

# The Role of Coastal Zones in Global Biogeochemical Cycles

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The unique and dynamic coastal ocean is a significant source and sink of a multitude of atmospheric species of importance to global biogeochemical cycles and climate. The transition zone between land and ocean, including the atmosphere as a medium for the exchange of matter and energy, is characterized by a strong physical-biogeochemical coupling, resulting in an inherently complex system. Important biogeochemical exchanges occurring in the coastal zone involve water, nutrients (e.g., nitrogen, phosphorous, iron, and silica), salts (e.g., chlorine, bromine, and iodine), carbon (e.g., dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), particulate organic carbon (POC), and carbon dioxide ( $\text{CO}_2$ )), reactive organic trace gases (e.g., nitrogenous, halogenated, and sulfurous hydrocarbons), and inorganic trace gases (e.g., nitrous oxide,  $\text{N}_2\text{O}$ ).

Coastal zones are of particular importance to humans, as they are characterized by high per area productivity and are responsible for the majority of the world's fish catch. In addition, coastal ecosystems play an important role in the global carbon cycle as large fluxes of carbon and carbon-related tracers move between the land, ocean, and atmosphere in these regions. Most of the world's population lives near coastal zones, and anthropogenic changes and related climate change in these regions can pose serious consequences not only for fisheries but also for global biogeochemical cycles.

A workshop was convened to bring together junior scientists from universities and the National Center for Atmospheric Research (NCAR) to discuss the role of the coastal zone in global biogeochemical cycles. The workshop took place in the summer at NCAR in Boulder, Colorado, and was sponsored by NCAR's Early Career Scientist Assembly (ECSA) and Advanced Study Program.

The main discussions centered on identifying a research agenda within the following topics: (1) How do coastal zones impact the carbon cycle? (2) How do coastal zones impact atmospheric chemistry and aerosols? Subtopics within these themes included how coastal ecosystems can be represented in global models and how humans affect coastal zone biogeochemistry.

The complexity of coastal zones was evident at the onset of the meeting as discussions focused on defining the extent of the coastal zone. A broad definition of the coastal zone as the interface between the land and ocean can also include continental shelves, estuaries, bays, coastal upwelling areas, and terrestrial shoreline ecosystems. More precise boundaries can be delineated when put in the context of specific processes.

## *Coastal Zone Impacts on the Carbon Cycle*

The role of the coastal zones and continental margins in the global carbon cycle is poorly understood. Recent studies in the East China

Sea and off the west coast of Europe have suggested that these regions play a significant role in the global carbon cycle. Although the preanthropogenic coastal zone may have been a net  $\text{CO}_2$  source to the atmosphere due to the large riverine inputs of inorganic carbon and organic carbon that is quickly remineralized, more recent studies suggest that coastal zones are global net sinks for atmospheric  $\text{CO}_2$ . Overall, coastal zones represent the largest unknown fluxes in the oceanic carbon budget. This uncertainty is caused by the difficulty in measuring the small net fluxes of  $\text{CO}_2$  compared with gross fluxes in the coastal zone, and by the poor resolution of coastal zones in the global analysis and modeling of net air-sea exchange.

## *Coastal Zone Impacts on Atmospheric Chemistry and Aerosols*

Coastal zones can influence atmospheric chemistry through the transfer of biogenic trace gases and sea-salt aerosols to the atmosphere. The coastal oceans are the dominant marine sources of some climatically significant gases (e.g.,  $\text{N}_2\text{O}$ , carbonyl sulfide, and methane). Coastal ecosystems are also major sources for several halogenated compounds that can influence atmospheric ozone chemistry and possibly also influence new particle production in coastal areas.

In a larger context, this direct influence on atmospheric composition and aerosol formation from biogenic trace gases can affect Earth's radiative balance. Conversely, atmospheric chemistry can influence the coastal zones through the deposition of inorganic (e.g., nitrate, ammonium) and organic nitrogen species. Nitrogen deposition to the coastal zones can change the productivity in the coastal areas and potentially lead to large enhancements in coastal  $\text{N}_2\text{O}$  emissions.

## *Feedbacks and Human Interactions*

Coastal regions cannot be studied independent of their adjacent environments. They are, for example, dynamically coupled to the open ocean through physical processes. Winds and currents along the coastline result in mesoscale eddies, meandering jets, and squirts (one-way jets) causing transport of coastal waters to the open ocean with varying degrees of magnitude. Surface drifters show about a 2-week transport time for the movement of coastal water to hundreds of kilometers offshore. In turn, open-ocean waters are returned to the coast within a larger-scale onshore flow.

