’s two carbon cycles.

*The biospheric carbon cycle*

The major process by which carbon is transferred between biospheric reservoirs is the fixation of CO2 to biomass via photosynthesis and the corresponding respiration of organic matter back to CO2:

CO2 + H2O ⬄ CH2O + O2 (1)

where CH2O represents organic carbon contained in biomass (OCbio). Globally, if photosynthesis outpaces respiration, then this process results in a net increase in the size of surficial OC reservoirs and therefore a decrease in *p*CO2, while the opposite is also true. However, it is well known that the biosphere is nearly entirely self-contained, resulting in a near-perfect balance between photosynthetic CO2 fixation and subsequent respiration on a global scale (Sarmiento and Gruber, 2006). Despite this, small imbalances do persist, resulting in a "leaky" biosphere and the accumulation of OCbio within marine sediments (Figure 1.1).

One process by which sedimentary OC accumulation can occur is the erosion of terrestrial landscapes and transport of particulate OC (POC) to coastal margin sediments via rivers (Ludwig et al., 1996; Schlünz and Schneider, 2000). Although fluvial POC export flux represents only a small fraction of net primary production (*i.e.*<1%; Galy et al., 2015), this process continuously removes OC from the terrestrial biosphere that could have otherwise been respired. If this material subsequently escapes remineralization in marine sediments, as has been observed in many fluvial fan settings (France-Lanord and Derry, 1997; Burdige, 2005; Galy et al., 2007; Hilton et al., 2008), then riverine POC transport can constitute a quantitatively important atmospheric CO2 sink over geologic timescales.

Because fluvial suspended sediment and POC fluxes are known to depend on hydrology and river discharge (Milliman and Farnsworth, 2011), which is itself controlled by precipitation patterns (*e.g.* Jian et al., 2009), this process describes a direct response of the carbon cycle to changing climate – that is, riverine carbon export constitutes a climate feedback. Furthermore, POC yield depends on the rate at which river networks are able to erode the landscape (Ludwig et al., 1996; Ludwig and Probst, 1998; Galy et al., 2015). In addition to climatic factors, erosion rates strongly depend on geologic variables such as lithology, landscape slope, and tectonic uplift rate (Dadson et al., 2003; Milliman and Farnsworth, 2011; Hilton, 2016). Fluvial POC export therefore represents the intersection between hydrologic and geologic carbon cycle controls. However, the relative responses to changes in such controls remain largely elusive, hindering our ability to quantitatively reconstruct the role of fluvial climate feedbacks in the past and to predict future changes.

*The geologic carbon cycle*

In addition to the transport and burial of OCbio, highly erosive river networks draining meta-sedimentary lithologies incorporate a significant amount of rock-derived OC (OCpetro; *e.g.* Hilton et al., 2011; Galy et al., 2015). Because they integrate the slowly subducted and lithified marine sediments on timescales of millions to tens of millions of years (Figure 1.2), meta-sedimentary rocks represent the largest global OC stock by nearly 3 orders of magnitude (Figure 1.1). While the vast majority of this reservoir is effectively decoupled from surface processes on shorter timescales, respiration of exposed OCpetro during fluvial transit represents an atmospheric CO2 source (Galy et al., 2008; Bouchez et al., 2010; Hilton et al., 2014). Because OC­petro available for weathering is roughly double that of atmospheric CO2 (*i.e.* 1100 PgC in the upper 1 m; Copard et al., 2007), even a small perturbation in oxidation rates could lead to large changes in the resulting atmospheric CO2 flux.

