Section I

Introduction

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An introduction to the biogeochemistry of river-coastal systems

T. S. Bianchi, M. A. Allison, and W.-J. Cai

1. Introduction

The coastal zone is a dynamic region where the rivers, estuaries, ocean, land, and the atmosphere interact (Walsh 1988; Wollast 1998; Liu et al. 2009; Cai 2011; Canuel et al. 2012). Although the coastal zone, as defined by the recent Land-Ocean Interactions in the Coastal Zone (LOICZ) project, comprises less than 20% of the Earth's surface, it contains greater than 40% of the human population, borders 75% of the megacities in the world, and yields 90% of the global fisheries (Crossland et al. 2005). Rivers provide connectivity between terrestrial and ocean environments, the two largest global sinks for atmospheric CO_2; however, this connectivity often is greatly modified in the coastal zone. The world's 25 largest rivers drain nearly half of the Earth's land surface and account for approximately 40% of the fluvial sediments and 50% of the freshwater entering the ocean (Milliman and Meade 1983; Meade 1996; Vorosmarty and Peterson 2000). However, studies of small and medium-sized rivers form the basis of most of our knowledge about how rivers function (Milliman and Farnsworth 2011).

A relatively comprehensive understanding about the flux, characteristics, and processing of carbon exists for smaller rivers, relative to the world's largest rivers, which are often in remote areas that are logistically challenging to study. In most cases, large rivers have been examined in an "expedition" mode. Our knowledge of carbon in these rivers is based on only a few field studies or relies on data collected at the last hydrological station of a river above the reach of tides, which is often hundreds of kilometers upstream from the ocean interface. Nevertheless, comparisons that have been made between small "flashy" rivers (e.g., Eel River [United States]) and larger systems such as the Amazon have shown the relative importance of storage and transit time on the composition of particulate organic carbon (POC) delivered to the continental margin (Blair et al. 2004). For example, in the Eel River system, there is "mass wasting" in the watershed, which delivers bedrock and vascular vegetation (as indicated by the $\delta^{13}C$-depleted values) from soils – with minimal transformation during transport to the coast (Blair et al. 2003). Conversely, the Amazon, which has a much larger watershed, with extensive storage and processing time of organic carbon (OC) in lowland soils, allows for enough time for the OC signature to be altered before being deposited and buried on the continental margin. In the present, riverine delivery of organic matter (OM) to continental margins is the dominant means by which terrigenous production is preserved, influencing global biogeochemical cycles and the ocean's ability to sequester atmospheric CO_2. The main premise of this introductory chapter is that

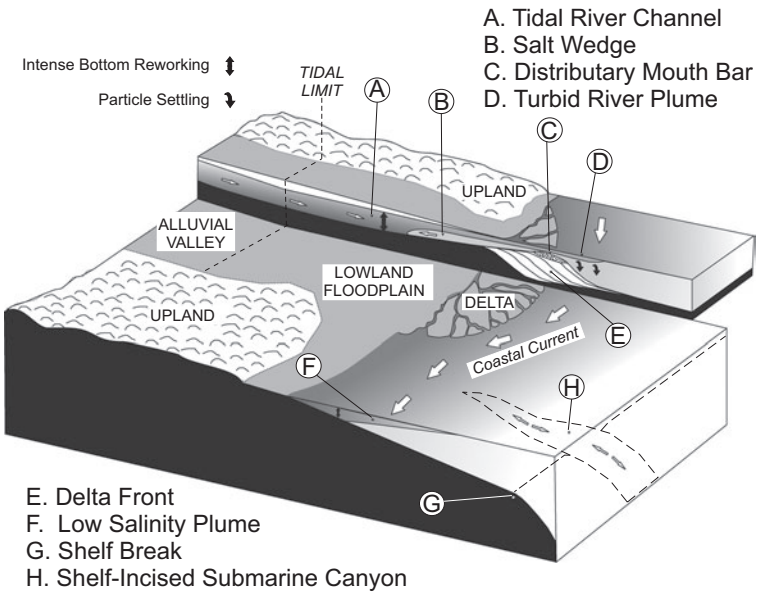

Figure 1.1. There are regional geomorphogical domains and associated sedimentary deposits with river-ocean mixing zone that have significant effects on biogeochemical processes in the coastal zone (modified from Bianchi and Allison, 2009).

the material flux from rivers has a profound impact on the biogeochemistry of the world's ocean and, through this river-ocean interaction, plays an important role in global biogeochemical cycles of elements such as carbon and nitrogen and in sediment delivery to the global ocean.

