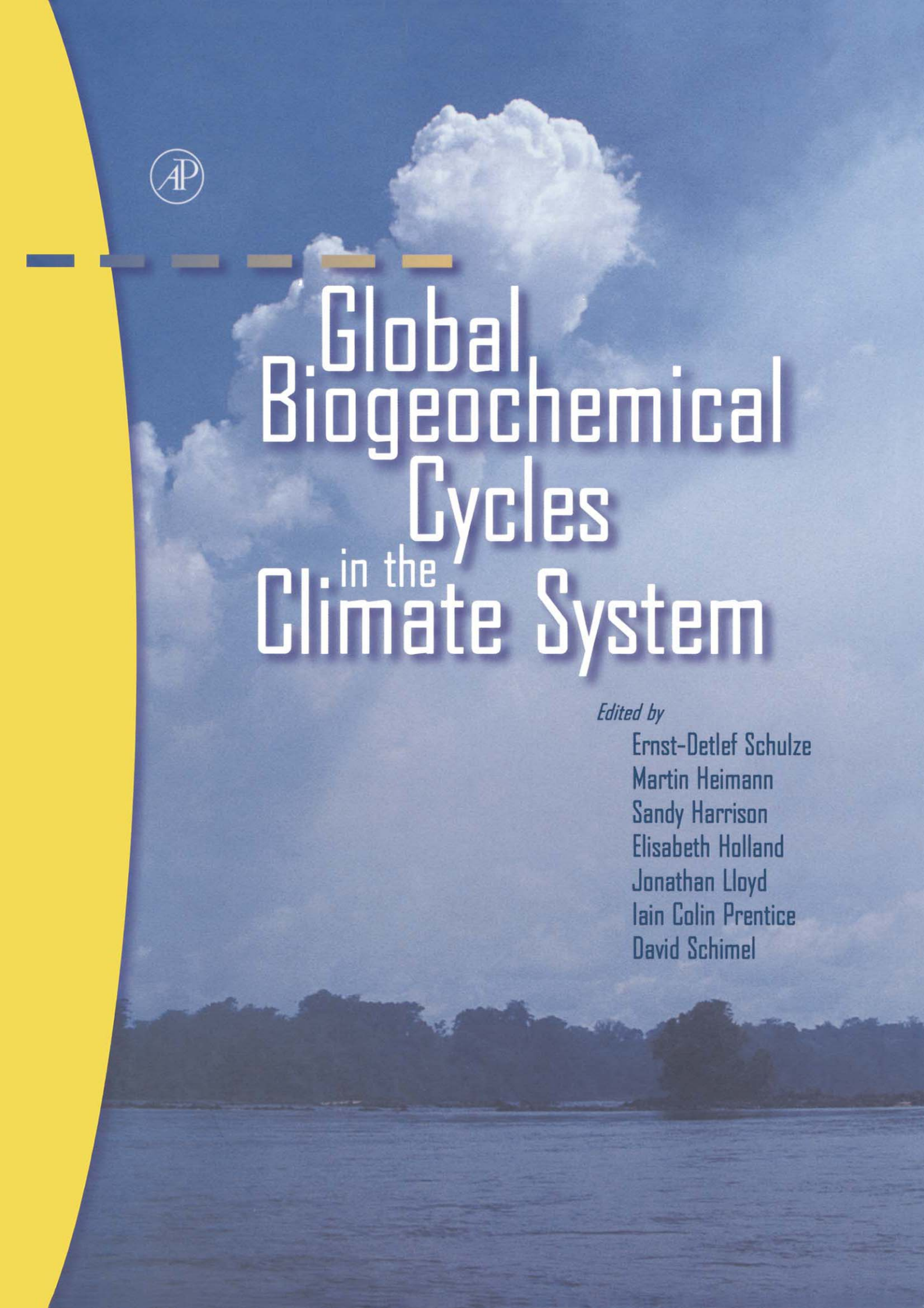
Global Biogeochemical Cycles in the Climate System
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Foreword