While it is currently estimated that the fluvial OCbio export flux to the coastal ocean is 3 times greater than that of OCpetro (Galy et al., 2015), atmospheric CO2 emissions due to OCpetro oxidation remains elusive (Galy et al., 2008; Bouchez et al., 2010; Hilton et al., 2014), largely due to the fact that the kinetic, environmental, and compositional controls on this flux are poorly constrained. For example, because there exist few measurements of oxidation rate constants (Chang and Berner, 1999), it remains unknown if OCpetro weathering is limited by erosion rates or kinetic controls, while the roles of partial oxidation (Schillawski and Petsch, 2008) and OCpetro chemical composition (Galy et al., 2008) have additionally received little attention. Furthermore, the relative response of OCbio burial and OCpetro oxidation to changing climatic and geologic processes is not fully understood. For example, it has been proposed that high runoff due to increased intensity and frequency of tropical storms during periods of elevated atmospheric CO2 should lead to increased export and burial of OCbio, thus lowering *p*CO2 (*i.e.* a negative feedback loop; Hilton et al., 2008). However, high runoff has also been shown to result in elevated sediment yield and denudation rates, potentially increasing the exposure of freshly uplifted OCpetro to weathering and resulting in a positive feedback (Hilton et al., 2014).

The net effect of OC incorporation, transport, and evolution within fluvial systems on *p*CO2 must reflect the balance between: *(i)* burial of recently fixed OCbio and *(ii)* oxidation of eroded OCpetro (Figure 1.2). Constraining the response of these two processes to both climatic and geologic perturbations is therefore a major motivating factor for this thesis.

Motivation for this work

*Constraining feedback mechanisms*

While critically important for understanding the global carbon cycle, quantifying modern fluvial fluxes alone (Figure 1.1) does not offer insight into the governing mechanisms that control OC source, transport, and fate. On the global scale, the importance of constraining such feedback mechanisms has long been recognized in order to reconstruct changes in atmospheric CO2 concentration over geologic timescales (Berner and Caldeira, 1999). However, this has only recently been applied to modern fluvial systems. For example, recent studies (*e.g.* Hilton et al., 2008; Hilton et al., 2012; Galy et al., 2015) highlight the importance of erosive processes and sediment yield in determining both OCbio and OCpetro export fluxes, suggesting that increased storm-driven erosion due to elevated *p*CO2 could provide a negative feedback by increasing OCbio burial in marine sediments.

Furthermore, it is now known that OC transport through river networks is not passive. Rather, fluvial transit integrates the complex interactions between multiple biogeochemical processes, each of which has the ability to alter the evolution of OC quality and quantity (Cole et al., 2007; Aufdenkampe et al., 2011; Bianchi, 2011). This has lead to a new paradigm in our understanding of passive-margin systems in which OC is continuously deposited, chemically altered, and resuspended during transit (the so-called "river continuum"; Figure 1.3; Blair and Aller, 2012). In contrast, active-margin systems are now recognized not only as regions of intense erosion and OCbio export, but also for OCpetro weathering due to uplift of OC-rich meta-sedimentary rocks (Figure 1.3; Milliman and Syvitski, 1992). Therefore, based on this current understanding, passive-margin and active-margin systems should respond to environmental perturbations in fundamentally unique ways.

This thesis aims to advance our mechanistic understanding of fluvial carbon cycle feedbacks. To do so, I compare two end-member systems: *(i)* the Congo River representing large, floodplain-dominated, and low-erosion environments in order to isolate climatic controls; and *(ii)* rivers draining the highly erosive Central Range of Taiwan in order to determine geologic controls on active margins.

*The need for time-series measurements*

Fluvial systems are inherently dynamic in nature. However, there exist surprisingly few studies that consider riverine carbon export in a time-series manner, especially when including suspended sediments and particulate OC. Although such studies are logistically difficult, they provide critically important information regarding the seasonal variability and long-term evolution of river basins (*e.g.* Peterson et al., 2002; Raymond and Cole, 2003; Milliman and Farnsworth, 2011; Voss et al., 2015). In addition to refining our estimates of carbon flux (Figure 1.1), time-series measurements have revealed that OC composition exhibits significant temporal variability that is related to hydrology (Voss et al., 2015; Hemingway et al., 2016). Furthermore, time-series studies provide a necessary link between the synoptic, "campaign-style" results that describe most of our knowledge on modern river systems and paleoclimate reconstructions utilizing sediments deposited in river-dominated margins. In this thesis, I attempt to further develop this emerging "time-variable river continuum" model by utilizing a 34-month time-series of monthly measurements on the Congo River in addition to a high-resolution (sub-daily) sampling scheme across three successive typhoon events in Taiwan.