River systems and their directly affected coastal margin areas can be divided into three strongly interactive domains: (1) the drainage basin, extending from upland streams to the tidally influenced lower river; (2) the river-ocean mixing zone, extending from the tidally influenced freshwater portion of the river to the river mouth; and (3) the margin, which extends from the inner shelf, adjacent to the river mouth, to the shelf-slope break/canyon (Fig. 1.1). The river-ocean mixing zone, however, often extends to the shelf or further in the form of a low-salinity plume. The importance of large river source-to-sink systems to global OC burial (Hedges and Keil 1995) is evidenced by the sheer magnitude of material fluxes to the margin in these systems (Milliman and Farnsworth 2011). Our conceptual framework here is built on the idea that strong interactions and feedbacks between physical, geological, and biogeochemical processes control the net change in OC within the coastal zone (Fig. 1.1). For example, the position and intensity of the frontal zone between the freshwater outflow and marine water (controlled by the interaction of discharge, channel morphology, and tidal forcing) greatly influences the dominant sediment processes (e.g., flocculation, sorting, sinking, deposition, and resuspension) for a given time and space scale. These physical processes thus determine the microenvironment of particles, which in turn influences the rates and mechanisms of chemical alterations within the land-water interface. Understanding these complex interactions (and feedbacks) between processes is a critical first step toward building a predictive capability for estimating changes

in OM inputs to the ocean under changing global conditions – such as climate changes that result in an increase/decrease in precipitation and runoff, or changes in the magnitude and/or phasing of annual river hydrographs due to natural or anthropogenic causes (Arora and Boer 2001). By better understanding the processing of OM within the river-ocean mixing zone, we will be more fully prepared to predict how the global carbon cycle, including CO_2 fluxes between various carbon reservoirs, will be affected by river responses to global change.

2. Riverine inputs of particulate and dissolved organic matter to the coastal ocean

Approximately 87% of Earth's land surface is connected to the ocean by rivers (Ludwig and Probst 1998). The annual flux of carbon from rivers to the ocean is approximately 1 Pg C (1 Pg = 10^{15} g, or = 1 gigaton), which is of the same order as the global net ocean-atmosphere exchange of CO_2 (Mackenzie et al. 2004; Mackenzie and Lerman 2006 and references therein; Takahashi et al. 2009). Annually, rivers transport an estimated 20 Pg of fluvial sediments to the coastal margin (Meybeck 1982; Meade 1996). Associated with this sediment loading is an estimated 0.21 Pg of POC (Hedges and Keil 1995). Global estimates of the riverine flux of dissolved organic carbon (DOC) to the oceans range from about 0.25 to 0.36 Pg C y^{-1} (Meybeck 1981; Degens et al. 1991; Aitkenhead and McDowell 2000). Thus a terrestrial total DOC (TDOC) flux is about 0.5 Pg C y^{-1}, although a few others have suggested a much higher flux (see Cai 2011). In modern marine environments, riverine delivery of OM to continental margins is the dominant means by which terrigenous OM production is preserved (through burial), influencing global biogeochemical cycles and the ocean's ability to sequester atmospheric CO_2. However, there remains considerable uncertainty in our ability to adequately quantify carbon exchange from land to the coastal ocean and in our understanding of the processes influencing the fate of terrigenous carbon in coastal and deep sea sediments (Berner 1982; Sarmiento and Sundquist 1992; Hedges and Keil 1995; Schlünz and Schneider 2000; Galy et al. 2007, 2008; Hilton et al. 2010; Cai 2011; Galy and Eglinton 2011; Hilton et al. 2011).

2.1. The conundrum of missing OC

Berner (1989) suggested that most POC burial occurs in river deltas at a rate of 0.114 Pg C yr^{-1}. In contrast, little POC is buried in open ocean sediments (~0.006 Pg C yr^{-1}). Hedges and Keil (1995), however, suggested that POC burial in non-deltaic shelf sediments is equally as important as that in deltaic sediments (each ~0.070 Pg C yr^{-1}). Burdige (2007) further estimated an additional POC burial of 0.070 Pg C yr^{-1} in the 200- to 1,000-m depth range. In summary, among the 0.5 Pg C yr^{-1} of terrestrial POC export, no more than 25% to <50% (0.12 to 0.22 Pg C yr^{-1}) is found in marine sediments (also, isotopic signal of the POC suggests that they are only partially terrestrial). Therefore, one must conclude that most terrestrial POC is respired in sediments and water column via microbial decomposition and that the respiration occurs mostly in ocean margins, although we know little about the detailed pathway of terrestrial POC decomposition in ocean margins.

