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October 31, 1983 - November 29, 1984

A study of the remineralization of organic carbon was conducted in the organic-rich sediments of Buzzards Bay, MA. Major processes affecting the carbon chemistry in sediments are reflected by changes in the stable carbon isotope ratios of dissolved inorganic carbon (XCO_2) in sediment pore water. Six cores were collected seasonally over a period of two years. The following species were measured in the pore waters: JCO_2 , & $^{13}C-2CO_2$, $P0_4$, JH_2S , Alk , DOC , and Ca . Measurements of pore water collected seasonally show large gradients with depth, which are larger in summer than in winter. The $\delta^{13}C$ (PDB) of ICO_2 varies from 1.3 ‰ in the bottom water to approximately -10 ‰ at 30 cm. During all seasons, there was a trend towards more negative values with depth in the upper 8 cm due to the remineralization of organic matter. There was a trend toward more positive values below 8 cm, most likely due to biological irrigation of sediments with bottom water. Below 16-20 cm, a negative gradient was re-established which indicates a return to remineralization as the main process affecting pore water chemistry. Using the XCO_2 depth profile, it was estimated that 67-85 gC/m² are oxidized annually and 5 gC/m²-yr are buried. The amount of carbon oxidized represented remineralization occurring within the sediments. This estimate indicated that approximately 20% of the annual primary

productivity reached the sediments. The calculated remineralization rates varied seasonally with the high of 7.5×10^{-1} mol/L-sec observed in August 84 and the low (0.6×10^{-1}) in December 83. The calculated remineralization rates were dependent on the amount of irrigation in the sediments; if the irrigation parameter is known to $\pm 20\%$, then the remineralization rates are known to this certainty also. The amount of irrigation in the sediments was estimated using the results of a seasonal study of $^{22}Rn/^{222}Ra$ disequilibria at the same study site (Martin, 1985). Estimates of the annual remineralization in the sediments using solid-phase data indicated that the solid-phase profiles were not at steady-state concentrations. The isotopic signature of $2CO_2$ was used as an indicator of the processes affecting ICO_2 in pore water. During every month, the oxidation of organic carbon to CO_2 provided over half of the carbon added to the ICO_2 pool. However, in every month, the $\delta^{13}C$ of XCO_2 added to the pore water in the surface sediments was greater than -15 ‰, significantly greater than the $\delta^{13}C$ of solid-phase organic carbon in the sediments (-20.6 ‰). The $\delta^{13}C$ of ICO_2 added to the pore water in the sediments deeper than 7 cm was between -20 and -21 ‰, similar to the organic carbon in the sediments. Possible explanations of the ^{13}C -enrichment observed in the surface sediments were: a) significant dissolution of $CaCO_3$ ($\delta^{13}C = +1.7$ ‰) b) the addition of significant amounts of carbonate ion from

bottom water to pore water c) an isotopic difference between the carbon oxidized in the sediments and that remaining in the sediments. The effect of $CaCO_3$ dissolution was quantified using measured dissolved Ca profiles and was not large enough to explain the observed isotopic enrichment. An additional source of ^{13}C -enriched carbon was bottom water carbonate ion. In every month studied, there was a net flux of $2CO_2$ from pore water to bottom water. The flux of pore water $2CO_2$ to bottom water ranged from a minimum of 10×10^{-12} mol/cm²-sec in December 83 to a maximum of 50×10^{-12} mol/cm²-sec in August 84. However, because the pH of bottom water was about 8 while that of the pore water was less than or equal to 7, the relative proportion of the different species of inorganic carbon (H_2CO_3 , HCO_3^- , CO_3^{2-}) was very different in bottom water and pore water. Thus, while there was a net flux of ICO_2 from pore water to bottom water, there was a flux of carbonate ion from bottom water to pore water. Because bottom water JCO_2 was more ^{13}C -enriched than pore water JCO_2 , the transfer of bottom water carbonate ion to pore water was a source of ^{13}C -enriched carbon to the pore water. If the $\delta^{13}C$ of CO_2 added to the pore water from the oxidation of organic carbon was -20.6 ‰, then the flux of ^{13}C from bottom water to pore water must have been 10-30% of the total flux of $2CO_2$ from pore water to bottom water. This is consistent with the amount calculated from the observed gradient in carbonate ion.