*Current methodological limitations*

Currently, most studies aimed at constraining the source and composition of exported fluvial OC utilize the following techniques: *(i)* conservative tracers of bulk OC composition (*e.g.* 14C content, 13C content, N/C ratios, *etc.*); *(ii)* compound-specific biomarker concentrations and isotope composition (*e.g.* *n*-alkyl lipds, sterols, lignin oxidation products); and *(iii)* high-resolution non-quantitative mass spectrometry. When used in tandem, these techniques offer a powerful approach to understanding OC sources.

However, each comes with its own drawbacks. For example, bulk measurements provide a weighted-average view of the composition of all OC contained within a sample, but require *a priori* knowledge of end-member compositions in order to un-mix source contributions (Perdue et al., 2007; Weijers et al., 2009; Hilton et al., 2010; Hossler and Bauer, 2012). In contrast, biomarker concentration and isotope measurements provide information specific to a particular OC source, but individual compounds typically constitute <1% of total OC and are subject to potentially large and unknown production biases (Garcin et al., 2014; Ponton et al., 2014). To address these drawbacks, a 4th class of organic geochemical techniques is emerging – reaction monitoring methods (*e.g.* Rosenheim et al., 2008; Follett et al., 2014; Beaupré et al., 2016). In addition to geochemical applications using time-series fluvial sediments, this thesis aims to advance our theoretical understanding one such reaction monitoring technique, specifically the "Ramped PyrOx" (RPO) serial oxidation method. By heating a sample at a constant ramp rate and "binning" evolved CO2 for isotope measurements, this technique directly relates OC (thermo-)lability and isotope composition, and is therefore a promising method for monitoring OC degradation kinetics in the environment and for un-mixing OC sources.

Thesis outline

This thesis is motivated by a set of questions that aim to further our understanding of the environmental processes governing the role of rivers in the global carbon cycle. Thematically, these questions can be separated into two main sections:

1. **Ramped pyrolysis/oxidation (RPO) instrumental development, theory, data treatment, and post-processing** (Chapters 2 and 3).
   1. What is the contribution by contaminant ("blank") carbon in the RPO instrument, and how can this be corrected for? Does the RPO instrument impart any isotope fractionation?
   2. Can profiles of OC thermal recalcitrance be related to intrinsic molecular properties, and what are the governing kinetic reactions?
   3. How can RPO-derived thermal profiles and isotope results be combined to advance our understanding of OC sources and processing in the environment?
2. **Application of organic geochemical methods to riverine suspended sediments and soils** (Chapters 4, 5, and 6).
   1. How do the signals recorded in the fluvially exported POC integrate processes throughout the basin? Are they representative of upstream sources?
   2. Do these signals respond to environmental variability (*e.g.* hydrology, temperature) on seasonal and inter-annual timescales? How does this knowledge affect our interpretation of paleoenvironmental reconstructions using sedimentary archives?
   3. How would changes in environmental conditions affect the stability of carbon reservoirs (*e.g.* soils, rock-derived organic carbon) and the corresponding CO2 flux from these reservoirs to the atmosphere?

In practice, this thesis is articulated around the following chapters:

**Chapter 2**

This chapter describes recent developments to the RPO radiocarbon instrument located at the National Ocean Sciences Accelerator Mass Spectrometer (NOSAMS) facility. This method aims to separate individual components contained within complex OC mixtures based on thermo-lability and to evaluate the range of both stable carbon (13C and 12C) and radiocarbon (14C) composition contained within a given sample. Here, the contribution and isotope composition of contaminant ("blank") carbon is constrained and corrected for. Additionally, the isotope fractionation due to mass-balance effects is determined based on a compilation of 66 samples that have been analyzed over ~4 years, while the fractionation due to kinetic effects is evaluated using a set of standard reference materials.