Interestingly, another conundrum in chemical oceanography over the past few decades has been that although the amount of DOC discharged by rivers can account for the renewal of DOC in the global ocean (every ~4,000–6,000 yr; Williams and Gordon 1970), riverine DOC, which is widely

believed to be composed of TDOC, is recognized as accounting for only a small fraction of oceanic DOC (Meyers-Schulte and Hedges 1986; Hedges et al. 1997; Opsahl and Benner 1997). Interestingly, there is two times as much C that is delivered to inland waters (1.9 Pg C yr^{-1}) than is delivered to the ocean (0.9 Pg C yr^{-1}) – suggesting that in these systems, C is consumed more actively than previously thought. Moreover, recent estimates of CO_2 efflux from streams and rivers suggest that TDOC is not as recalcitrant as previously thought (Cole et al. 2007 and references therein).

One possibility is the "priming" of OM degradation, a process discovered by Lohnis (1926), who revealed that rates of soil humus mineralization were enhanced by the addition of fresh organic residues. Although the importance of photodegradation and bacterial consumption of TDOC in freshwaters have been widely investigated, the role of priming processes has been totally ignored. Therefore, we propose that a focus on priming will transform our understanding of carbon cycling in inland and coastal waters. Past work has shown that during transport through the freshwater-marine continuum, TDOM is continually exposed to solar irradiance. Here, photoreactions convert chromophoric dissolved OM (DOM) to dissolved inorganic carbon (DIC) in a globally significant component of the carbon cycle (e.g., Kieber et al. 1990; Mopper et al. 1991; Miller and Moran 1997; Xie et al. 2004). Recently, it was observed that at the mouth of the Congo River, which delivers 12.4 Tg DOC yr^{-1} to the ocean (5% of the global DOC export by rivers), much of TDOC is altered by photoreactions to produce carboxylic-rich alicyclic molecules (CRAM) (Stubbins et al. 2010) – highly recalcitrant and ubiquitous components of oceanic DOM (Hertkorn et al. 2006). Other work has shown that bacterial consumption of modified lignin derivatives can be responsible for as much as 30% of the carbon photooxidation in surface waters of the Mississippi River plume (Hernes and Benner 2003). Recently, Bianchi (2011) suggested that priming is likely important in carbon transformations in many aquatic ecosystems, because recent work has shown much higher TDOC consumption in inland and coastal waters than reported in the past (Cole et al. 2007). This change in perception has occurred due to more extensive and accurate measurements of CO_2 fluxes and TDOC in inland waters (e.g., rivers lakes), confirming that TDOC, from soils and plant litter, is being consumed more efficiently than previously reported. This greater apparent stability may in part be the result of priming, which to date has not been investigated. Although priming studies have been conducted extensively in soil systems, research in aquatic systems has lagged considerably. Although mention of priming, or in some cases "cometabolism" effects, can be found in the aquatic literature, the process has largely been supported by superficial or equivocal evidence. We posit here that this process is more important than previously recognized in understanding coastal OM processing.

3. Transport processes and controls on OM preservation

Controls on the abundance of terrestrial and algal-derived POC in river/coastal systems include losses from in situ bacterial and photochemical breakdown, flocculation/sinking, and deposition followed by diagenesis in bed sediments (Amon and Benner 1996; Opsahl and Benner 1998; McKee and Baskaran 1999; Guo and Santschi 2000; Mannino and Harvey 2000; Mitra et al. 2000; Benner and Opsahl 2001; Duan and Bianchi 2006). Losses of terrestrial POC in river-dominated continental margins such as the Fly (New Guinea), Huang He or Yellow River (China), Columbia (United States), and Mississippi indicate globally significant losses of fluvial POM in these highly dynamic regions.