Laboratory experiments were conducted to determine whether the $\delta^{13}\text{C}$ of CO_2 produced from the oxidation of organic carbon ($\delta^{13}\text{C}$ -OCOX) was different from the $\delta^{13}\text{C}$ of organic carbon in the sediments ($\delta^{13}\text{C}$ -SOC). In the laboratory experiments, mud from the sampling site was incubated at a constant temperature. Three depths were studied (0-3, 10-15, and 20-25 cm). For the first study (IE1), sediment was stirred to homogenize it before packing into centrifuge tubes for incubation. For the second study (IE2), sediment was introduced directly into glass incubation tubes by subcoreing. The second procedure greatly reduced disturbance to the sediment. Rates of CO_2 production were calculated from the concentrations of ^{14}C measured over up to 46 days. In both studies, the values of R_e in the deeper intervals were about 10% of the surface values. This was consistent with the field results, although the rates decreased more rapidly in the field. In all cases, the remineralization rates during the beginning of IE1 were much greater than those at the beginning of IE2. The sediment for IE1 was collected in February 84. The measured value of R_c in the surface sediment of the laboratory experiment (24×10^{-9} mol/L-sec) was much greater than the value of R_c observed in the field in another winter month, December 83 (6.2×10^{-9}). The sediment for IE2 was collected in August 85. The measured values of R_e in the surface sediment (6.6 - 12×10^{-9} mol/L-sec) were consistent with the field values

from August 84 (7.5×10^{-9}). The XCCO_2 results indicated that IE2 reproduced field conditions more accurately than IE1 did. The isotopic results from the experiments strongly suggested that $\delta^{13}\text{C}$ -OCOX in the surface sediments ($-17.8 \text{ o/oo} \pm 1.9 \text{ o/oo}$) was greater than $\delta^{13}\text{C}$ -SOC ($-20.6 \pm 0.2 \text{ o/oo}$). The magnitude of the observed fractionation was small enough that the observed values of $\delta^{13}\text{C}$ - CO_2 in the pore waters could be explained by fractionated oxidation coupled with the diffusion of carbonate ion from bottom water to pore water. The observed fractionation was most likely due to the multiple sources of organic carbon to coastal sediments. A study of the natural levels of radiocarbon in these sediments indicated that the carbon preserved in the sediments is approximately 30% terrestrial while the rest is from phytoplankton. The great geologic and climatic diversity of the Fraser River basin in southwestern Canada render it an excellent location for understanding biogeochemical cycling of sediments and terrigenous organic carbon in a relatively pristine, large, temperate watershed. Sediments delivered by all tributaries have the potential to reach the ocean due to a lack of main stem lakes or impoundments, a unique feature for a river of its size. This study documents the concentrations of a suite of dissolved and particulate organic and inorganic constituents, which elucidate spatial and temporal variations in chemical weathering (including carbonate weathering in certain

areas) as well as organic carbon mobilization, export, and biogeochemical transformation. Radiogenic strontium isotopes are employed as a tracer of sediment provenance based on the wide variation in bedrock age and lithology in the Fraser basin. The influence of sediments derived from the headwaters is detectable at the river mouth, however more downstream sediment sources predominate, particularly during high discharge conditions. Bulk radiocarbon analyses are used to quantify terrestrial storage timescales of organic carbon and distinguish between petrogenic and biospheric organic carbon, which is critical to assessing the role of rivers in long-term atmospheric CO_2 consumption. The estimated terrestrial residence time of biospheric organic carbon in the Fraser basin is 650 years, which is relatively short compared to other larger rivers (Amazon, Ganges-Brahmaputra) in which this assessment has been performed, and is likely related to the limited floodplain storage capacity and non-steady-state post-glacial erosion state of the Fraser River. A large portion of the dissolved inorganic carbon load of the Fraser River (>80%) is estimated to derive from remineralization of dissolved organic carbon, particularly during the annual spring freshet when organic carbon concentrations increase rapidly. This thesis establishes a baseline for carbon cycling in a largely unperturbed modern mid-latitude river system and establishes a framework for future process studies on the mechanisms of organic