**Chapter 3**

Here, a framework in which to interpret RPO isotope and kinetic results is proposed. OC decomposition kinetics are described as a continuous superposition of parallel first-order decay reactions that are governed by the Arrhenius equation. The distribution of activation energy required to explain observed thermal profiles is then constrained by solving the regularized inverse problem, thus relating RPO experimental results with intrinsic chemical properties of a given sample. To robustly verify the assumptions built into this model, a set of test samples was analyzed under a range of experimental conditions. Lastly, this chapter discusses how the RPO instrument presents a novel approach for separating carbon sources and understanding OC transformation processes.

**Chapter 4**

This chapter concerns the seasonal and inter-annual variability of vascular-plant-derived biomarker concentrations and δ13C values exported from the Congo River. Changes in the composition of vascular plant lipids (*n*-alkanes, *n*-alcohols, and *n*-alkanoic acids) extracted from fluvial sedimentary archives are commonly used as a tracer for changes in past ecosystem structure and carbon export. However, few studies have monitored the role of inter-annual variability on these signals. Using a 34-month time-series collected from the Congo River at Brazzaville, this chapter shows that alkyl lipid compound classes variably track upstream ecosystems and that *n*-alcohols and *n*-alkanoic acids are more susceptible to seasonal variability than are *n*-alkanes.

**Chapter 5**

Using the same Congo River sample set, this chapter constrains the source of exported particulate OC using bulk conservative tracers (δ13C, ∆14C, N/C) and microbial glycerol dialkyl glycerol tetraether (GDGT) biomarkers. Variability in POC sources is shown to be driven by inter-annual hydrodynamic variability, with exported POC being dominated by significantly pre-aged material eroded from the *Cuvette Congolaise* swamp forest during periods of high northern-hemisphere discharge. Compared to published time-series data from an upstream tributary (Oubangui River), these results offer insight into the dilution and replacement of upstream POC by downstream sources during fluvial transit. Combined, Chapters 4 and 5 constrain the environmental processes governing Congo River OC export by highlighting the importance of seasonal and inter-annual hydrologic variability.

**Chapter 6**

Lastly, using a combination of bulk measurements, alkanoic acid biomarkers, and RPO results, this chapter reveals that the oxidation of rock-derived OC in the highly erosive Central Range of Taiwan is governed by microbial processes, a phenomenon that has previously been observed in laboratory incubation experiments but has yet to be verified as quantitatively important in the field. Additionally, the resulting CO2 flux to the atmosphere is constrained to be roughly equal to that of CO2 drawdown due to silicate weathering and burial of biospheric OC in this system. Because microbial oxidation appears to be rapid, it is likely not kinetically limited and resulting CO2 fluxes are governed by the rate of exposure of bedrock material to the weathering front (*i.e.* erosion rate).

**Conclusion**

One of the fundamental goals of Earth science is to understand, in a predictive manner, how the global carbon cycle adapts and responds to external perturbations, both in the past as well as the future. The importance of this knowledge becomes especially apparent in the context of anthropogenic climate change – how will Earth's natural cycles respond to this massive unnatural forcing? As a conclusion, I propose a set of thought experiments to highlight how the results contained within this thesis might offer novel insight into this understanding, and bring attention to the work that lies ahead.

The global carbon cycle

It has long been realized that atmospheric CO2 concentrations (*p*CO2) have remained relatively stable throughout much of Earth's history despite global-scale variability in tectonics, temperature, ice cover, *etc*. Therefore, to prevent runaway CO2 emission (*i.e.* "hot-house" climate) or consumption (*i.e.* "ice-house" climate), it is canonically thought that the global carbon cycle is controlled by an intricate network of positive and negative feedback mechanisms acting over geologic timescales (106 – 107 yr). This interpretation, commonly attributed to the late Bob Berner, inherently implies that *p*CO2, and therefore global temperature via the greenhouse effect, is the “master variable” to which all feedbacks respond (Figure 7.1).

