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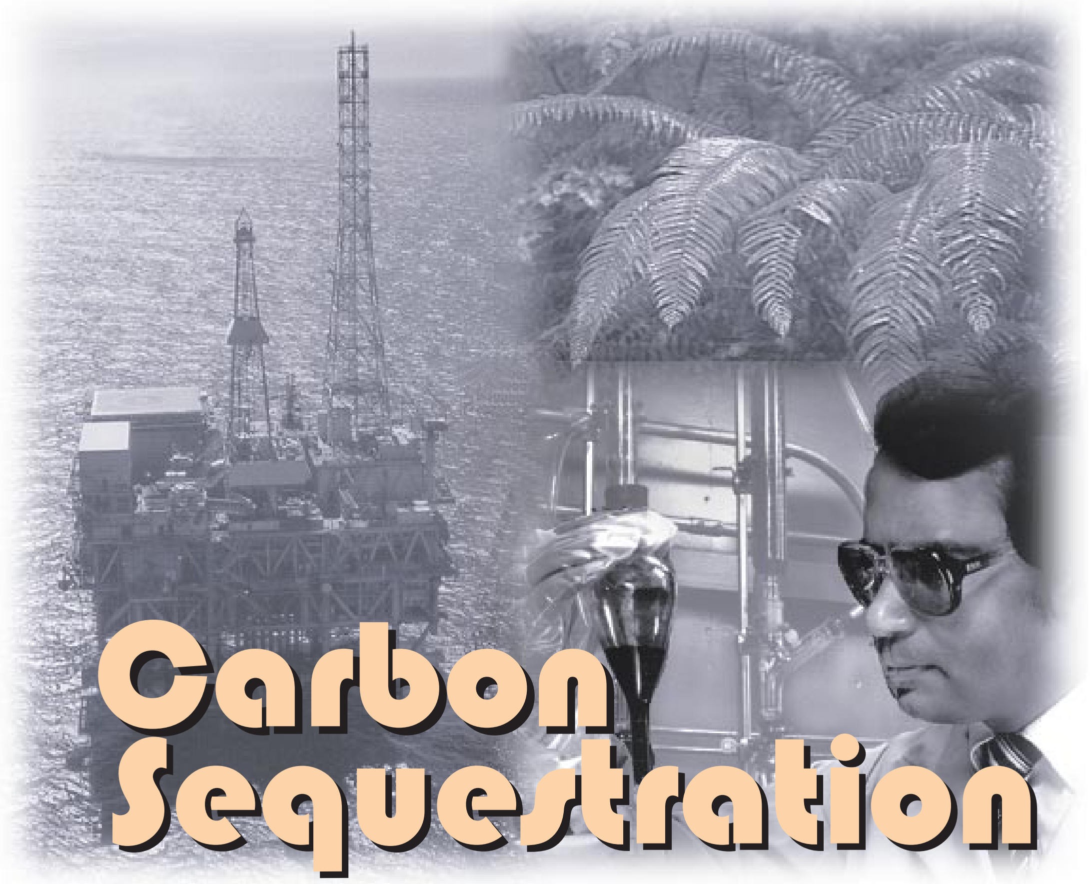

Carbon Sequestration

State of the Science

A working paper for *roadmapping*
future carbon sequestration R&D

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WORKING PAPER ON CARBON SEQUESTRATION SCIENCE AND TECHNOLOGY

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ABBREVIATIONS, ACRONYMS, AND INITIALISMS

BER	Office of Biological and Environmental Research (DOE)
BES	Office of Basic Energy Sciences (DOE)
CO	carbon monoxide
CO_2	carbon dioxide
DEA	diethanolamine
DOE	U.S. Department of Energy
EOR	enhanced oil recovery
ESA	electrical swing adsorption
FACE	Free Air CO_2 Enrichment
GtC	billion tonnes of atmospheric carbon
H_2	hydrogen gas
HNLC	high-nutrient, low-chlorophyll (ocean waters)
IEA	International Energy Agency
IGCC	integrated gasification combined cycle
IPCC	Intergovernmental Panel on Climate Change
m	meter
MBARI	Monterey Bay Aquarium Research Institute
MDEA	methyldiethanolamine
MEA	monoethanolamine
MIT	Massachusetts Institute of Technology
MPa	million Pascal (a measure of pressure)
nm	nanometer
NO_x	oxides of nitrogen
OCMIP	Ocean Carbon-Cycle Model Intercomparison Project
OGCM	ocean general circulation model
PCAST	President’s Council of Advisors on Science and Technology
POC	particulate organic carbon
ppm	parts per million
PSA	pressure swing adsorption
R&D	research and development
ROV	remotely operated vehicle
SO_x	oxides of sulfur
TSA	thermal swing adsorption

EXECUTIVE SUMMARY

Predictions of global energy use in the next century suggest a continued increase in carbon emissions and rising concentrations of carbon dioxide (CO_2) in the atmosphere unless major changes are made in the way we produce and use energy—in particular, how we manage carbon. For example, the Intergovernmental Panel on Climate Change (IPCC) predicts in its 1995 "business as usual" energy scenario that future global emissions of CO_2 to the atmosphere will increase from 7.4 billion tonnes of carbon (GtC) per year in 1997 to approximately 26 GtC/year by 2100. IPCC also projects a doubling of atmospheric CO_2 concentration by the middle of next century and growing rates of increase beyond. Although the effects of increased CO_2 levels on global climate are uncertain, many scientists agree that a doubling of atmospheric CO_2 concentrations could have a variety of serious environmental consequences.

One way to manage carbon is to use energy more efficiently to reduce our need for a major energy and carbon source—fossil fuel combustion. Another way is to increase our use of low-carbon and carbon-free fuels and technologies (nuclear power and renewable sources such as solar energy, wind power, and biomass fuels). Both approaches are supported by the U.S. Department of Energy (DOE) and are not the focus of this report.

The third and newest way to manage carbon, capturing and securely storing carbon emitted from the global energy system (carbon sequestration), is truly radical in a technology context. The development of today's fossil energy-based system is rooted in the Industrial Revolution. For over 200 years, the development of energy technology has been focused on lowering costs through increased efficiency to support economic growth. Because of their abundance, availability, and high energy content, coal, oil, and natural gas have proved to be attractive energy sources to produce electricity, run industrial processes, propel transportation vehicles, and provide energy for residential and commercial applications. As fossil energy use increased and adverse environmental effects became apparent, energy technology also evolved to minimize them. However, all of this enormous technology development has assumed that the free venting of CO_2 to the atmosphere was environmentally harmless. Only recently has the increasing concentration of CO_2 in the atmosphere been considered to represent a serious environmental problem. The consequence is that we have developed an intricate, tightly coupled energy system that has been optimized over 200 years for economy, efficiency, and environmental performance, but not for the capture and sequestration of its largest material effluent, CO_2.

The goal of this report is to identify key areas for research and development (R&D) that could lead to an understanding of the potential for future use of carbon sequestration as a major tool for managing carbon emissions. Under the leadership of DOE, researchers from universities, industry, other government agencies, and DOE national laboratories were brought together to develop the technical basis for conceiving a science and technology road map. That effort has resulted in this report, which develops much of the information needed for the road map.

This report identifies the R&D topics necessary to understand and develop critical options for the capture, transport, conversion, and sequestration of carbon. It addresses known sources of carbon (industrial sources, power plant flue gases, preprocessed fossil fuels before combustion); carbon forms for sequestration (CO_2, elemental carbon, and minerals that contain carbon); and options for sequestration sinks—oceans, geologic formations, soils and vegetation (see Chaps. 3 through 7).

THE ROAD MAP VISION AND GOALS

The vision for the road map is to

Possess the scientific understanding of carbon sequestration and develop to the point of deployment those options that ensure environmentally acceptable sequestration to reduce anthropogenic CO_2 emissions and/or atmospheric concentrations. The goal is to have the potential to sequester a significant fraction of 1 GtC/year in 2025 and 4 GtC/year in 2050.

The purpose of carbon sequestration is to keep anthropogenic carbon emissions from reaching the atmosphere by capturing them, isolating them, and diverting them to secure storage and/or to remove CO_2 from the atmosphere by various means and store it. Any viable system for sequestering carbon must be safe, environmentally benign, effective, and economical. In addition, it must be acceptable to the public.

Why is carbon sequestration important? Given the magnitude of carbon reductions needed to stabilize the atmosphere, capture and sequestration could be a major tool for reducing carbon emissions to the atmosphere from fossil fuels; in fact, sequestration may be essential for the continued large-scale use of fossil fuels. It will allow greater flexibility in the future primary energy supply. In addition, it could offer other benefits such as the manufacture of commercial products (e.g., construction materials and plastics); improved agricultural practices that could reduce soil erosion, conserve water, and increase the sustainability of food production; the restoration of wetlands, which would help preserve wildlife and protect estuaries; increased biodiversity; enhanced recovery of oil and methane (from coal beds); and the development of exportable technologies to help the U.S. economy.

THE GLOBAL CARBON CYCLE AND FOSSIL FUELS

Most anthropogenic (human-activity-related) emissions of carbon to the atmosphere result from combustion of fossil fuels for the economical production of energy. If the demand for energy continues to increase, it is possible that the only way that fossil fuels can be used for large-scale energy production is through the development and implementation of carbon capture and sequestration options.

Given the magnitude of carbon emission reductions needed to stabilize the atmospheric CO_2 concentration, multiple approaches to carbon management (i.e., improved energy efficiency and clean energy systems) will be needed. All potentially important technical options should be explored.

SCIENTIFIC AND TECHNICAL NEEDS FOR CARBON SEQUESTRATION

STRATEGIC ISSUES

Following are the general recommendations of the report addressing strategic issues regarding a comprehensive carbon sequestration program.

- Sequestration R&D could expand the world's future options for dealing with greenhouse gases.
- Many carbon sequestration options are particularly amenable to improving existing activities—such as CO_2 injection during secondary oil recovery—and often provide important secondary benefits, such as improving ecosystems during reforestation.
- Some carbon sequestration options, such as improved agricultural practices, are available practically immediately. Examining ongoing, field-scale sequestration investigations in terrestrial, geological, and ocean systems can provide critical experience for designing the necessary environmental research programs.
- Some carbon sequestration options that have limited capacity or relatively short carbon residence times could nonetheless make important near-term contributions during a transition to other longer-term carbon management options. Other carbon sequestration options can provide significant long-term contributions.
- For carbon sequestration to be a viable option, it needs to be safe, predictable, reliable, measurable, and verifiable; and it needs to be competitive with other carbon management options, such as energy-efficient systems and decarbonized energy technologies.
- Carbon sequestration is an immature field, so multiple fundamental R&D approaches are warranted and significant breakthroughs can be expected. The federal government is an appropriate sponsor of carbon sequestration R&D.
- Integrated analyses of the carbon sequestration system should be periodically updated to evaluate the potential contributions, costs, and benefits of various carbon sequestration options.
- The information from the R&D program should be provided to policy makers to aid them in developing policy and selecting the most efficient and effective solutions to the issues of climate change.

Separation and Capture of CO_2 from the Energy System

Several currently available technologies can be used to separate and capture CO_2 from fossil-fueled power plant flue gases; from the effluents of industrial processes such as iron, steel, and cement production; and from hydrogen production by reforming of natural gas. However, these technologies have not been applied at the scale required to use them as part of a CO_2 emissions mitigation strategy. CO_2 can be absorbed from gas streams by contact with amine-based solvents or cold methanol. It can be removed by adsorption on activated carbon or other materials or by passing the gas stream through special membranes.

Geologic or ocean storage sequestration options that use a concentrated source of CO_2 require low-cost carbon separation and capture techniques to be viable options. The scale of the industrial system required to process gigatonnes of carbon warrants investigation into new solvents, adsorbents, and membrane separation devices for either pre- or post-combustion separation.

Advanced methods might include adsorbing CO_2 on zeolites or carbon-bonded activated carbon fibers and separating it from flue gases or process gases from industrial operations using inorganic membranes. The use of commercial CO_2-removing processes that scrub gases with amine-based solvents is projected to raise the cost of producing electrical power from coal-fired power plants using existing technology. Capture and sequestration could increase the cost of electrical power generation from coal by as much as 20 to 30 mills/kWh. Thus, although CO_2 separation is done routinely, dramatic improvements are necessary to make the process economical (Chap. 2). Techniques will be needed to transform the captured CO_2 into materials (1) that can be economically and safely transported and sequestered for a long time or (2) that can be used to make commercial products (e.g., construction materials) that could offset the costs of separation and capture.

There are numerous options for the separation and capture of CO_2, and many of these are commercially available. However, none has been applied at the scale required as part of a CO_2 emissions mitigation strategy, nor has any method been demonstrated for all the anthropogenic sources considered in this R&D map. Many issues remain regarding the ability to separate and capture CO_2 from anthropogenic sources on the scale required, and to meet the cost, safety, and environmental requirements for separation and capture. In our assessment of the scientific and technological gaps between the requirements for CO_2 separation and capture and the capabilities to meet these requirements, many explicit and specific R&D needs were identified.

- A science-based and applications-oriented R&D program is needed to establish the efficacy of current and novel CO_2 separation processes as important contributors to carbon emissions mitigation. Important elements of such a program include the evaluation, improvement, and development of chemical and physical absorption solvents, chemical and physical adsorbents, membrane separation devices with selectivity and specificity for CO_2-containing streams, molecular and kinetic modeling of the materials and processes, and laboratory-scale testing of the selected processes.

- Field tests are needed of promising new CO_2 separation and capture options in small bypass streams at large point sources of CO_2, such as natural gas wells and hydrogen production plants.

Sequestration in the Oceans

The ocean represents a large potential sink for sequestration of anthropogenic CO_2 (Chap. 3). Two methods are proposed for the sequestration of carbon in the ocean: (1) A relatively pure CO_2 stream that has been generated by a power plant, decarbonized fuel production system, or industrial facility could be injected

The ocean provides a large potential reservoir. Active experiments are already under way in iron fertilization and other tests of enhanced marine biological sequestration, as well as deep CO_2 injection. Improvements in understanding marine systems will be needed before implementation of major marine sequestration campaigns.

directly into the ocean. The injected CO_2 may become trapped in ocean sediments or ice-like solids, called hydrates. (2) The net oceanic uptake from the atmosphere could be enhanced through a method such as iron fertilization. These approaches will require better understanding of marine ecosystems to enhance the effectiveness of applications and avoid undesirable consequences.

- Field experiments of CO_2 injection into the ocean are needed to study the physical/chemical behavior of the released CO_2 and its potential for ecological impact.
- Ocean general circulation models need to be improved and used to determine the best locations and depths for CO_2 injection and to determine the long-term fate of CO_2 injected into the ocean.
- The effect of fertilization of surface waters on the increase of carbon sequestered in the deep ocean needs to be determined, and the potential ecological consequences on the structure and function of marine ecosystems and on natural biogeochemical cycling in the ocean need to be studied.
- New innovative concepts for sequestering CO_2 in the ocean need to be identified and developed.

Sequestration in Terrestrial Ecosystems

The terrestrial biosphere is a large and accessible reservoir for sequestering CO_2 that is already present in the atmosphere. Natural carbon fluxes are huge, so that even small forced changes resulting from R&D advances would be very significant. It will be important to address the consequences of altering the natural flux.

Terrestrial ecosystems, which are made up of vegetation and soils containing microbial and invertebrate communities, sequester CO_2 directly from the atmosphere (Chap. 4). The terrestrial ecosystem is essentially a huge natural biological scrubber for CO_2 from all fossil fuel emissions sources, such as automobiles, power plants, and industrial facilities. Computer models indicate that terrestrial ecosystems—forests, vegetation, soils, farm crops, pastures, tundras, and wetlands—have a net carbon accumulation of about one-fourth (1.5 to 2 GtC) of the 7.4 GtC emitted annually into the atmosphere by fossil fuel combustion and land use changes. If there were an increased focus on practices to enhance the natural carbon cycle, the potential for terrestrial ecosystems to remove and sequester more carbon from the atmosphere could be increased by, for example, improving agricultural cultivation practices to reduce oxidation of soil carbon and enhancing soil texture to trap more carbon, and protecting wetlands.

- The terrestrial ecosystem is a major biological scrubber for atmospheric CO_2 (present net carbon sequestration is ~2 GtC/year) that can be significantly increased by careful manipulation over the next 25 years to provide a critical "bridging technology" while other carbon management options are developed. Carbon sequestration could conceivably be increased by several gigatonnes per year beyond the natural rate of 2 GtC per year, but that may imply intensive management and/or manipulation of a significant fraction of the globe's biomass. However, those potentials do not yet include a total accounting of economic and energy costs to achieve these levels. Ecosystem protection is important and may reduce or prevent loss of carbon currently stored in the terrestrial biosphere. The focus for research, however, should be on increasing the rate of long-term storage in soils in managed systems.

- Research on three key interrelated R&D topics is needed to meet goals for carbon sequestration in terrestrial ecosystems:
    - Increase understanding of ecosystem structure and function directed toward nutrient cycling, plant and microbial biotechnology, molecular genetics, and functional genomics.
    - Improve measurement of gross carbon fluxes and dynamic carbon inventories through improvements to existing methods and through development of new instrumentation for in situ, nondestructive below-ground observation and remote sensing for aboveground biomass measurement, verification, and monitoring of carbon stocks.
    - Implement scientific principles into tools such as irrigation methods, efficient nutrient delivery systems, increased energy efficiency in agriculture and forestry, and increased byproduct use.

- Field-scale experiments in large-scale ecosystems will be necessary to understanding both physiological and geochemical processes regulating carbon sequestration based upon integrative ecosystem models. Such carbon sequestration experiments are needed to provide proof-of-principle testing of new sequestration concepts and integration of sequestration science and engineering principles.

Sequestration in Geologic Formations

Limited geological sequestration is being practiced today, but it is not yet possible to predict with confidence storage volumes and integrity over long time periods. Many important issues must be addressed to reduce costs, ensure safety, and gain public acceptance.

Three principal types of geologic formations are widespread and have the potential for sequestering large amounts of CO_2. They are active and uneconomical oil and gas reservoirs; aqueous formations; and deep and unmineable coal formations. About 70 oil fields worldwide use injected CO_2 for enhanced oil recovery. CO_2 sequestration is already being practiced in a sub-seabed reservoir in the North Sea of Norway. The United States has sufficient capacity, diversity, and broad geographic distribution of potential reservoirs to use geologic sequestration in the near term (Chap. 5). The primary uncertainty is the effectiveness of storing CO_2 in geological formations—how easily CO_2 can be injected and how long it will remain. Only through experience will enough knowledge be gained to assess the ultimate sequestration potential of geologic formations.

- Fundamental and applied research is needed to improve the ability to understand, predict, and monitor the performance of sequestration in oil, gas, aqueous, and coal formations. Elements of such a program include multiphase flow in heterogeneous and deformable media; phase behavior; CO_2 dissolution and reaction kinetics, micromechanics and deformation modeling; coupled hydrologic-chemical-mechanical-thermal modeling; and high-resolution geophysical imaging. Advanced concepts should be included, such as enhancement of mineral trapping with catalysts or other chemical additives, sequestration in composite geologic formations, microbial conversion of CO_2 to methane, rejuvenation of depleted oil reservoirs, and CO_2-enhanced methane hydrate production.

- A nationwide assessment is needed to determine the location and capacity of the geologic formations available for sequestration of CO_2 from each of the major power-generating regions of the United States. Screening criteria for choosing suitable options and assessing capacity must be developed in partnership with industry, the scientific community, and public and regulatory oversight agencies.

- Pilot-scale field tests of CO_2 sequestration should be initiated to develop cost and performance data and to help prioritize future R&D needs. The tests must be designed and conducted with sufficient monitoring, modeling, and performance assessment to enable quantitative evaluation of the processes responsible for geologic sequestration. Pilot testing will lay the groundwork for collaboration with industrial partners on full-scale demonstration projects.

Advanced Biological Processes

> Advanced biological techniques may produce options too radical to predict. Some biologic processes can sequester carbon products at low cost. New carbon sequestration options could become feasible and others could be improved using advanced biological techniques.

Advanced biological processes (Chap. 6) could be developed and implemented to limit emissions and capture and sequester carbon from both relatively concentrated utility and industrial combustion gases, as well as from dispersed point sources. Bacteria and other organisms could be used to remove carbon from fuels and to recycle carbon from man-made waste streams. In addition, crop wastes and dedicated crops could be used as feedstocks for biological and chemical conversion processes to manufacture fuels and chemicals. Advanced crop species and cultivation practices could be designed to increase the uptake of atmospheric CO_2 by terrestrial and aquatic biomass and decrease CO_2 emissions to the atmosphere from soils and terrestrial and aquatic biomass.

The 21st Century has been referred to as the "Century for Biology." Indeed, many new molecular tools have been developed that will aid in new discoveries and assist in providing solutions to key problems facing humankind and the planet. The difference that advanced biological techniques can make will be evident when they are integrated with land, subsurface, and ocean management practices. The following recommendations will promote cost-effective and stable biological solutions to carbon sequestration.

- Research should be initiated on the genetic and protein engineering of plants, animals, and microorganisms to address improved metabolic functions that can enhance, improve, or optimize carbon management via carbon capture technology, sequestration in reduced carbon compounds, use in alternative durable materials, and improved productivity.

- The objectives and goals of the advanced biological research should be linked to those specific problems and issues outlined for carbon sequestration in geological formations, oceans, and soils and vegetation so that an integrated research approach can elucidate carbon sequestration at the molecular, organism, and ecosystem levels.

- Short-, mid-, and long-term goals in advanced biological research should be instituted so that scale-up issues, genetic stability in natural settings, and efficacy in the field can be assessed.

Advanced Chemical Approaches

> Most carbon sequestration options rely on chemical reactions to achieve benign, stable, and inert products. Studies to enhance the relevant chemistry almost certainly will reduce the costs or increase the effectiveness of these options. Results from R&D on advanced chemical topics also may make it possible to generate useful and marketable byproducts.

Many of the sequestration technologies described in this document depend on chemistry. Improved methods of separation, transport, and storage of CO_2 will benefit from research on and development of advanced chemical techniques to address sequestration via chemical transformations (Chap. 7). Any viable sequestration technique must store vast amounts of carbon-rich materials, so environmental chemistry will be valuable to determine whether these materials will be stable when sequestered. Many issues pertaining to aqueous carbonate/bicarbonate chemistry are relevant to sequestration of carbon in oceans, geological formations, and groundwater. Carbonate chemistry in very basic solutions may lead to a method for extracting CO_2 from air. Clathrates, compounds that can enclose molecules such as CO_2 within their crystal structure, may be used to separate CO_2 from high-pressure systems. Learning clathrate properties may be important to understanding chemical approaches to ocean storage of carbon, and subsurface arctic and marine hydrate formations may also be evaluated as geologic sequestration options.

- The proper focus of R&D into advanced chemical sciences and technologies is on transforming gaseous CO_2 or its constituent carbon into materials that either are benign, inert, long-lived and contained in the earth or water of our planet, or have commercial value.
  - — Benign by-products for sequestration should be developed. This avenue may offer the potential to sequester large (gigatonne) amounts of anthropogenic carbon.
  - — Commercial products need to be developed. This approach probably represents a lesser potential (millions of tonnes) but may result in collateral benefits.
- The chemical sciences can fill crucial gaps identified in the other focus areas. In particular, environmental chemistry is an essential link in determining the impact and consequences of these various approaches. Studies to address the specific gaps identified in Chap. 7 should be conducted to ensure that other focus areas meet their potential.

DEVELOPING A CARBON SEQUESTRATION ROAD MAP

An emerging science and technology road map seeks to identify the scientific and technological developments needed to achieve a specific policy goal. The process of identifying the needed science and technology must be focused by developing a concept of the technological system (Chap. 8). This task is particularly difficult in the case of carbon capture and sequestration because the understanding necessary to design such a system is still immature.

Today, carbon is emitted to the atmosphere from many sources that were not designed to capture, let alone sequester, these emissions. There are many ideas for, and even demonstrations of, technology to capture and sequester carbon from fossil fuel combustion. Many of the requisite new energy production technologies are already under development at DOE. However, the current energy system probably must be modified significantly to make an economical capture and sequestration system possible. Thus, the emerging technology road map for carbon capture and sequestration cannot be constructed apart from consideration of current and emerging energy technologies. It will involve an iterative process to connect this road map with others being developed by DOE for various parts of the energy technology system.

This report is a significant first step toward the development of an emerging technology road map for carbon capture and sequestration. We start from a bold vision of having the scientific and technical knowledge to make carbon sequestration a major carbon management option by 2025. Guided by this vision, each of the technical focus chapters (2–7) identifies key areas for scientific and technical development, including new areas outside traditional energy technology development.

We have begun the process of exploring the mutual relationships and interdependencies of the scientific and technological developments in all these fields by building a series of road map linkages. This process has illuminated how progress in one area affects the total system. However, R&D priorities and performance requirements have not yet been defined. Nor has the phasing of potential R&D schedules been considered. Developing linkages has allowed us to eliminate overlaps to some extent, but gaps in the technology needs have not yet been examined. Before proceeding much further, much more work must be done on specifying the economic constraints and technology needs of the integrated carbon capture and sequestration system. The road map outline presented in this document, especially the research needs delineated in chapters 2–7, provides the sound basis for taking these next steps toward a fully realized program in carbon sequestration. This report should be used as a framework in organizing a wider examination by diverse stakeholders of the science and technology required for carbon capture and sequestration.

1

CARBON SEQUESTRATION: A THIRD APPROACH TO CARBON MANAGEMENT

Vision

The vision for the road map is to possess the scientific understanding of carbon sequestration and develop to the point of deployment those options that ensure environmentally acceptable sequestration to reduce anthropogenic CO_2 emissions and/or atmospheric concentrations. The goal is to have the potential to sequester a significant fraction of 1 GtC/year in 2025 and 4 GtC/year in 2050.

1.1 CARBON MANAGEMENT

1.1.1 The Challenge

In the past 60 years, the amount of anthropogenic carbon dioxide (CO_2) emitted to the atmosphere, primarily because of expanding use of fossil fuels for energy, has risen from preindustrial levels of 280 parts per million (ppm) to present levels of over 365 ppm (Keeling and Whorf 1998).

Predictions of global energy use in the next century suggest a continued increase in carbon emissions and rising concentrations of CO_2 in the atmosphere unless major changes are made in the way we produce and use energy—in particular, how we manage carbon. For example, the widely cited IS92a ("business as usual") energy scenario developed by the Intergovernmental Panel on Climate Change (IPCC 1995) predicts that future global emissions of CO_2 to the atmosphere will increase from 7.4 billion tonnes of atmospheric carbon (GtC) per year in 1997 to approximately 26 GtC/year by 2100. Although the effects of increased CO_2 levels on global climate are uncertain, there is scientific consensus that a doubling of atmospheric CO_2 concentrations could have a variety of serious environmental consequences in the next century.

What would it take to stabilize the atmospheric concentrations of CO_2? Two widely used scenarios, a "business as usual" and an atmospheric stabilization scenario, are compared in Fig. 1.1. The difference between the two scenarios, about 1 GtC per year in 2025 and about 4 GtC per year in 2050, represents one estimate of the CO_2 reductions required to reach atmospheric stabilization. This road map identifies a framework for research and development (R&D) that would

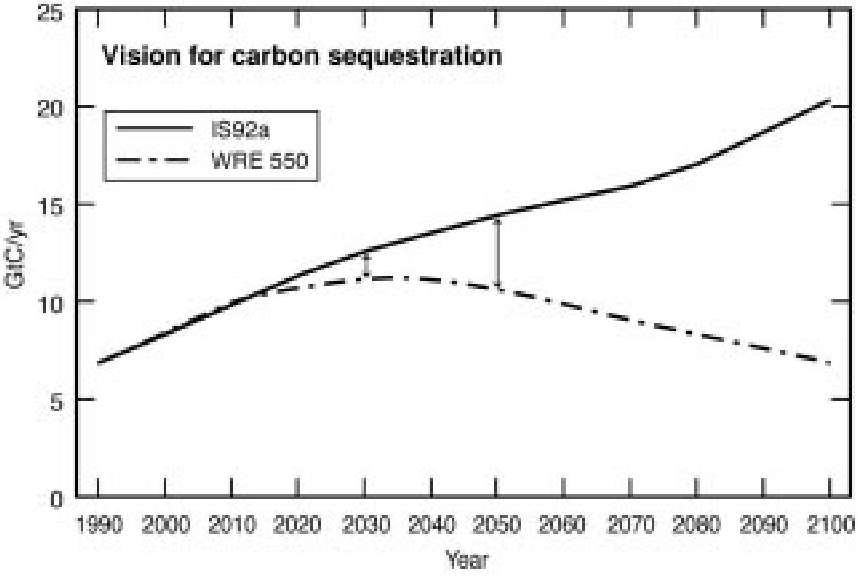

Fig. 1.1. One representation of the reductions in CO_2 that would be necessary to reach atmospheric stabilization compares the IS92A (business as usual) scenario with a scenario (WRE550) that leads to stabilized atmospheric CO_2 concentrations of 550 ppm (about twice preindustrial levels). The WRE550 scenario is commonly used by analysts of climate change. *Source:* Wigley, Richels, and Edmonds 1996.

allow carbon sequestration to provide a significant fraction of that reduction.

1.1.2 The Vision

The vision for the road map is to possess the scientific understanding of carbon sequestration and develop to the point of deployment those options that ensure environmentally acceptable sequestration to reduce anthropogenic CO_2 emissions and/or atmospheric concentrations. The goal is to have the potential to sequester a significant fraction of 1 GtC/year in 2025 and 4 GtC/year in 2050.

1.1.3 Three Approaches to Carbon Management

Carbon sequestration is distinguished from, but complements, two other approaches to carbon management that are supported by the U.S. Department of Energy (DOE) (National Laboratory Directors 1997).

The first approach is to increase the efficiency of primary energy conversion and end use so that fewer units of primary fossil energy are required to provide the same energy service. DOE is sponsoring a variety of R&D programs to develop more efficient supply- and demand-side technologies (e.g., more efficient fossil-fuel-fired power plants, buildings, appliances, and transportation vehicles) and to find ways to produce and deliver electricity and fuels more efficiently. More efficient energy conversion and end use will result in lower CO_2 emissions per unit of energy service.

A second approach is to substitute lower-carbon or carbon-free energy sources for our current sources. For example, this strategy might involve substituting lower-carbon fossil fuels such as natural gas for coal or oil; using renewable energy supplies such as solar, wind, or biomass; or increasing the use of nuclear power. DOE has major R&D programs to develop more efficient fossil energy as well as renewable energy and nuclear energy technologies.

Carbon sequestration could represent a third approach in addition to efficiency improvements and evolution toward low-carbon fuels. However, it has received much less attention to date than these other two approaches.

1.1.4 What is Carbon Sequestration?

Carbon sequestration can be defined as the capture and secure storage of carbon that would otherwise be emitted to or remain in the atmosphere. The idea is (1) to keep carbon emissions produced by human activities from reaching the atmosphere by capturing and diverting them to secure storage, or (2) to remove carbon from the atmosphere by various means and store it.

One set of options involves capturing carbon from fossil fuel use before it reaches the atmosphere. For example, CO_2 could be separated from power plant flue gases, from effluents of industrial processes (e.g., in oil refineries and iron, steel, and cement production plants), or during production of decarbonized fuels (such as hydrogen produced from hydrocarbons such as natural gas or coal). The captured CO_2 could be concentrated into a liquid or gas stream that could be transported and injected into the ocean or deep underground geological formations such as oil and gas reservoirs, deep saline reservoirs, and deep coal seams and beds. Biological and chemical processes may convert captured CO_2 directly into stable products. Atmospheric carbon can also be

Why is Carbon Sequestration Important?

It is important to carry out research on carbon sequestration for several reasons:

- Carbon sequestration could be a major tool for reducing carbon emissions from fossil fuels. However, much work remains to be done to understand the science and engineering aspects and potential of carbon sequestration options.

- Given the magnitude of carbon emission reductions needed to stabilize the atmospheric CO_2 concentration, multiple approaches to carbon management will be needed. Carbon sequestration should be researched in parallel with increased energy efficiency and decarbonization of fuel. (These efforts should be closely coordinated to exploit potential synergies.)

- Carbon sequestration is compatible with the continued large-scale use of fossil fuels, as well as greatly reduced emissions of CO_2 to the atmosphere. Current estimates of fossil fuel resources—including conventional oil and gas, coal, and unconventional fossil fuels such as heavy oil and tar sands—imply sufficient resources to supply a very large fraction of the world's energy sources through the next century.

- The natural carbon cycle is balanced over the long term but dynamic over the short term; historically, acceleration of natural processes that emit CO_2 is eventually balanced by an acceleration of processes that sequester carbon, and vice versa. The current increase in atmospheric carbon is the result of anthropogenic mining and burning of fossil carbon, resulting in carbon emissions into the atmosphere that are unopposed by anthropogenic sequestration. Developing new sequestration techniques and accelerating existing techniques would help diminish the net positive atmospheric carbon flux.

captured and sequestered by enhancing the ability of terrestrial or ocean ecosystems to absorb it naturally and store it in a stable form.

1.1.5 Necessary Characteristics for Carbon Sequestration Systems

Any viable system for sequestering carbon must have the following characteristics.

Capacity and price. The technologies and practices to sequester carbon should be effective and cost-competitive. This road map will focus on options that allow sequestration of a significant fraction of the goal.

Environmentally benign fate. The sheer scale and novelty of sequestration suggests a careful look at environmental side effects. For example, the long-term effects of sequestration on the soil or vegetation need to be understood. Until recently, dilution into the atmosphere was considered acceptable. Vast quantities of materials would be generated. The safety of the product and the storage scheme have to be addressed.

Stability. The carbon should reside in storage for a relatively long duration.

1.2 THE GLOBAL AND THE FOSSIL FUEL CARBON CYCLES

Carbon sequestration is intimately tied to two carbon cycles— the natural and the fossil fuel cycles. Understanding aspects of both cycles provides a context for developing carbon sequestration options.

1.2.1 The Global Carbon Cycle

Improving our understanding of the global carbon cycle, its fluxes, and its reservoirs, is intimately tied to successful implementation of carbon sequestration technologies. Decreasing atmospheric CO_2 concentrations by reducing CO_2 emissions or by changing the magnitude of the fluxes between reservoirs is controlled by the carbon budget of a reservoir. From a carbon sequestration perspective, understanding the potential to alter carbon budgets through the intervention of carbon sequestration technologies to reduce future atmospheric CO_2 concentrations is one of the principal challenges.

Human activities during the first half of the 1990s have contributed to an average annual emission of approximately 7.4 GtC into the atmosphere (Fig. 1.2). Most of these emissions were from fossil fuel combustion. The net result of these CO_2 emissions during the first part of the 1990s was an annual net emissions increment to the atmosphere of 3.5 GtC. Storage of carbon in terrestrial systems due to photosynthesis and plant growth was 1.7 GtC. Another 2.2 GtC per year was taken up by oceans.

Carbon fluxes between the atmosphere and ocean/terrestrial reservoirs are quite large (hundreds of GtC per year), while net carbon exchange is over an order of magnitude smaller. For example, the average net ecosystem accumulation of the terrestrial biosphere was 0.3 GtC per year (1.7 GtC per year net ecosystem production diminished by 1.4 GtC per year due to land clearing), while terrestrial

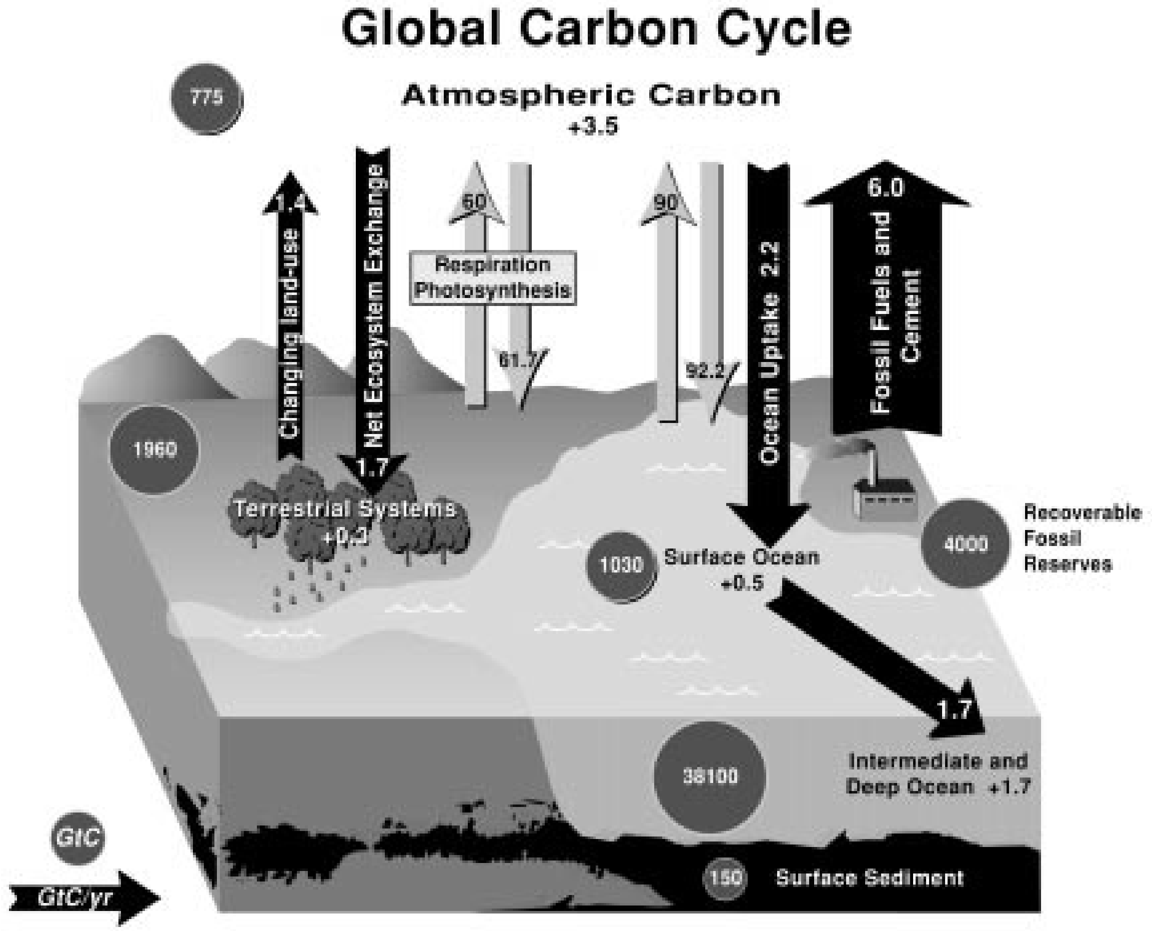

Fig. 1.2. Human-induced changes in the global carbon cycle resulting from increases in the combustion of fossil fuels and changing land-use patterns. Solid arrows indicate the average magnitude of perturbation in carbon fluxes and the fate of carbon resulting from these activities averaged for the first half of the 1990s. Net fluxes (black arrows) and gross fluxes (gray arrows) are in billions of tonnes of carbon per year. Annual net additions of carbon (shown as + numbers) to the atmosphere, ocean subsystems, and terrestrial systems from anthropogenic sources are in billions of tonnes of carbon per year. Pool sizes (circles) are shown in billions of tonnes of carbon. For more information, see Houghton 1995 and Marland et al. 1998. *Source: Technology Opportunities to Reduce U.S. Greenhouse Gas Emissions*, modified from IPCC 1995.

ecosystems photosynthetically fixed 61.7 GtC per year—the photosynthesis uptake being offset by 60 GtC per year due to plant/soil respiration. Similarly, the net ocean uptake of 2.2 GtC per year is the difference of ocean/atmosphere fluxes each exceeding 90 GtC per year. The significance of understanding these complicated carbon exchanges is that developing the ability to alter these gross annual carbon exchanges of the global carbon cycle by a small percentage through carbon sequestration technologies would increase net storage of carbon in the major reservoirs and lessen atmospheric carbon concentrations.