carbon turnover and organic matter-mineral associations in river systems. River Pollution 1: Chemical Analysis discusses methods of detecting and determining the various forms of pollution and the interpretation of results. It aims to provide a chemical background for, and supplement to, the information on analytical methods, and to review critically other methods which may be useful in certain circumstances for research, control work, and field tests. The book begins with a description of river surveys, and physical and chemical methods for determining river pollution. Separate chapters cover methods to determine the presence of dissolved oxygen, combined nitrogen, sulfur compounds, carbon dioxide, free chlorine, metallic contaminants, and carbon compounds. Subsequent chapters discuss the estimation of less important substances which may sometimes be encountered in pollution problems; and the significance of chemical and physical tests and the interpretation of the results of an analysis. This book is intended for those interested in chemical analysis as applied to river pollution problems, sewage, and trade wastes. This book is written as a reference on organic substances in natural waters and as a supplementary text for graduate students in water chemistry. The chapters address five topics: amount, origin, nature, geochemistry, and characterization of organic carbon. Of these topics, the main themes are the amount and nature of dissolved organic carbon in natural waters (mainly fresh water, although

seawater is briefly discussed). It is hoped that the reader is familiar with organic chemistry, but it is not necessary. The first part of the book is a general overview of the amount and general nature of dissolved organic carbon. Over the past 10 years there has been an exponential increase in knowledge on organic substances in water, which is the result of money directed toward the research of organic compounds, of new methods of analysis (such as gas chromatography and mass spectrometry), and most importantly, the result of more people working in this field. Because of this exponential increase in knowledge, there is a need to pull together and summarize the data that has accumulated from many disciplines over the last decade. This dissertation consists of several studies conducted at various spatial and temporal scales designed to identify the important processes that affect organic matter (OM) inputs from the Andes mountains to the Amazon headwaters, as well as carbon (C) and nitrogen (N) cycles in the rivers themselves. Andean rivers supplied approximately equal amounts of fine and coarse sediments to the Amazon, but most coarse sediments were retained in the Andean foreland while fine sediments continued downstream. Terrestrial plant $\delta^{13}\text{C}$ increased with elevation, but terrestrial soil $\delta^{13}\text{C}$ did not and was enriched by 1-3% over plants. Particulate organic matter (POM) concentrations were generally low, with periodic high concentrations during storms. There were

significant differences in the isotopic composition of POM between seasons (wet vs. dry), reflecting changes in sediment source. During high flow, POM resembled terrestrial materials, but during drier periods there was evidence for a resuspended bottom sediment or algal source. During wet periods, OM content of soils and river POM decreased downstream, but the POM trend was complicated during drier months. $\delta^{14}\text{C}$ of POM decreased downstream, suggesting that young, fresh OM introduced in small headwater streams was respired preferentially in rivers or diluted with older material downstream. Fine suspended POM was higher in $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ than coarse POM, indicating either greater degradation in the fine fraction or sorption of isotopically enriched dissolved OM. Deforestation is reflected in suspended POM in small headwaters, with enrichment in both ^{13}C (due to introduced C_4 grasses) and ^{15}N . Epiphytic plants living in forest canopies were $\delta^{15}\text{N}$ -deplete compared to rooted plants, and the biomass of these epiphytes was so high that their $\delta^{15}\text{N}$ was reflected in stream POM. Precipitation was a major source of isotopically enriched dissolved organic N (DON) to cloudforests in the central Andes. Inorganic N export from these systems in streams was very low, but this seems to be the result of high demand for DIN by microbes and fine roots in riparian soils, not a high reactivity of dissolved inorganic N (DIN) in the stream. Low deposition of and demand for inorganic N in