Especially during the past century, land use changes and agricultural and industrial activities have been growing so rapidly that their effects on the environment, including the chemical composition of the global atmosphere have become clearly noticeable on all scales. The first realization of the possibility of global effects was connected with the growth of the "greenhouse" gas carbon dioxide measured by C. D. Keeling and R. Revelle, on the basis of these measurements they stated that humanity had embarked on a global geophysical experiment potentially leading to climate warming. Other human-caused global disturbances in the atmosphere were discovered thereafter. In 1971 attention was called to the possible loss of stratospheric ozone, caused by NO_x catalysts in the exhaust of supersonic aviation. The projected large fleets of aircraft were never built. However, in 1974 an already existing, but late recognized threat to the ozone layer by ClO_x radicals produced in the stratosphere by the photochemical destruction of entirely man-made chlorofluorocarbon (CFC) gases was hypothesized and later confirmed by atmospheric observations. In fact, in 1985, scientists were caught totally by surprise when researchers of the British Antarctic survey reported much larger springtime ozone depletions, than originally estimated, on the order of 30%. It was found that the ozone loss was largest at altitudes between about 12 and 22 km, exactly the height region in which, under undisturbed conditions, maximum ozone concentrations had always been measured. At this location, it had always been thought that ozone was chemically inert. Since then, the "ozone hole" has grown in area and depth, so that by this year's spring total ozone had declined by more than 50% over a region three times the size of the United States. A couple of years of intensive research efforts showed that a chemical instability had developed, involving formation of ClO_x catalysts on ice particles under sunlit conditions, followed by rapid ozone destruction. The combination of special natural factors in early spring, cold temperatures, and availability of sunlight, together with about six times larger than natural loadings of chlorine gases, had led to this chemical instability over the Antarctic. Since 1996 the production of CFC gases on the industrial world has been forbidden. I have dwelled in this issue in some detail for two reasons. First, international political action would not have been taken without convincing scientific evidence that the CFC emissions were the cause of the heavy ozone loss. Second, it will be particularly important to determine where the world's complex environmental system may be most vulnerable to human perturbation. For this purpose, modeling alone will be far from sufficient. Surprises are not excluded, as the ozone hole story so drastically has demonstrated.

In the 1970s the substantial impact of the bioshpere on atmospheric chemistry was also realized. First, the main natural loss of stratospheric ozone occurs through reactions involving NO_x radicals that derived photochemically from the oxidation of N_2O, a by-product of the biological nitrogen cycle in soils and waters. Second, it was discovered that tropospheric ozone and its photochemical by-product, hydroxyl, are much influenced by chemical chain reactions involving CH_4 and other hydrocarbons, carbon monoxide, and NO_x. All these gases have both natural and anthropogenic sources. This is of the greatest importance, as the hydroxy1 radicals, also called the "detergent of the atmosphere," to a large degree determine the chemical composition of the atmosphere by reacting with almost all gases that are emitted by natural processes and human activities.

In addition to being chemically active in the stratosphere and troposphere, several of the afore-mentioned and other gases serve as "greenhouse gases," thereby significantly adding to the climate warming caused by CO_2. On the other hand, aerosol particles, in particular, sulfates derived by the oxidation of largely anthropogenic SO_2 from oil and coal burning, have a cooling effect on climate.

The estimation of the impact of various kinds of human activities on atmospheric chemistry and climate clearly requires a good understanding of the natural and anthropogenic sources of large number of trace gases, as well as particulate matter, and the biological processes creating them. This research not only deals with the present and future, but also profits much from the vast amount of information regarding climate parameters and chemical composition of the atmosphere cores that is deposited in sediments and in ice. The latter data clearly show that the biosphere does not counteract climate change in some Gaian fashion. On the contrary, during earlier glacial periods all greenhouse gases were less abundant in the atmosphere than during the interglacials. This research has received special international, political attention in connection with the proposed Kyoto protocol to reduce the emissions of CO_2 caused by fossil fuel burning and deforestation. As was the case with the CFC regulations, effective CO_2 emission control measures will rely also on a strong scientific base. It was the realization of these strong needs, requiring improved knowledge especially about the biogeochemical cycles of C, N, S, P, and trace compounds such as iron, that led to the creation of a Max Planck Institute for Biogeochemistry. During the initial discussions, involving the cream of the international, biogeochemical, and climate community, the proposal received enthusiastic endorsement, emphasizing the uniqueness of the institute on the global scence. The proposal was also well received by the scientific members and the senate of the Max Planck Society. The search for directors and key scientific personel of the institute proved highly successful, with several key recruitments coming from overseas, clearly showing the enthusiasm accompanying the creation of the institute.

The MPI for Biogeochemistry in Jena is one of several Max Planck Institutes involved in global change research. This book, based on the presentations given to celebrate the first anniversary of the institute shows many important examples of the breadth and excitement of Global Change research around the world, including legal/political aspects. I hope that the so successful creation sets an example and promotes initiatives elsewhere to enhance biogeochemical research efforts, and its connections to ecology, climate and atmospheric chemistry. Many Happy Returns.