1.2.2 The Fossil Fuel Cycle

About 75% of the world's commercial energy comes from fossil fuels, and about 84% of the energy used in the United States is derived from fossil fuels (EIA 1998a; PCAST 1997). Given the advantages inherent in fossil fuels, such as their cost-competitiveness, their availability, their ease of transport and storage, and the large fossil resources, fossil fuels are likely to remain a major player in global energy supply for at least the next century.

Figure 1.3 shows the energy flows through the U.S. economy from fossil and other fuels. This diagram helps to identify places where CO_2 could be separated and captured, but there are energy and cost implications that must be considered (Hoffert et al. 1998). In the near term, most CO_2 is likely to come from electricity generated from fossil fuels, because large quantities of it could be processed at fixed locations. However, other possibilities become more likely in the longer term. Fossil fuels, solid waste, or biomass can be "decarbonized" so that a higher-energy-content and environmentally benign fuel is separated from CO_2. For example, either a fossil energy source or another carbon source such as solid waste or biomass could be pretreated to produce hydrogen and CO_2. These central pretreatment facilities could become other new sources of carbon for capture.

1.3 APPROACH AND SCOPE OF THIS REPORT

The goal of this report is to identify key areas for R&D that could lead to a better understanding of the potential use of carbon sequestration as a major tool for managing carbon emissions. Under the leadership of DOE, researchers from universities, industry, other government agencies, and DOE national laboratories were brought together to develop the technical basis for developing an R&D road map. This report develops much of the information needed for the road map.

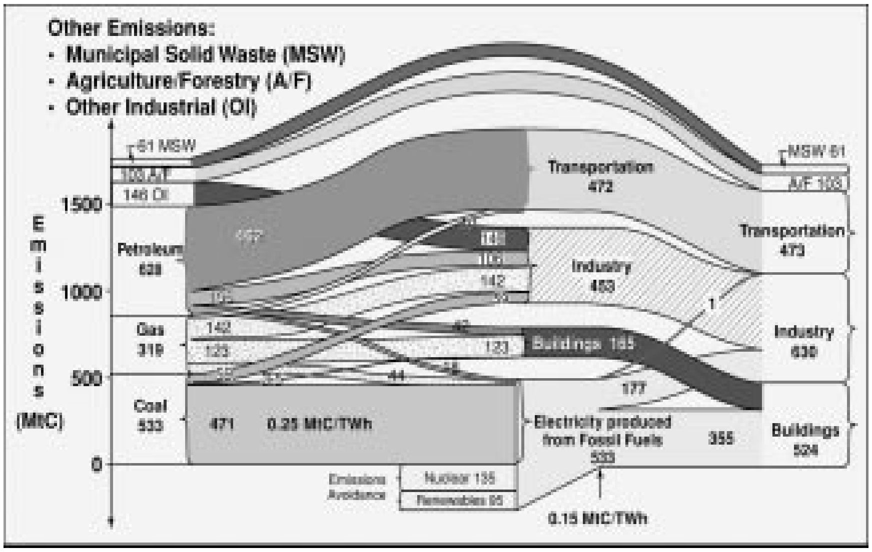

Fig. 1.3. Carbon flows in the energy system and sources of emissions in the United States in 1995 (in millions of metric tons equivalent). Electricity produced by the combustion of fossil fuels is likely to remain a significant contributor to greenhouse gas emissions. *Sources:* EIA 1998a,b.

Six scientific/technical “focus areas” relevant to carbon sequestration were identified, and groups of experts in each area reported on the R&D issues. These focus areas are

1. Separation and Capture of CO_2
2. Ocean Sequestration
3. Carbon Sequestration in Terrestrial Ecosystems (Soils and Vegetation)
4. Sequestration of CO_2 in Geological Formations
5. Advanced Biological Processes for Sequestration
6. Advanced Chemical Approaches to Sequestration

These six focus areas represent one way to organize the scientific and engineering issues underlying carbon sequestration.

Our vision for a carbon sequestration road map is to conduct the appropriate R&D so that options will be available for significantly reducing anthropogenic carbon emissions in the time frame of 2025 and beyond.

This report describes the R&D necessary to understand and develop to the point of deployment all critical options bearing on the capture, transport, conversion, and sequestration of carbon (Fig. 1.4). It addresses known sources of carbon (industrial sources, power plant flue gases, carbon split away from fossil fuels before combustion); carbon forms for sequestration (CO_2, elemental carbon, and minerals that contain carbon); and options for sequestration sinks (oceans, geologic formations, enhancing the natural carbon cycle).

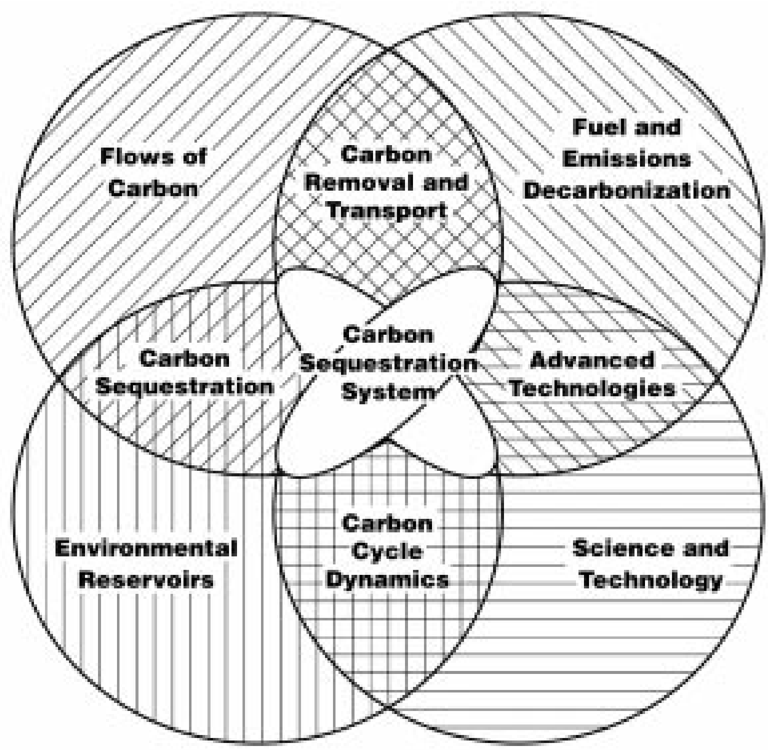

Fig. 1.4. Deploying an effective carbon sequestration system will require an integrated program of science, enabling technology, and advanced power systems—all dependent on better understanding of environmental carbon dynamics.

1.4 TOWARD DEVELOPMENT OF A CARBON SEQUESTRATION ROAD MAP

An emerging technology road map provides—and encourages the use of—a structured R&D planning process. Emerging technology road maps furnish a framework for managing and reviewing the complex, dynamic R&D process needed to achieve important strategic goals by identifying how specific R&D activities can relate to integrated technical capabilities needed to achieve strategic objectives. The process of identifying the needed science and technology must be focused by developing a concept of the technological system that would enable achievement of that goal. This task is particularly difficult in the case of carbon capture and sequestration because there has been, heretofore, no paradigm for such a system (Victor 1998).

Our road map gives a top-level picture of a carbon capture and sequestration system and its linkages to the energy system. We have concentrated principally on the development of scientific understanding that is needed for specific capture and sequestration functions, including specific changes in components of the existing energy system that would simplify and/or lower the cost of capture and disposal. Many capture and sequestration technologies are discussed in detail in Chaps. 2–7. Each can be developed and improved individually. However, the economic cost and effectiveness of the overall carbon capture and sequestration system depend on the effective combination of many scientific advances. Their relative importance must finally be judged in the context of the integrated technology system.

After identifying the technology goals and the integrated technology system needed to satisfy those goals, our next step was to assess the alternative technological pathways that might lead to an integrated carbon sequestration technology system. The approach was to construct these pathways within a technological hierarchy. The highest level of the hierarchy is the integrated technology system—in this case, the carbon capture and sequestration system. The hierarchy base is supported by the science and technology capabilities that are needed to develop the technologies that make the system economical and effective.

1.4.1 Foundations for an Expanded National Program in Carbon Sequestration

Sequestration studies began in 1977 (see End Note 1), but an upsurge of interest in them has occurred only recently. In the past two years, several key government studies of carbon management and energy have highlighted carbon sequestration as an approach with high potential where much R&D is needed.

For example, the potential importance of carbon sequestration has been underscored by the President's Committee of Advisors on Science and Technology report titled *Federal Energy Research and Development Agenda for the Challenges of the 21st Century* (PCAST 1997). Specifically, the report recommends that a much larger science-based CO_2 sequestration program be developed with the budget increasing from the current $1 million per year to the vicinity of tens of millions. The report further states that the R&D should be performed in a collaborative way between DOE's offices of Fossil Energy and Energy

Research (now Office of Science) and the U.S. Geological Survey. International collaboration is also strongly encouraged.

Although the current DOE carbon sequestration program is modest in scale, many of the foundations have already been built for significantly expanding this effort. The DOE Office of Science program on CO_2 sequestration includes both the Office of Basic Energy Sciences (BES) and the Office of Biological and Environmental Research (BER). The primary relevant goal for BES is to develop major new fundamental knowledge that crosscuts DOE's applied programs related to carbon management, including such disciplines as materials sciences, chemical sciences, geosciences, plant and microbial biosciences, and engineering sciences. BES has longstanding programs in fundamental research, such as improved materials synthesis and combustion engineering for more efficient energy technologies, improved catalysts for low-carbon industrial processes, improved understanding of biological mechanisms of carbon fixation, and improved understanding of fluid flow in the subsurface for geological sequestration (www.er.doe.gov/production/bes/bes.html).

In 1999, a new program in BES and BER will be initiated to conduct research in carbon management, including carbon sequestration, as a result of the climate change technology initiative. The subjects will include sequencing genomes of methane- and hydrogen-producing microorganisms; enhancing the natural terrestrial and oceanic fluxes of CO_2; and improving the understanding of biological carbon fixation, materials, catalysts, combustion chemistry, and physics and chemistry of geological reservoirs.

BER has a longstanding fundamental research program on the global carbon cycle. Current research focuses on atmospheric measurements of carbon fluxes and related processes, terrestrial carbon fluxes, and advanced biological investigations of carbon in terrestrial and ocean margin systems. A key element of terrestrial carbon research involves Ameriflux, which is a network of CO_2 flux measurements across North, Central, and South America to quantify net CO_2 exchange between the atmosphere and representative terrestrial ecosystems. Free Air CO_2 Enrichment (FACE) experiments provide information about changes in the carbon content of ecosystems under increased concentrations of atmospheric CO_2, altered temperatures, and altered precipitation regimes. Relevant information can be found at www.er. doe.gov/production/ober/gc/accc-fr.html and www.cdiac.esd.ornl.gov/programs/ameriflux. Ocean research focuses on molecular biological approaches to understanding the coupling between carbon and nitrogen cycles (www.er.doe.gov/production/ober/GC/acc-ft.html). BER also sponsors a program, Integrated Assessment of Global Climate Change, that supports research in understanding carbon management frameworks for integrated assessment modeling activities.

DOE's Office of Fossil Energy has a program on CO_2 capture and sequestration to develop and demonstrate technically, economically, and ecologically sound methods to capture, reuse, and dispose of CO_2. In 1998, DOE made awards for 12 "cutting-edge" research projects, ranging from the use of CO_2-absorbing algae growing on artificial reefs to deep-ocean or deep-saline-reservoir greenhouse gas disposal. Some of these projects may be selected for further development. (Details on this solicitation can be found at www.fe.doe.gov).

The Office of Fossil Energy has recently undertaken an initiative to provide formal management direction to sequestration program activities and to establish program content and funding priorities. A team has been assembled to define a research strategy clearly and to ensure coordination with internal and external stakeholders. In making its recommendations, the team will draw heavily from this report. In FY 1999, the second phase of the Fossil Energy novel concept investigations will obtain the required engineering and economic data to proceed to proof-of-concept. In the areas of geological and ocean sequestration, international government/industry projects will continue.

In 1991 the International Energy Agency (IEA) established a Greenhouse Gas R&D Programme focused on analyzing technologies for capturing, using, and storing CO_2. It has expanded to include methane, as well as forestation options. The program is currently in its third 3-year phase and has support from 16 countries (including the United States) and a growing number of industrial organizations. (Details on this program can be found at www.ieagreen.org.uk.)

In addition to government studies, industry is moving ahead with development of CO_2 sequestration technologies:

- The World Resources Institute has formed a consortium with General Motors, Monsanto, and British Petroleum to address the fundamental issues of global energy supply, climate change, and economic growth—paths to stabilizing CO_2 concentrations at levels reducing risks of climate change (WRI 1998).
- Since October 1996, STATOIL, a Norwegian energy company, has been separating CO_2 from natural gas and injecting it, at a rate of 1 million tonnes per year, into a deep saline reservoir 800–1000 meters below the ocean floor in the North Sea (see Chap. 5).
- About 70 oil fields use CO_2 injection to recover additional crude oil.
- Various oil companies have proposed to sequester CO_2 at the rate of 30 million tonnes of carbon per year in the deep aquifers adjacent to the Natuna gas field, in the South China Sea, when that field comes into production.
- Many domestic and international forest preservation and management projects sequester carbon by reducing deforestation and harvest impacts. Forest management can also enhance existing carbon sinks.

These industrial efforts are very important, but the amounts of CO_2 sequestered are very small compared with overall emissions. Considerable R&D investment by government and industry is needed to enable sequestration of sufficient quantities of CO_2 to mitigate any adverse effects resulting from CO_2 emissions.

1.4.2 The Need for a National R&D Plan for Carbon Sequestration

Carbon sequestration is promising as a carbon management strategy, but its potential cannot be evaluated and realized without a broad program of research, development, and demonstration. The specific components of such a plan are the subjects of Chaps. 2–7. The framework for an integrated carbon sequestration system is presented in Chap. 8.

There are many ways to move ahead on sequestration. Some technologies are already sufficiently developed to be tested in field research experiments (e.g., injecting CO_2 into a geological formation and monitoring its form, location, and stability). As technologies progress, their implications for global climate change policy should be evaluated (Parson and Keith 1998).

Many sequestration technologies and practices will require further fundamental scientific and engineering studies before field testing. For example, there are known agricultural practices for increasing storage of carbon in plant roots and soil, but much research needs to be done to design effective methods for enhancing carbon storage in ecosystems and determine their impacts.

1.5 END NOTES

1. Avoidance of CO_2 emissions through physical capture of CO_2 from power plants and disposal of CO_2 in the deep ocean was first proposed by Marchetti (1977). In the United States, preliminary studies were conducted at Brookhaven National Laboratory (Steinberg 1984).

   However, it was not until 1990 that planning research efforts were undertaken in this field. Since then, many conferences and studies have been conducted on options for the capture and disposal or reuse of CO_2 from large stationary sources. Much of this work has been done under the auspices of IEA's Greenhouse Gas R&D Programme and the successful conference series on CO_2 removal and disposal. It should also be noted that the Offices of Fossil Energy and Science jointly sponsored a research needs assessment (Herzog 1993) and a white paper (Herzog 1997) on this subject. Both of these reports were completed at the Massachusetts Institute of Technology.

   In the past two years, four important government documents have appeared that highlight the potential for carbon sequestration and the need for further work. There are recent reports by the President's Council of Advisors on Science and Technology; *the Federal Energy R&D Report*; the study by 11 DOE laboratories called *Technology Opportunities to Reduce U.S. Greenhouse Gas Emissions* (National Laboratory Directors 1997); *and Carbon Management: Assessment of Fundamental Research Needs*, a product of a series of DOE workshops (DOE 1997). Important conferences and workshops that have addressed carbon sequestration have been four international conferences on CO_2 removal, the International Conference on Greenhouse Gas Control Technologies in Interlaken, Switzerland in August 1998; the Fuels, Decarbonization, and Carbon Sequestration Workshop (Socolow 1997); the Stakeholders' Workshop on Carbon Sequestration (Herzog 1998); and "Carbon Sequestration in Soils: Science, Monitoring, and Beyond" held December 1998 in St. Michaels, Maryland, and organized by Pacific

Northwest and Oak Ridge National Laboratories. These reports and others indicate that the potential for sequestration is quite high but largely unexamined.

2. Several road-mapping activities under way at DOE are related to the development of this carbon sequestration road map. For example, the Office of Industrial Technologies is carrying out the Industries of the Future program that involves the development and implementation of technology road maps for the most energy-intensive industries, including aluminum, steel, chemicals, glass, and forest products. Among these activities is a joint effort under way with the chemicals, forest products, and agricultural industries to plan for the future of plant/crop-based resources, which includes the development of new bioenergy technologies for the coproduction of fuels, power, and industrial feedstocks.

   There is also a road map under development for power generation technologies by the offices of Fossil Energy, Nuclear Energy, and Energy Efficiency and Renewable Energy in collaboration with the heat and power generation industries. The Electric Power Research Institute is developing technology road maps for electric power generation, transmission, distribution, storage, and end use. These efforts all involve the joint development and deployment by government and industry of advanced technologies, many of which will result in lower carbon emissions, thus affecting the source and amount of man-made carbon emissions to be sequestered in the future.

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1.7 ACKNOWLEDGMENTS

Special appreciation is due to Michael P. Farrell for providing the discussion of the global carbon cycle in Sect. 1.2.1 and to Marilyn A. Brown for translation of the Energy Information Administration (EIA) U.S. energy flow data into carbon equivalents in Fig. 1.3.

2 SEPARATION AND CAPTURE OF CARBON DIOXIDE

2.1 CHARACTERIZATION OF CARBON FLOWS (SOURCE TERMS)

This chapter and road map address the separation and capture of anthropogenic CO_2 only. Separation and capture have been identified as a high-priority topic in other reports (Socolow 1997; Herzog 1998; FETC 1998). The costs of separation and capture, including compression to the required pressure for the sequestration option used, are generally estimated to make up about three-fourths of the total costs of ocean or geologic sequestration (Herzog 1998). A study conducted for the IEA Greenhouse Gas R&D Programme suggests that significantly increased power generation costs will result from CO_2 separation and capture (IEA 1998). Using a base case pulverized coal plant with flue gas desulfurization for comparison, the cost of eliminating CO_2 emissions from advanced power generation plants ranged from $35 to $264 per tonne of CO_2, and power cost increases ranged from 25 to 215 mills/kWh.

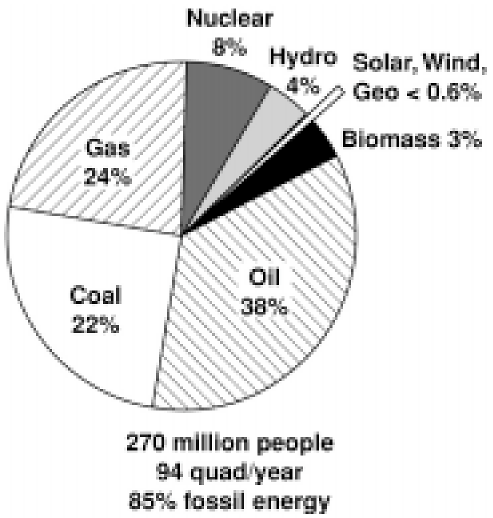
The wide range of costs is indicative of the peculiarities of the advanced power generation plants and the wide range of separation and capture possibilities. Although some of the more expensive methods may be used in certain production enterprises with high–value-added products, the less expensive approaches will likely be used in conventional and advanced power plants. These less expensive approaches are appropriate for power generation, and an independent analysis (Herzog 1998) suggests these separation and capture approaches would increase power generation costs by about 20 to 30 mills/kWh.

The scope of this element of the road map includes all anthropogenic emissions of CO_2, with a focus on those sources most amenable to various

Vision

By 2020, possess the scientific understanding of CO_2 separation and capture techniques and have developed to the point of deployment readiness those techniques that ensure the delivery of a stream of CO_2, or other carbon form, at acceptable costs and of acceptable purity at the requisite conditions of pressure and temperature for the respective sequestration options discussed in subsequent chapters.

Primary Energy Sources



This chart depicts energy use in the United States by primary energy sources. For the last 4 years, coal production in the United States has been at record levels of over a billion short tons per year. Most of the coal is consumed in power generation, as is some natural gas. Most of the natural gas is used for space heating and other domestic, commercial, and industrial applications. The great majority of oil produced is used for transportation, and essentially none is used for electricity generation. This road map focuses on the CO_2 sources most adaptable to separation and capture; these include, primarily, power generation, hydrogen production, natural gas production, refineries, and industrial processes.

separation and capture methods. Sources that appear to lend themselves best to separation and capture technologies include large-point sources of CO_2 such as conventional pulverized-coal steam power plants; natural-gas-fired combined cycle plants; and advanced power generation systems, including coal or natural gas combustion plants employing enriched air or oxygen to support combustion with CO_2 recycling, integrated coal gasification (especially oxygen-based) combined cycles, hydrogen turbines, and fuel cells. Many of the advanced systems will use enriched air or oxygen to support the combustion process. The reduction or elimination of the large volume of diluent nitrogen in process and flue gases dramatically improves the opportunity for the separation and capture of CO_2 from these systems. The equipment used for combustion and processing will range from existing technology (e.g., coal-fired steam plants and gas turbines) to advanced technology (e.g., production of hydrogen from fossil fuels).

In addition to power plants, numerous other high-CO_2-emitting industrial sources are being considered for application of capture and sequestration technologies. In natural gas production, CO_2 is often generated as a by-product. Natural gas may contain significant amounts of CO_2 (20% or more by volume), most of which must be removed to produce pipeline-quality gas. Therefore, sequestration of CO_2 from natural gas operations is a logical first step in applying CO_2 capture technology, as demonstrated by the Sleipner West project in Norway, the proposed Natuna project in Indonesia, and the proposed Gorgon project in Australia. Other significant industrial sources of CO_2 include oil refineries, iron and steel plants, and cement and lime producers. Although these sources contribute only a small fraction of total CO_2 emissions, separation and capture of these emissions are feasible and would contribute significantly to overall CO_2 emission reduction goals.

Dispersed sources of CO_2 emissions, particularly residential buildings and mobile spark ignition and diesel

Advanced Power Plants

Advanced coal-fired power plants, such as this 800-ton-per-day coal gasification pilot/demonstration plant, will have energy conversion efficiencies 20 to 35% higher than those of conventional pulverized coal steam plants. These advanced plants are also much more amenable to carbon management than are conventional plants. *(Photo courtesy of Tom Lynch of Dynegy)*

engines, are especially challenging sources for applying cost-effective separation and capture methods. Although these sources are collectively large, they are not a primary focus of our road map. However, the introduction of fuel cells for vehicular propulsion and power generation may occur within the time frame of this road map, and depending on the extent of their deployment, the need to use fossil fuels to produce hydrogen (H_2) for fuel cells could have a significant impact on CO_2 separation and capture. For example, if buses and vehicle fleets move toward on-board H_2 storage, central H_2 production facilities may be built that would allow CO_2 separation and capture. Such central H_2 production facilities are considered in this road map. Other advanced power systems, such as hydrogen turbines that would use H_2 as fuel, also have important implications with respect to the need for central H_2 production facilities and the opportunity for CO_2 separation and capture. Electric vehicles may also come into widespread use during the time frame of this road map. Should that occur, separation and capture of CO_2 at the central power stations that produce the electricity for recharging electric vehicle batteries would indirectly reduce CO_2 emissions from the transportation sector. However, one of the consequences of the deregulation of the electric power industry may be the introduction of a significant distributed power supply. Depending on the size and nature of these power generation plants, such a change might have a negative impact on the ability to separate and capture CO_2.

Carbon dioxide concentrations in effluent streams will range from ~5% for current power generation plants to almost 100% for some advanced technologies. All separation and capture feed streams are likely to contain small amounts of impurities such as oxygen, sulfur oxides, and nitrogen oxides from combustion of natural gas or advanced processing of fossil fuels to yield hydrogen. For some current and emerging technologies involving combustion of coal, the feed streams will contain large amounts of nitrogen, oxygen, water vapor, particulates, and volatile and semivolatile chemical species as well. The feed stream may also be contaminated with chemicals used to remove other constituents (e.g., sulfur or nitrogen oxides). Feed-stream pressures will range from essentially ambient for current technologies to tens of atmospheres for some advanced processes. Feed-stream temperatures will range from very warm (~50°C) to hot (hundreds of degrees).

2.2 CURRENT AND POTENTIAL SCIENCE AND TECHNOLOGY REQUIREMENTS

The goal of CO_2 separation and capture is to isolate carbon from its many sources in a form suitable for transport and sequestration. The technology required to perform this function depends on the nature of the carbon source and carbon form(s) that are suitable for subsequent steps leading to sequestration. Many forms are possible, including gaseous and supercritical CO_2 and even clathrates. High levels of purity (99+%) are possible, but at significant cost.

The impurities in the product must be of sufficiently low concentrations that transportation and sequestration operations are not compromised. The purity requirements imposed by sequestration operations are not known because sequestration technology is being developed concurrently. Some initial investigation to develop provisional purity requirements will be necessary and will be reviewed and modified as the requirements of various sequestration options become clear. End-state specifications may be for the final product of separation and capture or for an intermediate product that is converted to another form (e.g., a carbonate) before transport. Separation and capture processes that operate on effluent streams, as well as those that are integral elements of optimized advanced processing flow sheets, will be considered.

2.3 CURRENT AND POTENTIAL SCIENCE AND TECHNOLOGY CAPABILITIES

Categorized in this section are what are believed to be conventional separation and capture options that are applicable for anthropogenic CO_2 emissions. It is not presumed that the categories or methods within the categories are exhaustive; certainly, little-known or as-yet-unknown techniques could ultimately become preferred options. For those CO_2 separation and capture methods identified, performance characteristics, including CO_2 product purity and operating conditions, differ because of operational or technical considerations. These characteristics of CO_2 separation and capture technologies are the basis for matching them with the technologies that are the anthropogenic sources of CO_2.

The most likely options currently identifiable for CO_2 separation and capture include

- chemical and physical absorption
- physical and chemical adsorption
- low-temperature distillation
- gas-separation membranes
- mineralization and biomineralization
- vegetation

These were identified and included as probable options because of process simplicity, environmental impact, and economics. Currently, several CO_2 separation and capture plants use one or more of these methods to produce CO_2 for commercial markets. The vegetation separation and some mineralization methods are also sequestration methods and are discussed in the appropriate focus area chapters.

2.3.1 Chemical and Physical Absorption

Carbon dioxide can be removed from gas streams by physical or chemical absorption. Physical absorption processes are governed by Henry's law (i.e., they are temperature and pressure dependent with absorption occurring at high pressures and low temperatures). Typically, these processes are used when the concentration (i.e., partial pressure of CO_2) is high (>525 kPa). The removal of 0.1 to 6% CO_2 from natural gas production wells by chemical absorption using amines can be deployed conveniently in remote fields. Currently, this approach represents the most widely deployed commercial technology for capture. However, in other commercial applications, the typical solvents for physically absorbing CO_2 include glycol-based compounds (e.g., the dimethylether of polyethylene glycol) and cold methanol.

Chemical absorption is preferred for low to moderate CO_2 partial pressures. Because CO_2 is an acid gas, chemical absorption of CO_2 from gaseous streams such as flue gases depends on acid-base neutralization reactions using basic solvents. Most common among the solvents in commercial use for neutralizing CO_2 are alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). Other chemical solvents in use are ammonia and hot potassium carbonate. Flue gases are typically at atmospheric pressure. Depending on the CO_2 content of the flue gas, the partial pressure of CO_2 can vary from 3.5 to 21.0 kPa. At such low partial pressures, alkanolamines are the best chemical solvents to enable good CO_2 recovery levels; however, use of these solvents must be balanced against the high energy penalty of regenerating them using steam-stripping.

Flue gases typically contain contaminants such as SO_x, NO_x, O_2,

Sleipner T Platform

The Sleipner T (T = treatment) platform in the North Sea is used by Statoil, the Norwegian state oil company, to remove CO_2 from sub-quality natural gas. An amine absorption process is used to remove the CO_2, which is then compressed and piped to the adjacent Sleipner A platform for injection into the Utsira formation 1000 m below the seabed (see Chap. 5). Sleipner T is representative of the absorption technology that could be used for separation and capture of CO_2, and it is used specifically as a CO_2 mitigation strategy. This is the largest CO_2 separation, capture, and sequestration operation in the world, sequestering about a million tones of CO_2 per year. *(Photo courtesy of Olav Kaarstad of Statoil.)*

hydrocarbons, and particulates. The presence of these impurities can reduce the absorption capacity of amines as well as create operational difficulties such as corrosion. To avoid such problems, these contaminants are often reduced to acceptable levels through the use of suitable pretreatment techniques. Some commercial processes handle these difficulties through pretreatment and/ or the use of chemical inhibitors in the absorption process. However, these processes tend to be more expensive than conventional alkanolamine-based absorption processes.

Some of the typical operating problems encountered in using conventional trayed or packed columns for gas-liquid contact are foaming, vapor entrainment of the solvent, and the need to replenish the solvent in low quantities. However, these problems have a relatively small effect on the total system costs of the alkanolamine-based absorption process. Membrane contactors that typically use polymeric membranes can offer some advantages over conventional contactors, which are expected to be most advantageous where system size and weight need to be minimized (e.g., on ocean platforms). Potential benefits include the elimination of foaming and vapor entrainment, as well as the ability to maintain liquid and gas flow rates independently.

CO_2 Separation in Hydrogen Production

Separation of CO_2 and other contaminant gases using adsorption systems is a commercial practice in the production and purification of hydrogen. The reformer hydrogen plant shown produces 35 million standard cubic feet of hydrogen and about 9 million standard cubic feet of CO_2 per day. These plants are not usually operated in a mode that results in complete conversion of methane to hydrogen and CO_2. However, operational modifications could be made in which essentially pure hydrogen and CO_2 would be produced. Numerous plants such as this one are in use worldwide, but the CO_2 is typically vented to the atmosphere. *(Photo courtesy of Joe Abrardo of Air Products and Chemicals)*

2.3.2 Physical and Chemical Adsorption

Selective separation of CO_2 may be achieved by the physical adsorption of the gas on high-surface-area solids in which the large surface area results from the creation of very fine surface porosity through surface activation methods using, for example, steam, oxygen, or CO_2. Some naturally occurring materials (e.g., zeolites) have high surface areas and efficiently adsorb some gases. Adsorption capacities and kinetics are governed by numerous factors including adsorbent pore size, pore volume, surface area, and affinity of the adsorbed gas for the adsorbent.

An IEA study (1998) evaluated physical adsorption systems based on zeolites operated in pressure swing adsorption (PSA) and thermal, or temperature, swing adsorption (TSA) modes. In PSA operation, gases are adsorbed at high pressures, isolated, and then desorbed by reducing the pressure. A variant of PSA, called vacuum swing adsorption, uses a vacuum desorption cycle. In TSA operation, gases are adsorbed at lower temperatures, isolated, and then desorbed by heating. These processes are somewhat energy-intensive and expensive. The IEA report concludes that PSA and TSA technologies are not attractive to the gas- and coal-fueled power systems included in that study. Nevertheless, PSA and TSA are commercially practiced methods of gas separation and capture and are used to some extent in hydrogen production and in removal of CO_2 from subquality natural gas. Therefore, these methods clearly are applicable for separation and capture of CO_2 from some relatively large-point sources.

2.3.3 Low-Temperature Distillation

Low-temperature distillation is widely used commercially for the liquefaction and purification of CO_2 from high-purity sources (typically a stream with >90% CO_2). In low-temperature distillation, a low-boiling-temperature liquid is purified by evaporating and subsequently condensing it. However, such processes are not used for separating CO_2 from significantly leaner CO_2 streams. The application of distillation to the purification of lean CO_2 streams necessitates low-temperature refrigeration (<0°C) and solids processing below the triple point of CO_2 (–57°C). A patented process to separate CO_2 from natural gas, providing liquid CO_2, is an example of such a low-temperature process (Valencia and Denton 1985; Victory and Valencia 1987).

Distillation generally has good economies of scale, as it is cost-effective for large-scale plants, and it can generally produce a relatively pure product. Distillation is most cost-effective when feed gases contain components with widely separated boiling points, and when the feed gas is available at high pressure and most of the products are also required at high pressure. Low-temperature distillation enables direct production of liquid CO_2 that can be stored or sequestered at high pressure via liquid pumping. The major disadvantage of this process is that, if other components are present that have freezing points above normal operating temperatures, they must be removed before the gas stream is cooled to avoid freezing and eventual blockage of process equipment. Another disadvantage is the amount of energy required to provide the refrigeration necessary for the process.

Most CO_2 emissions being considered for CO_2 capture are produced in combustion processes. Such streams contain water and other trace combustion by-products such as NO_x and SO_x, several of which must be removed before the stream is introduced into the low-temperature process. These by-products are usually generated near atmospheric pressure. These attributes, coupled with the energy intensity of low-temperature refrigeration, tend to make distillation less economical than other routes. The application of low-temperature distillation, therefore, is expected to be confined to feed sources at high pressure and with high CO_2 concentrations (e.g., gas wells).

2.3.4 Gas-Separation Membranes

Gas-separation membranes are of many different types, and although the efficacy of only a few of these types in separating and capturing CO_2 has been demonstrated, their potential is generally viewed as very good. Diffusion mechanisms in membranes are numerous and differ greatly depending on the type of membrane used. Generally, gas separation is accomplished via some interaction between the membrane and the gas being separated. For example, polymeric membranes transport gases by a solution-diffusion mechanism (i.e., the gas is dissolved in the membrane and transported through the membrane by a diffusion process). Polymeric membranes, although effective, typically achieve low gas transport flux and are subject to degradation. However, polymer membranes are inexpensive and can achieve large ratios of membrane area to module volume.

Palladium membranes are effective in separating H_2 from CO_2, but gas fluxes are typically very low, and palladium is subject to degradation in sulfur-containing environments. Porous inorganic membranes, metallic or ceramic, are particularly attractive because of the many transport mechanisms that can be used to maximize the separation factor for various gas separations. Porous inorganic membranes can be 100 to 10,000 times more permeable than polymeric membranes. (Permeance is the volume of gas transported through a membrane per unit of surface area per unit of time per unit of differential pressure.) However, the cost for inorganic membranes is high, and the ratio of membrane area to module volume is 100 to 1000 times smaller than that for polymer membranes. These factors tend to equalize the cost per membrane module. The inorganic membrane life cycle is generally expected to be much longer. Inorganic membranes can be operated at high pressures and temperatures and in corrosive environments, yet still have very long life cycles. They are also less prone to fouling and can be used in applications where polymer membranes cannot.

Considerable interest and R&D are being focused on zeolite-type materials to achieve a membrane with molecular sieving characteristics. However, the permeance of such membranes tends to be substantially lower than desired. These are high-cost membranes because the methods for fabricating them are expensive.

Inorganic membranes can be made with effective pore diameters as small as 0.5 nm and as large as desired. Membranes can be made with a wide range of materials, and pore size and material can be changed to improve permeance and separation factor. Large separation factors are essential to achieve desired results in a single stage. Inorganic membranes can be made to separate small molecules from larger molecules (molecular sieves) or to separate certain large molecules from smaller molecules (enhanced surface flow). This latter effect is important because it allows separation that will keep the desired gas either on the high-pressure or the low-pressure side of the membrane. Note that the operating conditions play an important role in determining the change in mole fraction across a membrane and the amount of the desired gas that can be recovered (captured). There must be a partial pressure gradient of the desired gas across the membrane to achieve a flow of that gas through the membrane.