these forests appear to explain low ambient stream DIN concentrations. The research reported on here sought to characterize natural organic matter (NOM) in dilute solutions and to isolate it without altering its properties, so that the effect of NOM in drinking water may be considered. Several NOM isolation methods were evaluated, including evaporation, reverse osmosis, nanofiltration, and adsorption. The effects of such isolation procedures on NOM's chemical composition and reactivity were considered. Based on these studies, the report presents conclusions regarding the feasibility and adequacy of in situ and ex situ techniques. Croue is affiliated with Laboratoire de Chimie de l'Eau de l'Environnement, Université de Poitiers. Annotation copyrighted by Book News, Inc., Portland, OR. After years of technological development and its important achievements to make our life easier and more comfortable, human society is going to face one of the most difficult challenges of the last century: to stabilize the concentration levels of greenhouse gases in the atmosphere to prevent harmful effects on the climate system. Through a delicate balance between photosynthesis and respiration, terrestrial ecosystems, and in particular forests, are today thought to take up a significant part of the carbon dioxide emissions in the atmosphere, sometimes called the "terrestrial carbon sink". However, the location, magnitude, and vulnerability of the carbon dioxide sink of the terrestrial biota are still uncertain. The suite of traditional tools in

an ecologist's toolbox for studying ecosystem productivity and carbon balance include leaf cuvettes, whole-plant and soil chambers for gas exchange, and biomass and soil carbon inventories. While each of the cited methods has distinct advantages, they are limited with regards to their ability to measure net carbon dioxide exchange of the whole ecosystem across a variety of time scales. This book presents a compendium of results of a European project (EURO FLUX), funded by the European Commission through its fourth framework program, aiming to elucidate the role of forests in continental carbon balance. The Bryan/College Station (B/CS) region has been reported to have elevated concentrations of dissolved organic carbon (DOC) in surface water. Increased DOC concentrations are worrisome as DOC has been shown to be an energy source for the recovery and regrowth of *E. coli* and many watersheds are impaired by high bacteria levels. To examine the sources and fates of DOC in rural and urban regions to better understand DOC movement through the environment, seven watersheds were studied. To investigate source, streams were analyzed using diffuse reflectance near infrared spectroscopy (DR-NIR) and carbon isotopes. Fate of DOC was determined through monthly streams samples, gathered between March 2011 and February 2012, which were incubated for biodegradable DOC (BDOC). Soil in the region was sampled based on land use categories. Soil was analyzed for DOC and

BDOC as well as DOC adsorption, the other major fate of DOC. Above ground vegetation was sampled in conjunction with soil and analyzed for BDOC. Data indicated that fecal matter from cliff swallows provided considerable organic material to streams in the B/CS region as shown through DR-NIR. Carbon isotope values in streams ranged from $-23.5 \pm 0.7\%$ to $-26.8 \pm 0.5\%$. Stream spectra may be able to predict carbon isotope values in streams (Adj. $R^2 = 0.88$). Mean annual stream DOC concentrations ranged from 11 ± 3 mg/L to 31 ± 12 mg/L, which represents a significant decrease in DOC between 2007 and 2011. Concurrent increases in pH and conductivity were also recorded. The decrease in DOC and the increases in pH and conductivity may be due to impacts of high sodium irrigation tap water. Biodegradable DOC was low in streams, which is likely due to DOC being present in streams in refractory forms that are resistant to microbial breakdown. Soil chemistry, including soil adsorption, was greatly influenced by sodium. The elevated adsorption coefficients and release values seen in highly developed and urban open areas can be attributed to frequent exposure to high sodium irrigation water. The results indicate that sodium is a major driver of DOC in the system. Sound management decisions concerning irrigation water chemistry and urban development might eventually emerge to protect water quality as a result of this research. Among the most valuable natural ecosystems, estuaries and marshes are areas of