Dr. Paul Crutzen

Preface

Biogeochemistry: The Jena Perspective

In the late 20th century, biogeochemistry emerged as a new discipline in which the biological, physical, and human sciences collaborate (CGCR, 1999; Schlesinger, 1997). Biological, because the chemical cycles of the planet are mediated by life (Table 1). Physical, because of the strong coupling between climate and atmospheric composition so evident in the glacial–interglacial record of the ice cores (Fig. 1). And, human, because of the massive human disruption of the planet's carbon and nitrogen cycles by fossil fuel burning (which produces CO_2 and a range of volatile nitrogen compounds) (Fig. 2).

From the three figures, one gets an overview of the way in which the field of biogeochemistry has emerged. The evidence for the importance of biology in the composition of the atmosphere (Fig. 2) was deduced from geochemical measurements of air enabled by advances in analytical technology. The chemistry of the atmosphere and the discipline of atmospheric chemistry provided a view of the biosphere not accessible from "within" the discipline. The atmosphere reflects biotic processes operating over "deep" time as well as processes operating on rapid time scales (especially with respect to the oxidized N species). Some compounds, especially the hydrocarbons, may reflect plant–insect coevolution, and so to understand the atmosphere requires a deep understanding of biology. When insights into atmospheric chemistry were combined with emerging ecosystem studies of nitrogen and other elements (e.g., Vitousek and Reiners, 1977), a paradigm emerged that enriched both ecology and geophysics (Andreae and Schimel, 1989).

The realization that ecosystem biogeochemistry and climate were dynamically coupled was nascent for most of the 20th century. The ice-core records showing the coordinated rhythm of temperature, CO_2, and methane provided conclusive evidence of interactions (Fig. 2). The ice cores show coupled changes in trace gases and climate. They preserve a tantalizing body of information about leads, lags, and amplification that is not yet fully unravelled. While variations in CO_2 are strongly governed by changes in ocean circulation, mass balance considerations and isotopes suggest land-ecosystem changes as well (Indermuhle *et al.*, 1999). Climate effects on terrestrial biogeochemistry are demonstrated by the patterns in methane (produced in terrestrial wetlands and ungulate mammals) and nitrous oxide. High-resolution records showing high-frequency changes in ice cores, and detailed records of the Holocene provide information on timescales tractable, or nearly so, in analysis using today's biogeochemical models. Again, the perspective from geophysical records provides a view of ecosystem processes different from, and most strongly complementary to, the paradigms emerging from within the discipline.

The scientific community was galvanized by the Mauna Loa curve of increasing carbon dioxide and the political ramifications of this scientific result will echo for the foreseeable future (Benedick, Chapter 26 of this volume). Geophysical measurements provide a trans-disciplinary view of human processes. Since biogeochemistry has a "basic science" character and remains concentrated in academia, the carbon and nitrogen cycles would be of far less interest without the challenges of carbon and climate change, acid rain, and tropospheric ozone increase. The Mauna Loa curve challenges both the policy-relevant and intellectual sides of biogeochemistry. The policy side is obvious—the rate of increase in atmospheric CO_2 is the index of humanity's export of carbon to the atmosphere.

Scientifically, the fraction of CO_2 released to the atmosphere that remains as CO_2 in the air (about half) is not yet explained on the basis of incontrovertible measurements. While the holy grail of explaining the "missing sink" grows asymptotically closer, the political stakes and hence the standard of proof required are growing. The interannual variability of the growth rate of CO_2 gives evidence of climate–carbon interactions. Subtle year-to-year variations in the increase in CO_2 reflect changes in land and ocean uptake. The measurement and modeling tools to understand these changes are emerging and provide a direct means of understanding how climate affects the carbon system at large scales. Changes in the carbon system are reflected also in changes in the pole-to-pole gradient of CO_2. That gradient reflects the balance of sources and sinks on large scales. Because the equilibration time (the interhemispheric transport time) is about a year, changes in the gradient are another source of information about interannual variability. The seasonal cycle of CO_2 provides information about the seasonal activity of the biosphere. Because the phase and amplitude of the seasonal cycle vary spatially (Fig. 3), they provide rich information about land ecosystems. To date, we cannot fully separate changes in carbon uptake (photosynthesis) and release (respiration) to provide unique explanations for the seasonal cycle and its variation. This remains a research challenge.

1. Research Challenges

The discipline of biogeochemistry confronts a wide array of scientific and methodological challenges, as is evident in the balance of this book. These are not limited to the cycles of carbon and nitrogen, but include the role of phosphorus, iron, calcium, aluminum, and acidity, to name just a few. In this section, I will identify four cross-cutting challenges that illustrate aspects of the science.