Biogeochemical processes influencing coastal regions include riverine and groundwater inputs, atmospheric inputs, benthic interactions of nutrients (including denitrification), suspension of sediments, upwelling, and sediment burial. The carbon budget in the coastal zone is strongly coupled to nitrogen

dynamics which are controlled by these processes. Anthropogenic inputs of nitrogen are predominantly the result of agriculture and the burning of fossil fuels. However, the forms of nitrogen and their transport to the coastal zone (e.g., runoff versus atmospheric) are very different for these two sources. Upwelling in coastal zones can be a large source of  $\text{CO}_2$ -rich waters, but it is not well known how much of this  $\text{CO}_2$  is eventually fixed by biological processes.

The pronounced heterogeneity of these coastal zones results in complicated biological responses. To understand the carbon cycling in the coastal zone, we need to accurately determine these biological responses and food web structures. Key to progress in these areas is the development of new remote and in situ observation systems.

Riverine inputs are exceptional sources of freshwater, particulate matter, and dissolved chemical species (organic and inorganic) to coastal regions. Most of this input occurs near the equator (the three largest rivers, Amazon, Congo, and Orinoco, discharge within  $10^\circ$  of the equator and account for nearly two thirds of the global sum) or in the northern hemisphere. Remote sensing images indicate a large-scale biological response due to the impact of these large rivers. Clear patterns of chlorophyll-*a*, phytoplankton abundance, and chromophoric dissolved organic matter (CDOM) are evident in these plumes. There is also a succession of phytoplankton species as these plumes travel out into the open ocean and age.

The coastal regions are also under the influence of intensified atmospheric deposition. This deposition can include both major macronutrients (e.g., nitrate, ammonium, and phosphate) and trace nutrients (e.g., iron). These loadings vary dramatically both regionally and seasonally; for example, anthropogenic atmospheric sources of nitrate and ammonia in North America result in their enhanced deposition to the coastal Atlantic region off the eastern seaboard. The coastal regions downwind of Asia also include enhanced atmospheric deposition of anthropogenic nitrate and ammonia, but with a strong dust component from arid regions of Asia. This mineral dust can be a source of micronutrients (e.g., iron) to these coastal regions.

## *Future Directions*

Obtaining global estimates of the importance of the coastal zone requires extrapolation of our knowledge from limited regions to large regions. Unfortunately, our main tool for doing this, global modeling, has difficulty in simulating the coastal zones with all of their heterogeneities. To represent coastal zones in global models, a classification system based on biogeographical factors is needed. We need to determine which coastal processes are relevant on a global scale and whether these processes can be parameterized and resolved in global models. One method for incorporating coastal processes into largescale (not yet global)

models is to embed coastal models with finer resolutions (temporal and spatial) into the larger-scale models.

We know that many biogeochemical aspects of the coastal zones are globally significant and directly relevant to human activity, but there is much more to be learned. We need to understand the influence of the coastal zone on the global carbon cycle. We need to better constrain the physical and biological processes that control trace gas exchange. The role of anthropogenic nutrient inputs in trace gas emissions is particularly important. There are also regions in the coastal zones, such as salt marshes and mangrove swamps, that are still relatively understudied with respect to these

processes. Remote sensing is also showing us that major rivers have a strong influence on biological processes far into the ocean basins.

There is clearly a strong need to better constrain the role of the coastal zones in biogeochemical cycles and feedbacks. Observations and models both will contribute to improving our understanding of the coastal zone with respect to the carbon budget, trace gas emissions, and influence on atmospheric chemistry and aerosols. New observation systems with better spatial and temporal resolution will help us to understand the heterogeneity of the coastal zone, define their various types, and parameterize their functions in global models. With improved prognostic modeling,

we can explore mechanisms of current variability and predict future change.

The University Corporation for Atmospheric Research (UCAR)/NCAR Junior Faculty Forum on Future Scientific Directions was held 23–25 June 2004, at NCAR in Boulder, Colorado.

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## Future Applications of Thorium-234 in Aquatic Ecosystems

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A fundamental and outstanding issue in marine biogeochemistry is understanding the mechanisms that control and enhance the flux of material from the surface ocean to depth. "Sinking particles" are the ultimate removal mechanism of many biologically and particle reactive elements from the ocean. This includes atmospheric carbon, which is converted from CO<sub>2</sub> to particulate phases during biological production and sequestered to deep waters via particle sinking. Unfortunately, the temporal and spatial magnitude of the sinking particle flux remains an elusive and difficult process to study.