Throughout the last half century, many feedbacks governed by fluvial processes have been proposed that involve a direct link between temperature and mechanisms acting to increase or decrease *p*CO2. One of the most widely invoked, dating to Walker et al. (1981), is the idea that the rate of CO2 drawdown due to silicate rock weathering followed by CaCO3 deposition in marine sediments is a function of global temperature, which, in turn, is a function of atmospheric *p*CO2. Increasing *p*CO2 therefore increases silicate weathering rates, especially in mountainous regions (Maher and Chamberlain, 2014), leading to elevated CO2 drawdown until a stable equilibrium is once again reached. Acting in parallel is the erosion and efficient export of OC derived from the terrestrial biosphere (OCbio), which is additionally biased toward high-elevation catchments (France-Lanord and Derry, 1997; Galy et al., 2007; Hilton et al., 2008; Galy et al., 2015). According to this mechanism, if increased *p*CO2 leads to elevated erosion due to an acceleration of the hydrologic cycle, then OCbio export and burial will subsequently increase, drawing down *p*CO2. Both of these mechanisms therefore emphasize the importance of elevation and catchment geometry in regulating feedback sensitivity.

However, they are likely balanced by positive feedbacks acting to amplify *p*CO2 perturbations. The two most significant pertaining to river catchments involve CO2 emissions due to the oxidation of rock-derived (“petrogenic”) organic carbon (OCpetro; Hilton et al., 2014; Chapter 6) or the oxidation of pyrite followed by subsequent acidification of CaCO3 (Torres et al., 2014), both of which should accelerate under warmer conditions, especially in mountainous catchments (Torres et al., 2016). While the controls on these mechanisms is just beginning to be understood, the importance of high-elevation regions with high sediment yield is already clear. Based on the this emerging understanding, I propose a nuanced update to the Berner paradigm – namely, that CO2 source and sink processes can directly respond to the same perturbation without invoking a feedback loop that includes temperature.

For example, OCpetro oxidation appears to be rapid and not kinetically limited, at least given the erosion rates observed in Taiwan, suggesting that increasing exposure of bedrock material to the surface via erosion will increase the rate of OCpetro oxidation (a CO2 source) in addition to OCbio burial and silicate weathering (CO2 sinks). However, this relationship should break-down under extraordinarily high erosion rates, as bedrock incision would export significant amounts of unweathered OCpetro­ and relatively little OCbio, dampening both mechanisms (Hilton et al., 2011). One important future direction for the work presented in Chapter 6, therefore, is to constrain microbially mediated OCpetro oxidation rates and fluxes in catchments experiencing a wide range of erosion rates and to determine the kinetic limits of this mechanism. Additionally, it is critical that we understand the relationship, if any, between OCpetro yield in fluvial sediments and oxidation fluxes on landscapes. Combined, this would allow us to predictively constrain CO2 emissions due to OCpetro oxidation a function of sediment yield, as has been done previously for OCbio export (Galy et al., 2015). Furthermore, the CO2 emission fluxes and governing mechanisms controlling pyrite weathering remain almost completely unknown (Calmels et al., 2007; Torres et al., 2014), presenting a pressing need for future research.

Still, with regards to organic carbon, the framework proposed here suggests that the net effect of fluvial systems as an atmospheric CO2 source or sink and their sensitivity to *p*CO2 perturbations is a function of erosion rate. To probe this conceptual understanding, first I consider a high-elevation Earth surface similar to that of Taiwan, while still allowing erosion rates to vary over many orders of magnitude. In this scenario, the fraction of OCpetro oxidized (*f*ox) appears to be <15% of the total yield due to high rates of bedrock incision and rapid export of unweathered material (Hilton et al., 2011). Using the power law relationships between OCbio, OCpetro, and suspended sediment yield of Galy et al. (2015), and assuming that 15% of the OCpetro yield in rivers is oxidized to CO2, fluvial OC processes in this conceptual Earth would represent a net CO2 sink until global sediment yield increased above ~ 104 to 105 t km-2 yr-1, depending on OCbio burial efficiency (Figure 7.2, blue shaded region). The magnitude of rivers as a CO2 sink would be maximized at slightly lower yields, between 103 and 104 t km-2 yr-1, and would decrease to zero with decreasing erosion.