high productivity, have high economic value, and provide numerous ecosystem services. However, there is still uncertainty in marsh and estuarine carbon budgets and in our overall understanding of the drivers, composition, and fluxes of organic matter in these habitats. Part of this uncertainty is due to high spatial and temporal variability within these habitats and the range of methods used in previous studies. While the number of studies is increasing, there are still large gaps in our knowledge of marsh-estuarine interface dynamics. This study examined the concentrations, fluxes, and composition of particulate and dissolved organic carbon (POC, DOC) and dissolved inorganic carbon (DIC), with a focus on the temporal patterns and drivers of carbon pools at the marsh-estuarine interface. Taskinas Creek, a Chesapeake Bay National Estuarine Research Reserve, was chosen for this study as it provides a near-pristine location to measure current baseline data and is equipped with long-term water quality and meteorological monitoring stations that provided valuable ancillary data. Water samples were collected from Taskinas Creek from 2013 to 2018 to measure POC, DOC, and DIC concentrations, stable isotopes of carbon and nitrogen, colored dissolved organic matter (CDOM), and lipid biomarker compounds. Linear mixed effects (LME) modeling identified that the total suspended sediments were the primary driver of POC concentrations and marsh sources were the primary drivers of both DOC and DIC.

Measured carbon concentrations were then used to calculate carbon fluxes based on parameters measured via continuous water quality monitoring at Taskinas Creek, allowing for a high-frequency, long-term carbon flux record. On an annual basis, the marsh acted as a source of carbon to the York River (53 g C m⁻² y⁻¹) but the fluxes of the different pools of carbon differed in direction and magnitude. On a net basis, the York River was a source of organic matter to the marsh (58 to 77 g POC m⁻² yr⁻¹ and 3.9 to 18 g DOC m⁻² yr⁻¹) whereas DIC was exported from the marsh (114 to 193 g DIC m⁻² yr⁻¹). Stable isotopes, lipid biomarkers, and CDOM were used to determine the primary sources of organic matter at Taskinas Creek. Lipid biomarker and stable isotope analyses revealed that POC was primarily derived from algal sources, likely originating from the adjacent York River. In contrast, CDOM spectral measurements and stable isotopes of DOC and DIC indicated that dissolved carbon was primarily marsh-derived, and CDOM was primarily composed of humic-like and fulvic-like compounds. These results agree with previous studies conducted in similar habitats and within the York River estuary. The import of labile POC into the marsh and the export of DOC, DIC, and CDOM to the estuary can have important consequences for marsh and estuarine food webs, marsh surface stability, and the overall biogeochemistry of these habitats. The results found in this study can be used to improve carbon budget models by not

only providing current baseline carbon concentrations, but also the primary drivers and sources of these carbon pools. As these drivers and sources may face changes in times of future anthropogenic and climate change, understanding how they affect carbon pools can enable better predictions of how these carbon pools will change in the future. Rivers are an important pathway of organic carbon mobilization in the arctic, and their influence is projected to grow as precipitation and soil temperatures increase in response to high-latitude warming. This study addresses the bioactivity of arctic riverine dissolved organic carbon (DOC) in three North Slope Alaskan rivers: the Kuparuk, the Colville, and the Sagavanirktok. While lability experiments have previously been conducted during late summer discharge on arctic rivers, none have analyzed the early hydrograph spring-melt peak DOC. During the summer of 2006, water samples were taken from significant periods of the hydrograph (upswing, peak, downswing, and quasi-stable summer) of the three rivers for DOC lability experiments. DOC from spring melt discharge proved to be highly labile and therefore dynamically different from summer DOC. Over a three-month sample incubation period, these samples lost up to 40 and 33 percent of their DOC (with and without added nutrients, respectively) while samples taken later in summer lost merely 9 and 5 percent. As spring melt contributes half of the total annual discharge and DOC flux of winter-freezing