Over the past decade, thorium-234 has increasingly been used to quantify particle fluxes from surface waters in both open-ocean and coastal environments. Thorium-234 ( $t_{1/2} = 24.1$  days) is a particle reactive radionuclide that is produced in seawater by radioactive decay of its dissolved conservative parent, <sup>238</sup>U. In principle, the disequilibrium between <sup>238</sup>U and the measured total <sup>234</sup>Th activity reflects the net rate of particle export from the surface ocean on timescales of days to weeks. Thus, <sup>234</sup>Th should serve as an integrative tracer that is relatively forgiving in terms of biological patchiness and temporal heterogeneity. Furthermore, it enables multiple sample collection at a suite of depths throughout the water column, enabling a closer examination of particle flux and remineralization patterns.

In spite of advances in sample collection, analytical methods, and technology, there remain a number of important questions concerning <sup>234</sup>Th speciation, reactivity, sample collection and analysis, and modeling strategies that affect our interpretation of <sup>234</sup>Th disequilibrium. The uncertainties and debate regarding these issues need to be resolved if <sup>234</sup>Th is going to continue to be successfully applied as an in situ tracer for the export of particulate organic carbon (POC) and associated biogenic and other particle reactive elements.

In August 2004, over 40 researchers from the United States, Europe, India, Australia, and China met at the Woods Hole Oceanographic Institu-

tion in Woods Hole, Massachusetts, for a workshop on the Future Applications of <sup>234</sup>Th in Aquatic Ecosystems (FATE). The purpose of the workshop was to bring together a number of international experts in the collection, analysis, and interpretation of <sup>234</sup>Th in aquatic ecosystems with diverse opinions and backgrounds. Geochemists not directly involved in <sup>234</sup>Th measurements were also present to provide outside perspective into the current status and future directions of <sup>234</sup>Th research. A number of students also attended the meeting and acted as scribes to record comments and ideas put forward during the working group sessions.

The participants were asked to discuss and define current issues in the use of <sup>234</sup>Th as well as a coherent strategy for future endeavors. Invited talks (available at <http://www.geol.sc.edu/cbnelson/Thmeeting/Index.htm>) focused on four main areas (see below) and set the stage for in-depth discussions. A brief overview of the working group discussions is presented here.

### Methodologies and Techniques

There are currently a number of techniques available for the measurement of <sup>234</sup>Th. These techniques have inherent strengths and weaknesses that are not necessarily clear to those outside the <sup>234</sup>Th community. Guidance and a consensus on where and when each method should or should not be used is needed, including specific recommendations regarding sample size and collection methods, preconcentration techniques, the use of yield monitors, counting procedures, and error analysis.

In addition, there are currently no specific <sup>234</sup>Th standards available for intermethod and interlaboratory comparisons. This is due in part to the fact that <sup>234</sup>Th has a very short half-life and is therefore not amenable to being distributed as a standard reference material. Many laboratories calibrate <sup>234</sup>Th to deep-water samples and assume equilibrium with <sup>238</sup>U (which is in turn derived from salinity).

However, sediment resuspension, deep-sea migrating zooplankton, and even the abundance

of deep particle layers, such as those produced from hydrothermal systems, may cause <sup>234</sup>Th:<sup>238</sup>U disequilibria in some instances. Small disequilibria in surface waters are common, and uncertainties in calibration assumptions can result in large errors in the <sup>234</sup>Th flux.

Given the wide range of procedures currently in use for the measurement of <sup>234</sup>Th activity, the community should strive to rigorously define analytical procedures that can be compared using standardized materials, such as aged seawater rather than deep seawaters. This includes the calibration of equipment for specific sample types, i.e., particles, and geometries being measured.

### Collection and Application of Particulate Organic Carbon/<sup>234</sup>Th Ratios

In order to convert <sup>234</sup>Th fluxes into export of a particular element of interest, it is necessary to quantify the elemental to <sup>234</sup>Th ratios of sinking particles at a given reference depth. The most common application is in determining the export of POC. POC/<sup>234</sup>Th ratios may vary widely depending on the geographical location, bloom versus nonbloom conditions, and collection technique (i.e., in situ pumps versus sediment traps).

While POC/<sup>234</sup>Th ratios may vary greatly within the upper 100 m and within coastal areas, evidence presented at the meeting provided convincing arguments that there is much less variability in open-ocean settings at depths just below the euphotic zone. The group agreed that at these depths POC/<sup>234</sup>Th ratios are often within a factor of 2–3. At least some of this range in the ratio of POC/<sup>234</sup>Th at depth is due to natural variability, but there are also differences in the POC/<sup>234</sup>Th ratio depending on the method of collection that needs to be further evaluated.

In essence, the thorium community has inherited the same issues encountered by the sediment trap community; there is no unbiased mechanism for collecting a representative "sinking particle." The group suggested that following specific protocols in the collection of particulate <sup>234</sup>Th will reduce the range and uncertainty of POC/<sup>234</sup>Th measurements and allow for better intercomparisons between data sets. Further characterization of samples using simultaneous particle collection by