With all the design parameters available, it is likely that an inorganic membrane can be made that will be useful for separating CO_2 from almost any other gas if appropriate operating conditions can be achieved. However, for multiple gas mixtures, several membranes with different characteristics may be required to separate and capture high-purity CO_2.

2.4 SCIENCE AND TECHNOLOGY GAPS

We present here our views on the gaps in science and technology and the R&D required to fill or span these gaps in order that our vision may be achieved. As a result in large measure of the state of separation and capture technology, the R&D projects required to address these needs will be of the type that has been described as "Pasteur's Quadrant" research. This type of research seeks to extend the frontiers of understanding but is also inspired by considerations of use. We extend that description somewhat in that our R&D recommendations refer to a science-based technology development approach.

2.4.1 Chemical and Physical Absorption

The issue of the recovery of volatile trace elements, such as mercury, in fossil fuel is a factor in the regulatory process and must be considered in the context of this road map. The optimal recovery strategy for trace elements may not be consistent with an optimal strategy for CO_2 capture. Also, using current technologies, minimizing energy costs for CO_2 capture will probably not be compatible with a 100% CO_2 capture strategy. Better options must be developed to reduce total system costs for CO_2 recovery. Specific needs are listed below.

- Significant development work on membrane contactors is needed to improve their chemical compatibility with alkanolamines and high-temperature resistance, as well as to lower costs.
- Commercially available alkanolamines such as MEA, DEA, and MDEA have different costs, rates of reaction with CO_2, absorptive capacities, and corrosion rates. Researchers have an opportunity to optimize existing solvents or develop new solvents to reduce total capital and operating costs. Some development of chemical and physical solvents and systems will be required to achieve the vision of this road map.
- It is likely that novel solvents and system components will reduce the capital and energy costs for flue gas treatment to separate and capture CO_2. Prudent courses of action include investment in R&D on novel solvents, particularly those amenable to use in advanced systems, and investment in system studies to identify the best possible configurations of processes and equipment, particularly as they relate to cost and process simplicity.
- Considerable interest has been shown in the concept of retrofitting conventional pulverized-coal boilers for CO_2 recycling to increase the CO_2 concentration to the point where recovery becomes economically feasible.

- Molecular modeling of the absorption process is indicated to aid in the selection of absorbents.
- Kinetic modeling is needed to establish or confirm rate-limiting steps in the absorption process.
- Synthesis of absorbents based in part on molecular and kinetic models is an appropriate R&D investment.
- Systems that use air to support combustion present difficulties in separation and capture of CO_2 because of the large amount (~80%) of nitrogen diluent in the process stream. Integrated gasification combined cycle (IGCC) power plants could provide an ideal opportunity for CO_2 capture when oxygen rather than air is used to support the gasification process. (In combined cycles, which include gas turbines and steam turbines, the hot exhaust gases from the gas turbines are used to generate steam to drive the steam turbines.) Coal-derived gas for gas turbines is produced in a highly concentrated, pressurized form that allows for the use of a variety of solvents that can capture CO_2 from the gas stream before combustion, which may also be in oxygen rather than air. As a baseline case, the cost and energy benefits of chemical absorption processes integrated into an IGCC or other advanced power system must be demonstrated in a commercial setting as a real-case option.
- Novel gas/liquid contactors must be developed to minimize mass- and heat-transfer effects in gas scrubbing. The contactors might take advantage of so-called “structured packing” or even “microchannel reactors.” Using microchannel hardware, highly compact and efficient absorption systems could be developed that consist of an absorber/heat exchanger and desorber. Because the dimensions of the channels are measured in micrometers, heat- and mass-transfer effects are limited. Isothermal operation could produce higher absorption capacity. The technical challenges for microchannel reactors will be cost containment, prevention of plugging, and high throughput. Other potential problems include scale-up, corrosion, and solvent carryover.

2.4.2 Physical and Chemical Adsorption

H_2 production plants that use PSA produce an impure CO_2 stream containing unrecovered hydrogen, methane, CO, and nitrogen. This stream is recycled to the reformer as fuel, becoming the flue gas from the reformer. Physical adsorbents suffer from low selectivity and low capacity, and they are limited to operation at low temperatures.

- Adsorbents that can operate at higher temperatures in the presence of steam must be developed and are already under consideration.
- Indicated programs include R&D aimed at the synthesis of adsorbents with increased adsorptive capacity and improved kinetics and capable of producing a pure CO_2 product, as well as R&D directed to improving methods for effecting the adsorption-desorption process.
- Molecular modeling of adsorbents is needed to aid in the identification of adsorbents selective to CO_2.

- Kinetic modeling to identify rate-limiting steps and to provide a focus for adsorbent development is needed.
- New steam-tolerant, high-temperature sorbent materials need to be developed and coupled with novel process concepts. Unlike zeolites and other inorganic sorbents, these sorbent materials would be capable of adsorbing CO_2 in the presence of steam. The sorbent would be regenerated in a low-energy-intensive manner. Regenerability would eliminate material-handling problems when nonregenerable natural minerals are used. Stability of the sorbent over thousands of cycles needs to be demonstrated.
- Other novel adsorption concepts for CO_2 separation and capture are likely, and R&D on novel concepts should be pursued. If adsorbents can be developed that are capable of adsorption at high temperature and desorption using novel processes, they could significantly improve the ability to control CO_2 emissions from fossil-fueled power systems.

2.4.3 Low-Temperature Distillation

To extend the viability of low-temperature distillation processes, several development activities would be required.

- Process cycle development and process integration studies for specific applications are needed.
- Integration with sequestration processes and development of efficient and novel refrigeration cycles may enable competitive low-temperature distillation processes. Comparison with other technology options will ultimately depend on the specific application and opportunity.

2.4.4 Gas-Separation Membranes

Considerable R&D is required to realize the potential of membranes for separation and capture of CO_2, particularly at higher temperatures and pressures.

- R&D on polymeric membranes is essentially restricted to changing the composition of the polymer to increase the dissolution and diffusion rates for the desired gas components.
- Experience has shown an apparent limit to the effectiveness of polymeric membranes. The polymer composition can be changed to increase the membrane permeance, which invariably decreases the separation factor. The converse is also true: changing the composition to increase the separation factor reduces the membrane permeance. Although there is not nearly so extensive an accumulation of data for inorganic membranes, the available data do not indicate a corresponding relationship for inorganic membranes.
- R&D in molecular modeling is needed to indicate the potential of membranes to separate CO_2.
- Kinetic modeling should be used to establish the potential flux of gases in membrane systems.
- Novel membrane synthesis methods should be developed.
- Inorganic, palladium-based membrane devices could be developed that reform hydrocarbon fuels to mixtures of hydrogen and CO_2 and that, at the same time, separate the high-value hydrogen. The remaining gas, predominantly CO_2, would be recovered in a compressed form. The hydrogen could be used in future fuel cell systems or advanced turbine power systems. Pure hydrogen, when

burned to generate power, produces water vapor as the only product of combustion. Daunting issues include capital costs and stabilization of the membrane in highly corrosive gases if coal is used.

2.4.5 Product Treatment and Conversion

As noted previously, the product of the separation and capture function will be CO_2. However, the attributes of the CO_2, such as its concentration, impurities, pressure, and temperature, will differ for the respective combinations of sources and separation and capture methods employed. Absorption processes, for example, may be manipulated to yield CO_2 streams of very high purity, and those CO_2 streams will generally be at source pressures. For those options that will sequester carbon as CO_2, it is assumed that the CO_2 will be subjected to the purification treatment and pressurization required for transportation and for sequestration. The CO_2 product may be provided at 90 to 99+% purity, at temperatures ranging from cryogenic to a few hundred degrees Celsius, and at pressures from atmospheric to more than 3.5 MPa. Different carbon forms (other than CO_2) may also be required for some of the sequestration options. R&D should address

- full-cycle analysis of product treatment and conversion to meet the requirements of transportation and sequestration
- conversion of CO_2 to the required form for the particular sequestration option
- the disposition of the variety of by-products that may be produced during conversion of the CO_2 to other products

2.4.6 Transportation

In some scenarios, the separation and capture process will be remote from the sequestration process. Any R&D program must include carbon transport to the sequestration site and should address primarily systems aspects such as optimization and integration of the carbon sources, separation and capture, transportation, and sequestration.

2.4.7 Advanced Concepts

This section addresses advanced concepts that have been identified and/or advocated as having significant potential for CO_2 separation and capture. In one advanced concept, CO_2-containing gases are dissolved in water, followed by the formation of CO_2 hydrates in which CO_2 is trapped in a crystalline ice-like solid. The process requires gases at about 0°C and 1 to 7 MPa, depending on the other gases present and on the partial pressure of CO_2 in the gas stream. The formation of CO_2 hydrates may be especially amenable to removal of CO_2 from pressurized gas streams with minimal energy losses.

An advanced approach, called electrical swing adsorption (ESA), that addresses many of the issues of PSA and TSA systems uses a novel carbon-bonded activated carbon fiber as the adsorption medium (Burchell et al. 1997). Activation conditions for these adsorbents may be varied to increase or decrease pore size, pore volume, and surface area to improve the effectiveness of the carbon fiber as a CO_2 adsorbent. This material is also highly conductive electrically, so adsorbed gases can be rapidly, effectively, and efficiently desorbed by passing a low-voltage electrical current through the material. This adsorption-desorption process may be used with no variation of system pressure and with minimal variation in system temperature. The electrical energy required for desorption is approximately equal to the heat of adsorption of the adsorbed gas; thus the ESA process is promising as an energy-efficient, economical gas separation and capture method.

Another novel technology is referred to as "chemical-looping combustion," or more recently as "sorbent energy transfer." In this process, the fossil fuel (gasified coal or natural gas) transfers its energy to reduce a metal oxide, producing steam and high-pressure CO_2 that can be sequestered with little additional compression energy. The steam is used in a steam turbine to produce electricity. The metal is then reoxidized in air, producing heat to raise the temperature of a high-pressure stream of air or nitrogen to drive a gas turbine to generate more electricity. The oxidized metal is sent to the reducing vessel to repeat the cycle. The barriers to any new combustion system are legion; this is also true even of conventional coal combustion using oxygen instead of air with CO_2 recycling.

2.5 ALIGNMENT OF REQUIREMENTS TO CAPABILITIES (R&D ROAD MAP)

As indicated in the preceding section, numerous R&D needs and opportunities exist for improvements and innovations related to CO_2 separation and capture. Figure 2.1 presents an R&D road map for pursuing the stated

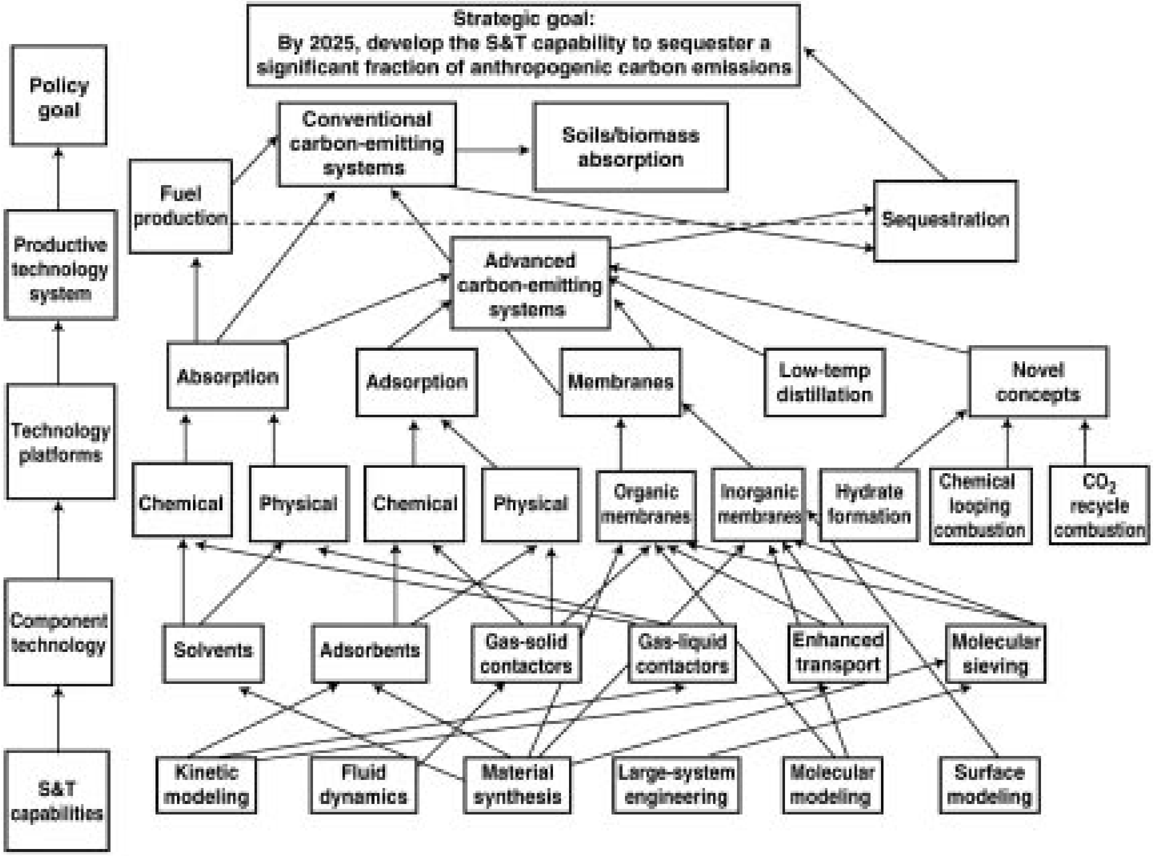


Fig. 2.1. Separation and capture R&D road map.

goal. Based on the analysis presented here, as well as analyses presented in the references to this chapter, separation and capture of CO_2 from anthropogenic sources for sequestration via any of several options appear to be possible. Notwithstanding this possibility, a disciplined R&D program directed to improvements in currently available technology, extension of current developments, and pursuit of innovative and novel approaches is critical to ensuring the ability to effectively and efficiently capture CO_2 at costs that are not prohibitive.

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3 OCEAN SEQUESTRATION

Vision

By 2025, develop (1) the technology to implement ocean sequestration of CO_2, (2) the knowledge to understand its effects on marine ecosystems and on the ocean's biogeochemical cycles, and (3) the modeling tools to determine the long-term fate of sequestered CO_2.

The ocean represents a large potential sink for sequestration of anthropogenic CO_2 emissions. Although the long-term effectiveness and potential side effects of using the oceans in this way are unknown, two methods of enhancing sequestration have been proposed:

- the direct injection of a relatively pure CO_2 stream that has been generated, for example, at a power plant or from an industrial process (see Sect. 3.1)
- the enhancement of the net oceanic uptake from the atmosphere, for example, through iron fertilization (see Sect. 3.2)

Other pathways are also possible but would probably require longer time frames to be developed (see Sect. 3.3). For a given pathway, our goal is to analyze the tradeoffs among cost, long-term effectiveness, and undesirable changes to the ocean ecosystem.

On average, the ocean is about 4000 m deep and contains 40,000 GtC (IPCC 1996). It is made up of a surface layer (nominally 100 m thick, but the depth varies), a thermocline (down to about 1000 m deep) that is stably stratified, and the deep ocean below 1000 m. Its waters circulate between surface and deep layers on varying time scales from 250 years in the Atlantic Ocean to 1000 years for parts of the Pacific Ocean. The amount of carbon that would cause a doubling of the atmospheric concentration would change the deep ocean concentration by less than 2%.

Currently, net oceanic uptake of 2 ± 0.8 GtC/year[1] results from the growth of anthropogenic

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[1] This number for net ocean uptake is from IPCC and is based on data for the mid-1980s. Changes in sea-air forcing since then should have increased this flux slightly.

CO_2 in the atmosphere. On a time scale of 1000 years, about 90% of today's anthropogenic emissions of CO_2 will be transferred to the ocean (see Fig. 3.1). Ocean sequestration strategies attempt to speed up this process to reduce both peak atmospheric CO_2 concentrations and their rate of increase.

Although the ocean's biomass represents about 0.05% of the terrestrial ecosystem, it converts about as much inorganic carbon to organic matter (about 50 GtC/year) as do processes on land. The photosynthetic fixation of CO_2 by ocean organisms, followed by the sinking and remineralization (conversion to CO_2) of organic carbon, is a natural process for sequestering CO_2 in the deep sea. This process is often referred to as the "biological pump" (see Fig. 3.2).

The question is whether we can use the deep sea as a site for sequestration of additional anthropogenic CO_2. Many people are wary of ocean sequestration, including some authors of this chapter, because it is known that small changes in biogeochemical cycles may have large consequences, many of which are secondary and difficult to predict. Nevertheless, ocean sequestration is occurring on a large scale today, and entrepreneurs are already trying to commercialize ocean sequestration technologies. Therefore, it is imperative to conduct research to better understand the risks as well as the opportunities. The ocean plays an important role in sustaining the biosphere, so any change in ocean ecosystem function must be viewed with extreme caution.

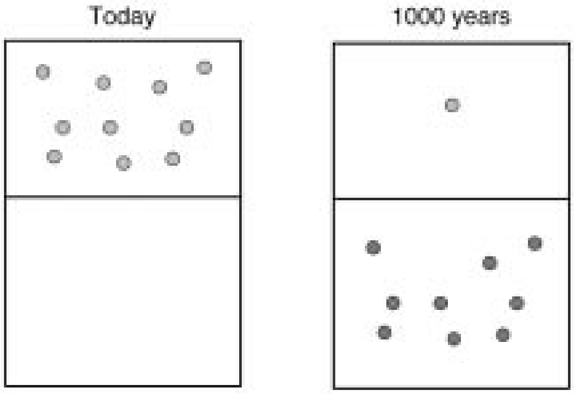

Fig. 3.1. Every year the ocean actively takes up one-third of our anthropogenic CO_2 emissions. Eventually (over 1000 years), about 90% of today's anthropogenic emissions of CO_2 will be transferred to the ocean. Ocean sequestration strategies attempt to speed up this ongoing process to reduce both peak atmospheric CO_2 concentrations and their rate of increase.

How much carbon can the ocean sequester? Because of high pressures prevailing in deep ocean environments, a large quantity of CO_2 (exceeding the estimated available fossil fuel resources of 5,000 to 10,000 GtC) may be dissolved in deep ocean waters. However, a more realistic criterion needs to be based on an understanding of the biogeochemistry of the oceans. At present, we do not have enough information to estimate how much carbon can be sequestered without perturbing marine ecosystem structure and function; obtaining this information is one of the goals of the proposed research (Takahashi et al. 1981; Sarmiento and Bender 1994).[2]

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[2] As an example calculation with no implications as to what an environmentally acceptable amount is, adding about 1300 GtC to the ocean would result in a pH decrease of 0.3. This pH change is similar to the change that will occur in the surface ocean as a result of doubling the preindustrial amount of atmospheric CO_2. The change in surface seawater pH today, from that of preindustrial times, is already 0.1.

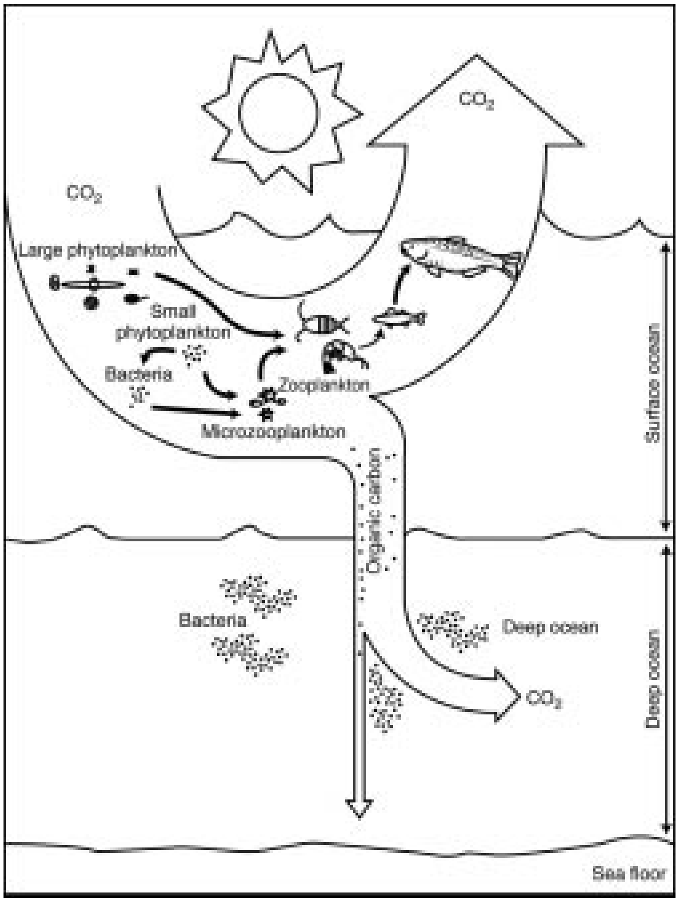

Fig. 3.2. A schematic diagram of the biological pump. In this generalized pelagic food web, CO$_2$ is being fixed by phytoplankton through photosynthesis. Phytoplankton are consumed by zooplankton that may, in turn, be consumed by higher trophic organisms, such as fish. Organic carbon in the form of detritus (e.g., fecal pellets, decaying organisms) sinks to the ocean depths, where it is remineralized to CO$_2$ by bacteria en route.

3.1 DIRECT INJECTION OF CO$_2$

The direct injection of CO$_2$ into the ocean requires starting with a fairly concentrated stream of CO$_2$ and delivering it to locations in the ocean where it will be effectively sequestered for hundreds of years, if not longer. To accomplish this, CO$_2$ will most likely be injected as a liquid below the thermocline at depths greater than 1000 m (Herzog 1998). One limitation of this approach is that it is best suited to large, stationary CO$_2$ sources with access to deep-sea sequestration sites—sources that may account for about 15 to 20% of our anthropogenic CO$_2$ emissions.

We have the technology to proceed with this option. However, we do not have the knowledge to adequately optimize the costs, determine the effectiveness of the sequestration (i.e., its impact in mitigating climate change), and understand the resulting changes in the biogeochemical cycles of the oceans. This section addresses how we may gain this knowledge.

3.1.1 Science and Technology Requirements

There are many technical options for sequestration by direct injection of CO$_2$. For example, injections may occur at moderate depths (1000–2000 m), at deep depths (>3000 m), in depressions on the ocean floor, or even into the suboceanic crust of the earth. The CO$_2$ may be sequestered by dissolution in the water column or by the formation of CO$_2$ hydrates, which are solid, ice-like compounds. The delivery of the CO$_2$ may be by pipeline or tanker. In all cases, on the scale of kilometers around the injection point, near-field computer models are needed to understand the physical and chemical interactions between CO$_2$ and seawater and the interaction between CO$_2$-enriched seawater and stratified surrounding water. One challenge is to determine how to use the buffering effect of bottom sediments (e.g., the ability of calcium carbonate to react with the CO$_2$) to increase the capacity and effectiveness of ocean sequestration (Archer 1996). Another challenge is to understand the kinetics associated with the formation of CO_2 hydrates and to try to take advantage of their properties (e.g., increased density, lower mass transfer coefficient) for carbon sequestration. Finally, engineering analysis is required to estimate the costs of the various injection pathways.

Sequestration effectiveness will depend on the exact depth and location of the injection. In general, the deeper the CO_2 is injected, the more effectively it is sequestered; but injecting deeper requires more advanced technologies and may increase costs. Regional and global ocean general circulation models (OGCMs) are required to quantify sequestration effectiveness by calculating the reduction in atmospheric CO_2 as a function of time as a result of various ocean sequestration strategies. However, OGCMs must be improved to reduce the uncertainty associated with their results.

Environmental impacts near the injection point must be detailed, and the long-term, broad-scale impacts on the function of the ocean ecosystem must be understood. The most significant environmental impact is expected to be associated with lowered pH as a result of the reaction of CO_2 with seawater. Non-swimming marine organisms residing at depths of about 1000 m or greater are most likely to be affected adversely by more acidic seawater; the magnitude of the impact will depend on both the level of pH change and the duration of exposure. The microbial community would also be affected, causing unknown impacts on biogeochemical processes that play a crucial role in the ocean carbon cycle. Local environmental impacts may be minimized by designing the injection system to disperse the CO_2. Specific needs for R&D include gathering baseline data and implementing cost-effective monitoring. Robust, predictive models could help reduce the costs of monitoring by focusing sampling on areas of greatest potential impact.

3.1.2 Current Scientific and Technological Capabilities

Led by offshore exploration and production activities of the oil and gas industry, great strides have been made in the development of undersea offshore technology. It is becoming routine to work in depths approaching 2000 m. Work at much deeper depths, even approaching 10,000 m, is possible at reduced scales and/or time horizons, as has been shown in deep drilling and other scientific programs. However, many technical challenges still exist in going deep at large scales for extended times. Therefore, as a first step, it appears that the best strategy is to discharge the CO_2 below the thermocline at moderate depths of 1000 to 2000 m.

To implement that strategy, several methods of injection have been proposed (Fig. 3.3). One method is to transport the liquid CO_2 from shore in a pipeline and to discharge it from a manifold lying on the ocean bottom, forming a rising droplet plume. Another method is to transport the liquid CO_2 by tanker and then discharge it from a pipe towed by the moving ship. Although the means of delivery are different, the plumes resulting from these two options would be quite similar and, therefore, research on these two injection methods should be considered complementary.

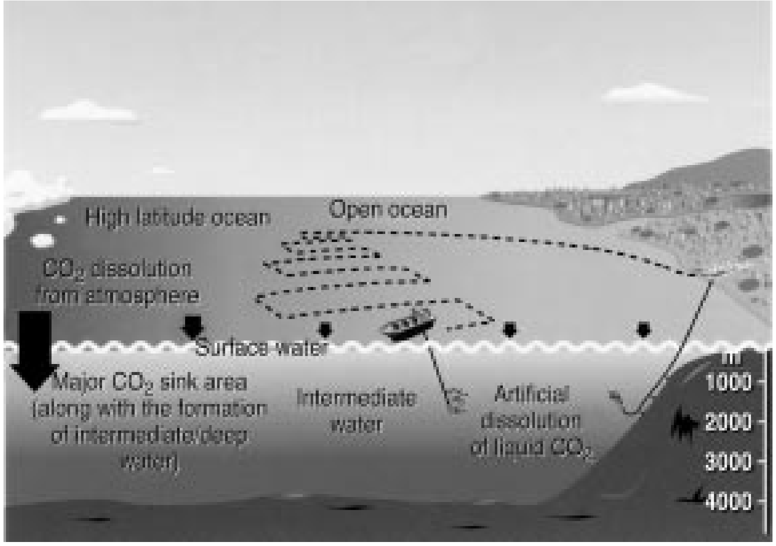

Fig. 3.3. For injection of CO_2 at depths of 1000 to 2000 m, it has been suggested that liquid CO_2 be transported from shore through a pipeline for discharge from a manifold lying on the ocean bottom. Another proposal is to transport the liquid CO_2 by tanker and then discharge it from a pipe towed by the moving ship.

Once the CO_2 leaves the pipe, our current capabilities are much more limited. Models do exist to characterize the near-field plume, but they have not been validated with experimental data. We know that CO_2 hydrates may be formed from the injected CO_2 (see the sidebar on formation of CO_2 hydrates). The thermodynamic behavior of hydrates is well understood and their kinetics have been extensively investigated. However, we do not fully understand the kinetics that will control the formation and dissolution of hydrates in seawater, especially under the dynamic conditions in the plume.

Regional and global OGCMs are available to describe the ultimate fate of the injected CO_2 by modeling its behavior in the mid-field (tens to hundreds of kilometers from the injection point) and in the far field (hundreds of kilometers and greater from the injection point) (Fig. 3.4). These models can simulate broad characteristics of observed transient tracer fields (e.g., chlorofluorocarbons, carbon-14, and tritium), whose movements can be detected in the open ocean. However, for modeling the fate of a point source such as injected CO_2, the uncertainties are large and the results will not be definitive.

Perhaps the area we are least capable of understanding is the environmental consequences of CO_2 injection. We do understand the ocean's capacity to neutralize the water that is acidified by injected CO_2. We have models to predict pH changes to tens of kilometers around the injection point. However, we have very little knowledge of how the pH change or other impacts due to CO_2 injection would affect the biogeochemistry and ecosystems in the deep ocean.

These are selected research activities now under way to evaluate the ocean sequestration of CO_2:

International Field Experiment. Is ocean sequestration of CO_2 technically feasible? What are its environmental impacts? Can these impacts be minimized economically? An international research project is addressing these questions. Japan, Norway, and the United States signed a Project Agreement for International Collaboration on CO_2 Ocean Sequestration in December 1997; since that time, Canada and ABB (Switzerland) have joined the project,

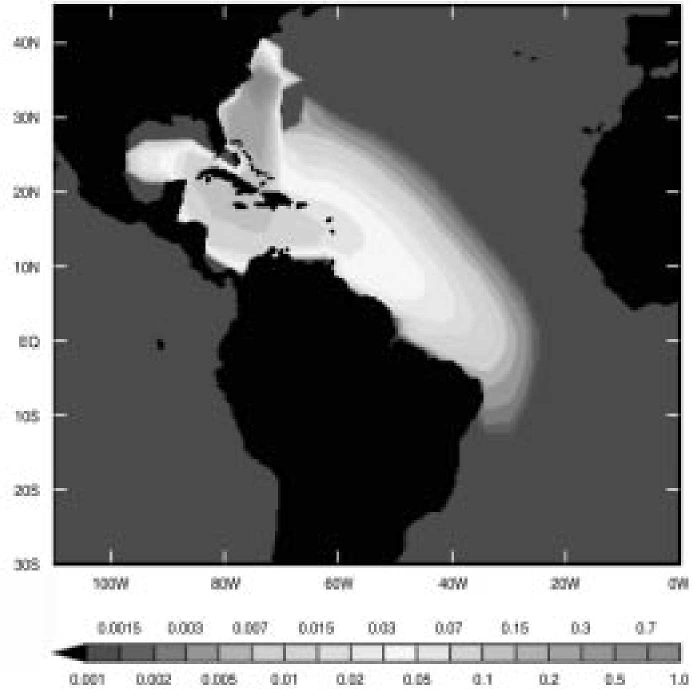

Fig. 3.4. Simulated distribution of carbon injected into the ocean at a depth of 1720 m off the coast of Cape Hatteras, North Carolina, after 20 years of continuous injection, as computed by the three-dimensional ocean model of Lawrence Livermore National Laboratory. At this depth, the model predicts that the carbon would be swept south with an undercurrent that flows beneath the Gulf Stream. This kind of simulation is necessary to determine the most effective depths and locations for deep-sea CO_2 injection.

which will continue through March 31, 2002. A field experiment will be performed in the summer of 2000 off the Kona Coast of Hawaii. The implementing research organizations are the Research Institute of Innovative Technology for the Earth (Japan), the Norwegian Institute for Water Research (Norway), the Institute of Ocean Sciences (Canada), and the Massachusetts Institute of Technology [(MIT) United States]. The general contractor for the project is the Pacific International Center for High-Technology Research in Hawaii. To investigate longer-term acute and chronic biological impacts, a phase 2 project may be conducted in an enclosure or at a semi-enclosed site such as a fjord (Adams et al. 1998).

Experiments at the Monterey Bay Aquarium Research Institute (MBARI). In April 1998, MBARI scientists successfully carried out a controlled experiment with a 9-L liquid CO_2 release at a depth of 3650 m (in situ temperature about 1.6°C) from *Tiburon*, an unmanned, remotely operated vehicle (ROV) tethered to a ship. For several hours they observed the transformation of liquid CO_2 into solid hydrate (see sidebar).

Comparison of Ocean Carbon Cycle Models. The International Geosphere-Biosphere Programme initiated the Ocean Carbon-Cycle Model Intercomparison Project (OCMIP) in 1995 through the Global Analysis, Interpretation, and Modeling task force. OCMIP is an international project devoted to improving marine carbon cycle models by comparing them with each other and by evaluating them using observational data sets. Thanks in part to some additional funding provided by the IEA Greenhouse Gas R&D Programme, the European research program on Global Ocean Storage and Anthropogenic Carbon will also look at global scientific aspects of the deep-ocean CO_2 sequestration issue. Specifically, the researchers will compare models of dispersion of CO_2 from seven hypothetical point sources to get a better understanding of sequestration efficiency. The U.S. component of OCMIP (funded by the National Science Foundation and the National Aeronautics and Space

Administration and involving MIT, Pennsylvania State University, the National Center for Atmospheric Research, Lawrence Livermore National Laboratory, and Princeton University) is positioned to perform the same set of analyses with U.S. models, but no funding is available yet for this activity.

The CO_2 Ocean Sequestration Project in Japan. In April 1997, a 5-year national program looking at ocean sequestration of CO_2 began in Japan. Annual funding is in excess of $10 million per year. The lead research institutes for this program are the Research Institute of Innovative Technology for the Earth and the Kansai Environmental Engineering Center. This project encompasses joint research activities involving national institutes, private companies, and universities. The R&D agenda includes studying the behavior of liquid CO_2 released into the ocean, developing an engineering system for CO_2 injection, assessing the impacts of CO_2 on marine organisms, developing a near-field environmental impact assessment model, predicting the long-term fate of sequestered CO_2, and participating in the international field experiment (Masuda 1998).

3.1.3 Science and Technology Gaps

By comparing our technical capabilities with the technical requirements for developing effective, economical, and environmentally acceptable ocean sequestration technologies, we identified the following gaps:

- Insufficient information is available to optimize an injection strategy. For example, we must obtain answers to these questions:
  – Should dilute CO_2 streams be injected to try to avoid any environmental impacts? Will this strategy have an impact on cost?
  – Should CO_2 streams be injected deep in the ocean to maximize retention time? Will it be worth the extra cost? Will the technical capability to do so be available by 2025?
- On the engineering side, these specific research gaps must be addressed:
  – Develop injection technology. Even though CO_2 can be injected now, we need a technology that is low in cost and maintenance and that can be used at greater ocean depths, if necessary.
  – Experimentally demonstrate the behavior of CO_2 near the injection point. This understanding may lead to injection strategies that can minimize any environmental impacts.
  – Better understand the dynamic response (i.e., kinetic behavior) corresponding to hydrate formation and dissolution. This is a first step in developing strategies that could use hydrate formation to our advantage for sequestering CO_2 (see Chap. 7).
  – Assuming no environmental constraints, develop strategies that maximize the neutralization of the acidified water by deep-ocean calcium carbonate sediments. This approach would have two positive effects: reducing pH changes in the water column and increasing the sequestration capacity of the ocean.
  – Develop monitoring technology to observe changes in the ocean's biogeochemical processes and ecosystems.
- Concerning the effectiveness of injection technologies, some

Formation of CO_2 Hydrates in the Deep Sea

The accompany photo from the MBARI experiment shows the overflow of liquid CO_2 onto the sea floor.

One suggested strategy for ocean sequestration of CO_2 by direct injection is to create a long-lived "CO_2 lake" on the ocean floor. To investigate this concept, a group of scientists at MBARI performed a series of deep ocean experiments for the disposal of fossil fuel CO_2 in the form of solid hydrate (CO_2 5.75 H_2O). One recent experiment was carried out with the MBARI ROV *Tiburon* off the central California coast. The ROV carried about 9 L of liquid CO_2 to a depth of 3650 m, where the pressure is ~36 MPa and the temperature is 1.6°C. The CO_2 was in a steel accumulator in which a piston continually adjusted to ambient pressure. The CO_2 was expelled by applying pressure on the piston from a water pump powered by vehicle hydraulics. Partly because CO_2 is denser than seawater at this depth, hydrate formation there dramatically differs from that observed at shallower depths.

MBARI scientists observed a rapid increase in the volume of the contained experiments as the CO_2-water interface rose, causing overflow of the liquid onto the sea floor about 100 min after the experiment started. They attributed this effect to the formation of a hydrate, readily seen as an accumulating mass at the bottom of the containers. This incorporation of large amounts of water in the solid phase resulted in an expansion of system volume by about a factor of 7, causing the remaining liquid CO_2 to spill over. High interfacial tension maintained a strong barrier, preventing the released liquid CO_2 from interacting with the sediments.

specific research gaps can be closed if researchers accomplish the following:
  - – Address weaknesses in OGCMs, specifically western boundary currents, ocean bottom currents, and sub-grid scale processes (e.g., eddies); and test the models using natural and, perhaps, experimentally released tracers.
  - – Couple near-field with far-field effects of CO_2 injection through a hierarchy of models (or nonuniform grids). Specifically, plume modeling should be coupled with basin- and global-scale ocean circulation models.

- Related to the environmental impacts of direct injection, some specific research gaps can be filled if researchers accomplish the following:
  - – Understand the carbon cycle of the ocean to determine the baseline. CO_2 goes into the ocean naturally, even with no enhancement or direct injection. These effects need to be understood.
  - – Determine parameters for direct injection of CO_2 that will minimize environmental impacts.
  - – Understand the effect of the sustained release of elevated

levels of CO_2 on ocean biogeochemistry and ecosystems. Are there any other impacts that are important beyond the lowering of pH?
  - Find answers to these questions: Should the injected CO_2 stream be pure (i.e., >99%)? Can ocean ecosystems tolerate other gases such as nitrogen, oxygen, hydrogen, CO, carbon oxysulfide, argon, hydrogen sulfide, NO_x, SO_2, and trace metals? To what levels? What effects do these gases have on ocean ecosystems?
  - Investigate the impact of CO_2 on bioturbation of sediments. (Bioturbation is the disruption of marine sedimentary structures by the activities of benthic organisms.) Bioturbation makes skeletal calcium carbonate buried in the upper 10 or more centimeters of sediments available for the neutralization reaction of sequestered CO_2.