Another possible control on the loss of terrestrially derived OM in rivers is through the mixing of algal and terrestrial OM, which is believed to promote oxidation of the more refractory terrestrial material through the action of cometabolism or co-oxidation (Canfield 1994). OC in the lower Mississippi River consists of POC and DOC derived from both terrestrial and phytoplankton sources (Benner and Opsahl 2001; Bianchi et al. 2002, 2004; Duan and Bianchi 2006). The relative importance of these different sources is generally controlled by discharge and suspended particulate matter (SPM), whereby more phytoplankton occur during low-flow stages, when there is more light availability – nutrient limitation is generally not a controlling factor here (Duan and Bianchi 2006). The higher the abundance of phytoplankton-derived POC, the greater the contribution of phytoplankton-derived DOC will be during these low-flow periods (Bianchi et al. 2004). The influence of marine-derived phytoplankton also varies proportionally with the intensity of the frontal zone exchange processes – primarily as river discharge changes seasonally.

Coagulation processes are affected by factors such as ionic strength, particle size and composition, and the concentration of DOM – all of which show sharp concentration gradients in coastal zones where the salt wedge migrates between the lower river and the shelf. The abundance of bacterioplankton and phytoplankton can also affect rates of flocculation by producing polymers (e.g., mucopolysaccharides), to which particles can adhere (van Loosdrecht et al. 1990). These flocs can also selectively scavenge components of the DOM pool as they move through the water column, thereby altering the composition of DOM before it is released to the coastal ocean. Although the complex interaction of salinity, organic content, suspended particle concentration, and turbulence that determines floc size remains unresolved (Geyer et al. 2004), recent results suggest that flocs may form or reform rapidly in the tidal freshwater zone of rivers and have settling rates that could allow the riverine layer to be the source of the ephemeral mud deposits below the salt wedge (Galler and Allison 2008). Observations by Eisma (1996), Milligan and Hill (1998), and Hill et al. (2001) in coastal environments suggests that floc size is independent of turbulence at low to moderate energies and then decreases abruptly at higher turbulences.

The importance of large river source-to-sink systems to global OC burial (Hedges and Keil 1995) is evidenced by the sheer magnitude of material fluxes to the margin in these systems. Approximately 80% of the total OC preserved in marine sediments occurs in "terrigenous-deltaic" regions near river mouths (Romankevich 1984; Berner 1989). Bianchi and Allison (2009) posited that large river delta-front estuaries (LDE) are both "drivers" and "recorders" of natural and anthropogenic environmental change. However, despite the importance of these environments, there remains a fundamental lack of understanding about OC dynamics operating within these regions and how this influences the magnitude and character of OC exported offshore. This lack of understanding is primarily due to the high heterogeneity in the sources of OC, which include (1) primary production by phytoplankton, and (2) discharge of terrestrially derived OC (OC_{terr}) by rivers, as well as the complex architecture of margin environments influencing pathways and transport rates along and cross-margin.

Typically, when sediment and OC is transported across the shelf break to the slope, there is only modest early diagenesis taking place in the first few tens of centimeters below the sediment-water interface and have oxygen penetration depths of several centimeters that tend to increase with increasing water depth (e.g., Reimers et al. 1992; Cai and Sayles 1996). This reflects increased oxygen exposure time and extent of organic matter degradation (e.g., Hartnett et al. 1998; Hedges et al. 1999).

Notable exceptions are sediments found beneath highly productive overlying waters that have a high rain rate of POC, resulting in rapid and extensive diagenesis near the sediment-water interface, where formation of high concentrations of authigenic minerals is commonly observed (e.g., Rowe and Howarth 1985; Hedges and Keil 1995; Arthur et al. 1998).

There is now clear evidence from measurements of diagenetic processes that relatively rapid down-slope transport of OM, often associated with submarine canyons, can lead to significantly greater benthic metabolism and associated diagenesis than can be explained by POC input from overlying waters (e.g., Jahnke et al. 1990; DeMaster et al. 1994; Jahnke and Jahnke 2000). Studies such as those by Silverberg et al. (2000) and Arnosti and Holmer (2003) have also demonstrated that the intensity of diagenetic activity is often not well predicted by sediment total organic carbon (TOC) content and characteristics in continental margin sediments. These earlier studies provide sound examples of the importance of measuring diagenetic processes in association with the study of OM transport and deposition in slope environments. It has been shown that labile OM, likely produced by in situ diatom production in the Mississippi River plume, is rapidly transported to the Mississippi Canyon (Bianchi et al. 2006; Waterson and Canuel 2008; Sampere et al. 2008, 2011). Preliminary results suggest that productive LDEs, such as the Mississippi, may be important conduits for transporting fixed carbon from highly productive plume waters on the shelf to deeper benthic communities. Observations of an active benthic community within the Mississippi Canyon provide further support for this view (Bianchi et al. 2006). The pioneering work of Aller and his associates (e.g., Aller et al. 1996; Aller 1998; Aller and Blair 2006; Blair and Aller 2012) has shown the importance of mobile muds as an "incinerator" of OC and, in the proposed diagenetic studies, mobile muds are also inherently linked with the transport of OC offshore. Complementing this body of work, Arzayus and Canuel (2004) showed that degradation of more refractory OM was facilitated in mobile, physically mixed estuarine sediments.