ivers, a significant portion of annual arctic DOC is labile and is therefore a large input of bioactive organic DOC to the Arctic Ocean carbon cycle. "The organic carbon (C) stocks contained in peat were estimated for a wetland-rich boreal region of the Mackenzie River Basin, Canada, using high-resolution wetland map data, available peat C characteristic and peat depth datasets, and geostatistics." -- Abstract Carbon dioxide, bicarbonate ion, and carbonate ion comprise the most important acid-base system in natural waters, and the equilibria between them regulate the pH of seawater, as well as most rainwater, stream water, river water, and groundwater. Carbon Dioxide Equilibria and Their Applications provides a clear, compact presentation of this topic, which is central to geochemistry and environmental engineering. It emphasizes a rigorous mathematical and thermodynamic basis for calculations and their application to realistic problems. The book's first four chapters present the basic equations, mathematical techniques for visualizing and manipulating them, and data on equilibrium constants and activity coefficients. These are presented in the general context of acid-base titration and solubility of CaCO₃. The remaining chapters show how these concepts and techniques are applied to geochemistry and oceanography, in addition to their applications to water conditioning. Specific topics discussed include acid rain, freshwater, seawater, carbonate sediments in the deep oceans, the

effects of increased atmospheric CO₂ on the oceans, estuarine waters, brines, hydrothermal solutions, pH adjustment, prediction of calcium carbonate saturation, corrosion inhibition, and water softening. Research conducted on the Waipaoa and Waiapu Rivers on the North Island of New Zealand has recognized and characterized geomorphologic and geochemical processes responsible for the control and delivery of sediment and associated OC to the adjacent margin. Clay mineral compositions from specimens of bedrock, volcanic soils and tephra, suspended river sediment, and recent marine sediments were studied. Identification of the clay minerals was made chiefly by X-ray (XRD), infrared (FTIR), and selective mineral dissolution analyses. Geochemical analyses included organic carbon (OC) concentrations and stable carbon isotopic compositions. Characteristic clay minerals indicative of bedrock contributions include chlorite and illite. Smectite and kaolinite are also present but in lesser quantities. Soil and tephra mineralogy could not be as easily quantified from x-ray diffraction due to the presence of poorly crystalline minerals (i.e. allophane). FTIR spectrometry proved to be a beneficial tool for the identification of clay minerals in the soil. Allophane and the higher concentration of smectite signify material being derived from the soils and tephra. Suspended sediment samples collected during moderate to high river flows exhibited a mixed clay mineral composition derived from both bedrock and

soil. Within the Waiapu River, bedrock contributions appeared to be greater due to gullying being the more dominant geomorphologic process. The Waipaoa River showed soil contributions to be as important as rock contributions. Recent marine sediments off the Waiapu River were similar in composition to the suspended Waiapu River sediment. Spatial variability in clay mineralogy associated with cross shelf transport reveal chlorite increases at the expense of illite off the Waiapu shelf. A downcore study was conducted on the Waipaoa shelf to examine temporal variability. The sediments in the flood layer and below resemble the river suspension, with smectite being the dominant clay min. Abstract: Chemical weathering of silicate bedrock and sediment in soil consumes atmospheric CO₂ and produces clay minerals that control organic carbon burial in river-dominated ocean margins. The high standing islands of Oceania, Papua New Guinea (PNG) in particular, are globally important sources of weathering and organic carbon fluxes. The Fly River is the largest river in PNG, and an important system to study in order to understand the global significance of this critical region. We measured the chemistry of bedrock, soils, sediment and solutes in the Fly River basin to understand weathering sources and fluxes from this system. Although weathering of carbonate rocks dominates the river's solute flux, weathering of silicates consumes 36-46 x 10⁹ mol/y of atmospheric CO₂ in our study area.