3.1.4 Research and Development Plan

To close the gaps, these specific line items are recommended for an R&D plan:

- Increase understanding of the behavior of CO_2 released in the ocean through laboratory studies, small-scale field experiments (e.g., the international field experiment and MBARI experiments) as well as near-field modeling efforts.
- Perform laboratory experiments to measure the effects of changes in pH and in CO_2 concentrations on organisms from mid-water and deep-sea habitats.
- Determine the environmental impacts of the business-as-usual scenario (i.e., natural CO_2 uptake by the ocean).
- Improve global/regional modeling to quantify benefits and identify sites.
  - Conduct an OGCM intercomparison exercise on point sources of CO_2 in the deep ocean with the goal of answering two questions: How good are the models? How can the models be improved?
  - Support measurement programs that can provide validation data, including the results of better analyses of natural tracers.
- Conduct a pilot experiment to determine the feasibility of CO_2 injection, monitor its ecological impact, and characterize its far-field effects by collecting time-series data.
- Integrate the results of the previous efforts into specific injection scenarios (including recommended sites and modes of discharge) that optimize the tradeoffs among cost, environmental impacts, and effectiveness.

3.2 ENHANCEMENT OF NATURAL CARBON SEQUESTRATION IN THE OCEAN

The natural process of carbon fixation by phytoplankton (primary production) results in sequestration of carbon in the deep ocean via the biological pump (see Fig. 3.2). The biological pump involves the gravitational settling, decomposition, and burial of biogenic debris formed in the upper levels of the ocean. Phytoplankton in surface waters are rapidly grazed by zooplankton, which in turn may be consumed by larger animals such as fish. While it is estimated that 70–80% of the fixed carbon is recycled in surface waters (Sarmiento 1993), the rest is exported as particulate organic carbon (POC) to the deep ocean, where it is slowly mineralized by bacteria.

Fertilization of the oceans with micronutrients (such as iron) and macronutrients (such as nitrogen and phosphorus) is a strategy that is being considered to enhance drawdown of CO_2 from the atmosphere and thus accelerate the biological pump. Because certain areas of the ocean have low levels of phytoplankton yet a high concentration of nitrogen and phosphorus, it was realized that a lack of iron might limit phytoplankton growth (see the IRONEX sidebar) (Chisholm 1992). Initial studies of iron fertilization in high-nutrient, low-chlorophyll (HNLC) waters have demonstrated that in situ fertilization of surface waters with iron to promote growth of phytoplankton is feasible at scales of tens of square kilometers (Coale et al. 1996).

Some commercial ventures are trying to capitalize on ocean fertilization for increasing their fish harvest. While these ventures have a primary goal other than carbon sequestration, the strategies of fertilization and potential for environmental impact are the same, and all commercial ventures using fertilization to enhance fish production also claim carbon sequestration as a secondary benefit. For example, Ocean Farming, Inc., has planned a large-scale fertilization of the coastal waters of the Marshall Islands with iron, silicon, and phosphorus to increase the yield of tuna. This enterprise claims carbon sequestration as a secondary goal. Similarly, MARICULT, a European consortium of government and industry, is currently exploring the commercial feasibility of fertilizing coastal waters to increase the fish harvest. These commercial ventures are proceeding even though the

IRONEX: Iron Fertilization Experiments

The equatorial Pacific and Southern Oceans have excess macronutrients, nitrogen and phosphorus, in their surface waters. The late John Martin of Moss Landing Laboratories hypothesized that these nutrients are abundant in these regions because the micronutrient iron is very scarce, thus limiting phytoplankton growth. To test this hypothesis, two unenclosed transient iron fertilization experiments (IRONEX I and II) were conducted in the equatorial Pacific in 1993 and 1995, and a third experiment is being planned for the Southern Ocean. The results from IRONEX II, in which 500 kg iron was added to a 72 km^2 patch of surface water, were particularly dramatic. Quantum yield of photosynthesis increased significantly within 2 hours, nitrogen and phosphorus were drawn down, and chlorophyll concentrations increased 30-fold within a week, approaching levels typical of coastal waters. The species composition of the phytoplankton community shifted dramatically, with larger cells dominating by the end of the experiment. The bloom caused a decrease in the partial pressure of CO_2 in the middle of the patch and a three-fold increase in dimethyl sulfide production, both of which have implications for climate regulation. The duration of the experiment was 18 days—not long enough for significant changes at higher trophic levels—and the bloom dissipated shortly after the last injection of iron. It is not at all clear how sustained fertilization would affect ecosystem structure, export of carbon to the deep sea, and fluxes of greenhouse gases. These effects cannot be predicted from a transient experiment, so longer-term fertilization experiments are needed.

potential ecological consequences of ocean fertilization are not yet known. Such consequences could range from changes in species diversity to induction of anoxia and significant adverse effects on community structure and function. The fundamental question that should be answered is whether any alterations in the ocean ecosystem are justified relative to the benefits to society.

3.2.1 Science and Technology Requirements

An urgent need exists to determine the potential ecological consequences of large-scale ocean fertilization on the biosphere and on biogeochemical cycling. We need to be able to predict accurately how ecosystems will change in response to either short-term or sustained fertilization of the oceans. We also need to understand overall natural carbon sequestration efficiency in the oceans. Moreover, the feasibility of ocean fertilization will depend on optimization of fertilizer design, delivery, and ecological monitoring. Long-term ecological monitoring may prove extremely costly, so robust, dynamic models that predict ecosystem response will be the key to designing an economical and effective monitoring strategy.

3.2.2 Current Science and Technology Capabilities

Small-scale ocean fertilization is feasible from both an engineering and an economic perspective. The technology for fertilizing surface waters is fairly straightforward; it involves releasing microalgal nutrients such as iron, phosphorus, or nitrogen from platforms such as boats or airplanes. Recent iron fertilization experiments (IRONEX I and II) demonstrated that a deficiency of iron limits primary production (photosynthesis) in HNLC areas of the ocean where nitrogen and phosphorus are abundant (see the IRONEX sidebar). The application of 500 kg of iron to 72 km^2 in the equatorial Pacific resulted in a 30-fold increase in phytoplankton biomass, a dramatic shift in species composition and elevated carbon fixation rates.

A number of technologies are available for monitoring ecosystem response to fertilization (or deliberate CO_2 injection), including assays for primary and secondary production using radiotracer techniques. Determining ecosystem response below the euphotic zone (the zone where the net rate of photosynthesis is positive) could use in situ filtration techniques that determine size distributions and chemistry of POC with minimal disturbance to the samples (Bishop et al. 1987; Bishop 1999) (see Fig. 3.5). An ocean carbon inventory survey will

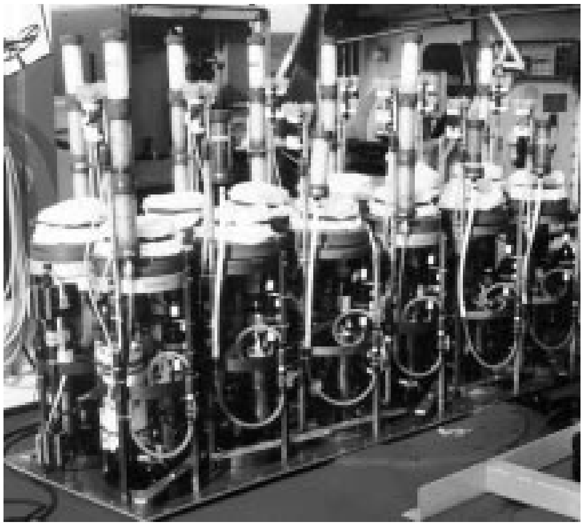

Fig. 3.5. The multiple unit large-volume in situ filtration system (MULVFS) allows the precise determination of properties of particulate matter that is needed for a systematic survey of ocean carbon inventory and for the evaluation of ecosystem function. MULVFS samples are large enough to meet the diverse needs of multiple research groups.

use improved technologies to characterize the dissolved and particulate organic and inorganic carbon pools and ecosystem function. More efficient shipboard sampling technologies for many key parameters have been developed or are under development. A growing suite of autonomously operating carbon and nutrient sensors is under development for deployment on moored, floating, or autonomous profiling platforms. The use of optical approaches for remote sensing of water column primary productivity and carbon biomass is rapidly progressing.

To simulate the effectiveness of ocean fertilization as a CO_2 sequestration strategy, two challenges must be met. First, we must be able to predict the change in biological carbon export from the surface ocean to the deep ocean as a result of ocean fertilization. Second, we must be able to predict the fate of this carbon after it reaches the deep ocean.

The problem of predicting changes in carbon export from the surface ocean resulting from fertilization is a difficult one, because it depends on hard-to-predict changes in ecosystem structure. Surface ocean biology models have simulated biological carbon export at specific locations reasonably well, but these models have generally been “tuned” to match some observations at these locations. Work is under way to try to develop a single model that can be applied across the global ocean to predict carbon export from physical and nutrient conditions alone. Although much progress has been made in this area, this goal has not yet been attained. It will be important to monitor closely any ocean fertilization experiments to develop solid data sets for use in evaluating ocean biology and ecosystem models.

Predicting the fate of biogenic carbon after it is transported to the deep ocean is also a thorny problem. An important component of this prediction is the estimation of the depth at which the organic carbon will be oxidized, and this depth will depend on whether the organic carbon is particulate or dissolved, the size of the particles, and other factors. Once the organic carbon has oxidized in the deep ocean, the problem is largely equivalent to the deep-ocean CO_2 injection problem—predicting ocean transport, CO_2 degassing (returning to the atmosphere), and sediment interactions. Several simulations of this aspect of the problem have already been made using assumptions about the change in ocean biological carbon export and the depth of its oxidation. These studies have concluded that the effectiveness of ocean fertilization as a CO_2 sequestration strategy is very sensitive to the rate of ocean mixing between the ocean’s surface layers and its deep layers. If some carbon in the deep layers is brought to the surface through mixing, then it could return to the atmosphere through degassing rather than become buried in the sediments.

3.2.3 Science and Technology Gaps

A number of critical gaps exist in our understanding of ocean fertilization as a strategy for enhanced carbon sequestration.

- The impact of long-term ocean fertilization on the structure and function of marine ecosystems is unknown. Changes in phytoplankton structure are an inevitable consequence of fertilization, and this would lead to changes in ocean food web structure and dynamics. Such changes could have long-term (both positive and negative) impacts on

fisheries, many of which are already declining primarily because of over-fishing. Fertilization with iron and phosphorus in lake ecosystems selects for the growth of cyanobacteria over other types of phytoplankton; this proliferation could be a problem because certain species of cyanobacteria produce powerful toxins. Whether a toxic form of cyanobacteria might occur in marine ecosystems is unknown at present.
- The impact of sustained fertilization on the natural biogeochemical cycles in the ocean is completely unknown. The biogeochemical cycles of carbon, nitrogen, phosphorus, silicon, and sulfur in marine environments are highly complex and intertwined, and recent evidence suggests that they are regulated by the availability of iron on a global scale. A perturbation of one elemental cycle can have repercussions that are unanticipated.
- The potential risk of fertilization leading to eutrophication must be determined. Eutrophication causes oxygen depletion, which could kill species that require oxygen; in some cases, it can lead to the production of methane (another greenhouse gas) by microorganisms. On the other hand, lack of oxygen in the sediments of the ocean floor could lead to an increase in the preservation of buried carbon due to slow rates of mineralization. The impact of fertilization on sediment-dwelling (benthic) organisms is unknown.
- At present, we do not have a good understanding of the effectiveness of ocean fertilization at a large scale. Will enhanced carbon fixation in surface waters result in an increase in carbon sequestered in the deep ocean? Some preliminary modeling work has been done, but these models are based on simplified biological assumptions and have not been validated against real-world data.

3.2.4 Research and Development Plan

Sustained longer-term fertilization experiments are vitally important to assess the ecological consequences of in situ fertilization. More important, such experiments yield information that is vital to understanding the mechanisms that have triggered past climate changes such as glacial-interglacial transitions. We need to know how marine food webs change in response to nutrient enrichment. At a minimum, such research should seek to accomplish the following:

- Increase understanding of the existing “biological pump” and identify the nutrients that regulate it on a global scale. Naturally occurring fertilization by upwelling, wind-driven dust deposition, or iron-rich coastal runoff may provide insights into the role of nutrients in ocean sequestration of carbon.
- Determine to what extent increased primary production in surface waters enhances the biological pumping of carbon to deeper waters. This determination will require an inventory of ocean carbon, including export of POC and particulate inorganic carbon to the deep sea and the mineralization (oxidation) or dissolution of all carbon at depth. Development of technologies for autonomous determination of all forms of carbon is needed.
- Determine the impact of sequestration on biogeochemical cycling.

For example, if carbon is sequestered, the available nitrogen and phosphorus in surface waters will be reduced. How long will it take for natural nitrogen and phosphorus to be replenished to support ongoing primary production?

- Determine the relationship between iron and nitrogen fixation. Would fertilization with iron and phosphorus in the ocean cause cyanobacterial blooms that would increase the oceans' nitrogen inventory? Would an increase in nitrogen lead to an increase in carbon export?
- Monitor the effects of fertilization on phytoplankton community structure and trophic dynamics. Can nutrient ratios be "designed" to increase productivity without changing the community structure, thus minimizing environmental impacts?
- Validate models of sustained fertilization with improved biological parameterization. We need to couple physical, chemical, and biological models to predict the effectiveness of ocean sequestration. We especially need to know how long anthropogenic carbon will remain sequestered in the ocean.

3.3 LONGER-TERM, INNOVATIVE CONCEPTS FOR OCEAN CO_2 SEQUESTRATION

Whereas most of the research in ocean CO_2 sequestration has been in the areas of deep-sea CO_2 injection and ocean fertilization, both of these concepts are less than 25 years old, and a plan written 25 years ago might have missed these strategies. Therefore, we should encourage the development of innovative concepts for sequestering CO_2 in the oceans that may be the basis for advanced technologies in the coming years and decades. A few concepts are described below for illustrative purposes only—at present we do not have enough information to judge their feasibility.

- **Converting concentrated CO_2 at a power plant to relatively strong carbonic acid, using the acid to dissolve carbonate minerals, and then releasing the dissolved carbonate and dissolved fossil-fuel CO_2 into the ocean.** This technique would greatly enhance ocean storage capacity and would eliminate concerns about changes in pH because the dissolved carbonate mineral would neutralize much of the acidity of the carbonic acid. This approach would greatly diminish eventual degassing back to the atmosphere, circumventing the need for pumping CO_2 to great distances and depths. Limitations of the concept include the need for large amounts of water and the need to transport as much carbonate mineral as coal to the power plant.

- **Burial of organic carbon in the ocean.** Organic waste could be stored as a thick layer on the ocean bottom. Sources of this organic carbon could include farm waste, carbon-black from decarbonized fuel, or organic-rich dredged sediments. Biomass from fast-growing sea grasses, kelp forests, or terrestrial plants could be harvested for burial in the ocean. Transportation of large volumes of biomass to the ocean depths, however, may prove too costly. Moreover, anoxia and the production of methane may present a serious problem with this approach.

- **Mining hydroxides and bicarbonates (e.g., sodium hydroxide, potassium hydroxide, sodium bicarbonate) and dissolving them in the ocean**. These minerals, when dissolved, will neutralize the acidity produced by anthropogenic CO_2 and will effectively sequester that CO_2 in the oceans. The limited availability of these materials in nature may preclude this approach.

3.4 CONCLUSION

Because the ocean already is a large repository for carbon on the planet, it is not unreasonable to consider direct injection of CO_2 or enhancement of CO_2 fixation through fertilization as possible options for carbon sequestration. Technologies exist for direct injection of CO_2 at depth and for fertilization of the oceans with microalgal nutrients. However, we lack sufficient knowledge of the consequences of ocean sequestration on the biosphere and on natural biogeochemical cycling. Such knowledge is critical to responsible use of oceans as a carbon sequestration option. Long-term studies on the impact of ocean sequestration on ecosystem dynamics and global biogeochemical cycling are needed (Fig. 3.6). The ocean plays an important role in sustaining the biosphere, so any change in ocean ecosystem function must be viewed with extreme caution.

Public perception of ocean sequestration will undoubtedly be an issue for its broader acceptability. Much of the public, as well as ocean advocacy groups, believe that the oceans must remain as pristine as possible. The fisheries industry will also be concerned about possible economic impacts resulting from ocean sequestration activities. Legal issues will undoubtedly be complicated. With the exception of the coastal economic zones, the ocean is international in domain and is protected by international treaties or agreements such as MARPOL or the Law of the Sea. Ultimately, both scientific understanding and public acceptability will determine whether ocean sequestration of carbon is a viable option.

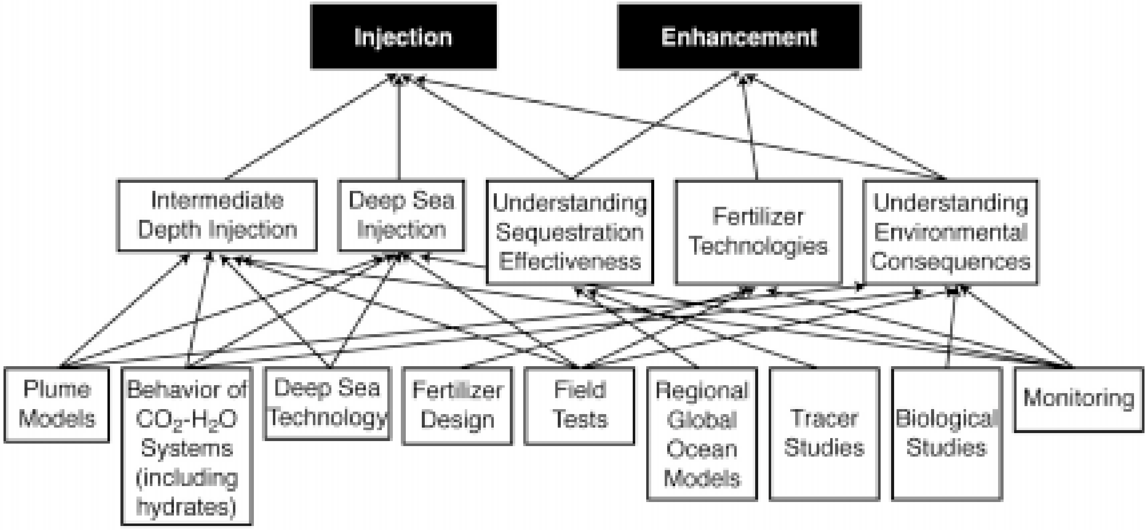

Fig. 3.6. R&D road map for ocean sequestration of CO_2.

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Vision

Research and development accomplishments by the year 2025 that will lead to an ability to understand, predict, assess, measure, and implement substantially increased sequestration of carbon in soil and vegetation systems.

4 CARBON SEQUESTRATION IN TERRESTRIAL ECOSYSTEMS

This chapter addresses the scope of the potential for sequestering carbon in the terrestrial biosphere. The aim of developing enhanced carbon sequestration in the biosphere is to enable a rapid gain in withdrawal of CO_2 from the atmosphere over the next 50 years in order to allow time for implementation of other technological advances that will help mitigate CO_2 emissions.

Carbon sequestration in terrestrial ecosystems is either the net removal of CO_2 from the atmosphere or the prevention of CO_2 net emissions from terrestrial ecosystems into the atmosphere. Carbon sequestration may be accomplished by increasing photosynthetic carbon fixation, reducing decomposition of organic matter, reversing land use changes that contribute to global emissions, and creating energy offsets through the use of biomass for fuels or beneficial products. The latter two methods may be viewed more appropriately as carbon management strategies. However, because of the need to integrate R&D issues related to ecosystem dynamics, we include information on these but focus primarily on sequestration.

The terrestrial biosphere is estimated to sequester large amounts of carbon (~2 GtC/year). Our vision is that we will increase this rate dramatically while properly considering all the ecological, social, and economic implications. There are two fundamental approaches to sequestering carbon in terrestrial ecosystems: (1) protection of ecosystems that store carbon so that sequestration can be maintained or increased and (2) manipulation of ecosystems to increase carbon sequestration beyond current conditions. We emphasize manipulative strategies and the R&D necessary to understand, measure, implement, and assess these strategies.

Soil—The Earth's Living Membrane

Soil, which has been described as a living membrane between bedrock and the atmosphere (CNIE 1998), is actually a diverse ecosystem containing microorganisms and many types of invertebrates and vertebrates as residents. Soils are critical to plant production, but they also are essential for carbon sequestration (soils currently contain ~75% of the terrestrial carbon). Soils in which high levels of carbon are present as soil organic matter (SOM) exhibit improved nutrient absorption, water retention, texture, and resistance to erosion, making them particularly useful for both plant productivity and sequestration. R&D is needed to better manage soils to increase carbon sequestration.

Storage of carbon in belowground systems is the best long-term option for carbon storage in terrestrial systems because most SOM has a longer residence time than most plant biomass. SOM is a complex mixture of compounds with different residence times. The more stable compounds are the most important for carbon sequestration because they have turnover times of hundreds to thousands of years. R&D can determine ways to increase the presence of the most stable compounds in SOM.

Prevention of erosion can be a major contributor to carbon sequestration. The Food and Agricultural Organization (FAO 1992) estimates that 25 billion tons of soils are lost through erosion each year. The Committee for the National Institute for the Environment (CNIE 1998) provides a dramatic description for this lost soil: "If dropped on Washington, D.C., this amount of soil would cover the city under more than 100 meters, burying the Capitol dome." If this soil contained an average of 4% soil organic carbon, that would be equivalent to emissions of roughly 1 GtC/year (CNIE 1998). Even though erosion cannot be completely prevented, research may identify possible strategies to enhance the capture and longevity of SOM released by erosion and transported by rivers into wetlands and coastal areas.

Land-use management and agricultural practices have great potential to sequester carbon by protecting soils. About one-third of the current 1.5 billion tonnes of carbon emitted to the atmosphere because of changes in tropical land use is from oxidation of soil carbon. It is estimated that 40 to 60 billion tonnes of carbon may have been lost from soils as the result of forest clearing and cultivation since the great agricultural expansions of the 1800s. When land is converted from natural perennial vegetation and cultivated, SOM generally declines by 50% in the top 20 cm of soil and 20 to 30% in the top meter of soil. Because less organic matter is introduced to the soil and because soil aggregates are destroyed (causing the loss of physical protection mechanisms that trap soil carbon), SOM declines significantly. In addition, cultivated soil is exposed to the air, so, during decomposition by soil organisms, the SOM is oxidized and the carbon carried off as CO_2. With good management to protect soils and the development of methods to improve texture of soils so they trap more carbon, it may be possible to exceed the original native SOM content of many soils.

In this chapter, we review the inventories of carbon in terrestrial ecosystems and the roles of the biosphere in the global sequestration process and then estimate the potential for carbon sequestration in each of them (Sects. 4.1 and 4.2). We next summarize the current capabilities in carbon sequestration (Sect. 4.3). The gap between the potential for carbon sequestration and the current capabilities establishes the drivers for R&D needs. Section 4.4 begins the actual road map. It starts at the system level with our vision for carbon sequestration in the terrestrial ecosystem. From this, we establish three objectives (Sect. 4.4.1) and then propose strategies that will help in meeting those objectives (Sect. 4.4.2). The final leg of the road map is to identify the R&D that is required to realize the strategies (Sect. 4.4.3).

The world's terrestrial environment comprises a wide diversity of ecosystem types that can be categorized into several biomes to address unique aspects of their carbon sequestration potential. A single, realistic set of R&D needs covering all issues in these highly variable systems cannot be stated. Therefore, we developed a primary set of R&D needs that represent cross-cutting topics. These R&D needs, which are broadly applicable to several of the major ecosystems, are discussed in the main body of this chapter. Appendix B contains information specific to each of the ecosystems.

4.1 TERRESTRIAL ECOSYSTEMS: NATURAL BIOLOGICAL SCRUBBERS

The total amount of carbon "stored" in terrestrial ecosystems is large (~2000 ± 500 GtC). Table 4.1 shows estimates of the distribution of this carbon among the major ecosystems of the world. Carbon sequestration in these terrestrial ecosystems will be enhanced by increasing the amounts of carbon stored in living plant matter, roots, and soil carbon (inorganic and organic) and in long-lived materials that contain woody matter, or by processing wood into long-lived carbon products. Net removal of CO_2 from the atmosphere by terrestrial ecosystems (~2 GtC/year) occurs when plant photosynthesis exceeds all processes of consumption and respiration, resulting in aboveground plant growth and increases in root and microbial biomass in the soil. Plant matter is consumed when it is eaten, dead or alive, by an animal. In addition, plants return stored carbon to the atmosphere through respiration, as do animals through their waste or death and decay. When a plant sheds leaves and

Multiple Benefits of Terrestrial Sequestration of Carbon

Increasing the storage of carbon in vegetation and soils could offer significant accompanying benefits: improved soil and water quality, decreased nutrient loss, reduced soil erosion, better wildlife habitats, increased water conservation, and more biomass products. Restoring wetlands to sequester larger quantities of carbon in sediment will also preserve wildlife and protect estuaries. Understanding how to increase soil carbon stocks in agricultural lands is critical to increasing sustainability of food production. Finally, creating conditions for higher plant productivity and accumulation of soil carbon to increase carbon sequestration will have the side benefit of restoring degraded ecosystems worldwide.

Increases in soil carbon sequestration alone can provide significant benefits by delaying the need for more technically complex solutions. Edmonds et al. (1996, 1997) estimated that, for agricultural soil carbon only, 35 years of time might be "bought" (potentially saving at least $100 million) before major adjustments in the world's energy production system would be required to meet a goal of 550 ppmv atmospheric CO_2. As a result, over the next quarter century, other carbon management options could be evaluated and implemented.

Table 4.1. Global estimates of land area, net primary productivity (NPP), and carbon stocks in plant matter and soil for ecosystems of the world

Ecosystem	Area (10^{12} m^2)	NPP (gC/m^2/year)	NPP (Pg C/year)	Plant C (g/m^2)	Plant C (Pg)	Soil C[a] (g/m^2)	Soil (Pg)	Total (Pg)
Forest, tropical	14.8	925	13.7	16500	244.2	8300	123	367
Forest, temperate and plantation	7.5	670	5.0	12270	92.0	12000	90	182
Forest, boreal	9.0	355	3.2	2445	22.0	15000	135	157
Woodland, temperate	2.0	700	1.4	8000	16.0	12000	24	40
Chaparral	2.5	360	0.9	3200	8.0	12000	30	38
Savanna, tropical	22.5	790	17.8	2930	65.9	11700	263	329
Grassland, temperate	12.5	350	4.4	720	9.0	23600	295	304
Tundra, arctic and alpine	9.5	105	1.0	630	6.0	12750	121	127
Desert and semi-desert, scrub	21.0	67	1.4	330	6.9	8000	168	175
Desert, extreme	9.0	11	0.1	35	0.3	2500	23	23
Perpetual ice	15.5	0	0.0	0	0.0	0	0	0
Lake and stream	2.0	200	0.4	10	0.0	0	0	0
Wetland	2.8	1180	3.3	4300	12.0	72000	202	214
Peatland, northern	3.4	0	0.0	0	0.0	133800	455	455
Cultivated and permanent crop	14.8	425	6.3	200	3.0	7900	117	120
Human area	2.0	100	0.2	500	1.0	5000	10	11
Total	150.8		59.1		486.4		2056	2542

[a] Soil C values are for the top 1 m of soil only, except for peatlands, in which case they account for the total depth of peat.

Source: Amthor et al. 1998.

roots die, this organic material decays, adding carbon to the soil. Soil carbon is lost to the atmosphere through decomposition by soil organisms (e.g., fungi and bacteria). This process also mineralizes organic matter, making available the nutrients needed for plant growth. The total amount of carbon stored in an ecosystem reflects the long-term balance between plant production (inputs) and all respiration and decomposition (losses).

Biological transformation of carbon has been, and quite likely will continue to be, a primary mechanism for removing CO_2 from the atmosphere. This is reflected in the standing stock of vegetation and the accumulation of soil organic matter. Methods that rely on biological transformation can play a central role in the management of carbon sequestration in the future. This biospheric carbon sequestration is essentially a huge natural biological scrubber for all emission sources (e.g., fossil fuel plants, cement plants, automobiles). The value of 2 GtC/year removed from the atmosphere each year by the earth's mantle of vegetation is the net ecosystem production. This value is uncertain because it is an estimated difference between photosynthesis and respiration—both very large fluxes and highly uncertain (Chap. 1). We can "observe" the contemporary, world-wide *net difference* between global carbon uptake by photosynthesis (P) and releases by respiration (R) through measuring annual changes in atmospheric CO_2 and accounting for oceanic carbon dynamics. However, we cannot use this information to assess how the biosphere will regulate atmospheric CO_2 in the future. This is because the P:R ratio is highly sensitive to environmental variables such as temperature, moisture, and nutrient availability and differs among ecosystems. If atmospheric CO_2 increases enough to cause climate change, the global P:R ratio may change in ways that we cannot now predict accurately. Small changes in these large numbers could dwarf any carbon management strategy imposed by humans.

4.2 POTENTIAL FOR CARBON SEQUESTRATION

The biomes that make up the terrestrial ecosystem are categorized in Table 4.2. The estimates of potential carbon sequestration include the current natural rate of carbon sequestration, which totals about 2 GtC/year. Note that achieving the potential indicated in the table, particularly the higher numbers, may imply an intensive management and/or manipulation of a significant fraction of the globe's biomes. The table also does not reflect estimates of economic, energy, or environmental costs to achieve such a rate, which could be unacceptably large for higher numbers. The assumptions also include expected advances from an intensive R&D program.

Estimating the potential for increasing carbon sequestration in terrestrial ecosystems is difficult because the biogeochemical dynamics that control the flow of carbon among plants, soils, and the atmosphere are poorly understood. Additionally, there will be socioeconomic issues, energy costs (such as possible hydrocarbon feedstock for fertilizers), and potential ecological consequences that would need to be compared with the benefits of sequestration or other carbon management options. However, the upper limit on terrestrial sequestration is large should extraordinary measures be needed at some time in the future.

Table 4.2. The categorization of biomes used in this road-mapping exercise
The primary method of carbon sequestration is rated as high (H), medium (M), and low (L) levels of sustained management intensity required over the long term. Global potential carbon sequestration rates were estimated that might be sustained over a period of 25 to 50 years

Biomes	Primary method to increase CS	Potential CS (GtC/year)[a]
Agricultural lands	Management (H)	0.85-0.90[b]
Biomass croplands	Manipulation (H)	0.5-0.8[c]
Grasslands	Management (M)	0.5[d]
Rangelands	Management (M)	1.2[e]
Forests	Management (M)	1-3[f]
Urban forest and grasslands	Creation and maintenance (M)	g
Deserts and degraded lands	Manipulation (H)	0.8-1.3[h]
Terrestrial sediments	Protection (L)	0.7-1.7[i]
Boreal peatlands and other wetlands	Protection (L)	0.1-0.7[j]
Total		5.65-10.1

[a] R&D allows improvements in carbon sequestration implementation; management intensity includes fertilization, irrigation, pesticides, and heavy equipment usage; no reallocation of land use from Table 4.1 except for 10-15% of agricultural land to biomass crop lands. The totals include the current natural rates.

[b] Soil carbon only; recovery of an amount equivalent to what was lost from native soils prior to agricultural use; implementation of best available management (e.g., no-till, intensified production and residue inputs, intensified rotations with crop rotation, double cropping, greater use of perennials) and new technologies such as discussed in the chapter with some CO_2 fertilization.

[c] An average annual aboveground productivity level of 13.2 Mgdwt/ha/year (6t/ac). Belowground storage of carbon is 1.75 MgC/ha/year and is assumed to be "permanent" and not to provide any negative feedback on further storage. Short rotation woody crop and perennial grass production are assumed to provide equivalent carbon storage benefits. The energetic costs of producing and harvesting switchgrass result in a biomass energy return ratio (energy in harvested biomass divided by production energy costs) of 12.3 and an energy gain of 343% for ethanol production. The carbon gain from substitution of ethanol for gasoline (2.48 MgC/ha/year) after subtracting carbon costs of production (0.60 MgC/ha/year) and adding an average belowground sequestration rate of 1.75 MgC/ha/year provides an annual carbon savings of (2.48 + 1.75- 0.60) = 3.60 MgC/ha/year. Trees and grasses are assumed to be equally efficient at net carbon production and sequestration, and it is assumed that production of ethanol and electricity provide equivalent net benefits in terms of carbon savings. A conversion of 10% of current crop to biomass crops for energy represents a realistic target; under more favorable conditions a 15% conversion might be achievable on a world basis.

[d] Intensification of management with fertilization, controlled grazing, and species improvements; 25% increase in belowground carbon stocks; linear increases through 2050.

[e] Total increase of 27 GtC through 2050; rehabilitation of degraded rangeland and fertilization by increasing CO_2.

[f] Watson et al. (1996) estimate 1-1.6 GtC/year (Table 14) and include above- and belowground vegetation, soil carbon, and litter. Their estimate does not include R&D to increase carbon sequestration. Trexler (1998) suggests a rate of 2 GtC/year may be plausible. With focused R&D, both these values may be exceeded.

[g] No estimate available.

[h] From Table 23 of Lal, Hassan, and Dumanski (1998). Soil carbon emphasis; erosion, desertification, and global warming effects are controlled; includes restoration of lands; reclamation of salt-affected soils; agricultural intensification on nondegraded lands (~0.015 GtC/year); and fossil fuel carbon offset of ~0.2 GtCg/year; includes accretion of inorganic carbonates.

[i] Estimate from Stallard (1998), which is for current sequestration, increased by 15% to account for benefits from R&D on approaches to better sequester carbon in sediments. We do not imply increasing erosion, but better managment of existing and future sediments. Although they are not truly an ecosystem, we categorize sediments because of the large potential to store carbon and the recent acknowledgement that they may be a key part of the carbon inventory.

[j] Assumes the impact of recent global warming on net carbon balance can be reversed (Oechel et al. 1993) and the future warming can be controlled (Goulden et al. 1998); sequestration of plant carbon will be increased by management of soil carbon and perhaps limited conversion to forest or grassland vegetation where ecologically acceptable.

Using the estimated distribution of carbon stored in the major ecosystems of the world (Table 4.1), we projected possible rates of carbon sequestration, assuming advances from R&D and a global emphasis on carbon sequestration. These are presented for each of the nine biomes in Table 4.2. Although land-use changes, such as growing new forests and decreasing deforestation, have great potential to mitigate increasing carbon emissions, the carbon sequestration potential for such optimization across global systems requires a more comprehensive and systematic analysis than was possible during this effort. The major land-use change incorporated into the present analysis was an assumption that the results of R&D would allow 10 to 15% of agricultural crop land to be converted to biomass energy crop production. The estimate for deserts and degraded lands also contains several assumptions with respect to land-use change (Lal, Hassan, and Dumanski 1998). With the caveat of the assumptions noted above, and in Table 4.2, it is possible that ~5 to 10 GtC/year could be sequestered globally when all ecosystems are considered, compared with current rates of ~2 GtC/year. One of the key research questions is how long these rates of carbon sequestration in these biomes could be maintained. Also, there clearly will be some maximum capacity for sequestration, but that capacity is far from certain. Refining such estimates should be one of the R&D tasks undertaken.

Although perhaps surprisingly large, these relatively high ranges of potential carbon sequestration may not be unreasonable. For example, a 5% increase in the total carbon contained in global terrestrial ecosystems over a 25-year period would sequester >100 GtC. Sequestering 100 GtC over 25 years requires increasing the rate of carbon sequestration in terrestrial ecosystems (~2000 GtC) by an average of only 0.2% per year—roughly half what our provocative estimates project as possible.

Strategies for sequestration a few decades from now will be implemented in a world different from today’s. Human responses to climatic change and other environmental issues, population growth, economic development, and technological change may well lead to changes in patterns of land use, settlement, and resource management. It seems unlikely that carbon sequestration will be the highest-priority use for any land; instead, sequestration will have to be compatible with a host of other demands on ecosystem goods and services.

There are some limitations and uncertainties related to carbon sequestration potential in terrestrial ecosystems. First, it is critical at the outset to take a whole ecosystem approach. Having the capability to assess potential impacts on a particular ecosystem from an emphasis on sequestering carbon is a major need. For example, the dynamics of carbon storage and allocation are at present not well known under temperature, moisture, and nutrient conditions of a changing climate. Second, carbon sequestration strategies may have consequences beyond simply increasing carbon storage. Increasing organic matter in wetlands could result in higher emissions of methane, a greenhouse gas with a 20 times higher contribution to global warming than CO_2, although hydrologic controls or increases in the fraction of recalcitrant organic matter could offset this process. Converting croplands to grasslands may increase emissions of nitrous oxide (N_2O), another greenhouse gas, to the atmosphere (Marland et al. 1998).

Third, land use and sequestration actions also could alter the flow of micronutrients. For example, as a result of controls on erosion, might the fluxes of phosphorous and nitrate in aquatic systems increase or decrease to levels that cause ecological impacts? Strategies to “improve” carbon sequestration in deserts through increases in drought-tolerant vegetation could lead to decreased fluxes of wind-blown nutrients such as iron, with possible adverse impacts on the ability of the ocean to sequester carbon through iron-fertilized phytoplankton (Chap. 3). Thus research should support the development of effective yet flexible strategies for carbon sequestration and seek understanding of the interplay of these strategies with other human activities and goals.