At the opposite extreme, I consider a case where all fluvially exported OCpetro is the residual of oxidation on landscapes – that is, uplift is fast enough to continuously expose fresh bedrock to the surface, but low enough to prevent landsliding and incision, therefore preventing the export of unweathered OCpetro. Assuming the *f*ox value of 73+2/-3% calculated in Chapter 6 applies globally, OCpetro oxidation in this scenario out-paces OCbio burial above a sediment yield of ~ 102 to 103(Figure 7.2, red shaded region), similar to the modern global average of 176 t km-2 yr-1 (Galy et al., 2015). In reality, there likely exists a transition between the high-*f*ox scenario at low sediment yield and the low-*f*ox scenario at high sediment yield. Nonetheless, these thought experiments demonstrate the high sensitivity of counter-balancing positive and negative feedbacks in active margin systems that respond, in parallel, to the same *p*CO2 perturbation. Understanding this relationship will form an important component of my future research.

Finally, I consider how a low-elevation Earth would respond to *p*CO2 changes. For passive-margin, climate-controlled systems such as the Congo River, the results of Chapters 4 and 5 indicate that exported POC is largely derived from downstream regions, and that hydrology is a key control on OC source. Because both silicate weathering and OCbio burial flux would decrease in this low-erosion system relative to modern Earth, fluvial feedbacks would become less efficient at regulating atmospheric *p*CO2. This can be seen by the fact that net CO2 flux due to OC processes is largely insensitive to changes in sediment yield in passive margins, regardless of *f*ox (Figure 7.2). While limited in geographic extent today, a low-elevation Earth could be described by significant proliferation of permanently inundated swamp-forest regions such as the middle Miocene Pebus System located in the modern-day Amazon basin (Hoorn, 1994). Using the *Cuvette Congolaise* as an example, this would likely lead to an increase in terrestrial OC storage and longer fluvial residence times due to widespread anoxia. Therefore, OCbio storage in intermediate anoxic reservoirs could become more important in determining the role of rivers as a negative feedback to *p*CO2 perturbations in this end-member system.

The results of Chapter 5, combined with those of Schefuß et al. (2016), suggest that the ability of anoxic reservoirs to act as an atmospheric CO2 sink depends on hydrology and discharge. When *p*CO2 is high and the hydrologic cycle is amplified, high discharge through lowland depressions would expand the geographic extent of anoxic soils and therefore stabilize this OC reservoir (Schefuß et al., 2016). However, as *p*CO2 declines leading to lower monsoon intensity and lower discharge, these regions could become exposed and oxidized, not entirely unlike what is occurring in modern-day permafrost soils. Chapters 4 and 5 of this thesis highlight the importance of anoxic regions in driving OC export from large, passive-margin systems despite their small geographic extent (*e.g.* the *Cuvette Congolaise* constitutes ~4% of the total Congo Basin; Mayaux et al., 2003).

A final thought

In reality, Earth exists between these two extremes. While the end-members presented here provide a useful thought exercise, to properly understand fluvial responses to *p*CO2 perturbations we must turn to systems such as the Amazon or Ganges-Brahmaputra that contain both high-erosion headwaters *and* large floodplains. In the coming years, I plan further investigate the importance of OCpetro oxidation and OCbio export, in addition to pyrite weathering, by incorporating time-series sample sets from such systems. Furthermore, I stress the importance of continuing the collaborations and time-series sample collection presented in this thesis. To fully constrain the response of fluvial carbon cycle to a changing climate, in addition to the threats currently posed by deforestation and land-use change, it is critical that we continue these analyses and generate multi-decadal records of riverine OC export.

Lastly, I emphasize the utility of developing novel instrumental methods. One of the main challenges facing organic geochemists is the fact that any given sample contains a complex OC mixture representing a rage of chemical composition, environmental residence time, and susceptibility to degradation. Only by continuing to push the technical envelope will we be able to sufficiently meet this challenge.