This amounts to the 6th highest area-normalized CO₂ consumption rate of the world's 60 largest rivers. The majority of the Fly River's solute flux is generated in the highlands, but sediments deposited in the floodplains of the system continue to mature chemically, consuming at least 1.8×10^9 mol/y of atmospheric CO₂ in the basin of the Middle Fly River, -5% of the river's total silicate CO₂ consumption. Along with silicate weathering, burial of organic matter is second major sink for atmospheric CO₂ on geologic time scales. Soil organic matter appears to be the largest source of particulate organic material (POM) delivered to the Gulf of Papua from the Fly River, while freshwater algae is a secondary source of POM. A 2.7‰ enrichment in the $\delta^{13}\text{C}$ of organic matter in the Fly River delta/clinoform compared to POM in the river itself is attributed to diagenetic remineralization of organic carbon in surface sediments of the delta/clinoform. The final chapter of this thesis focuses on the ancient carbon cycle, specifically during the Paleocene-Eocene Thermal Maximum. We see no peak in the concentration of sedimentary graphitic black carbon (GBC, a paleo-wildfire tracer). Furthermore, a shift in $\delta^{13}\text{C}$ of GBC indicates a recent, rather than fossil, organic matter source for this GBC. Our data appear to refute, but cannot rule out, biomass burning as the cause of the PETM. Climate-driven changes in Arctic hydrology and biogeochemistry are impacting transport of water and water-borne

material from land to ocean. This includes massive amounts of organic matter that are mobilized and exported from the pan-Arctic watershed via rivers each year. Dissolved organic matter (DOM), an important part of the Arctic carbon cycle, has received growing attention in recent years, yet long-term studies of riverine biogeochemistry remain rare in these remote and logistically challenging regions. Remote sensing of chromophoric dissolved organic matter (CDOM, the portion of the DOM pool that absorbs light), provides a unique opportunity to investigate variations in DOM in major Arctic rivers over multiple decades. CDOM is a useful proxy for dissolved organic carbon (DOC) and is essential to photochemical processes in surface waters. This dissertation presents the development and application of remote sensing regression models across six major Arctic rivers: the Kolyma, Lena, Mackenzie, Ob', Yenisey and Yukon. Frozen, archival samples of CDOM were used to develop calibration data for remote sensing regressions. Remote sensing methods estimated CDOM with R² of 85% across all rivers, although individual rivers varied in their predictability in association with sediment loading and hydrology. As with previous studies of Arctic systems, concentrations and export of CDOM and DOC were highest during spring freshet in most of these rivers. Interannual variability in DOM export may be linked to the Arctic Oscillation. Within the Mackenzie, Ob', and Yenisey rivers, observations of DOM

concentration and export were extended back to the 1980s, the first known empirical records of this length for Arctic rivers that span both continents. Although no pan-Arctic trends in CDOM export were detected, there is some evidence of long-term changes in riverine DOM. For example, discharge-specific CDOM concentrations decreased in the Yenisey River and increased in the Ob' River. Additionally, CDOM concentrations increased over the past ~30 years within the Mackenzie River. This dissertation also includes results from experiments used to quantify the effects of cryopreservation on CDOM analyses, and potential approaches for ameliorating freezing effects. These experiments showed that freezing for preservation introduces some error into CDOM measurements, although these effects vary between river systems. Sonication may improve CDOM measurements in some river systems, but the effects of both cryopreservation and sonication should be quantified on a case-by-case basis. Overall, this dissertation work demonstrates that 1) remote sensing of CDOM is a viable tool for tracking fluvial DOM in the major Arctic rivers, 2) only the Mackenzie River showed significant increases in CDOM concentration from the 1980s to present and 3) long-term changes in discharge-specific CDOM concentrations have occurred in the Yenisey and Ob' rivers. These long-term trends cannot be definitively linked to climate change, but may be related to effects of warming on permafrost, hydrology, and