4.3 CURRENT CAPABILITIES

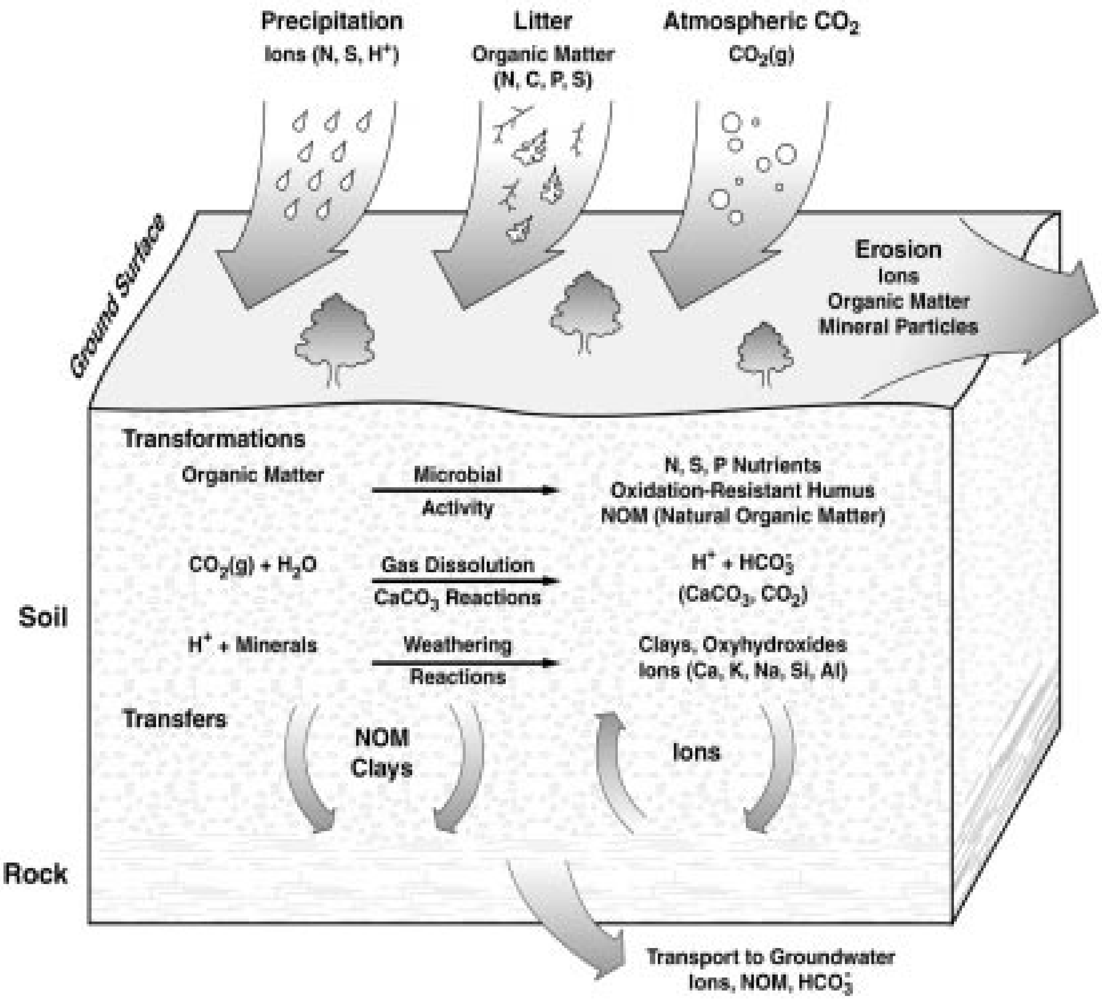
Historically, little emphasis was given to developing strategies for carbon sequestration. Rather, other priorities and practices actually promoted carbon release. For example, in the United States, 50% of the original wetlands have been lost. Fortunately, the trend now is to protect or even increase wetland acreage to preserve ecosystems and maintain biodiversity. Globally, losses of wetlands are not well documented but probably are as great as they are in the United States on a percentage basis. Changes in forest stocks and land clearing are continuing throughout most of the world.

Implementation of no-till practices, return of residues to soil, and the activities of the Conservation Reserve Program are increasing the amount of carbon in agricultural systems. (The main reason: the soil is less exposed to air, so less soil carbon is oxidized and carried off as CO_2.) Estimates suggest that the potential for soil carbon sequestration may be 8 to10 teragrams per year (Tg/year, or 10^{12} g/year), offsetting a third of the 28 TgC/year of fossil carbon emissions from agricultural production (Lal et al. 1995; Lal, Kimble, and Follett et al. 1998). The concomitant increase in belowground carbon can be substantial; there is some evidence that levels of soil organic carbon have doubled over the past 20 years in the upper 18 cm of soil placed in the Conservation Reserve Program (Gutknecht 1998).

The cutting of forests of eastern North America in the previous century is now being replaced by forest regrowth, and North America might even be a sink for carbon at this time (Fan 1998). Forests in the United States are being managed to maintain cover, increase water storage, and retain litter. Globally, however, there are still major challenges to slowing the rate of deforestation. The challenge is to reverse deforestation to gain 1.4 GtC/year and go beyond that to perhaps >2 GtC/year. Trexler (1998) and Sohngen et al. (1998) summarize modeling studies that suggest forests could sequester from 200 to 500 GtC by 2090.

Although the use of biomass as an alternative fuel supply is not implemented yet on a large scale, the R&D program is succeeding in showing the promise of this renewable

Soil Processes that Influence Carbon Fate and Transport



The dynamics of carbon transformations and transport in soil are complex and can result in either carbon sequestration or even increased emissions of CO_2. Bicarbonate (HCO_3) ions dissolved in water could be sequestered if the dissolved carbonate enters a deep groundwater system that has a residence time of hundreds to thousands of years. Natural organic matter is another type of soil carbon that could be transported to deep groundwater systems. Natural organic matter can be mobilized during intense precipitation following prolonged dry periods, based on observations at Walker Branch Watershed in Oak Ridge. This carbon-rich material may be sequestered if it is transported to deeper groundwater systems or deposited deeper in soil. Thus there may be opportunities to encourage geohydrologic systems to promote the deep transport of carbon into groundwater systems.

energy technology. Perhaps sequestration of 0.5 to 0.8 GtC/year from crop-to-biofuel conversion could be achieved by converting 10 to 15% of agricultural cropland to energy crops. It is important to point out that the use of biomass products can have additional benefits beyond sequestration in carbon management. For example, they may replace a product that is energy-intensive to manufacture (e.g., cotton can replace fiberglass as insulation), or they may be more energy-efficient in performance (e.g., plastic car panels manufactured from biomass feedstock are lighter than steel).

For tundra and taiga, unfortunately, the trend is in the wrong direction. These areas are being impacted so as to become carbon sources rather than sinks. Desertification and land degradation are still increasing globally, and little emphasis is being placed on how to use these areas for carbon sequestration. Lal, Hassan, and Dumanski (1998) and Lal, Kimble, and Follett et al. (1998) show that soil carbon sequestration can be a major benefit in these systems. Urbanization eliminated 10 million hectares (ha) of agricultural and forested land in the United States between 1960 and 1980. These highly impacted environments offer interesting opportunities. The density of carbon under these “intensively managed” systems (e.g., lawns with trees) is high—attributable to the high rates of fertilization and irrigation, with nitrogen oxide pollutants perhaps playing a minor role. Ancillary benefits from urban forestation might include local cooling effects and water retention that would reduce emissions from fossil fuel use.

In summary, despite historical and present practices such as deforestation, many beneficial practices that sequester carbon are either in place or being developed for implementation. However, these alone cannot meet the vision for carbon sequestration. More specific and focused efforts will be required.

4.4 TERRESTRIAL ECOSYSTEM SCIENCE AND TECHNOLOGY ROAD MAP

Figure 4.1 summarizes the entire science and technology road map for terrestrial ecosystems. Our estimated target for sequestering carbon in terrestrial ecosystems is 4 to 10 GtC/year. One of the first R&D needs is to refine these targets and assess the feasibility of reaching the goals (i.e., the limits on the sequestration rate and capacity).

The technology system level of Fig. 4.1 illustrates one of the major R&D linkages: the development of products from biomass using advanced chemical or biological methods (note the linkage circle labeled “Biomass Products”).

Recall the importance of looking at the major ecosystems of the world, as was discussed earlier. The system level is expanded in Fig. 4.2 to illustrate a detailed view of the road map that includes the major ecosystems categorized by management intensity. In this figure and following road map figures, the level of the road map being discussed in detail is highlighted at the far left of the figure.

After establishing a vision, objectives are defined to meet that goal. Sect. 4.4.1 and Fig. 4.3 present the three technology objectives that, if met, would allow the vision to be achieved. After objectives have been established, a variety of strategies can be developed that would focus on meeting the

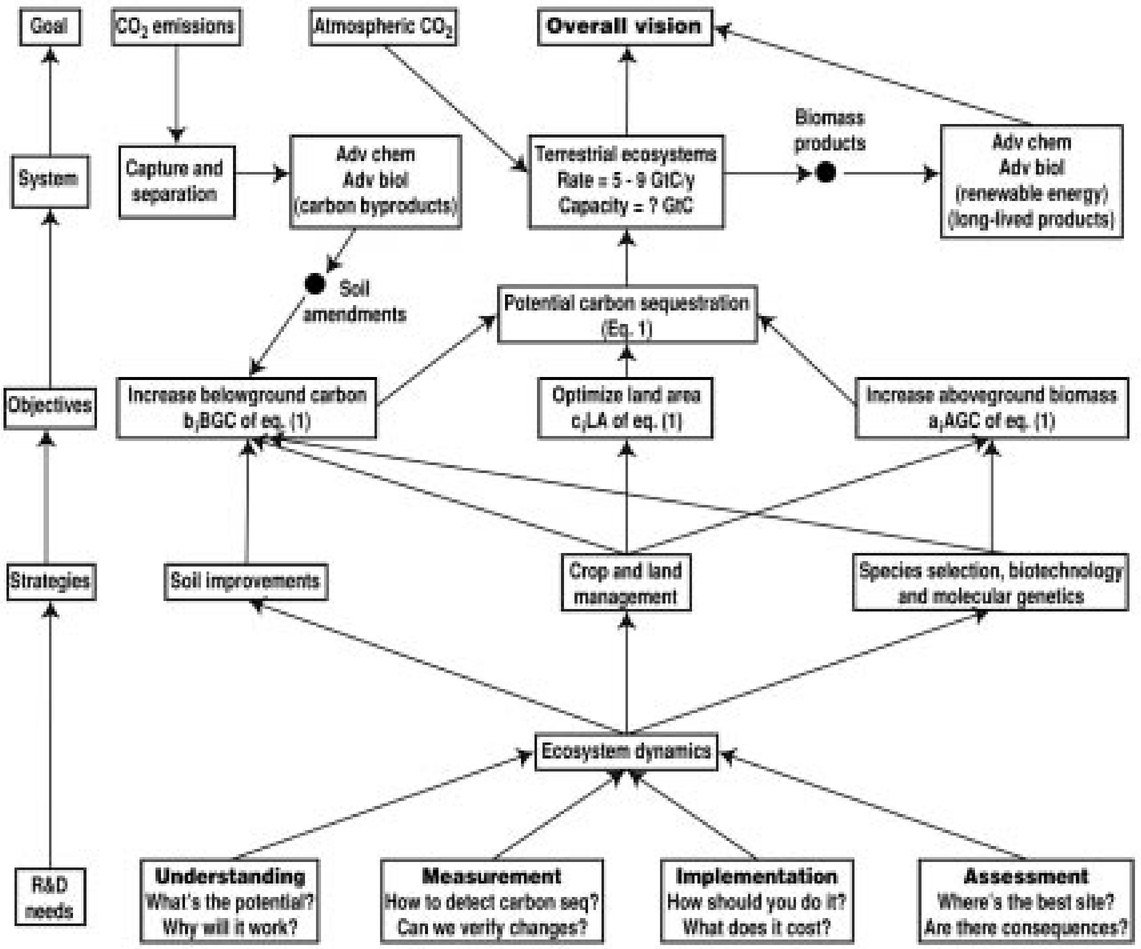


Fig. 4.1. Overall system view of the science and technology road map for the terrestrial ecosystems.

objectives (see Sect. 4.4.2 and Fig. 4.4). The final step is to identify R&D to support implementation of the strategies (see Sect. 4.4.3 and Fig. 4.5).

4.4.1 Objectives

Our carbon sequestration system has three objectives (Fig. 4.3): increase the amount of carbon in belowground systems (soil or sediment), increase the carbon in aboveground biomass, and/ or manage land area with an emphasis toward carbon sequestration. A simplified representation of how one might quantify the potential carbon sequestration (PCS) is

$$PCS = \sum (a_iAGC_i + b_iBGC_i) \times c_iLA_i \qquad (1)$$

where

a_i = potential increase in above-ground carbon in the i^{th} ecosystem;

b_i = potential increase in below-ground carbon in the i^{th} ecosystem;

c_i = potential change in land area due to management for carbon sequestration in the i^{th} ecosystem;

AGC_i = aboveground carbon; biomass of the i^{th} ecosystem in the index year;

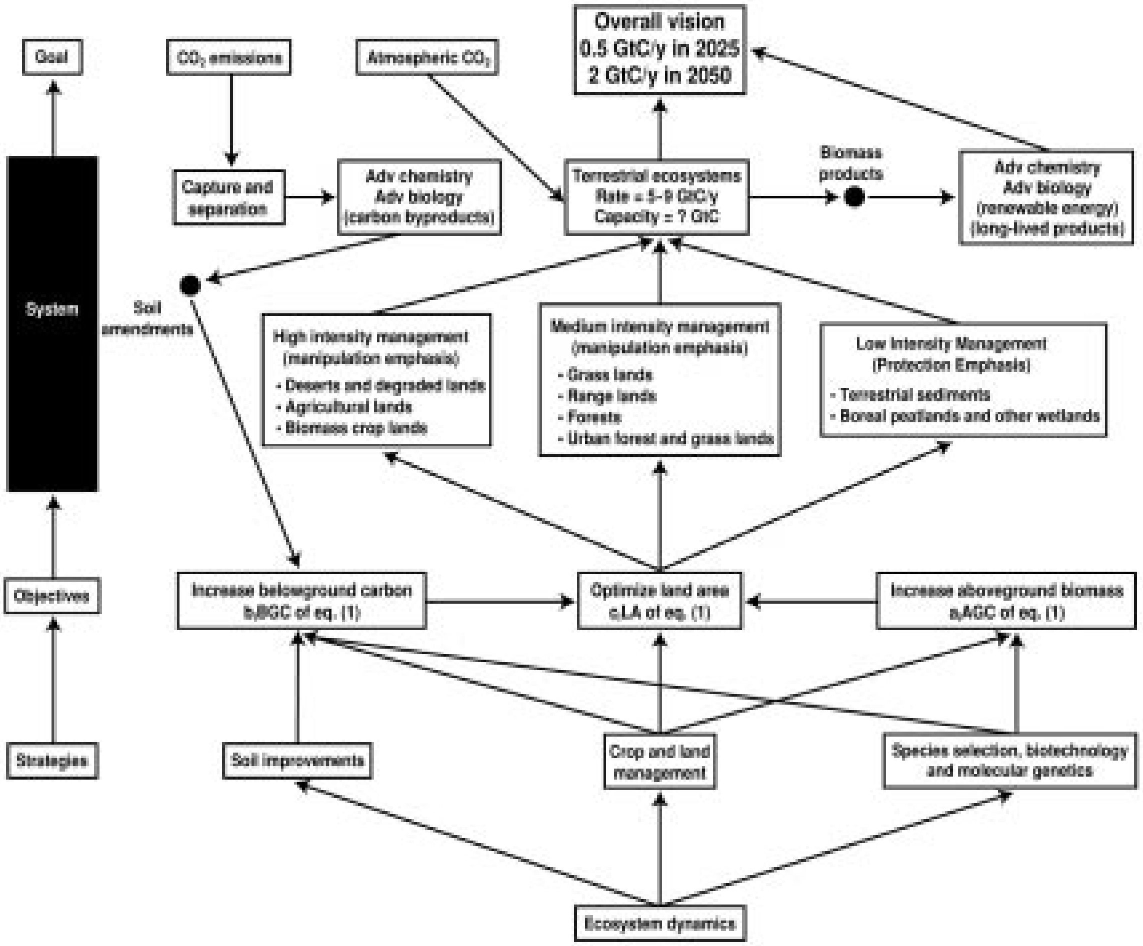


Fig. 4.2. Detailed view of the system level showing the ecosystem categories that are part of the overall system.

BGC_i = belowground carbon; root biomass + soil carbon (organic and inorganic) in the ith ecosystem in the index year;
LA = land area of each ecosystem in the index year.

To arrive at a global total for potential carbon sequestration, we must obtain the above- and belowground carbon inventory for each ecosystem in the index year, multiply that number by the potential change coefficient, assume an optimization of land use to maximize carbon storage potential, and sum across all ecosystems.

Although represented as independent variables, the three terms (aboveground carbon, belowground carbon, and land area) can be tightly coupled. There can be great synergism among plant biomass and soil organic carbon. Changes in the allocation of land area between different ecosystem types (e.g., conversion of annual cropland to biomass plantations) can increase aboveground carbon, which can lead to increases in belowground carbon. The rate of increase in aboveground carbon will initially be much faster than increases in belowground carbon, but the rates of change will depend on the type of land use reallocation. In addition, major changes in both rates are possible within ecosystem types (independent of land reallocation) through various types of management

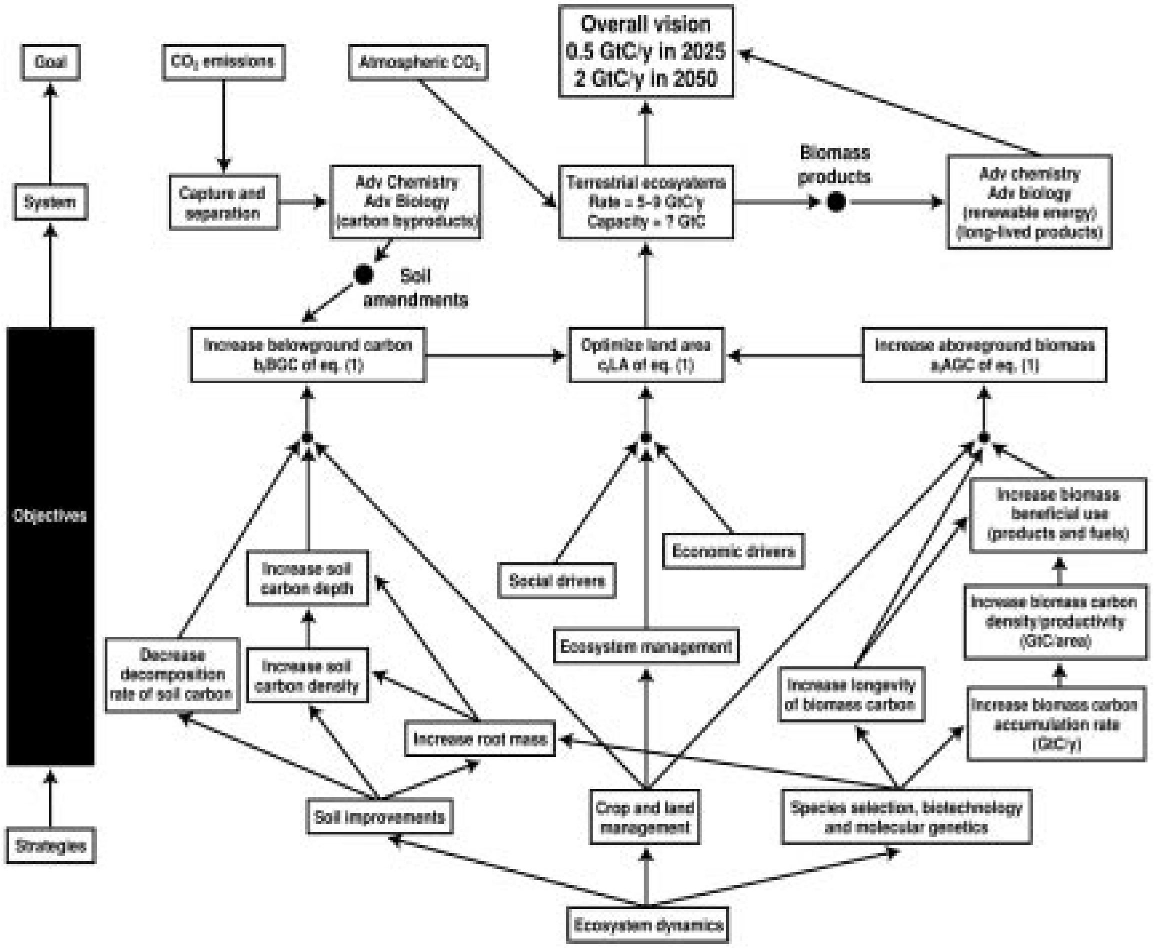


Fig. 4.3. Detailed view of the objectives level showing the various components that feed into the three primary objectives that are described in equation (1).

interventions. We use the equation simply as a means to highlight objectives for carbon sequestration and to drive the development of R&D needs.

Using potential carbon sequestration (Eq. 1) to define sequestration options, we discuss each of the variables separately. The detailed view of the objectives in Fig. 4.3 illustrates four ways to increase belowground carbon:

- increase the depth of soil carbon
- increase the density of carbon (organic and/or inorganic) in the soil
- increase the mass and/or depth of roots
- decrease the decomposition rate of soil carbon

One key link to another technology system is the possible use of byproducts created by advanced chemical or biological methods as soil additions to increase organic content, water retention, and protection of organic matter, and to improve the texture of the soil so that it can hold more carbon. An example might be creation of “smart fertilizers” or the use of mixtures of minerals (e.g., carbonates, silicates, and oxides) formed at fossil fuel power plants (Chap. 7) blended with biosolids such as sewage sludge. See the “Soil

Amendments” link between advanced chemical and biological processes to belowground carbon in Fig. 4.1.

For the aboveground system, there are also four ways to increase carbon sequestration (Fig 4.3):

- increase the rate of accumulation of aboveground biomass
- increase the density of total biomass per area and/or the density of carbon in the aboveground biomass
- increase the longevity of biomass carbon (decrease decomposition rate)
- increase beneficial use of biomass carbon in long-lived products

An important component from the aboveground carbon term is the use of biomass products. Increasing the density of total biomass or the accumulation rate offers high carbon sequestration potential. However, storage due to increased plant productivity is most efficient if the carbon is moved to a long-term pool, such as long-lived woody biomass or soils. Another alternative is to substitute products manufactured from biomass for products that are made using fossil fuels, addressing both sequestration and management. Obvious examples that address both carbon management and sequestration include biofuels and wood products. Less obvious but perhaps important examples that are focused on carbon sequestration might include the use of biomass products in structural materials (e.g., cement) or combined with other materials to create new soils. These are illustrated by the “Biomass Product” link to “Advanced Chemical and Biological” at the system level (Fig. 4.2).

The land area term is the large multiplier. As seen by the large areas in Table 4.1, in some ecosystems, a small change in carbon content could result in large increases in total carbon sequestered. Although the total land area of the world cannot be increased, R&D might allow the land area term to increase total carbon sequestration by any or all of the following detailed objectives:

- social drivers
- economic drivers
- ecosystem management drivers

Optimization among ecosystems for carbon sequestration will be a complex function. Research in this area should include issues such as transforming land from low carbon sequestration uses to high carbon sequestration uses, as well as reversing land use changes that have made land areas into sources of CO_2 emissions.

4.4.2 Strategies

The next level of the road map addresses strategies (Fig. 4.4) that support the objectives. Three general strategies directly support the objectives of terrestrial ecosystems. The fourth strategy is an integrative one that is absolutely critical to consider as carbon sequestration is attempted in terrestrial ecosystems:

- **Soil improvements** primarily to support the objective of increasing belowground carbon
- **Crop and land management** to influence the aboveground biomass objective, the belowground carbon objective, and the optimization of land area
- **Species selection, biotechnology, and molecular genetics** that would directly benefit both above- and

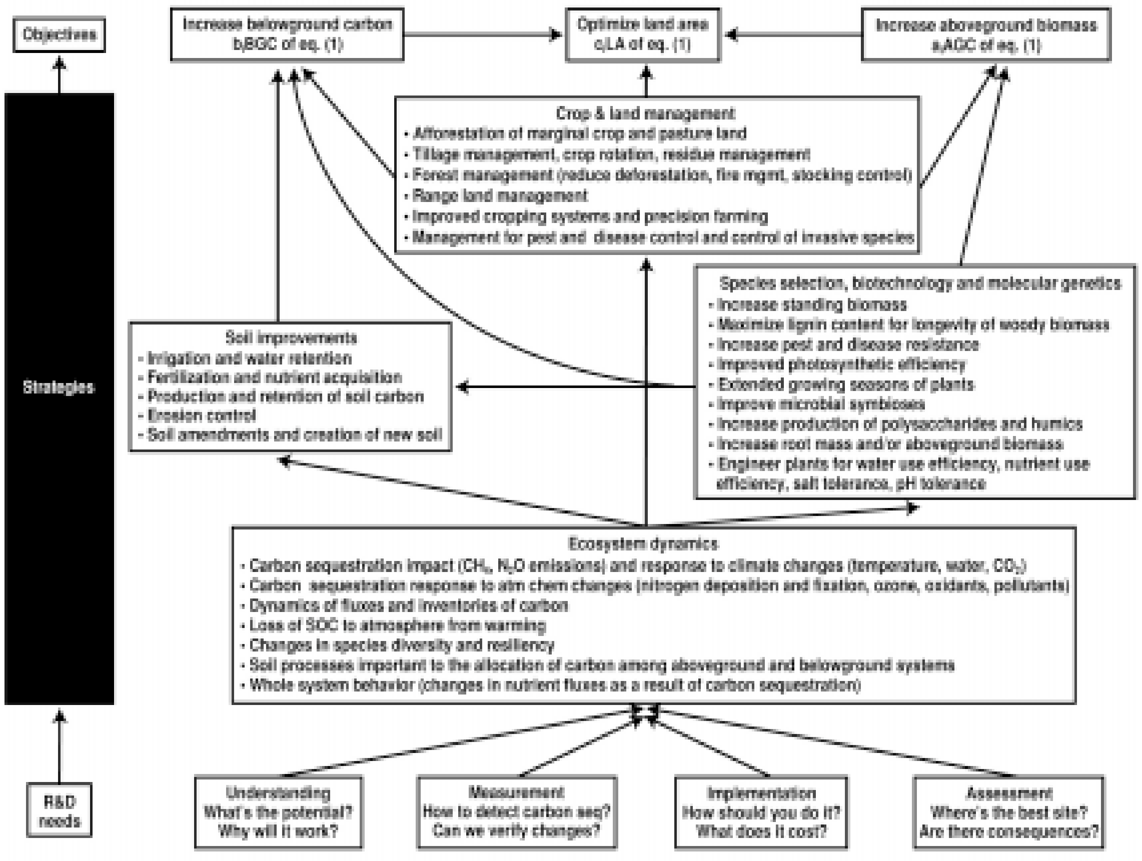


Fig. 4.4. Detailed view of the strategies level illustrating the options for which R&D will be required for effective implementation.

belowground systems and, indirectly, land use through, for example, increased agricultural production to free land for carbon sequestration

- **Ecosystem dynamics** focused on whole ecosystem behavior to optimize carbon sequestration performance, as well as on assessing potential negative feedback to other ecosystem features

4.4.2.1 Soil improvements

A variety of detailed strategies could be implemented or developed to increase the carbon content of soil, increasing belowground carbon directly and aboveground carbon indirectly. One of the key questions is whether soil texture, topographic position, and climate ultimately determine the carbon content of a soil or whether it can be changed by manipulation. We know little about the processes of humification (formation of humus, which consists of decayed organic matter that provides nutrients for plants and increases the soil's retention of water) or stabilization of decomposable organic carbon in soils. However, our current level of understanding is adequate to begin to address the questions: To what degree can these processes of stabilization be managed? What would be the consequences for plant productivity and ecosystem functions?

Figure 4.4 offers a detailed view of components of the soil improvement strategy. Opportunities for innovation exist in the following areas if R&D can address these key questions:

- **Irrigation and water retention.** How can we minimize the amount of water required, or perhaps use water of lower quality to increase carbon accumulation? For example, groundwater of marginal quality could be used for restoration of large tracts of degraded lands. Urban forests and grasslands would benefit from utilization of “gray” water from homes, businesses, or cities rather than irrigation using potable water supplies. Surface treatments or soil amendments that improve retention of water in soil between rain events and irrigation would also be of great benefit. Could desalination be linked to irrigation and carbon sequestration via production of carbonates with brines and CO_2?
- **Fertilization and nutrient acquisition.** Can we improve the efficiency at which nutrients are taken up by plants through novel microbial manipulations or soil amendments? Can we determine and enhance the role of mycorrhiza (a mutual association between a fungus and the root of a seed plant it invades) in carbon fixation and plant productivity? We must address the availability of other critical nutrients and trace elements, not just nitrogen and phosphorous.
- **Enhance production and retention of soil carbon.** Can the formation of strongly-adsorbing and highly-recalcitrant organic macromolecules be enhanced through soil amendments, microbial manipulation, or genetic selection of biomass? Can soil organic carbon profiles be deepened to provide a greater mass of soil available for carbon sequestration? Can inorganic carbon formation be enhanced in an arid system?
- **Erosion control.** Beyond no-till agriculture, what methods can be used to minimize soil erosion? Are there soil additions or surface treatments that will significantly inhibit the susceptibility of soils to water erosion? Are there engineering innovations to at least trap organic matter that might be released from erosion (e.g., sediment trapping to enhance wetlands)? Can the current ~0.5 GtC (Stallard 1998) trapped in sediments each year behind dams be permanently sequestered?
- **Soil amendments or creation of new soil.** Can waste byproducts (e.g., fly ash, concrete, sewage sludge) be used alone or mixed with other materials to improve soil characteristics safely and economically to help the retention of carbon? Can materials created from byproducts be used to reclaim degraded lands, or perhaps even help mitigate land subsidence while at the same time sequestering carbon?

4.4.2.2 Crop and land management

Opportunities for increasing carbon sequestration by management practices vary in intensity and are specific to each ecosystem. There are also complexities to implementing some strategies. For example, no-till practices reduce oxidation of soil organic matter but do not necessarily promote increased incorporation of surface organic matter into the soil to potentially enhance soil organic carbon in the long term. There are opportunities to use natural biodiversity as well. For example, a shift from annual to perennial grains would benefit soil carbon sequestration. Management of agricultural ecosystems by planting trees and legumes mixed with crop plants can add organic carbon to soil. Proposed strategies include:

- afforestation of marginal crop and pasture land
- tillage management, crop rotation, residue management
- forest management (reducing deforestation, improving stocking control, implementing fire management)
- range land management
- improved cropping systems and precision farming focused on soil management
- management for pest and disease control and control of invasive species
- decrease urbanization and land conversion of forests to agricultural use

4.4.2.3 Species selection, biotechnology, and molecular genetics

Opportunities to select or genetically engineer species for carbon sequestration behavior can directly impact both aboveground and belowground carbon. It will be important to understand carbon partitioning into biomass as we attempt to engineer or select for carbon sequestration traits. R&D can also indirectly make more land area available for carbon sequestration (e.g., by improving food production per hectare so that more land is available for carbon sequestration). This strategy should include (1) research on plants and microbial communities with a focus on near-term (next 25 years) biotechnology options and species selection using extant knowledge and (2) relevant fundamental research on functional genomics that will have impacts in later years (>50 years).

For research in plant genetics, genes must be available for insertion into the plant of choice. Many genes in agriculture have come from a small set of annual plants (e.g., *Arabidopis*), for which information on gene function (e.g., disease resistance or flower formation) is easily obtained. Most of the genes found in such plants would not have direct value to a carbon sequestration strategy because genes for long-term carbon storage may have little agronomic value. Thus, to enable use of genetic engineering for carbon sequestration, there is a need to discover genes in perennial plants that allocate more carbon to belowground components, that code for higher content of extractives (components desired from the plant), or that provide resistance to microbial degradation. To enable the discovery of such genes, a functional genomics effort must precede the genetic engineering efforts.

It is not always necessary to start with functional genomics to modify the plant genome. For example, genes for producing higher lignin content in maize have been bred out of current varieties. (Lignin is a complex polymer that hardens and strengthens the cell walls of plants and that does not decompose easily.) Genetic stocks possessing higher lignin content exist, and these could be reintroduced if the objective were to produce this characteristic for carbon sequestration. R&D on altering the Rubisco enzyme to increase biomass production through a more efficient uptake of carbon also might have huge potential benefits. Opportunities in this area and others are discussed in more detail in Chap. 6. Strategies central to this theme include developing methods to

- increase standing biomass
- maximize lignin content for longevity of woody biomass
- increase pest and disease resistance
- improve photosynthetic efficiency
- extend growing seasons of plants
- increase root:shoot ratios
- increase carbon allocation in belowground components of less decomposable carbon compounds (e.g., lignin, phenolics)
- engineer new plants that have improved water efficiency, nutrient utilization, salt tolerance, and pH tolerance

Metting et al. (1998) provide details on some of the microbial biotechnology options available for sequestering more carbon in soil and vegetation, including species selection and genetic engineering to

- improve microbial symbioses (mycorrhizal fungi, bacterial fixation of nitrogen, and other nutrient acquisition features of soil)
- grow mycorrhizal fungi in pure culture (especially those that might improve water and nutrient uptake)
- increase production of polysaccharides and humic substances to stabilize soil organic matter

4.4.2.4 Ecosystem dynamics

A rational strategy to sequester carbon must consider all the components of the terrestrial ecosystem. Single tree species cannot be considered in isolation from other plant species or from soil because of the interactions and interdependencies among species in an ecosystem. Likewise, soil management cannot be separated from plant productivity. This integrative strategy element—ecosystem dynamics—is driven by four basic needs:

- Balance decomposition of biomass and soil organic matter as a source of carbon loss to the atmosphere against decomposition as a source of nutrients essential to plant growth. Sequestration strategies that attempt to decrease decomposition rates may inadvertently result in lower ecosystem carbon storage because, without decomposition, insufficient nutrients are available for plant growth. Plants, soil, and nutrient cycling must be considered together.
- Balance instantaneous or optimum plant productivity with the desire for long-term, predictable/stable productivity. An ecosystem that is managed for a single species likely will not maintain productivity under a wide range of conditions, such as climatic anomalies or disease outbreaks, without intensive management inputs. Target species, species diversity, and ecosystem resilience must be considered together.
- Design strategies that are compatible with other human demands on land and natural resources. It is necessary to understand both the impacts of carbon management on other ecosystem services and ways to design carbon management strategies that work in concert with other goals for terrestrial ecosystems, such as production of food, fuel, and fiber; clean water; climate moderation; or aesthetic or cultural value.
- Determine the potential feedback from carbon sequestration actions. What is the impact of carbon sequestration on the production or consumption of trace gases that

affect radiative forcing (N_2O and CH_4) or that otherwise have significant roles in atmospheric chemistry (CO and NO)? For example, increased organic matter content in wetlands might increase net methane emission. Will increased reservoirs of organic matter in soils significantly affect weathering and subsequent transport in rivers of iron, silica, and other micronutrients? If so, in what direction might changes occur, and what are the potential impacts? What consequences would an emphasis on desert carbon sequestration have on a eolian transport of iron and other metals or nutrients to the oceans or other terrestrial ecosystems?