Canyons are deep incisions of the continental shelf and slope. Despite their prevalence on both active and passive continental margins (Harris and Whiteway 2011), they remain understudied regions with respect to OC dynamics. One reason for this paucity of data is their complex wall and floor terrain, which results in high spatial variability and makes detailed OC studies based on only a few sediment cores difficult. Despite a rarity of in-depth OC studies, canyons are known to be (1) characterized by high faunal biomass, (2) important conduits for delivery and burial of OC in the oceans, and (3) "fast-track corridors" for sediment and carbon transported from land to the deep sea (Weaver et al. 2000; Liu and Lin 2004; Kiriakoulakis et al. 2011). The proximity and orientation of river mouth–canyon systems relative to alongshore sediment transport pathways lead to differences in the capture of riverine sediment and OC between large river source-to-sink systems (McKee et al. 2004; Walsh and Nittrouer 2009).

The OC and sediment connectivity between modern coastal systems and the deep sea has been the subject of considerable attention in recent years. For example, a primary goal of the National Science Foundation MARGINS Source-to-Sink program was to develop a quantitative understanding of sediment dispersal systems, including OC export from river mouth and shelf regions. Many large river margins are believed to export a relatively small volume of river-derived particulate matter seaward of the shelf break either due to (1) their location on wide, passive continental margins where deltaic sedimentation is confined to the inner shelf, or (2) because they are located where along-shelf–dominant coastal currents are present (McKee et al. 2004). This belief has led to the

prevailing view that sediments reach the continental slope through hemipelagic means (Shanmugam and Moiola 1985; Stow et al. 1985). However, it has been increasingly recognized that some large river margins (e.g., Sepik, Congo, Ganges-Brahmaputra, Eel, Rhone) are characterized by direct export of large volumes of sediment and OC to the lower continental margin due to either a (1) narrow (active continental margin) shelf (Kineke et al. 2000; Mullenbach and Nittrouer 2006); (2) progradation of the deltaic clinoform in the late Holocene near to the shelf edge (Coleman et al. 1998); (3) density-driven, cold shelf water (winter) advection (Puig and Palanques 1998); (4) landward incision of the associated submarine canyon so that it intercepts along-shelf transport pathways (Johnson et al. 2001; Michels et al. 2003); or (5) large-scale sediment remobilization from hurricane activity (Sampere et al. 2008, 2011).

4. CO_2 fluxes in coastal waters

Globally, estuaries are a major source of CO_2 to the atmosphere. In general, CO_2 degassing flux is more intensive in lower latitude estuaries than in high latitudes. Earlier estimates suggested that estuarine CO_2 degassing flux was as high as 0.5 Pg C yr^{-1}, equivalent to the annual riverine TOC flux (Borges 2005). More recently, it is generally agreed that the likely flux is about 0.25 Pg C yr^{-1}, even though both spatial and temporary resolutions of the available field measurements are low and thus uncertainty of the global flux synthesis is still high (Cai 2011 and references therein). In addition, the exact sources supporting this CO_2 degassing flux are unknown but include microbial decomposition of riverine terrestrial materials, inputs of high CO_2 soil and groundwater in the river basin, and inputs of both CO_2 and OC (and the subsequent respiration) from the coastal wetlands. Cai (2011) postulated that the latter is the major source supporting CO_2 degassing in low- to middle-latitude estuaries.