biogeochemistry within in Arctic watersheds with consequences for carbon cycling on both regional and global scales. Inland freshwater ecosystems, though comprising a small portion of the earth's surface, are thought to be important in the global carbon (C) cycle. Carbon processing by heterotrophic microbes (bacteria) is a critical process, contributing considerably to overall ecosystem production and processing of dissolved organic carbon (DOC). This study assesses spatial variation in C processing by heterotrophic bacterioplankton in a semi-arid river network: the Rio Grande/Rio Bravo del Norte in Texas, USA. I examined how bacterial metabolism and C processing varied with spatial differences in physicochemical conditions and patterns in DOC lability in this highly impacted riverine network. Physicochemical and biological data were collected at 14 sites from March - December of 2010. I additionally analyzed phytoplankton biomass, bacterial density, bacterial community metabolic rates [bacterial respiration (BR), bacterial productivity (BP), and bacterial growth efficiency (BGE)], and C quality parameters at a subset of nine sites within this drainage. Across the drainage, hydrology and landscape position (i.e., biogeoclimatic conditions, presence of reservoirs, and groundwater contribution to flow) substantially influenced in-stream physicochemical conditions, leading to spatial patterns in bacterial density, phytoplankton biomass, and bacterial metabolism. Bacterial C

metabolism was influenced by both physicochemical and C quality - quantity gradients present within the drainage. Bacterial production and BR responded to different environmental gradients, with BP being driven by C quality and inorganic nutrients. This resulted in a negative correlation between BGE and the bacterial respiration of refractory C. Results from this study indicate that natural variation and anthropogenic impacts influence the physicochemical and biotic conditions across the Rio Grande/Rio Bravo del Norte drainage and these effects have implications for C sequestration, transformation, and transport, as well as for organic matter (OM) delivery to the Gulf of Mexico. The Congo River basin (CRB) is the second largest drainage basin on Earth after the Amazon in terms of discharge and basin area. It also contains the second largest area of rainforest (1.8 million km²) that also hosts the single largest peatland deposit found (145,500 km²) in the Tropics. The Cuvette Centrale is the quarternary "sag" basin found at the center of this basin that receives flows from all the principal tributaries located in the right bank, left bank and the upper Congo River. While a few studies of the hydrology, sediments and organic matter biogeochemistry of the CRB have been made, there is a need to better constrain the lateral fluxes of material that pass through the Cuvette in order to best understand its role in the basin biogeochemistry at a daily time step. With the aid of the Soil and Water Assessment Tool

(SWAT) hydrological model calibrated using scarce data, and validated with remote sensing products, biogeochemical and hydrological models, we have established the role of the Cuvette Centrale as a source of water to the main River during low flow periods for the 2000-2012 simulation period. Furthermore, an analysis of the sediment dynamics in the 2000-2012 period revealed that the Cuvette Centrale is capable of retaining over 23 megatons of material annually produced within the Cuvette Centrale and from upland sources. The models for DOC and POC revealed that hydrology and slope are primary controls on these fluxes. The results revealed that between 1.2 to 1.5 megatons of DOC is produced in the Cuvette Centrale with 0.9 megatons of POC retained in the Cuvette Centrale. At the basin outlet, a flux of 13.4 Mt yr⁻¹ for DOC and 2.2 Mt yr⁻¹ of POC was estimated, consistent with previous estimates. The flux, preservation, and accumulation of organic carbon in marine systems are controlled by various mechanisms including primary p- duction of the surface water, supply of terrigenous organic matter from the surrounding continents, biogeochemical processes in the water column and at the seafloor, and sedimentation rate. For the world's oceans, phytoplankton productivity is by far the largest organic carbon source, estimated to be about 30 to 50 Gt (10 tonnes) per year (Berger et al. 1989; Hedges and Keil 1995). By comparison, rivers contribute -1 about 0. 15 to 0. 23 Gt y of particulate organi.