R&D related to sequestering carbon in soils and vegetation will be diverse and must include integrated assessment to address several features that will influence, or be influenced by, other carbon sequestration strategies. Key features of these assessments will be (1) land use inventories, (2) assessments at scales from watersheds to global, and (3) life-cycle analysis, which is the estimation of all costs (real dollars and carbon costs) to perform R&D and implement carbon sequestration options. Many dynamic parameters and processes must be measured and assessed over time, including

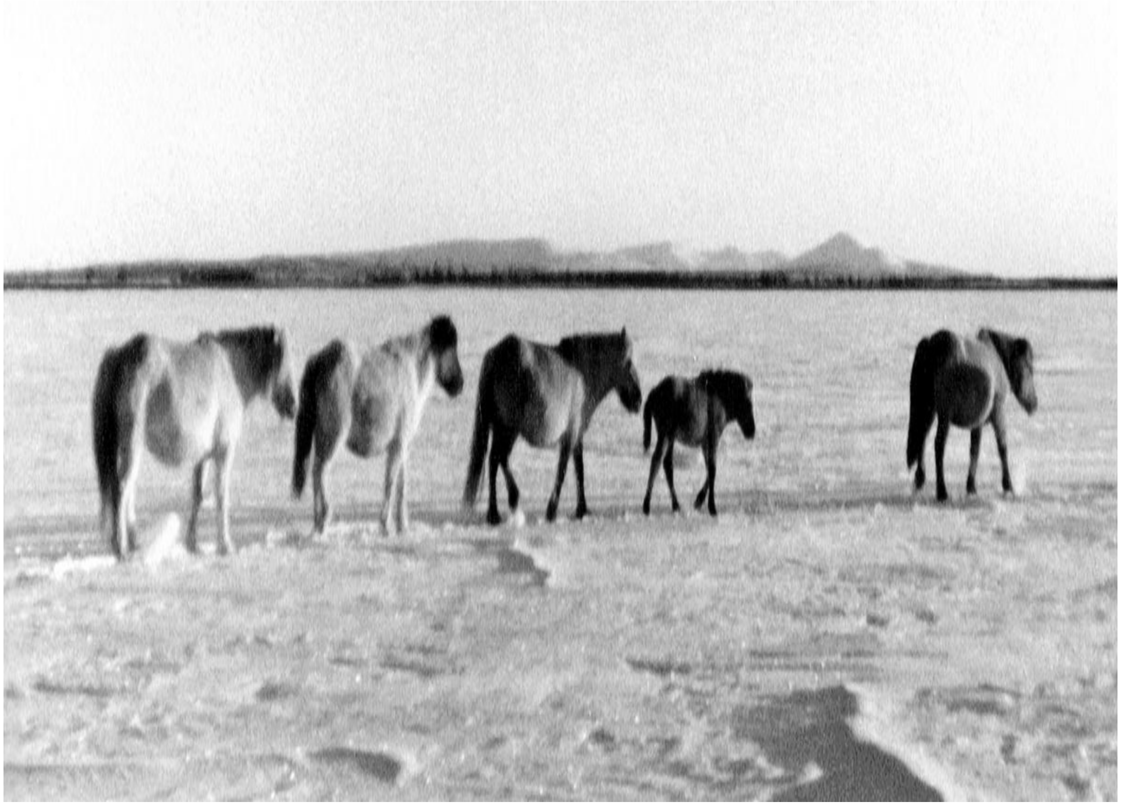
- Carbon sequestration impacts to the atmosphere (e.g., increased CH_4, CO, or N_2O emissions) and responses to climate changes (temperature, water, CO_2), in addition to CO_2 withdrawal by carbon sequestration
- Loss of sequestered soil carbon to the atmosphere as a result of global warming
- Carbon sequestration responses to atmospheric chemistry changes (nitrogen deposition and fixation, ozone, oxidants, other pollutants)
- Dynamics of fluxes and inventories of carbon at all scales as they change with response to carbon sequestration
- Changes in species diversity and resiliency (e.g., if you design a plant species for early rapid growth, you may limit its long-term growth and/or life expectancy) as a response to carbon sequestration
- Soil processes important to the allocation of carbon among above- and belowground systems (transformations, transport, and fate)
- Whole ecosystem behavior as a response to carbon sequestration (e.g., alteration of nutrient fluxes as a result of a sequestration emphasis, including soils, wind transport of iron and silica to oceans, and transport of organic matter to aquatic systems)

4.4.3 Research and Development Needs

We have now reached the bottom and final level of the road map—science and technology needs. The R&D recommended to address these cuts across several ecosystems and is intended to be general so as to stimulate thought rather than prescribe research for investigators. There are four critical aspects to be considered in planning an R&D program to address carbon sequestration in terrestrial ecosystems

Understanding. What is the potential for a given strategy to actually work? What are the scientific principles that govern carbon sequestration?

Assessment R&D Opportunity—A Pleistocene Park



The arctic tundra and boreal taiga currently store much of the world's soil organic matter. Although few readily apparent opportunities exist for greatly increasing carbon stores in these regions, there is one novel opportunity for enhanced carbon storage in the tundra—restoring and managing the Siberian loess-derived grasslands.

Russian and American scientists seek to create a grassland ecosystem maintained by large northern herbivores similar to that which existed in the region 10,000 to 100,000 years ago during the late Pleistocene Epoch (Stone 1998). The test area of Pleistocene Park is 150 km^2, but the Siberian region covered by loess that could potentially be managed for grassland restoration is approximately 10^6 km^2. Bison, horses, musk oxen, caribou, and moose would be introduced to "Pleistocene Park," a scientific reserve in northeast Siberia. This region supported large herds of these animals, as well as mammoths, during the Pleistocene. These animals were important in maintaining this grassland ecosystem just as large grazers currently maintain African grasslands.

The proposed transplant would reestablish a significant area of northern grassland, an ecosystem type that has disappeared but was formerly one of the world's most widespread biomes. Significantly, this ecosystem is characterized by much higher soil carbon (and total ecosystem carbon) than the shallow-rooted northern ecosystems found in this region today. The vegetation transition is expected to result in warmer, drier soils that would promote deeper-rooting grassland species. *Excerpted with permission from a proposal by Zimov and Chapin* (1998).

Measurement. How can we measure the rates of current carbon sequestration by terrestrial ecosystems? Are these rates likely to change significantly as a result of changes in atmospheric chemistry and climate? Can we detect changes in carbon sequestration rates after implementing various strategies? Can these changes be verified at large scales?

Implementation. If a strategy appears feasible, how should it actually be pursued? What advances in engineering are required? What are the costs associated with implementation? These costs can be in terms of actual dollars but also in terms of costs of carbon as fuel or materials (e.g., fertilizer may be required). How can we verify that a particular carbon sequestration implementation is effective and not the consequence of simultaneous changes in other factors?

Assessment. Where are the best opportunities to implement various strategies? What are the possible consequences of implementation over both the short and long term to the landscape, local, regional, or global ecosystems?

Process-level research will directly address the questions that must be answered to increase our understanding of carbon sequestration systems. This research is closely linked to and dependent on research into **measurement and sensing** methods to enable study of processes at a variety of scales. New measurement methods can also lead to new breakthroughs in our understanding of key processes. Advances in measurement and sensing directly support the critical need for verification and monitoring of carbon sequestration. Both of these areas will provide direct benefits to research in **ecosystem response and modeling**. This R&D area primarily links to the needs in assessment and represents an integrative R&D topic. Clearly, advances in **engineering technology** will be required to support the implementation of carbon sequestration strategies. As engineering advances are developed, though, information should be linked to ecosystem response and modeling so as to support assessment. We present specific R&D topics as itemized bullets for clarity to align with the details of the road map found in Fig. 4.5.

This discussion is intended to highlight the integrative nature of R&D for carbon sequestration in terrestrial ecosystems. In the road map, this importance is illustrated by the links from all R&D needs (Understanding, Measurement, Implementation, and Assessment) into the strategy “Ecosystem Dynamics” (Fig. 4.5), as well as the multiple links feeding the ecosystem response and modeling R&D needs.

4.4.3.1 Process-level research

Process-level research in the following areas will directly aid our understanding of carbon sequestration systems. R&D is needed to focus on the following:

- Biogeochemical dynamics of carbon, nitrogen, phosphorus, calcium, magnesium, potassium, and trace elements that control transformations of carbon and its transport and fate among plants, soil, water, and the atmosphere. The dynamics must be investigated within the context of a system that includes soil, water, plant, microbe, and climate interactions.

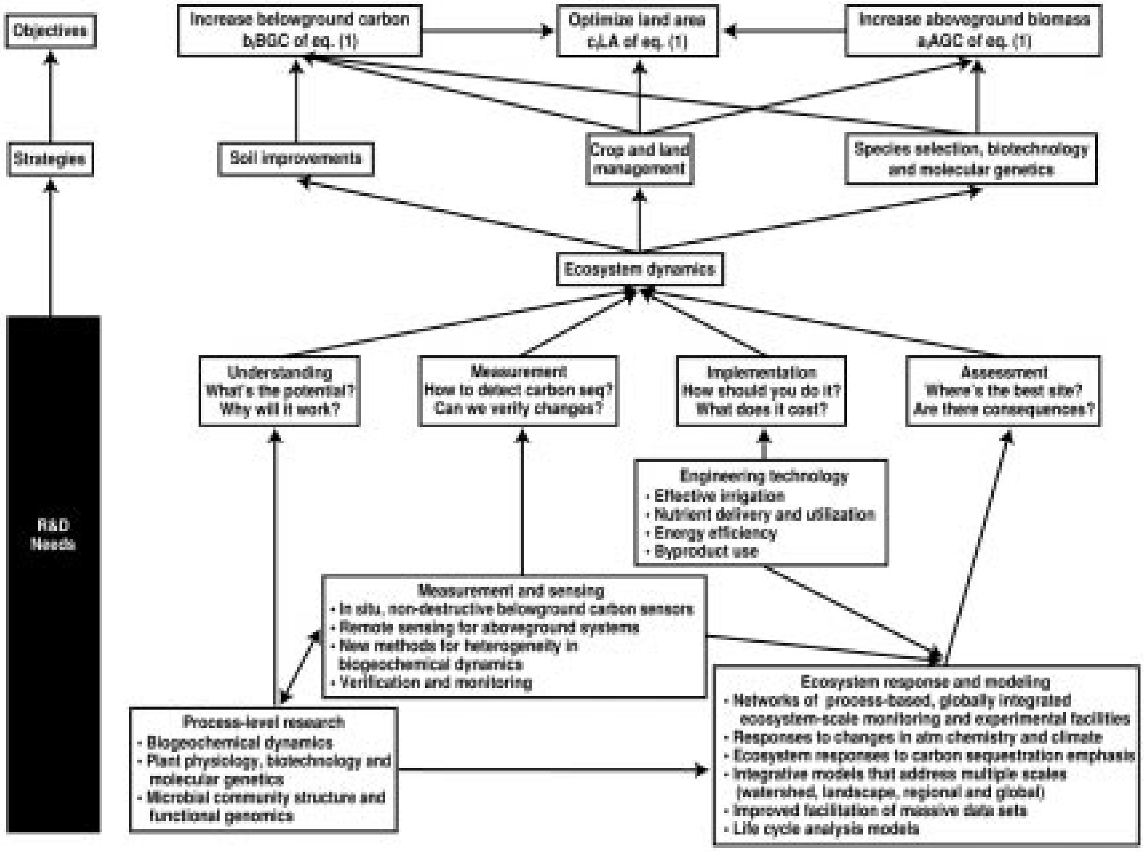


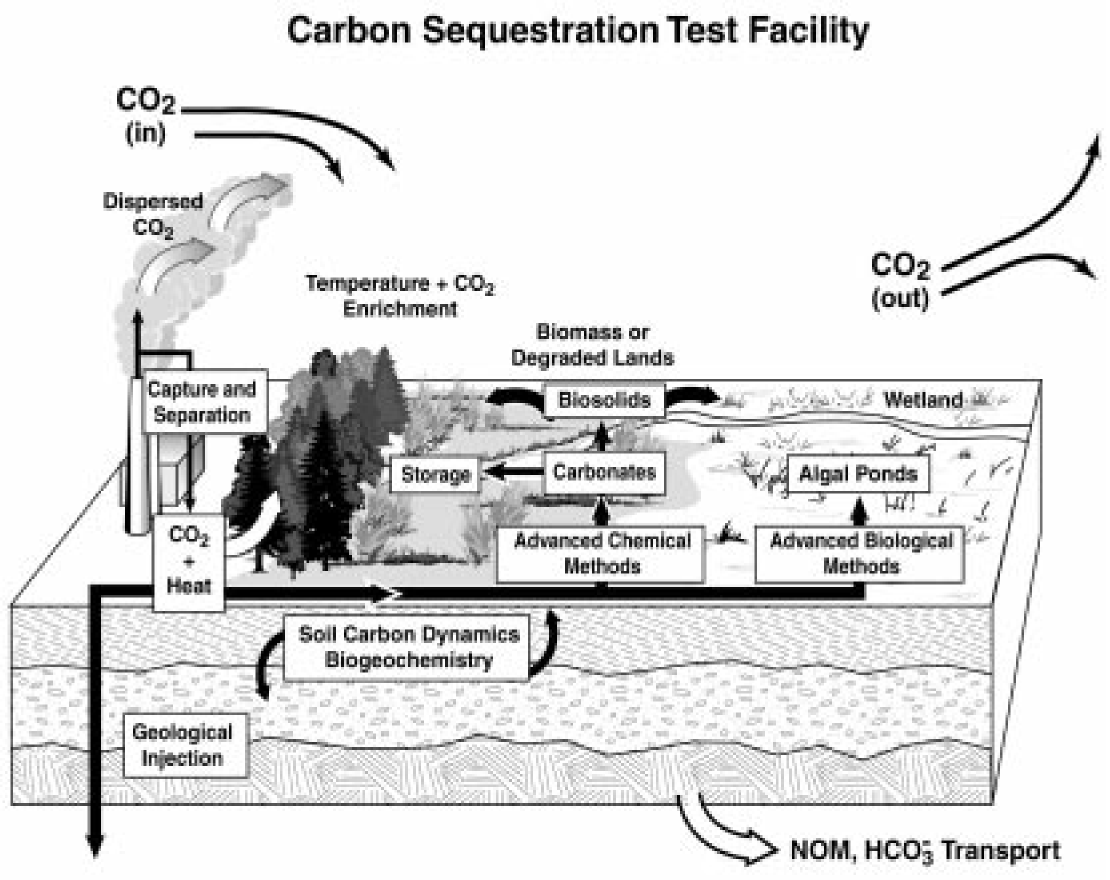
Fig. 4.5. Detailed view of the R&D needs level illustrating the fundamental R&D needed to support the development of carbon sequestration options for terrestrial ecosystems.

- Plant physiology, biotechnology, and molecular genetics. R&D topics would include development of methods to select and engineer plant species for improved nutrient acquisition, growth, carbon density, and/or carbon sequestration. How can we alter the composition of cellular components and design plants for effective byproduct use by increasing energy content, durability, and lignin content to reduce decomposition rates, or recyclability? How can pest and disease resistance be improved? (See also Chap. 6.)
- Microbial community structure and functional genomics. R&D should be directed toward (1) plant rhizosphere microbial community functions, (2) the microbial community role in stabilizing soil organic matter or slowing decomposition of organic matter, and (3) impact studies of effects of altered soil processes on nitrogen mineralization and fixation and plant acquisition of other nutrients.

4.4.3.2 Measurement and sensing

Developing measurement and sensing techniques to verify the occurrence of carbon sequestration in terrestrial ecosystems and to monitor its effects will be challenging (Post et al. 1998). Methods are needed to ensure that researchers sample sites where the changes are occurring in ways that reduce sampling errors. Detection of changes in terrestrial carbon at large scales will also offer challenges. It is

Field-Scale R&D on DOE Reservations



Advancing the science and technology needed to enable the mitigation of climate change resulting from CO_2 emissions through carbon sequestration will require long-term research, evaluation, assessment, and demonstration. DOE lands and associated facilities offer research sites and test beds for evaluating sequestration in terrestrial ecosystems. DOE lands offer great diversity—from shrub-steppe at Hanford, Washington, to tall-grass prairie at Argonne, Illinois, to deciduous forest at Oak Ridge, Tennessee (Brown 1998). Our vision is to have an integrated program of field-scale research, development, and assessment that would allow evaluation of CO_2 separation science and terrestrial sequestration options. Early research at field scale often results in meaningful feedback to guide process-level research. DOE lands represent well-studied sites, offer good opportunities to involve the public in evaluating carbon sequestration, and could assess transportation and other costs of sequestration at a small scale in early studies.

possible that rules of thumb could be determined for carbon sequestration accomplished by certain practices, but at this time the basis for developing quantitative rules is severely lacking. Because of these challenges, we believe the following R&D topics are particularly important.

- In situ, nondestructive belowground sensors are needed to quantify rates and limits of carbon accumulation both spatially and temporally. Three areas of importance are (1) soil carbon, water, and nutrients as a function of depth; (2) biomass (root and microbial community) imaging; and (3) porosity or soil structure changes. An example of a sensor that might be developed to measure changes in carbon concentrations in soil would be a miniaturized nuclear magnetic resonance imaging device for scanning a volume of soil below ground.

- Remote sensing (e.g., by satellite imaging) is needed for aboveground biomass systems. Improvements are needed in the frequency, accuracy, and scale of measurements to evaluate land cover and management differentiation and address the variability caused by heterogeneity at these scales.
- New methods of extrapolating across the scale of belowground processes are needed to enable tracking of changes measured in biogeochemical dynamics.
- Verification and monitoring. Will new sensors be required or will process knowledge (rules of thumb) be sufficient to estimate carbon sequestration based on the implementation of observable practices?

4.4.3.3 Engineering technology

Once new concepts based on understanding are put forth, some key engineering issues must be addressed to allow for effective implementation of strategies. We offer the following examples:

- Effective irrigation. How can water usage be minimized? Are there opportunities to develop gray water management for urban areas? How might wetland restoration be combined with waste water treatment? What are the implications of using groundwater of marginal quality?
- Nutrient delivery and utilization. A key issue will be nitrogen fixation. Also, with a mandate to reduce organic matter decomposition, nutrient availability will be an issue. Are there innovative soil amendments that can be developed? How can more litter be incorporated effectively into the soil? Are there ways to use large volumes of animal wastes or sewage sludge to improve carbon sequestration while solving this vexing environmental challenge?
- Energy efficiency. Many carbon sequestration methods will require the use of materials that must be handled with heavy equipment: how can the energy penalty be minimized? What alternatives to classic fertilizers can be developed to avoid the fossil fuel emissions from fertilizer production?
- Byproduct use. There are important R&D links to existing programs. For example, the DOE biomass program is examining fossil fuel displacement and the DOE Office of Industrial Technology is investigating feedstock programs. Are there innovative options to store or bury harvested biomass products? How can biomass products like wood be included in structural materials (e.g., to replace cement, which is produced by a CO_2–emitting process) to both sequester carbon and reduce CO_2 emissions?

4.4.3.4 Ecosystem response and modeling

The fundamental R&D needed for Ecosystem Response and Modeling falls into two broad categories. First, key measurements will be required for computer models that will evaluate the long-term effects of carbon sequestration. These measurements differ in emphasis from those in Sect. 4.4.3.2 by requiring larger scales, probable manipulative experiments, and integrated measurement strategies. Second, integrative models will be required at scales from landscapes to global ecosystems.

- Networks of process-based, globally integrated ecosystem-scale monitoring and experimental facilities.
- Measurement of plant and ecosystem-scale responses to changes in atmospheric chemistry and climate variables such as CO_2, temperature, water, nutrients, ozone, and pollutants. For example, increases in emissions of CO, N_2O, and CH_4 as a feedback from increased carbon sequestration activities.
- Measurement of ecosystem responses to sequestration. For example, species diversity and resiliency may be affected by implementation of some strategies.
- Integrative models that address plant-, watershed-, landscape-, and ecosystem-scale processes up to regional and global systems. These models must also make use of and facilitate use of massive data sets that will be collected through some of these activities. For example, work is needed to assess possible impacts from a focus on restoration of degraded lands, or carbon sequestration and erosion control in deserts that could reduce transport of iron and silica micronutrients by air currents to the ocean.
- Life-cycle analysis models that can identify opportunities for biomass gains, evaluate social and economic issues, and estimate total system costs (real costs and carbon costs).

4.5 SUMMARY

Carbon sequestration in terrestrial ecosystems will provide significant near-term benefits (over the next 25 years), with the potential for even more major contributions in the long-term (> 50 years). There are many ancillary positive benefits from carbon sequestration in terrestrial ecosystems, which are already a major biological scrubber for CO_2. The potential for carbon sequestration appears to be large for terrestrial ecosystems (5–10 GtC/year). However, this value is speculative, and a primary R&D need is to evaluate this potential and its implications for ecosystems. In addition, economic and energy costs were not fully considered in the analysis to estimate the carbon sequestration potential. As carbon sequestration strategies are developed, a whole ecosystem approach under changing climate conditions must be considered. Potential feedback mechanisms (both positive and negative) must be addressed.

Our primary focus has been on manipulative strategies to increase carbon sequestration rather than protect ecosystems. We wish to emphasize that carbon stored below ground is more permanent than plant biomass. However, even soil carbon must be managed in the long term. One of the key questions is whether soil texture, topographic position, and climate ultimately determine the carbon content of a soil, or whether it can be permanently changed by manipulation and to what extent. For plant biomass, transformation of carbon into long-lived products or belowground storage is essential. With this perspective, it appears that the following ecosystems offer significant opportunity for carbon sequestration (not in any order of priority):

- **Forest lands.** The focus should include belowground carbon and long-term management and utilization of standing stocks, understory, ground cover, and litter.
- **Agricultural lands.** The focus should include crop lands, grasslands, and range lands, with an emphasis on increasing long-lived soil carbon.
- **Biomass croplands.** As a complement to ongoing efforts related to biofuels, the focus should be on long-term increases in soil carbon.
- **Deserts and degraded lands.** Restoration of degraded lands offers significant benefits and carbon sequestration potential in both below- and aboveground systems.
- **Boreal wetlands and peatlands.** The focus should include management of soil carbon pools and perhaps limited conversion to forest or grassland vegetation where ecologically acceptable.

In developing the road map, we established three interrelated objectives that transcend ecosystems: increase belowground carbon (soil carbon), increase aboveground carbon (plant biomass), and optimize land area for sequestration of carbon.

These objectives can be accomplished by the following strategies: improve soil characteristics, manage crops and lands for sequestration, select and engineer species for sequestration, and assess impacts to ecosystem dynamics from sequestration.

Research on four key interrelated R&D topics is needed to meet goals for carbon sequestration in terrestrial ecosystems:

1. **Increased understanding** of ecosystem structure and function directed toward nutrient cycling, plant and microbial biotechnology, molecular genetics, and functional genomics.

2. **Improved measurement** of gross carbon fluxes, dynamic carbon inventories with the development of new or improved instrumentation for in situ, nondestructive belowground observation, remote sensing for aboveground biomass measurement, and verification and monitoring of carbon stocks.

3. **Implementation of improved knowledge and tools** such as better irrigation methods, efficient nutrient delivery systems, increased energy efficiency in agriculture and forestry, and increased byproduct use.

4. **Assessment of ecosystem responses** to changes in both atmospheric chemistry and climate, and other processes that might be impacted by implementation of carbon sequestration strategies. Suites of models would be used, integrating across scales ranging from physiological processes to regional scales as inputs to global-scale modeling and including life cycle analysis models.

Finally, field-scale research should be implemented in the near term with manipulations in large-scale ecosystems aimed at clarifying both physiological and geochemical processes regulating carbon sequestration. This research should be closely linked to integrative ecosystem modeling. The creation of such carbon sequestration test facilities on DOE reservations would provide proof-of-principle testing of new sequestration concepts and an integration of diverse sequestration science and engineering challenges.

4.6 ACKNOWLEDGMENTS

All members of the team who helped develop this chapter are identified in Appendix A. In addition, we express our appreciation to the following individuals who provided thorough and meaningful review comments: Gary King, David Nowak, Richard Pouyat, Jerry Tuskan, Donn Viviani, and Stan Wullschleger. Melissa and Terry Chapin provided a photograph for the Pleistocene Park concept and permission to include the concept in this report.

4.7 END NOTES

As discussed in Chaps. 1 and 2, several activities include R&D planning for carbon sequestration. One specific event that paralleled this road map activity, with a topic of close relevance, was the workshop entitled “Carbon Sequestration in Soils: Science, Monitoring and Beyond.” This workshop, organized by Oak Ridge and Pacific Northwest National Laboratories and the Council of Agricultural Science and Technology, was held December 3–5, 1998. It addressed the role of carbon sequestration in soils in far greater detail than does this road-mapping exercise. By engaging several participants in that workshop in our effort, we have tried to maintain a consistent view of the most important R&D topics. For excellent and detailed discussions on specific topics, consult the papers prepared for the workshop: Lal, Hassan, and Dumanski; Marland, McCarl, and Schneider; Metting et al.; and Post et al.

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5 SEQUESTRATION OF CARBON DIOXIDE IN GEOLOGIC FORMATIONS

Vision

By the year 2025, effective, safe, and cost-competitive options for geologic sequestration of all of the CO$_2$ generated from coal, oil, and gas power plants and generated by H$_2$ production from fossil fuels will be available within 500 km of each power plant.

5.1 SEQUESTRATION IN GEOLOGIC FORMATIONS BUILDS ON A STRONG EXPERIENCE BASE

Geologic formations, such as oil fields, coal beds, and aquifers, are likely to provide the first large-scale opportunity for concentrated sequestration of CO$_2$. In fact, CO$_2$ sequestration is already taking place at Sleipner West off the coast of Norway, where approximately one million tonnes of CO$_2$ are sequestered annually as part of an off-shore natural gas production project (see sidebar on the Statoil Project). Developers of technologies for sequestration of CO$_2$ in geologic formations can draw from related experience gained over nearly a century of oil and gas production, groundwater resource management, and, more recently, natural gas storage and groundwater remediation. In some cases, sequestration may even be accompanied by economic benefits such as enhanced oil recovery (EOR), enhanced methane production from coal beds, enhanced production of natural gas from depleted fields, and improved natural gas storage efficiency through the use of CO$_2$ as a “cushion gas” to displace methane from the reservoir.

5.1.1 Sequestration Mechanisms

CO$_2$ can be sequestered in geologic formations by three principal mechanisms (Hitchon 1996; DOE 1993). First, CO$_2$ can be trapped as a gas or supercritical fluid under a low-permeability caprock, similar to the way that natural gas is trapped in gas reservoirs or stored in aquifers. This mechanism, commonly called hydrodynamic trapping, will likely be, in the short term, the most important for sequestration. Finding better methods to increase the fraction of pore space

Statoil Sequesters CO_2 from Off-Shore Gas Production

Natural gas produced from the Sleipner West field in the North Sea contains nearly 10% by volume CO_2. To meet the sales specification of only 2.5% CO_2, most of the CO_2 must be removed from the natural gas before delivery. Statoil uses an amine solvent to absorb the excess CO_2. The separated CO_2 is injected into an aquifer 1000 m under the North Sea. Approximately one million tonnes of CO_2 are separated and sequestered annually. Over the project lifetime, 20 million tonnes of CO_2 are expected to be sequestered (Korbol and Kaddour 1995).

occupied by trapped gas will enable maximum use of the sequestration capacity of a geologic formation. Second, CO_2 can dissolve into the fluid phase. This mechanism of dissolving the gas in a liquid such as petroleum is called solubility trapping. In oil reservoirs, dissolved CO_2 lowers the viscosity of the residual oil so it swells and flows more readily, providing the basis for one of the more common EOR techniques. The relative importance of solubility trapping depends on a large number of factors, such as the sweep efficiency (efficiency of displacement of oil or water) of CO_2 injection, the formation of fingers (preferred flow paths), and the effects of formation heterogeneity. Efficient solubility trapping will reduce the likelihood that CO_2 gas will quickly return to the atmosphere.

Finally, CO_2 can react either directly or indirectly with the minerals and organic matter in the geologic formations to become part of the solid mineral matrix. In most geologic formations, formation of calcium, magnesium, and iron carbonates is expected to be the primary mineral-trapping processes. However, precipitation of these stable mineral phases is a relatively slow process with poorly understood kinetics. In coal formations, trapping is achieved by preferential adsorption of CO_2 to the solid matrix. Developing methods for increasing the rate and capacity for mineral trapping will create stable repositories of carbon that are unlikely to return to the biosphere and will decrease unexpected leakage of CO_2 to the surface.

Finding ways to optimize hydrodynamic trapping, while increasing the rate at which the other trapping mechanisms convert CO_2 to less mobile and stable forms, is one of the major challenges that must be addressed by an R&D program.

5.1.2 Sources and Forms of CO_2

For the purposes of this assessment, we assumed that CO_2 would be produced either by combustion of fossil fuels to generate electricity or by decarbonization of fossil fuels to produce hydrogen. Following generation, CO_2 would be separated from the waste stream to a purity of at least 90%. CO_2 would be transported as a supercritical fluid by pipeline to the nearest geologic formation suitable for sequestration. The technology, cost, and safety issues for transportation were not considered.

5.1.3 Capacity of Geologic Formations Suitable for Sequestration

Three principal types of geologic formations are widespread and have the potential to sequester large amounts of CO_2:

- active and depleted oil and gas reservoirs
- deep aqueous formations, including saline formations
- deep coal seams and coal-bed methane formations

Other geologic formations such as marine and arctic hydrates, CO_2 reservoirs, mined cavities in salt domes, and oil shales may increase sequestration capacity or provide site-specific opportunities but are likely to be developed only after other sequestration targets are explored.

Maps showing the location of active and abandoned oil and gas fields, deep-saline aquifers, and coal formations are provided in Figs. 5.1 through 5.3. Figure 5.3 also shows the location of fossil-fuel-fired power plants. As illustrated, one or more of these formations is located within 500 km of each of the fossil-fuel-burning power plants in the United States.

Estimates of sequestration capacity for each of these types of geologic formations are provided in Table 5.1. While the range and uncertainty in these estimates are large, and in some cases costs were not considered when they were developed, they suggest that a significant opportunity exists for CO_2 sequestration in geologic formations. More specifically, in the near term, the United States has sufficient capacity, diversity, and broad geographic distribution of geological formations to pursue geologic sequestration confidently as a major component of a national carbon management strategy. What is less certain is the ultimate capacity that geologic formations can contribute, over the centuries ahead, to sequestration of CO_2. Only through experience and application of systematic screening criteria will we gain enough knowledge to assess the ultimate sequestration capacity of geologic formations.

5.1.4 Drivers for R&D

Although the potential for CO_2 sequestration in geologic formations is promising, new knowledge, enhanced technology, and operational experience must be gained in a number of critical areas. The primary drivers for R&D include

- developing reliable and cost-effective systems for monitoring CO_2 migration in the subsurface

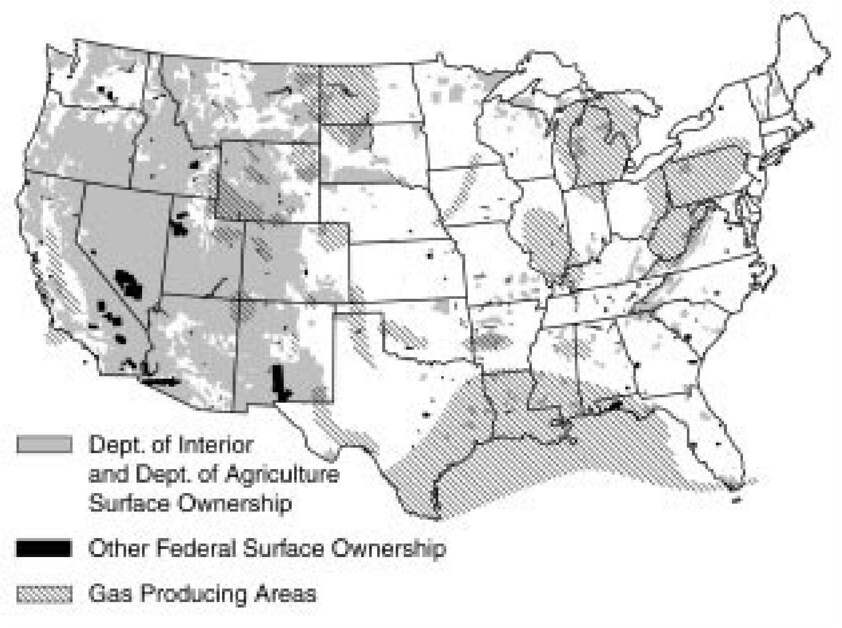


Fig. 5.1. Location of gas-producing areas in the United States.


Source: U.S. Geological Survey

Fig. 5.2. Location of deep saline aquifers in the United States.

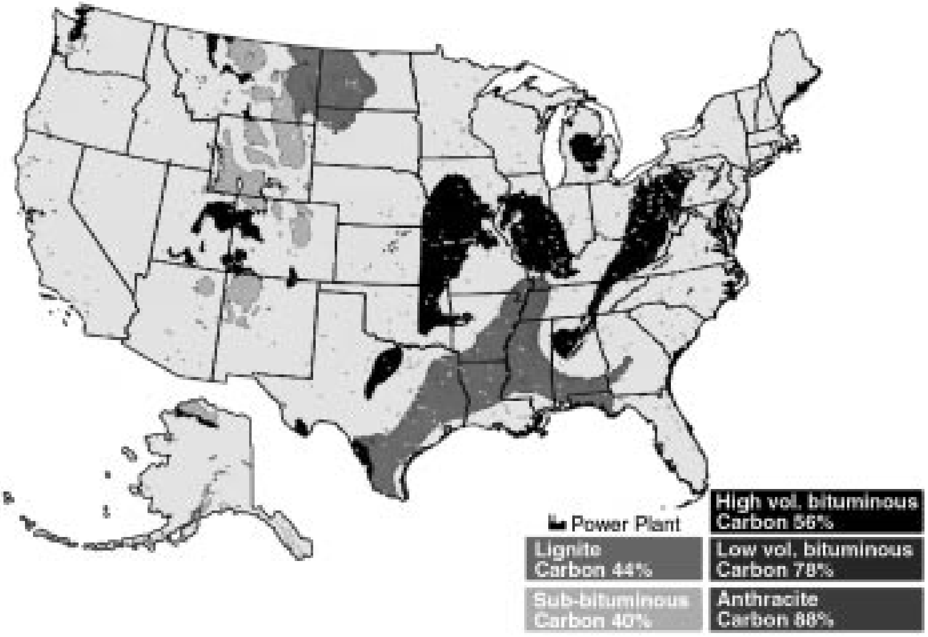


Fig. 5.3. Location of coal-producing areas in the United States and power plants.

Table 5.1. Range of estimates for CO_2 sequestration in U.S. geologic formations

Geologic formation	Capacity estimate (GtC)	Source
Deep saline aquifers	1-130	Bergman and Winter 1995
Natural gas reservoirs in the United States	25[a] 10[b]	R. C. Burruss 1977
Active gas fields in the United States	0.3/year[c]	Baes et al. 1980
Enhanced coal-bed methane production in the United States	10	Stevens, Kuuskraa, and Spector 1998

[a] Assuming all gas capacity in the United States is used for sequestration.
[b] Assuming cumulative production of natural gas is replaced by CO_2.
[c] Assuming that produced natural gas is replaced by CO_2 at the original reservoir pressure.

- assessing and ensuring long-term stability of sequestered CO_2 (<100 years)
- reducing the cost and energy requirements of CO_2 sequestration in geologic formations
- gaining public acceptance for geologic sequestration

This chapter outlines R&D needs to address these issues and provides a comprehensive road map of the critical elements needed to achieve the potential of geologic sequestration of CO_2.

5.2 ASSESSMENT OF CURRENT CAPABILITIES AND R&D NEEDS

The current capabilities and needs were evaluated in the following context for each major type of geologic formation.

Industrial experience: What related industrial experience provides the scientific, technological, and economic basis for evaluating sequestration in geologic formations?

Beneficial uses of CO_2: Are there beneficial uses of CO_2 that may offset the cost of sequestration or provide an additional incentive for developing CO_2 sequestration technology?

Regulatory, cost, and safety: What is known about the regulatory framework, cost, and safety aspects of CO_2 sequestration in geologic formations?

Operational drivers: What are the operational aspects that must be understood to enable cost-effective and safe sequestration of CO_2? These include

- *CO_2 trapping mechanisms:* Which of the trapping mechanisms is most important? How much do we understand about them? What are the key unresolved issues?
- *CO_2 waste stream characteristics:* What are the requirements for the CO_2 waste stream? How pure should it be? What are the effects of impurities on sequestration efficiency, cost, safety, and risk? What temperature and pressure are needed at the wellhead? What are the unresolved issues?
- *Formation characterization:* How can sequestration capacity and caprock integrity be assessed? What attributes are most important for assessing capacity and integrity?
- *Injection, drilling, and well completion technology:* How will CO_2 be injected into geologic formations? How will the wells be drilled and completed? Are there special material-handing issues for sequestration of CO_2?
- *Performance assessment:* What methods can be used to design, predict, and optimize sequestration of CO_2 in geologic formations? What new issues must to be addressed or new approaches will be required?
- *Monitoring:* How can migration of CO_2 in the subsurface be monitored? How can leakage be detected and quantified? How can we detect and monitor solubility and mineral trapping?

In the following sections, we first address these questions in the context of issues unique to each type of geologic formation. Next we address cross-cutting issues that are common to all formations.

5.2.1 Opportunities for CO_2 Sequestration in Oil and Gas Formations

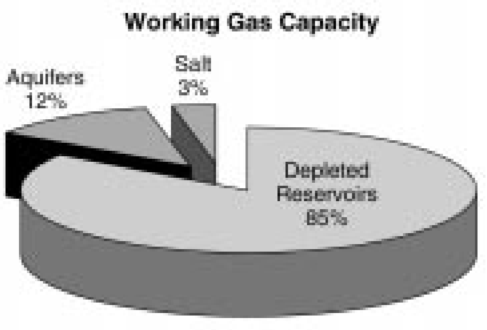
Oil and gas reservoirs are promising targets for CO_2 sequestration for a number of reasons. First, oil and gas are present within structural or stratigraphic traps, and the oil and gas that originally accumulated in these traps did not escape over geological time. Thus these reservoirs should also contain CO_2, as long as pathways to the surface or to adjacent formations are not created by overpressuring of the reservoir, by fracturing out of the reservoir at wells, or by leaks around wells. Second, the geologic structure and physical properties of most oil and gas fields have been characterized extensively. While additional characterization—particularly of the integrity and extent of the caprock—may be needed, the availability of existing data will lower the cost of implementing CO_2 sequestration projects. Finally, very sophisticated computer models have been developed in the oil and gas industry to predict displacement behavior and trapping of CO_2 for EOR. These models take into account the flow of oil, gas, and brine in three dimensions; phase behavior and CO_2 solubility in oil and brine; and the spatial variation of reservoir properties, to the extent it is known. These same processes are responsible for hydrodynamic and solubility trapping of CO_2 (see sidebar on natural gas storage).

The first and most viable option for CO_2 sequestration is to build upon the enormous experience of the oil and gas industry in EOR. Currently, about 80% of commercially used CO_2 is for EOR purposes. The technology for CO_2 injection is commercially proven and can be implemented without much difficulty (see sidebar on auxiliary benefits of CO_2 sequestration). EOR has the benefit of sequestering CO_2 while increasing production from active oil fields. In the long term, the volume of CO_2 sequestered as part of EOR projects may not be comparatively large, but valuable operational experience can be gained that will benefit geologic sequestration in other types of formations.

CO_2 could be sequestered in two types of natural gas fields: (1) abandoned fields and (2) depleted but still active fields where gas recovery could be enhanced by CO_2 injection. The map in Fig. 5.1 suggests that, except for the North Central and Atlantic Coastal states, abandoned gas fields are present in many parts of the United States. Deciding which abandoned gas fields could best be used in a CO_2 sequestration program would require a comprehensive review of the current conditions in abandoned fields and the economics of their rehabilitation. This would be a major program of investigation, but the necessary technology to carry out such a review is available and well known to the gas industry. Locating and sealing abandoned wells may be an ongoing challenge for sequestration in abandoned gas fields.