1.1 Large-Scale Carbon Sinks: Detection and Attribution

The problem of the terrestrial missing sink remains. Where and why is there net uptake in terrestrial systems? The two questions,

TABLE 1 Chemical Composition of the Atmosphere

Constituent	Chemical formula	Volume mixing ratio in dry air	Major sources and remarks
Nitrogen	N_2	78.084%	Biological
Oxygen	O_2	20.948%	Biological
Argon	Ar	0.934%	Inert
Carbon dioxide	CO_2	360 ppmv	Combustion, ocean, biosphere
Neon	Ne	18.18 ppmv	Inert
Helium	He	5.24 ppmv	Inert
Methane	CH_4	1.7 ppmv	Biogenic and anthropogenic
Hydrogen	H_2	0.55 ppmv	Biogenic, anthropogenic, and photochemical
Nitrous oxide	N_2O	0.31 ppmv	Biogenic and anthropogenic
Carbon monoxide	CO	50–200 ppbv	Photochemical and anthropogenic
Ozone (troposphere)	O_3	10–500 ppbv	Photochemical
Ozone (stratosphere)	O_3	0.5–10 ppm	Photochemical
Nonmethane hydrocarbons		5–20 ppbv	Biogenic and anthropogenic
Halocarbons (as chlorine)		3.8 ppbv	85% anthropogenic
Nitrogen species	NO_y	10 ppt–1 ppm	Soils, lightning, anthropogenic
Ammonia	NH_3	10 ppt–1 ppb	Biogenic
Particulate nitrate	NO_3^-	1 ppt–10 ppb	Photochemical, anthropogenic
Particulate ammonium	NH_4^+	10 ppt–10 ppb	Photochemical, anthropogenic
Hydroxyl	OH	0.1–10 ppt	Photochemical
Peroxyl	HO_2	0.1–10 ppt	Photochemical
Hydrogen peroxide	H_2O_2	0.1–10 ppb	Photochemical
Formaldehyde	CH_2O	0.1–1 ppb	Photochemical
Sulfur dioxide	SO_2	10 ppt–1 ppb	Photochemical, volcanic, anthropogenic
Dimethyl sulfide	CH_3SCH_3	10–100 ppt	Biogenic
Carbon disulfide	CS_2	1–300 ppt	Biogenic, anthropogenic
Carbonyl sulfide	OCS	500 pptv	Biogenic, volcanic, anthropogenic
Hydrogen sulfide	H_2S	5–500 ppt	Biogenic, volcanic
Particulate sulfate	SO_4^{2-}	10 ppt–10 ppb	Photochemical, anthropogenic

where and why, cannot be separated. Different parts of the world and differing ecosystem types are influenced by differing nitrogen additions, disturbance, and pollution. Answering the question "why is there a sink" requires explaining the differences between climate zones, management, and disturbance regimes and chemical climate. This is a practical problem because, in the future, there will be increasing pressure to manage carbon sinks. How can sinks best be induced and sustained? How can the effects of intentional measures be quantified and verified? What impacts does managing ecosystems for carbon storage have on other ecosystem goods and services, including diversity? Without scientific understanding, no intelligent design of management systems can emerge. Equally important is the fact that without scientific consensus there can be no political will to implement expensive management systems. Carbon science must integrate a basic understanding of process with powerful measurement techniques. Models are also required that have the credibility to be used in what-if exercises to aid in designing new management systems. Local models are crucial because sinks must be long lasting and management systems to store carbon must aim at a decadal to centennial timescale. The agronomic paradigm of "test plots" is needed but limited in utility because of timescale. Large-scale models are needed to test the global effect of an international regime, including the stability of induced ecosystem sinks to potential changes in the chemical, physical, and human environment.

1.2 New Methods for Measurement

Measurement capability has been a continual challenge to the carbon research community in accomplishing the ambitious goals. The foundation of carbon cycle research lies in stable absolute calibration, an initial priority of the Keeling Mauna Loa effort and a persistent feature of the community. New measurements, such as of stable and radio-isotopes, the O_2/N_2 ratio, and remote sensing have been developed and adopted by the community. Techniques for dealing with spatial heterogeneity are also in rapid evolution: these include ecosystems studies, local eddy covariance flux measures, mesoscale aircraft and tall-tower techniques, and continental to global inverse modeling techniques (Valentini *et al.*, 2000). As the scope of large-scale biogeochemical research expands beyond a carbon cycle and greenhouse gas focus, techniques will need to be developed for the spatial-temporal integration of a range of processes. It is likely that new techniques will be needed for the study of airborne and waterborne nutrient transport as in gas, suspended and dissolved water-borne and aerosol phases. Techniques for spatial integration of belowground processes are crucial—there still exist only rudimentary measures for root growth and soil C and N turnover at or above the plot scale (Valentini *et al.*, 2000). Continuing adoption and endogenous development of measurement and data analytical techniques is a priority for biogeochemistry.