Beyond estuaries in the continental shelves, CO_2 is generally supersaturated with respect to the atmosphere in proximal areas (i.e., inshore and near-shore areas and the inner shelf, generally to about 20 m) but undersaturated in distal areas (middle and outer shelves to about 200 m) (Cai et al. 2006). In addition, although shelves located in middle and high latitudes have lower surface water pCO_2, those in tropical and subtropical areas have higher pCO_2. Our knowledge of CO_2 distribution and flux in the continental shelves has improved rapidly in the past decade, although further improvement is still needed (Borges 2005; Cai et al. 2006; Chen and Borges 2009). The current consensus is that net global continental shelf sea-air CO_2 flux is an uptake of 0.25 Tg C yr^{-1} from the atmosphere (Cai 2011). Synthesis also revealed a striking latitudinal contrast in shelf sea-air CO_2 flux. Present-day shelves located between 30° and 90° are sinks of atmospheric CO_2 with a total uptake flux of 0.35 Pg C yr^{-1}, whereas those located from 0 to 30° are sources of CO_2 to the atmosphere with a total release flux of 0.10 Pg C yr^{-1} (Cai et al. 2006).

5. Possible links between coastal water CO_2 flux and riverine loadings

Rivers bring both inorganic nutrients and OC to the coastal zone and thus can influence metabolic state, carbon cycle, and air-sea CO_2 flux differently. In principle, terrestrial TOC loading drives the oceanic systems toward net heterotrophy, as it is eventually decomposed to CO_2. However, dissolved inorganic nitrogen (DIN) flux should lead coastal waters to net autotrophy because the use of DIN

in the ocean by phytoplankton leads to net synthesis of OC and net removal of CO_2. Globally, gross terrestrial "heterotrophic loading" greatly exceeds that of the "autotrophic loading" (Table 1–1, Cai 2011). However, in a few mid-latitude large rivers near population centers, for example, the Mississippi River, such loading ratios are more toward net autotrophy because of human-induced nutrient loadings (Cai and Lohrenz 2010). Most importantly, the relative terrestrial loadings have been altered in the past, in particular, recently from Holocene to Anthropocene. Historically, TOC loading had been increased over many centuries as humans expanded their occupation of the earth surface, but has been decreased substantially in the past century as humans built dams and reservoirs (Syvitski et al. 2003, 2005). Most noticeably, inorganic nutrient loadings, which have been increased greatly in many rivers, can potentially alter the trophic state of the affected coastal zones. However, the net role of this increased nutrient loading is unclear, as eventually most nitrogen nutrient is denitrified in coastal waters (Seitzinger et al. 2006).

It is also noted that rivers deliver freshwater, carbon, and sediments to the ocean unevenly (Borges 2005; Cai et al. 2006; Cai 2011). About two thirds of the terrestrial OC is supplied to lower latitude coastal oceans (Ludwig et al. 1996). In addition, it appears that OC is better preserved in cold high-latitude river delta sediments than in warm low-latitude marine sediments (de Haas et al. 2002). For example, terrestrial OC burial is ~50% in the Mackenzie River delta but less than 20% in the Amazon (de Haas et al. 2002; Showers and Angle 1986) and the Mississippi (Cai and Lohrenz 2010) systems. It is thus not unreasonable to speculate that lower latitude coastal oceans would release more CO_2. If 75% of the OC delivered to low-latitude coastal oceans is decomposed there, then this alone would generate a CO_2 flux of 0.25 Pg C yr^{-1} (note that two thirds of the global OC is delivered to the low-latitude margins; e.g., 0.5 Pg C yr^{-1} × 2/3 × 75%; see also Keil et al. [1997] for a similar estimate). Therefore, the observed air-sea CO_2 flux pattern in coastal estuaries and shelves are consistent with the nature of river inputs. However, with climate change resulting in greater flooding in some coastal regions, for example, coastal river plume regions that are typically net sinks for CO_2 (see Cai 2011; Cai et al. Chapter 7 of this book), recent work has shown that a large flooding event, such the flood of 2011 into the northern Gulf of Mexico, can be changed for a short period of time into a net CO_2 source with high loading and bacterial consumption of TDOC (Bianchi et al. 2013).

6. Directions for future research

In the coming decades, predicted changes in global climate are likely to have a dramatic impact on sediment and OC delivery of large rivers to the global ocean. Alteration to the magnitude and character of materials arriving from the drainage basin as a result of changing precipitation patterns, denudation rates, and land use are likely to even more strongly override biogeochemical processes in the coastal zone. Although existing studies outlined in the following chapters suggest that these changes to the OC budget of the oceans and atmosphere will be profound, a new generation of process studies will be necessary to quantify these impacts. By necessity, these studies will have to be coupled with a more comprehensive monitoring of key parameters in the lower rivers, coastal zone, and margin far-range areas.

One extreme example of the two central issues discussed in this book – land-ocean connectivity and impact of climate changes – can be found in Arctic rivers. First, although the Arctic Ocean