In nearly depleted gas fields, it is possible that injection could prolong the economic life of the field by maintaining reservoir pressures longer than would otherwise be possible. However, enhancing gas production through injection of another kind of gas (e.g., CO_2) while the field continues to operate has not been pursued in the

Natural Gas Storage in Geologic Formations



Daily and seasonal variability in demand for natural gas requires the storage of large volumes of natural gas that can be tapped as needed. Geologic formations are used to store natural gas. Currently, they provide 3 trillion ft^3 of working gas capacity. Most gas is stored in depleted gas fields, but aquifers and mined caverns in salt also contribute significantly to the existing capacity. Natural gas storage provides experience in and demonstrates the feasibility of the hydrodynamic trapping mechanism for use in sequestering CO_2 (Beckman and Determeyer 1995).

CO_2 Sequestration in Geological Formations Can Have Auxiliary Benefits

Recovering residual oil through the injection of CO_2 into oil reservoirs began on a large scale in 1972 in Texas. Carbon dioxide enhances oil production by two primary mechanisms. First, CO_2 gas displaces oil and brine, which are subsequently pumped from the wells. Second, injected CO_2 dissolves in the oil, leading to a reduction in viscosity and swelling of the oil, making it flow more easily and leading to enhanced production. The CO_2 used for EOR usually comes from naturally occurring CO_2-filled reservoirs. Pipelines carry CO_2 from its natural reservoirs to the oil field, where it is injected. Eventually, some of the injected CO_2 is produced along with the oil. At the surface, it is separated and injected back into the oil reservoir. EOR through CO_2 injection provides one example of the beneficial uses of CO_2 and operational experience to guide CO_2 sequestration.

In the future, CO_2 sequestered from power plants can be used to enhance coal-bed methane production. A pilot program of CO_2-assisted coal-bed methane production in the San Juan Basin, New Mexico, has been under way since 1996. This project, the Allison Unit Pilot run by Burlington Resources, is injecting 4 million ft^3/day of pipeline-fed CO_2 from a natural source into a system of nine injection wells located in the San Juan Basin. Preliminary results indicate that full-field development of this process could boost recovery of in-place methane by about 75%.

United States. Therefore, pilot tests augmented with laboratory and modeling studies will be needed to develop this technology. Some experience may be gained from Gaz de France, which for the past 10 to 15 years has been converting gas storage projects to operate with two kinds of gas: natural gas that is cyclically injected and withdrawn as needed and a low-cost cushion gas. A similar concept may be developed for combining CO_2 sequestration with enhanced natural gas production from depleted fields.

Table 5.2 lists the specific R&D needs for advancing the technology and acceptability of CO_2 sequestration in oil and gas reservoirs. Needs are divided into near-, mid-, and long-term efforts that together provide a comprehensive set of actions that will create a set of sequestration options.

5.2.2 CO_2 Sequestration in Aqueous Formations

Aqueous formations are the most common fluid reservoirs in the subsurface, and large-volume formations are available practically anywhere. For sequestration, deep (>2000 ft) formations that are not in current use are the most logical targets. As shown in Fig. 5.2, suitable deep formations, which are usually filled with brackish or saline water, are located across most of the United States.

Although there is little practical experience with CO_2 sequestration in aqueous formations, aquifer storage of natural gas provides a foundation of experience for identifying important technical issues. In addition, CO_2 sequestration in aquifers has been discussed in the technical literature since the early 1990s. Operational

Table 5.2. R&D priorities for CO_2 sequestration in oil and gas fields

Near-term R&D (<2005)	Mid-term R&D (2005-2010)	Long-term R&D (>2010)
Understand the importance of geochemical reactions on . seal integrity . long-term sequestration . subsidence in limestones . long-term oil recovery	Complete assessment of seismic monitoring methods for monitoring CO_2 invasion	Obtain cost and performance data from a full-scale integrated demonstration of CO_2 sequestration from a power plant in a depleted or abandoned gas field
Understand how natural CO_2 reservoirs are sealed and what this tells us about CO_2 sequestration potential	Enhance resolution of seismic monitoring methods	Develop methods to increase sequestration efficiency from current estimates (10-20% pore volume) to greater than 50%
Continue work on data integration to characterize variation of spatial properties in oil and gas reservoirs	Develop coupled H-M-C-T (hydrologic, mechanical, chemical, thermal) simulators for evaluating short- and long-term sequestration efficiency and safety	
Improve models of horizontal wells for CO_2 injection for EOR and sequestration efficiency	Conduct a small-scale pilot for improved gas recovery from a depleted gas field by CO_2 injection	
Assess and develop methods for detection of abandoned wells in oil and gas fields	Develop verification and monitoring capabilities for CO_2 sequestration in enhanced oil recovery applications	
Establish screening criteria for selecting sequestration sites in oil and gas fields . Highest priority should be given to EOR projects . Next highest priority to abandoned gas fields		
Match CO_2 generators to potential sequestration sites using screening criteria		

experience from aquifer gas storage and these studies indicate that from an engineering perspective, the main issues for CO_2 disposal in aquifers relate to (1) the disposal rate of CO_2; (2) the available storage capacity (ultimate CO_2 inventory); (3) the presence of a caprock of low permeability, and potential CO_2 leakage through imperfect confinement; (4) identification and characterization of suitable aquifer formations and caprock structures; (5) uncertainty due to incomplete knowledge of subsurface conditions and processes; and (6) corrosion resistance of materials to be used in injection wells and associated facilities.

The main trapping process affecting CO_2 sequestration in aquifers is well understood, at least in a generic sense. Injection of CO_2 into a water-filled formation results in immiscible displacement of an aqueous phase by a less dense and less viscous gas phase. Because CO_2 is soluble in water, some of the CO_2 will dissolve in the water. The thermophysical properties of water and CO_2 that determine flow behavior—such as density, viscosity, and solubility—are well known, as is their dependence on pressure, temperature, and salinity. Equilibrium solubility of CO_2 in water decreases by about a factor of 6 between 10 and 150°C, and it decreases with aquifer salinity ("salting out"). The rate at which gaseous CO_2 will dissolve in water depends on size and shape of the gas-water interfaces and may be subject to considerable uncertainty.

Uptake of CO_2 by water may be increased beyond what can be attributed to physical solubility by interactions with carbonate minerals. Minerals such as calcite would be dissolved in response to CO_2 injection. A considerably larger increase in storage capacity is possible from heterogeneous reactions with aluminosilicates ("mineral trapping"). There are indications that kinetics of reactions with carbonates may be fast, while kinetics of silicate interactions appear to be very slow, requiring tens or perhaps hundreds of years for substantial reaction progress.

Because CO_2 is considerably less dense and viscose than water, CO_2 injection into aquifers will be prone to hydrodynamic instabilities. The viscosity contrasts will lead to viscous fingering, and the density contrast will lead to gravity segregation. The specifics of each will depend on the spatial distribution of permeability at the actual site and on injection rates (Fig. 5.4). The effect of these complexities may be important in controlling the relative importance of the three primary trapping mechanisms. Detailed characterization of these

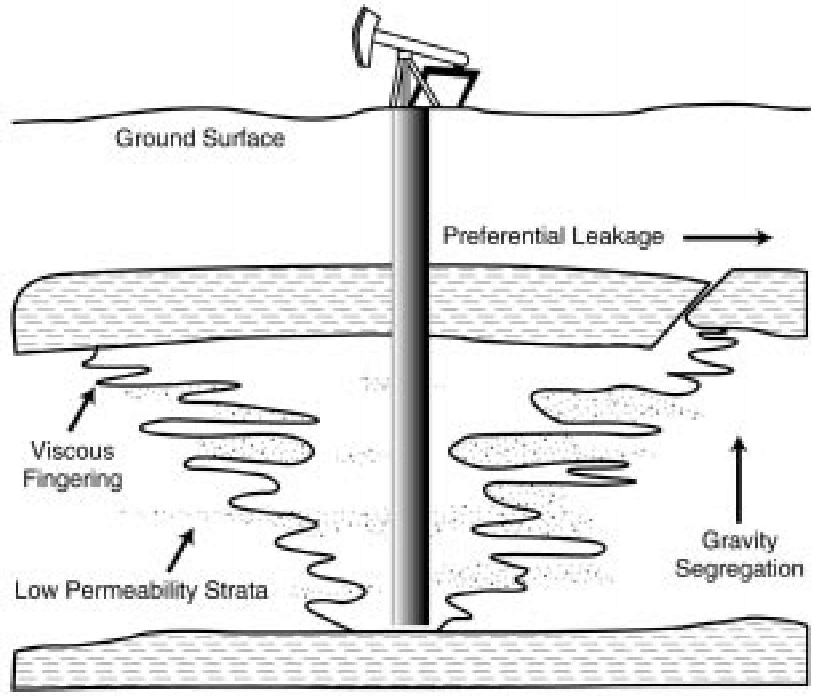


Fig. 5.4. Gravity segregation, viscous fingering, heterogeneity, and preferential flow through faulted cap rocks could influence CO_2 migration in the subsurface.

complexities will be difficult, but it may not be necessary for achieving engineering objectives.

Two key issues distinguish CO_2 sequestration in aquifers from sequestration in oil and gas reservoirs. First, oil and gas reservoirs occur by virtue of the presence of a structural or stratigraphic trap. This same trap is likely to retain CO_2. Identification of such effective traps may be more difficult in aqueous formations and may require new approaches for establishing the integrity and extent of a caprock. Second, injection of CO_2 into an aqueous formation is unlikely to be accompanied by removal of water from the formation. (In the case of EOR, oil is simultaneously withdrawn while CO_2 is injected.) Injection will therefore lead to an increase in formation pressure over a large area. Whether or to what extent large-scale pressurization will affect caprock integrity, cause land surface deformation, and induce seismicity must be better understood to design safe and effective sequestration.

A final issue concerning sequestration in aqueous formations is the acceptable leakage rate from the formation to overlying strata. Leakage of CO_2 may not pose a safety hazard and may, in some cases, be desirable if leakage to overlying units increases the opportunity for enhanced solubility or mineral trapping. Evaluating general and site-specific acceptable leakage rates should be part of a long-term strategy for CO_2 sequestration in aqueous formations.

Table 5.3 lists the specific R&D needs for advancing the technology and acceptability of CO_2 sequestration in aqueous formations. Needs are divided into near-, mid-, and long-term efforts that together provide a comprehensive set of actions that will create a set of sequestration options.

5.2.3 Opportunities for CO_2 Sequestration in Coal Formations

Coal formations provide an opportunity to simultaneously sequester CO_2 and increase the production of natural gas. Methane production from deep unmineable coal beds can be enhanced by injecting CO_2 into coal formations, where the adsorption of CO_2 causes the desorption of methane. This process has the potential to sequester large volumes of CO_2 while improving the efficiency and profitability of commercial natural gas operations (see sidebar on auxiliary benefits of CO_2 sequestration).

This method for enhancing coal-bed methane production is currently being tested at two pilot demonstration sites in North America. At one pilot production field in the San Juan Basin (New Mexico and Colorado), the operator has injected 3 million ft^3/day of CO_2 through four injection wells during a 3-year period. Preliminary results indicate that full-field development of this process could boost recovery of in-place methane by about 75%. The key technical and commercial criteria for successful application of this concept include (1) favorable geology such as thick, gas-saturated coal seams, buried at suitable depths and located in simple structural settings, which have sufficient permeability; (2) CO_2 availability, such as low-cost potential supplies of CO_2, either from naturally occurring reservoirs or from anthropogenic sources such as power-plant flue gas; and (3) gas demand, which includes an efficient market for utilization of methane, including adequate pipeline infrastructure, long-

Table 5.3. R&D priorities for CO_2 sequestration in aqueous formations

Near-term R&D (<2005)	Mid-term R&D (2005-2010)	Long-term R&D (>2010)
Conduct a small-scale pilot test of CO_2 injection into a shallow <3000-ft-deep aquifer or saline formation to guide R&D priorities	Understand the kinetics of CO_2 dissolution and mineral trapping	Obtain cost and performance data from a full-scale integrated demonstration of CO_2 sequestration from a power plant in moderate depth (2000-5000 ft) saline formation
Understand how the interplay of gravitational instability, viscous fingering, and formation heterogeneity influence CO_2 migration in aqueous formations	Understand how pressure buildup due to CO_2 injection influences caprock integrity	Develop technologies to mitigate or control CO_2 leaks
Continue work on data integration to characterize variation of spatial properties in aqueous formations	Develop coupled H-M-C-T (hydrologic, mechanical, chemical, thermal) simulators for evaluating short and long-term sequestration efficiency and safety	Develop advanced concepts and technologies for improving sequestration efficiency
Establish screening criteria for selecting sequestration sites in aqueous formations. Match CO_2 generators to potential sequestration sites using screening criteria	Understand the influence of microbial interactions on trapping efficiency and conversion of CO_2 to other forms of carbon	Develop remote or other cost-effective methods for monitoring CO_2 leaks
Evaluate and develop, if needed, methods for evaluating the integrity of caprocks	Evaluate the potential for induced seismicity associated with CO_2 injection.	
	Understand reservoir characteristics to minimize adverse effects on caprock integrity during CO_2 injection.	
Develop a safety analysis and technical strategy for the concept of an "allowable" leakage rate	Develop an appropriate technical basis for regulatory guidelines	
Use natural CO_2 reservoirs to understand how long-term mineral trapping may contribute to permanent sequestration	Develop methods for monitoring migration of CO_2 and its byproducts in the subsurface using a combination of hydrologic, seismic, tracer, and mechanical methods (e.g., tilt measurements)	

term end-users, and favorable wellhead gas prices.

A second pilot demonstration of this concept is located in Alberta, Canada. The Alberta project is testing a process of injecting CO_2 into one of Alberta's deep unmineable coal beds. Many of Alberta's coal deposits are rich in methane. Preliminary computer modeling suggests that selected techniques for fracturing the coals around wells could be improved with a substantial increase in primary methane. The initial field activities consist of a single well test, designed to measure reservoir properties, increase primary production by an effective fracturing technique, and evaluate CO_2-enhanced methane recovery. A detailed technical assessment will follow the field test in early 1999.

Coal-bearing strata include both thin and thick coal seams and interlayered sandstones, siltstones, and shales; and they are usually saturated with water. This complex interlayered formation defines the coal-bed reservoir interval. Coal-bed stratigraphy and the structure/porosity/permeability of interlayered and overlying strata are site-specific and will need to be individually characterized. Unlike in oil and gas reservoirs, however, the methane in coal beds is retained by adsorption rather than by trapping beneath an impermeable overlying/lateral seal. Therefore, the nature of overlying and adjacent strata becomes an important issue for retention of the CO_2 within the coal-bed reservoir interval until it is adsorbed, and for retention of the displaced methane until it can be withdrawn. Techniques to verify the capacity, stability, and permanence of CO_2 storage in coal-bed reservoir intervals are needed.

Table 5.4 lists the specific R&D needs for advancing the technology and acceptability of CO_2 sequestration in coal formations. Needs are divided into near-, mid-, and long-term efforts that together provide a comprehensive set of actions that will create a set of sequestration options.

5.3 CROSS-CUTTING R&D NEEDS FOR GEOLOGIC FORMATIONS

Operational requirements and R&D needs for sequestration in each of the three types of geologic formations were assessed independently. Not unexpectedly, needs common to all formations emerged and are summarized in this section. There are significant differences, however, in the maturity of technology and scientific understanding of the processes underpinning CO_2 sequestration in different types of geologic formations. Figure 5.5 highlights these similarities and differences.

5.3.1 CO_2 Trapping Mechanisms

Hydrodynamic and solubility processes responsible for trapping CO_2 in geologic formations are reasonably well understood, especially over the time frame associated with EOR (<20 years). Mineral trapping (i.e., reactions relying on the chemical reactions between the gas/liquid and solid phases) is less well understood, particularly with regard to how fast these reactions occur. Reactions between CO_2 and the microbial communities present in deep geologic formations are also poorly understood. Needs for new knowledge include

- hydrodynamics of CO_2 migration in heterogeneous formations (e.g., sweep efficiency, preferential flow, and leakage rates)
- CO_2 dissolution kinetics
- mineral trapping kinetics
- microbial interactions with CO_2
- influence of stress changes on caprock and formation integrity
- nonlinear feedback processes affecting confinement (e.g., mineral dissolution and precipitation that change rock permeability)
- CO_2–methane adsorption/exchange behavior on organic substrates

5.3.2 CO_2 Waste Stream Characteristics

A high-purity (>90% CO_2), dry waste stream is the most desirable for sequestration in geological formations,

Table 5.4. R&D priorities for CO_2 sequestration in coal formations

Near-term R&D (<2005)	Mid-term R&D (2005-2010)	Long-term R&D (>2010)
Understand the adsorption-desorption processes by which CO_2 substitutes for methane in coal formations	Develop modeling tools for simultaneous fluid flow, gas adsorption-desorption, deformation and gas-flow dynamics in coal-bed reservoir intervals	Obtain cost and performance data from a full-scale integrated demonstration of methane production, power generation, and CO_2 sequestration
Assess the absolute and relative porosity and permeability structure of various coals and coal-bed reservoir intervals, including expansion/contraction effects of CO_2-methane exchange at pressure	Assess the interaction of coal with compounds typically found in flue gases such as sulfur or nitrogen	Develop technologies and methods for injection and production in low-permeability and deep formations
Conduct pilot tests with sufficient monitoring to gain insights into how CO_2 injection increases production of methane from coal beds and how CO_2 is adsorbed onto coal	Conduct a pilot test of flue gas injection to evaluate ability of CO_2 to adsorb to the coal surface, displacing the methane, while the nitrogen sweeps the methane	Test CO_2, methane, coal interactions in water-saturated intervals to evaluate whether dewatering is needed prior to CO_2 injection
Develop reservoir screening criteria for assessment purposes. Match CO_2 generators to potential sequestration sites using screening criteria	Test the impact of various drilling methods (horizontal vs vertical) on injection and production dynamics of all gases and fluid phases	Test and monitor the ability of various coal formations to sequester CO_2 for a long time
Develop injection engineering and design techniques for optimizing CO_2 sequestration and methane production in coal beds	Develop methods for monitoring migration of CO_2 and its byproducts using a combination of hydrologic, seismic, tracer, and mechanical methods	
Understand how seismic wave propagation responds to CO_2 injection, adsorption, and coal deformation	Understand how the interactions between microorganisms, CO_2, and the solid matrix affect long-term sequestration	

based largely on considerations about volume reduction, costs for gas compression, and CO_2 handling issues (e.g., corrosion). Scoping studies are needed to evaluate beneficial or detrimental effects of waste stream characteristics on trapping efficiency, economics, and safety of CO_2 sequestration. Examples of research needs include

- analysis of the effect of waste stream characteristics on hydrodynamic, solubility, and mineral trapping/adsorption efficiency
- cost/benefit analysis for determining optimal CO_2 purity
- evaluation of the influence of other “contaminants” (e.g., mercury) on the safety and regulatory constraints on CO_2 sequestration

5.3.3 Formation Characterization

Ongoing efforts related to oil and gas production and groundwater remediation have led to development of

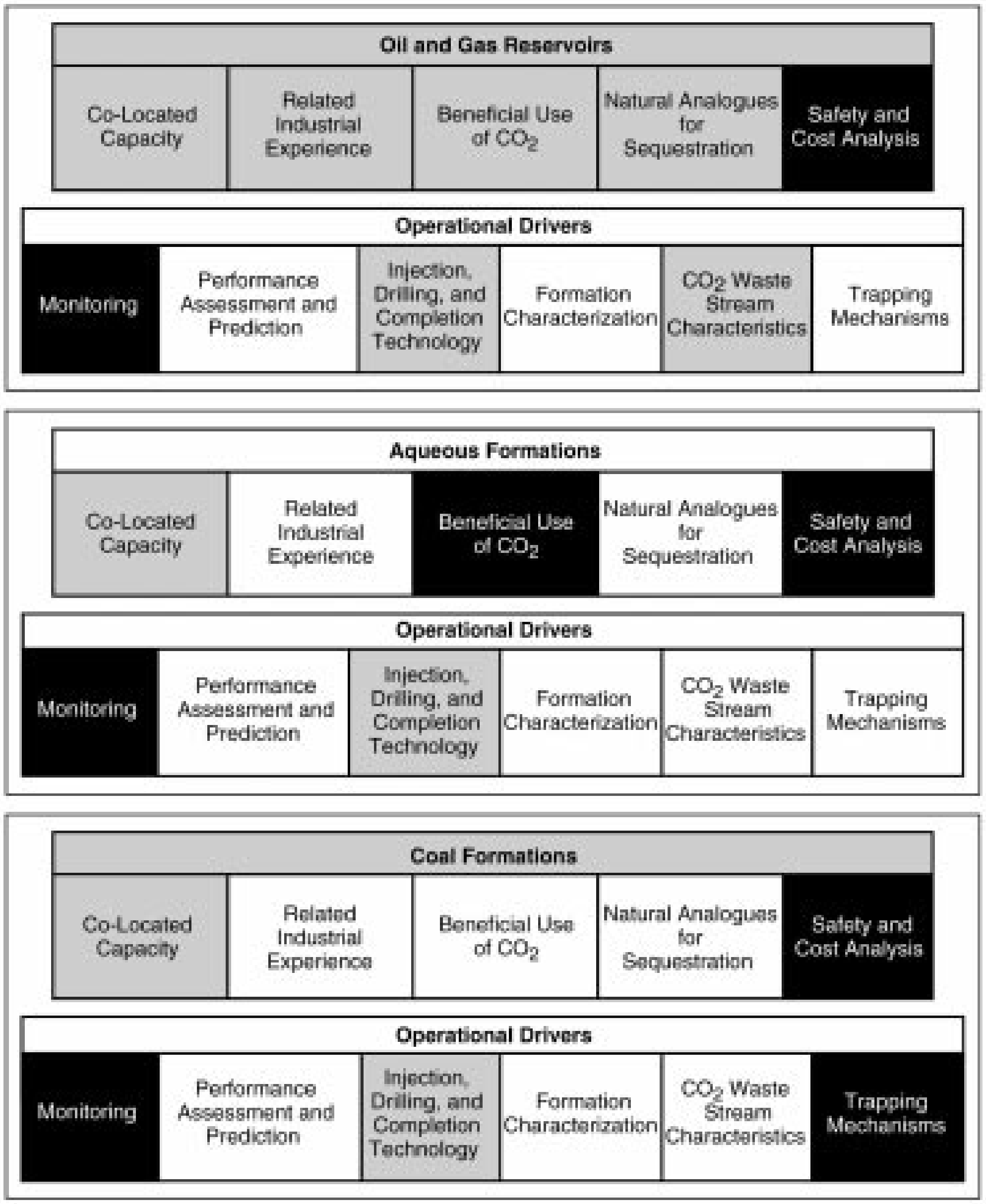


Fig. 5.5. Comparative evaluation of the technological and scientific maturity of operational requirements for sequestering CO_2 in geologic formations. Gray signifies that the technology and scientific understanding are mature and ready to go. White indicates that some experience base is available but more experience is needed to evaluate and improve sequestration options. Black signifies that key processes, parameters, technologies, and an understanding of fundamental processes must improve significantly to achieve our vision for geological sequestration.

hydraulic, geophysical imaging, and geostatistical techniques for characterizing the heterogeneity of sedimentary and fractured geological formations. These will be needed to predict the sweep efficiency in aqueous formations. Additional needs specific to sequestration include

- caprock characterization
- identification of leakage paths and rates

- evaluation of hydrologic isolation through the use of isotopic and other chemical analyses
- identification of mineral assemblages that influence mineral trapping and caprock integrity
- water encroachment in dewatered formations
- reservoir compartmentalization
- initial conditions and evolution of joints and fracture networks from stress and chemically induced deformation

5.3.4 Injection, Drilling, and Well Completion Technology

Injection, drilling, and completion technology for the oil and gas industry has evolved to a highly sophisticated state so that it is possible to drill and complete vertical, slanted, and horizontal wells in deep formations and wells with multiple completions, as well as to handle corrosive fluids. Optimization of these for CO_2 sequestration may require methods optimizing sequestration efficiency. Potential needs include

- methods of injecting additives for controlling the mobility of CO_2
- advanced well completion technology for enhancing sweep efficiency
- addition of chemical or biological additives for enhancing mineral trapping
- development and emplacement of in situ sensors for monitoring CO_2 migration
- injection technologies to limit CO_2 migration beyond “spill-points” and through leaks in the caprock

5.3.5 Performance Assessment

Multiphase, multicomponent computer simulators of subsurface fluid flow have been developed for oil and gas reservoirs, natural gas storage, groundwater resource management, and groundwater remediation. The accuracy of these simulators depends heavily on site- and project-specific calibration and improves by continual parameter adjustment over the project lifetime. Developing reliable tools for predicting, assessing, and optimizing CO_2 sequestration will require a similar level of experience under actual operating conditions. Additional needs specific to CO_2 sequestration include

- reactive chemical transport codes with precipitation-dissolution and adsorption-desorption kinetics and
- coupled H-C-M (hydrological-chemical-mechanical) models for long-term behavior and assessment of induced micro-seismicity.

5.3.6 Monitoring

Monitoring of CO_2 migration in the subsurface is needed for large-scale sequestration of CO_2. Tracking of the distribution of trapped CO_2 in the gaseous, dissolved, and solid phases is needed for performance confirmation, leak detection, and regulatory oversight. Existing monitoring methods include well testing and pressure monitoring; tracers and chemical sampling; and surface and borehole seismic, electromagnetic, and geomechanical methods such as tiltmeters. The spatial and temporal resolution of these methods is unlikely to be sufficient for performance confirmation and leak detection. Needs include

- high-resolution mapping techniques for tracking migration of sequestered CO_2 and its byproducts
- deformation and microseismicity monitoring

- remote sensing for CO_2 leaks and land surface deformation

5.3.7 Cross-Cutting Fundamental Research Needs

As the individual road maps for these geologic formations were developed, several cross-cutting fundamental research needs emerged. New and improved understanding of these issues will lead to safer and more cost-effective CO_2 sequestration. An expanded discussion of fundamental research needs can be found in Dove et al.

Multiphase transport in heterogeneous and deformable media: Gravity segregation, viscous fingering, and preferential flow along high-permeability pathways will play a dominant role in CO_2 migration in the subsurface. These difficulties will be compounded by deformation accompanying adsorption-desorption processes and precipitation-dissolution processes. A better fundamental understanding is needed to predict migration of CO_2 and to optimize sweep efficiency in geologic formations.

Phase behavior of CO_2/petroleum/water/solid systems: The partitioning of CO_2 between the aqueous, oil, gas, and solid phases is critical to understanding trapping mechanisms, as well as to predicting CO_2-enhanced oil recovery from petroleum formations and enhanced gas recovery from coal formations. Better understanding of the solid/fluid partitioning, particularly, is needed for optimizing enhanced gas recovery from coal-bed methane projects.

CO_2 dissolution and reaction kinetics: Although the principal reaction pathways between CO_2 and sedimentary formations are relatively well understood (e.g., reactions of feldspars with acid to form calcite, dolomite, siderite and clay; dissolution of carbonate minerals), the kinetics of CO_2 dissolution in the liquid phase and subsequent rock-water reactions are slow and poorly understood. If conversion of CO_2 to these stable mineral phases is to be an important component of sequestration in aqueous formations, understanding of the kinetics of these reactions and the processes controlling them is essential.

Micromechanics and deformation modeling: Production of oil and gas from geologic formations and subsequent sequestration of CO_2 into geologic formations will be accompanied by deformation of the reservoir formation. The influence of deformation on the hydraulic properties of the formation and integrity of the caprock must be better understood. In aqueous formations, unlike in oil and gas reservoirs where injection of CO_2 is accompanied by withdrawal of fluids, deformation is likely to be widespread as the pressure builds in the formation. The effects of deformation on the integrity of the caprock and its ability to induce seismic events must be better understood to ensure the long-term stability and safety of CO_2 sequestration.

Coupled H-M-C-T (hydrologic-mechanical-chemical-thermal) processes and modeling: Accurately predicting, assessing, optimizing, and confirming the performance of a sequestration project requires an accurate coupled model of all of the processes that influence repository performance and safety. While much experience in subsurface simulation has been gained from the oil and gas industry and from the groundwater management and remediation industries, other experience shows that the quality of our predictions depends strongly on having a simulator geared toward the specific application. Simulators tailored to the specific physical and chemical processes important for CO_2 sequestration must be developed, tested, calibrated, and refined through operational experience.

High-resolution geophysical imaging: High-resolution geophysical imaging offers the best potential for cost-effective monitoring of the migration and byproduct formation of CO_2 in subsurface environments. Three-dimensional and four-dimensional (time-lapse) images of geologic structures and pore fluids can be created with surface, surface-to-borehole, and cross-borehole techniques. The resolution needs to be improved if these methods are to be relied on to detect caprock leakage, formation of viscous fingers, and preferential pathways.

5.4 ADVANCED CONCEPTS FOR SEQUESTRATION IN GEOLOGIC FORMATIONS

The sequestration techniques described draw heavily from current approaches used by industry for production of oil, gas, and coal-bed methane and for storage of natural gas. Although these techniques provide reasonable near-term options for sequestration of CO_2, enhanced technology for CO_2 sequestration in geologic formations may significantly decrease costs, increase capacity, enhance safety, or increase the beneficial uses of CO_2 injection. Such enhanced technologies include the following:

- **Enhanced mineral trapping with catalysts or other chemical additives.** Conversion of CO_2 to stable carbonate minerals is expected to be very slow under the current scenarios envisioned for sequestration in geologic formations. Identification of chemical or biological additives that increase reaction rates could enhance the effectiveness of mineral trapping.

- **Sequestration in composite formations.** Multilayer formations, all with imperfect caprocks, may result in highly dispersed plumes of CO_2. The greater the degree of dispersion, the greater the opportunity for efficient solubility and mineral trapping. Developing design criteria that account for acceptable leakage across multilayer formations could increase the geographic distribution and capacity of geologic formations for sequestering CO_2.

- **Microbial conversion of CO_2 to methane.** Microorganisms that generate methane from CO_2 (methanogens) are known to exist in a wide variety of oxygen-depleted natural environments. If sequestration sites could be chosen to take advantage of this naturally occurring process, an underground “methane factory” could be created. Alternatively, additives that stimulate methanogenesis could be injected along with CO_2 to promote methane formation.

- **Rejuvenation of depleted oil reservoirs.** Injection of CO_2 into active oil reservoirs is a widely practiced EOR technique. However, even after the EOR process is no longer economically feasible, as much as 50% of the original oil in place may be left underground. CO_2 injection, followed by a quiescent period during which gravity drainage and gas cap formation redistribute the gas and liquid phases, may rejuvenate an oil formation that can no longer produce economically.

- **CO_2-enhanced production of methane hydrates:** Methane hydrates in ocean sediments and permafrost hold tremendous reserves of natural gas. Producing gas from these formations remains a challenge because of their complex structure, mechanical properties, and the thermodynamic behavior of hydrates. CO_2 injection into methane hydrate formations may enhance production while simultaneously sequestering CO_2.

5.5 OVERALL R&D PRIORITIES

Geologic sequestration is unique among the options for sequestration of CO_2 because of the extensive experience from related industries: oil and gas production, groundwater resource management, and groundwater remediation. Nevertheless, a number of critical needs must be addressed to make geologic formation a cost-competitive and safe option for sequestration of CO_2. These have been addressed in detail in the previous sections of the report. Figure 5.6 provides synthesis and a timeline for a key set of actions needed to accelerate development of a set of options for CO_2 sequestration in geologic formations. Short-term needs feed into longer term projects. Together these will provide a

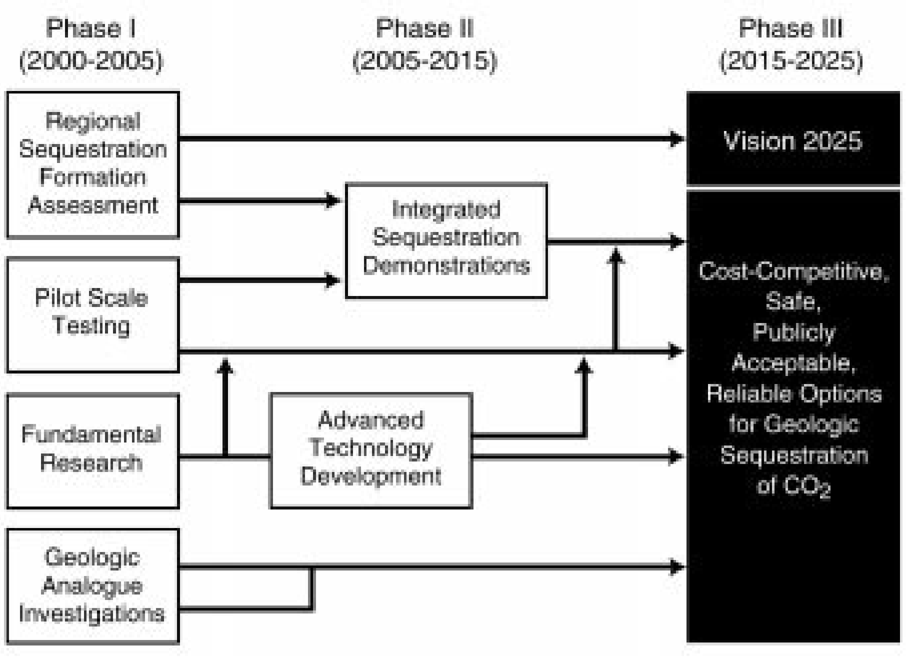


Fig. 5.6. Key elements of the R&D road map for sequestration of CO_2 in geologic formations.

realistic assessment and cost and performance data for large-scale sequestration of CO_2 in geologic formations. The paragraphs below elaborate on these key actions.

1. There must be a reliable assessment of geologic formations available for sequestration of CO_2 from each of the major power-generating regions of the United States. Screening criteria for choosing suitable options must be developed in partnership with industry, the scientific community, the public, and regulatory oversight agencies.
2. Pilot tests of geologic sequestration conducted early would help develop cost and performance data and help prioritize future R&D needs. These pilot tests should be designed and conducted with sufficient monitoring, modeling, and performance assessment to enable quantitative evaluation of the processes responsible for geologic sequestration.
3. Geologic analogues, such as CO_2 reservoirs and CO_2-rich aquifers, should be studied to determine the factors leading to caprock integrity and mineral-trapping mechanisms.
4. Fundamental research is needed to aid understanding of critical processes and parameters that will contribute to safe and effective CO_2 sequestration.
5. Advanced technologies are needed for (1) increasing the volume of the geologic formation filled by CO_2, (2) creating stable long-term sinks (stable mineral assemblages), (3) increasing solubility and perhaps diluting CO_2 to acceptable levels, and (4) tracking migration of CO_2 in the subsurface.
6. Full-scale demonstration projects, performed in partnership with industry, that integrate CO_2 separation and transportation with geologic sequestration are needed to provide cost, safety, and performance data on geologic sequestration of CO_2.

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6 ADVANCED BIOLOGICAL PROCESSES

Vision

Advanced biological processes will be developed and deployed to enable practices to sequester carbon in natural systems, remove or convert carbon from fossil energy systems into useful and refractory products, and recycle carbon through biological processes into end products that substitute for fossil carbon sources.

6.1 BACKGROUND AND RATIONALE FOR ADVANCED BIOLOGICAL PROCESSES TO SEQUESTER CARBON

By 2025, the goal is to implement advanced biological processes that would help limit emissions and sequester carbon from concentrated utility and industrial combustion gases and dispersed point sources. Advanced biological technologies will augment or improve natural biological processes for carbon sequestration from the atmosphere in terrestrial plants, aquatic photosynthetic species, and soil and other microbial communities. These technologies encompass the use of novel organisms, designed biological systems, and genetic improvements in metabolic networks in terrestrial and marine microbial, plant, and animal species. This strategy can be accomplished by developing

- faster-growing, healthier, and more stress-resistant crop and plants
- a better understanding of biological diversity, genetics, and processes
- ways to enhance or maximize geological carbon sequestration by use of microorganisms
- ways to enhance carbon sequestration in ocean systems through transgenic and genetic manipulation of members of the food chain
- alternative microbial polymers or genetically improved plants as durable materials

Enhanced biological carbon fixation significantly increases carbon sequestration without incurring costs for separation, capture, and compression. Higher ambient CO_2 concentrations increase biological carbon fixation. But the resulting biomass generally has a higher carbohydrate and lower lignin content. Thus increased photosynthate is trapped into readily degraded material.

Photosynthesis is a well-understood process. It is responsible for virtually all CO_2 fixation in nature. Naturally occurring non-photosynthetic microbial processes are also capable of converting CO_2 to useful forms such as methane and acetate. Although much remains to be learned about natural processes, we predict that focused research will create new opportunities to significantly enhance carbon sequestration by advanced biological processes.

Genetic engineering could increase carbon sequestration by developing durable new products that would not be consumed with release of CO_2. In addition, soil sequestration could be increased by altering the structure of plants to enhance carbon sequestration in soils. New plant species would have a higher percentage of biomass below ground, be resistant to decay, promote the formation of carbonate minerals, and interact with soil microbes to optimize the recycling of plant nutrients. Alternately, the structure and/or composition of aboveground plant structure biomass, including cell walls, could be altered to facilitate plant bioconversion processes and to render non-harvested biomass less degradable in the environment. The metabolic networks of plants and algae also could be altered to direct an increased share of photosynthate to desired products.

The four topic areas that comprise advanced biological technologies for carbon sequestration are carbon capture technology, sequestration in reduced carbon compounds, increasing plant productivity, and alternative durable materials. These have cross-disciplinary applications in terrestrial, geological subsurface, and ocean environments.

6.2 CARBON CAPTURE TECHNOLOGY SUPPORT

6.2.1 Current Science and Technology Capabilities

The prospects of using advanced biological processes to capture and reduce or sequester carbon from industrial processes are largely theoretical. However, the incentives for developing these processes are substantial because they are based on naturally occurring biological processes that do not require purified (or concentrated) CO_2 streams to be implemented effectively. Additional research will be required to determine the technical and economic feasibility of these approaches for terrestrial, geological, and ocean systems. Advanced biological processes have the potential to lower energy expenditures, reduce the need for chemical processing, increase recycling of carbon, and reduce the use of fossil fuels.

Sewage plants today are being affected by changes in community dynamics due to generation of new types of wastes from biotechnology facilities and “chip technology.” Engineers are just now beginning to work more closely with microbial ecologists, physiologists, and molecular biologists to better monitor the changes in the microbial diversity and metabolism that are requiring new paradigms for more effectively treating wastewater.

Subsurface microbiology and geomicrobiology researchers have seen an increase in funding for the characterization and monitoring of “rock”-inhabiting microorganisms. Through the use of molecular probes, polymerase chain reaction amplification, and even synchrotron technology, scientists are beginning to understand how these populations function in a world where there may be limited sources of carbon for energy. Through these studies, researchers have genetically identified and, in some cases, isolated new microorganisms that depend upon non-carbon sources of energy. These studies are laying the foundation for studies of microbial carbon sequestration and alternative energy sources.

6.2.2 Science and Technology Requirements

6.2.2.1 Energyplexes

Because of the high energy costs associated with current technologies for capture and separation at combustion sources with low-concentration CO_2 streams, the joint consideration of energy production and carbon capture might significantly lower costs. This may best be achieved by expanding the concept of "energyplexes" with integration of biological processes (National Laboratory Directors 1997). Biological processes integrated into energyplexes would produce energy, treat waste, sequester carbon, and produce useful end products. The integration at one site would minimize transportation costs, minimize the potential for environmental damage, and maximize yields. These concepts need further development, but some aspects, which include biological components, have been put into place on a limited scale

Waste treatment associated with landfills, sewage treatment facilities, or even release of sewage into water bodies produces significant CO_2 and other greenhouse gases (especially methane) from fixed carbon. This carbon represents a potential source of renewable energy. Molecular biology methods could be employed to slow the decomposition rates of solid wastes in landfills. In addition, the bioengineering technology to trap, separate, and recycle CO_2 and methane decomposition products at landfills and sewage treatment facilities needs to be improved.

Sewage treatment is designed to sanitize wastes and to reduce the carbon burden before discharge. Thus an implicit goal of sewage treatment is the production of CO_2. Most CO_2 is produced by the aerobic treatment stage. A shift to complete anaerobic fermentation could lower emissions. A modification of sewage treatment in this manner, via integration of physiological and genetic regulation, could generate more methane to meet the fuel demand of plant operation and could generate a higher-carbon end product for use in soil building and agriculture. Knowledge about physiological processes and end products must be expanded to design these plants.

Reductions in CO_2 emission could derive from more efficient operation of sewage treatment plants and landfills and integration of managed wetlands into waste treatment processes. Basic understanding of these biological processes must be expanded to allow more effective implementation of these options. Consideration should be given to the integration of these facilities into energyplexes to provide carbon and nutrients for other biological processes (e.g., production of carbonate rocks by metal-reducing organisms, production of biomass by algae).

6.2.2.2 Geological systems

Biological conversion of CO_2 into insoluble carbonate rocks, such as siderite ($FeCO_3$)—using metal-reducing bacteria and metal-containing fly ash or other low-value products—is technically feasible. If iron is abundant and available as a bioreductant, siderite can be formed. These materials could be used in roadbeds, as composite materials, or as fill. In any case, solid carbonate rock significantly simplifies storage and disposal of CO_2 by enormously increasing the density of the material to be handled. Either metal-reducing organisms or algae could be applied to precipitate carbonate rocks. Metals could be reduced by bacteria and precipitated as carbonates. Recent research on metal-reducing thermophilic bacteria has demonstrated that siderite production by these bacteria can be substantial.

6.2.3 Research Implementation

6.2.3.1 Energyplexes

The energyplex concept involves recycling CO_2 in waste flue gases from a power generation facility via photosynthesis to generate a store of reduced carbon in the form of algal biomass. Storage can take the form of polysaccharides or triglycerides, both of which are readily usable fuels, or of chemical feedstocks for downstream bioconversion processes. Although additional concepts will undoubtedly be developed and should be sought, initial efforts are likely to focus on several research areas, including integration of primary production using waste CO_2 and heat. These energyplexes could benefit from integration of sewage or other waste treatment because the nutrients and carbon could be used in biological processes at the site. Because of seasonal, land, and water limitations, this alternative may be applicable only in certain localities or specialized situations.

Energyplexes for Conventional Crops

An additional potential option is to use the CO_2 and the waste heat to promote the growth of more conventional agricultural crops. Use of CO_2 can lead to increases in productivity of plant growth in hydroponics or wetlands applications. Pilot projects are under way to capitalize on this concept.

One area that has been the focus of considerable research in the past is growth of algae for fuel production. Previous research focused on diesel replacements (“biodiesel”). In addition, the production of hydrogen and other chemical feedstocks using algae is worth additional investment in research. Some algae can be cultivated in saline or alkaline waters, which are available in the southwestern deserts, where land is relatively plentiful. This alternative might be limited by the costs of pond preparation, CO_2 injection, or algal harvest.

6.2.3.2 Geological systems

Microbial processes can probably be engineered to greatly accelerate the formation of carbonates from natural silicate minerals such as serpentinite (see Chap. 7). While it is known that the release of magnesium ions from crushed serpentinite is greatly enhanced in the presence of nitrifying bacteria (Lebedeva, Lyalikova, and Bugel’skii 1978), genetic manipulations, use of other chemotrophic organisms, and exploitation of microbial acid formation can be expected to further accelerate the decomposition of silicate minerals.

Knowledge about the factors that inhibit plant growth in serpentine soils (serpentine barrens, where little vegetation is found) can be used to design microorganisms that tolerate high magnesium concentrations and low calcium/magnesium ratios and resist heavy metal toxicity. Genetic engineering has the potential as well to endow these organisms with the capacity to use metal sulfide minerals as energy sources and CO_2 as the carbon source for growth. Carbon dioxide would be sequestered as magnesium carbonate and as microbial biomass.

Additional advanced concepts include the utilization of enzyme systems and catalysts for CO_2 capture. The goals of the research would be to achieve shorter residence times and higher throughput. A more innovative approach may be to develop biological catalysts for removal of CO_2. These may include "artificial photosynthesis" (microbial or self-assembly) applications with molecular devices that mimic photosynthesis. As some of the solvent-based CO_2 absorbents currently in use are organic compounds, biological production of solvents for CO_2 scrubbing is feasible.

6.3 SEQUESTRATION IN REDUCED CARBON COMPOUNDS

6.3.1 Current Science and Technology Capabilities

The feasibility of a significant midterm impact on global climate change by increasing the size of forests is firmly established. Algal biomass schemes for trapping CO_2 have advanced in recent years and should be explored as a possible supplement to forest management and advanced agricultural biotechnologies.

The surface area of the planet is dominated by oceans (75%), where bioproductivity is often limited by nutrient availability. As discussed in Chap. 3, nutritional enrichment could enhance ocean algal growth and marine productivity and might increase net oceanic CO_2 fixation. Advanced biological techniques could be used to increase phytoplankton productivity or to alter the competitive capacities of organisms that feed on algae. Marine algal production is not limited by water availability and affords greater opportunities to control nutrient delivery.

Algae are amenable to relatively simple genetic manipulations aimed at increasing photosynthetic efficiency, maximizing yields of desirable energy storage products, and optimizing conversion of photosynthetic products to fuels or chemical feedstocks. Such strategies could also be applied to terrestrial plant species.

6.3.2 Science and Technology Requirements

The goal is to have a mix of biological systems that will provide incremental but significant contributions to overall carbon management.

Research on using algae in pond systems for renewable energy is likely to have spin-offs for open-ocean carbon management schemes and could eventually lead to ocean harvesting–based renewable energy technologies. Recovery of other products from fermented algal biomass—for example, fertilizers for terrestrial crops or for open-ocean fertilization, or single-cell protein for animal nutrition—would improve overall economics.

Plant and microbial genomics projects currently under way will eventually provide detailed knowledge about organismal metabolic networks and interrelationships among different cells in a plant and different organisms in an ecosystem. Such knowledge will enable a better understanding of ecosystems and how to manage their productivities. We need more information about

- the function of genes being sequenced and computerized methods to manipulate and store the huge quantities of data pouring forth from genomics efforts
- how to introduce individual genes and pathways into a wide variety of plants and microbes
- gene replacement strategies for plant species
- artificial chromosomes for the introduction of large segments of genetic material into plants
- more rapid and reliable methods for screening candidate genetically engineered plants and for clonal propagation of engineered plants

6.3.3 Research Implementation

Most renewable energy schemes generate considerable recalcitrant biomass and therefore offer the opportunity for significant net carbon fixation in addition to their value in reducing the demand for fossil energy. Compared with the difficulties of CO_2 sequestration by separation, compression, and transport, the handling and storage of recalcitrant biomass is straightforward.

6.3.3.1 Sequestration of biological carbon in ocean sediments

Chapter 3 discusses enhancing the natural biological carbon cycle in the oceans. Research topics in advanced biology regarding this carbon mitigation option include the following:

- To what extent can biomass concentration and disposition be genetically manipulated?
- Are there feasible genetic manipulations of biomass that would alter the decreasing rate of biomass production in the open ocean?
- Can we develop an organism that will rapidly and costeffectively assess the ecological impacts of various nutrient stimulation scenarios?
- Can organisms be engineered so that deposition of biological carbon outweighs the adverse pH effects of carbonate deposition?
- Are there advanced biological approaches to increasing phytoplankton accumulation specifically in upwelling, nutrient-rich waters?
- Can genetic biomarkers be developed to monitor and assess the ultimate fate of biomass in deep ocean sediments? (In particular, we need a better understanding of the conversion of biomass to methane clathrates.)

An intriguing aspect of accumulating biomass in ocean sediments is the potential that this process could become an energy resource in the long-term. It is plausible that future energy scenarios would include methane recovery from clathrates located in well-defined deposits.

6.3.3.2 Alkaline ponds for carbon sequestration

The capacity of some blue-green algae to thrive essentially as monocultures in waters of high alkalinity creates the possibility of much more effective CO_2

sequestration than would be possible with other photosynthetic systems. The chemical hydration rate of CO_2 increases with pH, as does the amount of inorganic carbon that can be dissolved in aqueous solution. Alkaline ponds have the potential to trap virtually all of the smokestack CO_2 emissions as well as the major pollutant gases SO_2 and NO_x. Accumulation of biomass can be optimized by pH manipulations that suppress the biomass-consuming activities of respiring organisms. With appropriate mass culturing of suitable blue-green algae, photosynthetic activity can maintain alkaline pH while providing a renewable energy resource. The feasibility of mass culturing of microalgae in alkaline seawater has been established, demonstrating the potential for developing much larger mass culture systems than could be contemplated with freshwater ponds.

6.3.3.3 Schemes for producing refractory biomass from terrestrial plants

Two possibilities for fixing CO_2 into materials with recycle times much longer than wood can be considered: polymeric materials that are relatively refractory to biological degradation and inorganics (carbonates).

A large number of plant species synthesize diterpenoid resins or natural rubber, two materials that are relatively stable in the environment. Although few of these species are of economic significance, they are widespread and adaptable to a range of climates, could be grown on a large scale, and could be engineered for improved efficiency for conversion of CO_2 to product. These end products of plant metabolism could be deposited as such or cross-linked to minimize the possibility of biological degradation (e.g., vulcanized rubber).

The development of new materials (e.g., novel biomass-derived plastics), that would increase the use of reduced carbon compounds in the economy could be a significant element in carbon management. Another approach could be directed toward eliminating the irreversible conversion of petroleum to CO_2 by substituting “recyclable” plant products for fine and intermediate-scale chemicals and

Aquaculture in the Desert

In 1987, during Eritea’s war of independence from Ethiopia, simple ponds were dug along the shore to a depth of about 0.5 m below the low tide line and about 200 m^2 in area. The ponds were filled with sea water and chemical fertilizers to grow algae and inoculated with mullet fingerlings at a rate of one fingerling per square meter. After 4 months, each fish weighed about 1 lb. Less than 1% mortality was detected among these algae-eating fish, which are famous for their hardiness in resisting disease and coping with low oxygen concentrations. This is equivalent to a rate of production of about 15 tons/ha per year and demonstrated that desert shores could produce enough food to justify cultivation on a large scale. This was not surprising. In southeast Asia, freshwater ponds have been fertilized to grow algae and inoculated with algae-eating fishes for centuries. Their only variation on this time-proven practice was to substitute seawater for fresh water and marine fish and algae for freshwater fish and algae. (www.ibt.tamu.edu/invitro/guested.htmhttp) even transport fuels. These could include the plant essential oils, fixed oils, resins, and even heptane, which is a major component of turpentine and an excellent transport fuel. Genetic engineering of plants to improve the availability of these products is entirely feasible.

Lignin is relatively resistant to biodegradation, and increasing the lignin content of plants would slow the decay of biomass in soils. Plant geneticists have discovered mutations that decrease the lignin content of plants to increase nutritional value for ruminants. Moreover, as the biochemical pathways for lignin biosynthesis in plants became elucidated, the genes encoding lignin pathway enzymes were cloned and have recently been employed to alter the quantity and quality of lignin in poplar and aspen tree species. The technology of lignin manipulation could be applied to plants that are currently being considered for reforestation with the objective of increasing net carbon transfer.

It has been estimated that only 3% of the carbon in solid wood in landfills is converted to CO_2 or methane (Skog and Nicholson 1998). This limited decomposition of wood is attributed to the recalcitrance of lignin in anaerobic environments. Although anaerobic bacteria can degrade cellulose, much of the cellulose in solid wood is sequestered from bacterial action by a lignin barrier and therefore cannot be biodegraded. Even paper products undergo only partial decomposition in landfills. Currently, most of the wood and wood products in landfills is sequestered carbon. However, alterations in the structure of wood by decreasing lignin content could increase its biodegradability. It is likely that significant lignin would remain even in genetically modified woody plants and that landfills containing such plants would still sequester carbon. However, increasing biodegradability could increase methane yields from landfills, and the energy value of buried wood and wood products could provide an economic incentive for using woody materials for carbon sequestration. In contrast to reforestation or high-productivity agricultural schemes, there is an unlimited amount of carbon that could be sequestered in landfills.

6.4 INCREASING PLANT PRODUCTIVITY

Research would improve the ability to genetically manipulate plants to increase phototosynthetic activity and fix CO_2 and nitrogen more efficiently. Manipulation of plant genomes to obtain the desired effects is still a poorly developed field. Much more attention needs to be given to the fundamental mechanisms of cell development, cell wall biochemistry, plant photosynthetic processes, and primary and secondary metabolic processes.

More rapidly growing herbaceous agricultural plant species will enhance the removal of CO_2 from the atmosphere and trap it in photosynthate that can be readily converted into renewable fuels, chemicals, polymer precursors and foodstuffs. Rapidly growing woody species will trap CO_2 in durable timber that can be used for a wide variety of structures. Other fast-growing herbaceous and woody species will provide easily delignified fiber for paper, composites, and block copolymers.

6.4.1 Current Science and Technology Capabilities

The advent of modern molecular biology has enabled strategies for improvement of many different organisms through genetic engineering, including many agricultural and timber crop species. Our current understanding of the processes of photosynthesis, photorespiration, plant pathology, and wood structure and function, among others, suggests many strategies for increasing the rate of biological carbon sequestration. The 25-year time frame of the proposed R&D program would permit advances in several of these areas to be successfully deployed on a large commercial scale, which could have a significant impact on U.S. carbon emissions.

Plants get their carbon from CO_2, which makes up only 0.03% of the present-day atmosphere. Microscopic floating plants, phytoplankton, and other algae take up CO_2 dissolved in water. Both terrestrial and water plants require solar energy to reduce CO_2 to biomass. Photosynthesis is responsible for conversion of sunlight into chemical energy by essentially all primary producers in nearly all ecosystems. It provides the foundation of the food chain for life on Earth and is also the source of the oxygen in our atmosphere.

Sunlight provides the energy for the primary mechanism of carbon fixation from the atmosphere. The theoretical maximum efficiency of light energy capture and conversion into usable chemical energy is approximately 5% (expressed as a fraction of visible light energy available at the earth's surface). Plant photosystems seldom operate at anywhere near this efficiency, a fact that provides us with an excellent opportunity for carbon sequestration. Photosynthetic efficiency varies widely with the ecosystem and time of year. The efficiency of some forests can be as low as 0.1 to 0.05%, while that of marsh grasses can be as high as 2 to 4% in the early spring. The photosynthetic efficiency of corn and sugar cane can be as high as 3.5 to 4%.

Engineering Rubisco for Speed

Plants fix carbon by taking CO_2 from the air and adding it to small precursor sugars in plants. This step is carried out by an enzyme known as Rubisco. Rubisco is the most abundant protein in the world, making up 50% of all plant proteins. The Rubisco enzyme is slow and inefficient. It not only fixes carbon but, in an alternate reaction, adds oxygen to the precursor sugars and degrades them, diverting the enzyme from productive activity. It may be possible to engineer into Rubisco more efficient carbon-fixation mechanisms or to discover more efficient, naturally occurring forms of Rubisco in as yet poorly characterized or undiscovered organisms.

The activity of Rubisco is regulated by another enzyme called Rubisco activase. Rubisco activase controls the overall process of photosynthesis by making Rubisco activity responsive to light intensity. Researchers are currently changing a specific part of the Rubisco activase enzyme by genetic engineering to analyze its function. Information about the mechanism and structure of Rubisco activase eventually can be used to make changes that improve the activity of the enzyme and increase photosynthetic efficiency. (www.photoscience.la.asu.edu/Photosyn/faculty/salvucci.html)

Environmental conditions strongly affect photosynthetic efficiency, but the biochemistry of the photon capture and energy conversion system could be improved as well.

Photosynthetic carbon fixation is limited by the efficiency of two very important processes—conversion of incident light energy to captured chemical energy and the primary carbon fixation reaction catalyzed by the enzyme Rubisco (ribulose-1,5-bisphosphate carboxylase/oxygenase), the most abundant protein on Earth. Either or both of these processes may be limiting in terms of carbon sequestration rates, and it is thought that they could be enhanced significantly via advanced biological approaches.

Rubisco is not only a very slow enzyme, but is also inefficient because it can react with molecular oxygen in a process known as photorespiration. This results in a futile (nonproductive) metabolic cycle. As the ratio of CO_2 to O_2 in the atmosphere increases, the productive carboxylation efficiency will naturally increase. However, it may also be possible to discover more efficient, naturally occurring forms of Rubisco in as yet poorly characterized or undiscovered organisms, or to engineer into Rubisco an exaggerated preference for CO_2 over O_2 using modern molecular biological techniques (Mann 1999).

Some plant species have already developed a solution to the problem presented by Rubisco. A group of warm-climate grass species known as C_4 grasses (including corn, sorghum, and sugar cane) evolved a specialized leaf anatomy (Krantz anatomy; contrast C_3 and C_4 anatomy in Figs. 6.1 and 6.2, respectively). These plants show little or no photorespiration and are considerably more efficient because

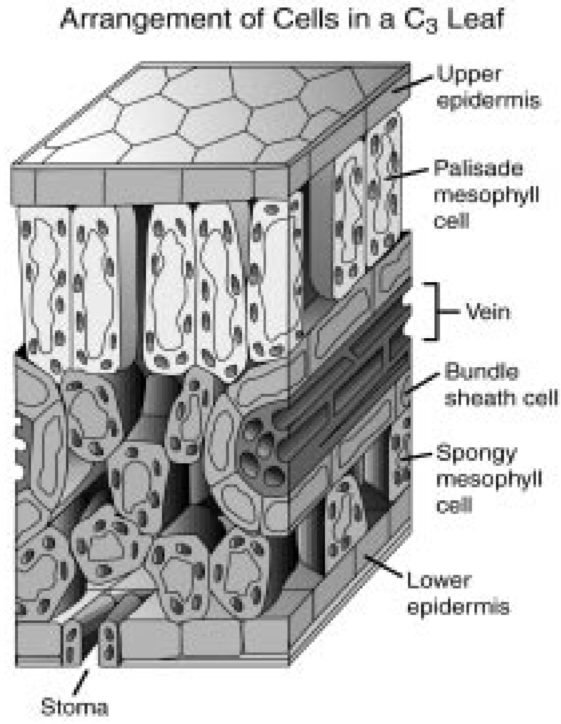

Fig. 6.1: Typical leaf anatomy in a C3 plant. (www.biology.arizona.edu/181/rick/photosynthesis/C4.html)

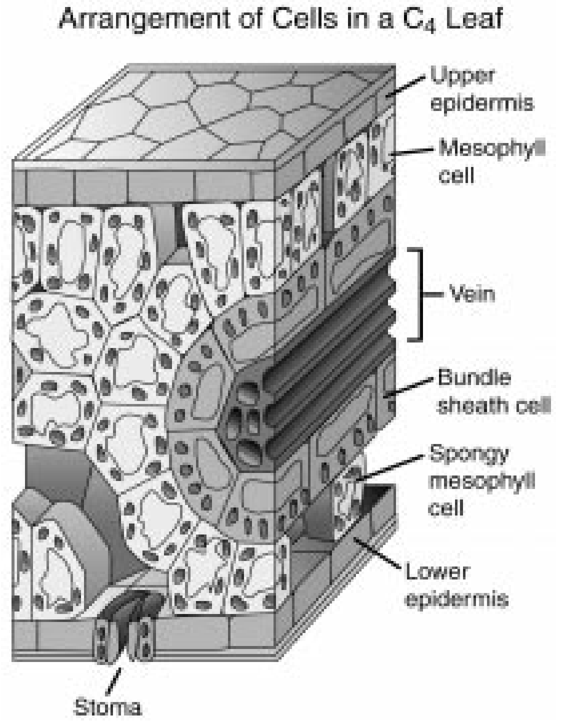

Fig. 6.2: Typical leaf anatomy in a C4 plant. (www.cme.msu.edu/WIT/Doc/mj_recon.html)

CO_2 is carried to sites of photosynthesis. This trapping of CO_2 is carried out via the Hatch-Slack pathway (Fig. 6.3), which is not affected by oxygen. Genetic manipulation, to optimize pathways for trapping CO_2, comprises significant research opportunities.

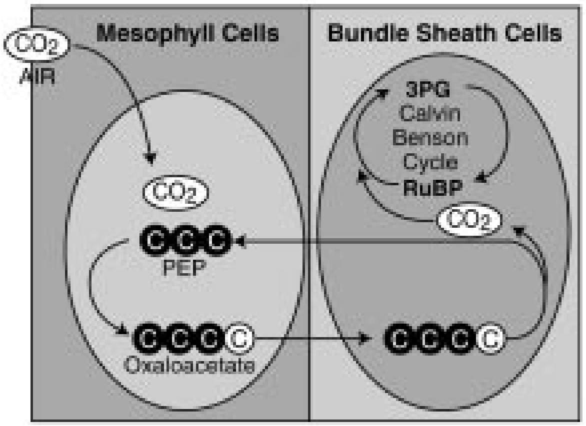

Fig. 6.3: Carbon fixation as it occurs via the Hatch-Slack pathway in C4 plants. (www.biology.arizona.edu/181/rick/photosynthesis/C4.html)

Although 78% of our atmosphere consists of nitrogen, plants are not capable of converting it into forms they can use. Certain bacteria, however, produce enzymes that facilitate the transformation of nitrogen gas into ammonia and other nitrogen-containing compounds that can readily be absorbed by plant roots and used by the plant. In nature, the natural decay of dead biomass releases nitrogen in forms that can often be absorbed by plants. This occurs both in terrestrial systems and in the oceans. Nitrogen availability is often growth-limiting and is routinely supplemented with fertilizers in agricultural practice. Some plant species, notably the legumes, do not require nitrogen fertilization because their roots are colonized by nitrogen-fixing microorganisms. Ammonia can be readily assimilated by plants and incorporated into other nitrogen-containing compounds, such as amino acids, which are essential for protein synthesis. The critical enzyme in nitrogen fixation is called nitrogenase, and it breaks the very strong triple bond of N_2. These complex and poorly understood enzymes require large amounts of energy to accomplish this reaction. In addition, nitrogenases contain an assortment of complex, iron-containing co-factors, which are essential for activity. Thus, iron is often rate-limiting for nitrogen fixation in the ocean.

When photosynthetic light capture, CO_2 fixation, and nitrogen availability no longer limit plant metabolism, one can improve regulation of and/or redesign secondary metabolic pathways for conversion and sequestration of the primary products. It is thus very important to understand both the spatial and temporal linkages among metabolic pathways in an organism, as well as modes of long-term storage of the sequestered products. Elucidation of these linkages and carbon storage capabilities will be best addressed by structural biology, plant and microbial molecular genetics, and computational simulation and theory.

Other environmental factors affecting carbon sequestration are predation by insects and microbial pathogens, which decrease global crop and forest yields. In addition, other stresses, such as drought, saline soils, heat and cold, pH, and the presence of heavy metals and other pollutants, limit plant growth rates and biomass accumulation. Ameliorating such stresses has been a target for improvement by agriculture and silviculture over the centuries. Modern plant science has mitigated crop losses, but there is still plenty of room for improvement, as evidenced by the prolific activity and investment in plant biotechnology.

It is advantageous to increase deposition of carbon in soils. This might be accomplished most effectively by increasing the transfer of photosynthate to root systems and by increasing the accumulation of recalcitrant bioproducts (such as lignin) in forest litter. Deposition of carbon in soil by agricultural and silvicultural systems might be increased by shifting photosynthate partitioning from aboveground to belowground organs via genetic means. Increasing the recalcitrance of root tissues should also be explored as a possibility. Root deposition might be particularly important in the restoration of degraded soils or cultivation of plants in marginal ecosystems.

Nitrogen fixation could also increase root deposition and stimulate root exudates. Soil microbes play an important but incompletely understood role in enabling nutrient uptake by plants. Microbes associated with plant roots are an essential component of biological nitrogen fixation. Carbohydrates and other nutrients secreted by plant roots foster microbial growth, and the associated bacteria and fungi mobilize minerals (such as phosphate) and fix nitrogen for plant use. By increasing secretion of photosynthate by roots, it might be possible to increase biological nitrogen fixation and the cultivation of crops in marginal lands. For example, specific plant-associated fungi are essential for the cultivation of softwood species on topsoil-deficient lands reclaimed from open pit mining. It seems likely that similar relationships might be important in other degraded environments.

Several significant non-photosynthetic CO_2 fixation reactions occur in nature (University of Chicago 1998). As much as 10% of the cellulose and hemicellulose in plant biomass might be converted in the anaerobic environment to methane and CO_2 by consortia of anaerobic bacteria. Acetogenic bacteria appear to play a major role in this process. At the global level, approximately 10 GT of acetate is metabolized annually in the anaerobic environment, and about 10% of this may be derived from CO_2 fixation via the acetyl-CoA pathway. Potentially important niches for acetogens include termites, monogastric and ruminant animal digestive systems, and forest soils.

If a source of hydrogen can be provided in a CO_2-rich, O_2-free environment, CO_2 can be fixed efficiently into nonvolatile carbon compounds. Interestingly, it has recently been discovered that the strictly chemical action of water on basaltic rock formations deep below the surface of the earth serves as a source of hydrogen for microbial ecosystems (Gollin et al. 1998). These reactions may be important for biosequestration in geologic formations, such as spent oil and gas wells.

The advent of genetic engineering has improved crop productivity by increasing disease resistance and improving the ability of engineered crops to compete with undesired plant species. Plant products, especially oilseed crops, have been altered to increase the production of marketable oils, and these engineered varieties are being grown commercially. Additional engineering could increase oil production or other desirable products. Several genetically engineered crop species are currently being grown in the United States and other countries and are rapidly capturing market share. For example, 40% of the Canola crops in Canada and 33% of the soybean crops in the United States are genetically engineered.

Research is under way to examine plant-insect interactions. The research usually focuses on combating a specific insect pest by producing transgenic plants (plants with genes from other species) that synthesize compounds that inhibit insect metabolism. Producing a disease-resistant transgenic plant requires that the molecular mechanisms involved in host plant resistance be elucidated. Unfortunately, these mechanisms vary greatly among plant pathogens.

Advances in gene technology have offered various novel routes to improve the disease resistance of crops. Resistance to a number of insect species has been created by use of genes encoding protease inhibitors and the *d*-endotoxin of *Bacillus thuringiensis*. Resistance against a number of viruses was obtained by expressing genes encoding for the viral coat protein, applying the principle of cross-protection.

6.4.2 Science and Technology Requirements

In order to realize the maximum benefit from biological fixation, we need more basic knowledge about what processes limit plant growth in many specialized crops for food, feed, fiber, fuel and structural uses. We also need more information about optimal cultivation and harvest methods, particularly in marginal environments where water or soil quality is limiting. Other growth-limiting factors such as disease and insect pests also require better understanding. Biotechnology and plant genomics will play large roles in reaching these goals.

6.4.3 Research Implementation

Plant productivity can be increased by

- improving photosynthetic efficiency by increasing light-trapping reaction efficiency and decreasing photorespiration (C4 pathway; engineering Rubisco efficiency and reaction rate)
- developing rapid methods for genetic manipulation of agricultural, tree, and nontraditional species with CO_2 sequestering potential (transformation and regeneration systems)
- developing new tools for manipulating fast-growing herbaceous and woody species (artificial chromosomes; gene replacement techniques)
- reducing the time required to create transgenic plants in the laboratory
- enhancing non-photosynthetic mechanisms for CO_2 fixation (bacterial methanogenesis and acetogenesis)
- genetically engineering the cell walls of agricultural species so that they can be more easily and economically converted to fuels and chemicals
- developing crops or processes that will biosynthesize functional feedstock chemicals for the synthesis of recalcitrant products (e.g., non-biodegradable plastics)
- improving nitrogen fixation in microbial symbionts of plants and/or by cloning genes into plants
- developing simplified nitrogenases that bypass the current mechanistic complexity, iron-dependence and energy intensity issues

- improving insect and disease resistance via transgenics and protein engineering

6.5 ALTERNATIVE DURABLE MATERIALS

6.5.1 Current Science and Technology Capabilities

6.5.1.1 Biopolymers

The past several years have seen dramatic growth in the use of enzymes for synthetic applications. This has been particularly apparent in the increased use of enzymes for polymer design and modification. Enzymes offer significant advantages over chemical catalysts in the synthesis of materials with highly specialized properties—including biodegradability, biocompatibility, inherent selectivity (e.g., enantio-, regio-, and chemo-), and easily tailored functionalities—all produced under conditions that minimize the formation of by-products and the avoidance of unwanted pollutants (Dorkick 1998).

The development of carbon feedstocks for chemical applications will reduce CO_2 emissions by displacing fossil hydrocarbons. Primary examples are the use of polymers derived from renewable agricultural resources, such as corn or sugar beets. These compounds are also commonly known as “bioplastics.” For many applications, the plastic “peanuts” used as packing material have been replaced by bioplastics. These bioplastics are displacing petrochemical-based polymers, such as polyethylene, polystyrene, and polypropylene. One class of bioplastics, the PLA resins, are composed of chains of lactic acid derived from conversion of starch to sugar followed by fermentation to lactic acid. Dow Chemical and Cargill have recently formed a joint venture to commercialize PLA on a large scale. Polyhydroxyalkanoates (PHAs), a chemically distinct family of biodegradable bioplastics, are being investigated by Monsanto and Proctor & Gamble for use as petro-plastic substitutes. Monsanto is looking at producing PHAs in crop plants instead of fermentation vats.

Turning Sugar into Better Polymers

The polymer polytrimethylene terephthalate (3GT) has enhanced properties compared with traditional polyester (2GT). Yet commercialization has been slow because of the high cost of making trimethylene glycol (3G), one of 3GT’s monomers; it is a two-step process. However, recently, through recombinant DNA technology, an alliance of scientists from DuPont and Genencor International has created a single microorganism with all of the enzymes required to turn sugar into 3G. This breakthrough is opening the door to low-cost, environmentally sound, large-scale production of 3G. The eventual cost of 3G produced by this process is expected to approach that of ethylene glycol (2G).

The 3GT that is created by a fermentation process requires no heavy metals, petroleum, or toxic chemicals. The primary material comes from agriculture—glucose from cornstarch. Rather than releasing CO_2 to the atmosphere, the process actually captures it because corn absorbs CO_2 as it grows and all liquid effluent is easily and harmlessly biodegradable. 3GT can also be subjected to methanolysis, a process that reduces polyesters to their original monomers. Used polyesters can be recycled indefinitely by being repolymerized. (www.dupont.com/corp/science/bionylon.html)

Bioplastics and biofuels are promising emerging technologies, but other technologies may have a greater long-range impact in terms of carbon sequestration. Bioplastics are expected to compete with petro-plastics on a cost/performance basis. If the carbon used in the process is from atmospheric sources (e.g., from biomass) the net result is carbon sequestration. The market for these materials may limit the carbon sequestration potential; however, other biological processes, especially when part of an integrated sequestration strategy, could have greater sequestration potential.

6.5.1.2 Microbial production of cellulose

Acetobacter xylinium, a non-photosynthetic bacterium most commonly used in the production of vinegar, can use glucose, sugar, glycerol, or other organic substrates and convert them into pure cellulose (Brown 1979). Weyerhaeuser, along with the now defunct Cetus Corporation, spent 7 years optimizing the production of bacterial cellulose, which has unique structural and absorption properties. Several patents have been filed on the applications of bacterial cellulose.

Microbial cellulose has been investigated as a binder in papers. Because it consists of extremely small clusters of cellulose microfibrils, it adds greatly to the strength and durability of pulp when integrated into paper. Ajinomoto Company and Mitsubishi Paper Mills in Japan are currently active in developing microbial cellulose for paper products (see patent JP 63295793 at www.botany.utexas.edu/facstaff/facpages/mbrown/position1.htm). This biopolymer is just one example of the many microbial polymers that have potential for use as alternative durable materials.

6.5.2 Science and Technology Requirements

Unfortunately, the plastic now produced by plants and bacteria is brittle and decomposes rapidly. Research into ways to improve the quality of bioplastics to enhance their usefulness in consumer goods is needed. Alteration of the biosynthetic pathways via gene shuffling, protein engineering, and improved fermentation technology at extreme temperatures must be integrated to achieve these improved bioplastics.

To overcome the drawbacks to successful commercialization of bacterial cellulose, efforts have centered on understanding the biosynthetic process itself, then trying to optimize the fermentation process to produce more cells and cellulose biosynthesis. Further genetic study of the operon-controlling cellulose

Cellulose Factories

Acetobacter xylinum is nature’s most prolific cellulose-producing bacterium. As many as a million cells can be packed into a large liquid droplet, and if each one of these “factories” can convert up to 10^8 glucose molecules per hour into cellulose, the product should virtually be made before one’s eyes. (www.botany.utexas.edu/facstaff/facpages/mbrown/position1.htm) synthesis is needed. Gene shuffling may have some applications also with respect to strain "quilting of genes" and selection of improved transformats.

Because microbial cellulose is an extracellular product that is excreted into the culture medium, special care and handling is necessary to maintain optimal production. The cellulose membrane itself can become a barrier for substrates and oxygen necessary for the cells to produce cellulose. Novel fermentation approaches have been developed to overcome some of the intrinsic difficulties for mass culture of *Acetobacter*, and a vigorous program of bacterial strain selection from regions all over the world has provided a stock resource of stable, efficient cellulose-producing strains.

What is needed at the present is a way to convert bench-scale fermentation to an efficient, large-scale fermentation technology. This research need for new development technology can be achieved through a combination of genetic engineering and a better understanding of microbial physiology in submerged culture.

6.5.3 Research Implementation

6.5.3.1 Biopolymers

Research to improve the desired characteristics of bioplastics includes the following:

- advances in elucidating structural biology
- genetic altering of enzymatic pathways
- improved protein crystallography
- computational biology to simulate structure and properties at extreme temperatures
- genetic engineering to improve durability and elasticity

6.5.3.2 Microbial cellulose

The recent success with cloning and sequencing the genes for bacterial cellulose synthesis (Saxena, Lin, and Brown 1990, 1991) plus functional genomic information (Saxena et al. 1994) will result in new ways to further optimize bacterial cellulose production by *Acetobacter xylinium* as well as other bacteria and algae that synthesize cellulose.

Continued efforts in integrating the physiology and molecular biology of bacterial polymers combined with structural and functional analysis via crystallography and synchrotron characterization should make these bacterial polymers even more attractive and affordable.

6.6 SUMMARY AND CONCLUSIONS

R&D efforts leading to sustained sequestration of gigatonnes of carbon per year from the atmosphere are prime sequestration options. Large-scale biological sequestration opportunities will require significant time and resources for deployment, so we envision successive technology deployments over 25 years (Fig. 6.4). Near-term measures (before 2005) have low technical risk and will have limited carbon sequestration effects at first, but they may become increasingly large sinks with time. Medium-term options will use more advanced strategies involving significantly higher technical risk but may permit higher carbon sequestration capacity with fewer resources. Long-term options are characterized as high-risk but may offer remarkable potential for carbon sequestration.

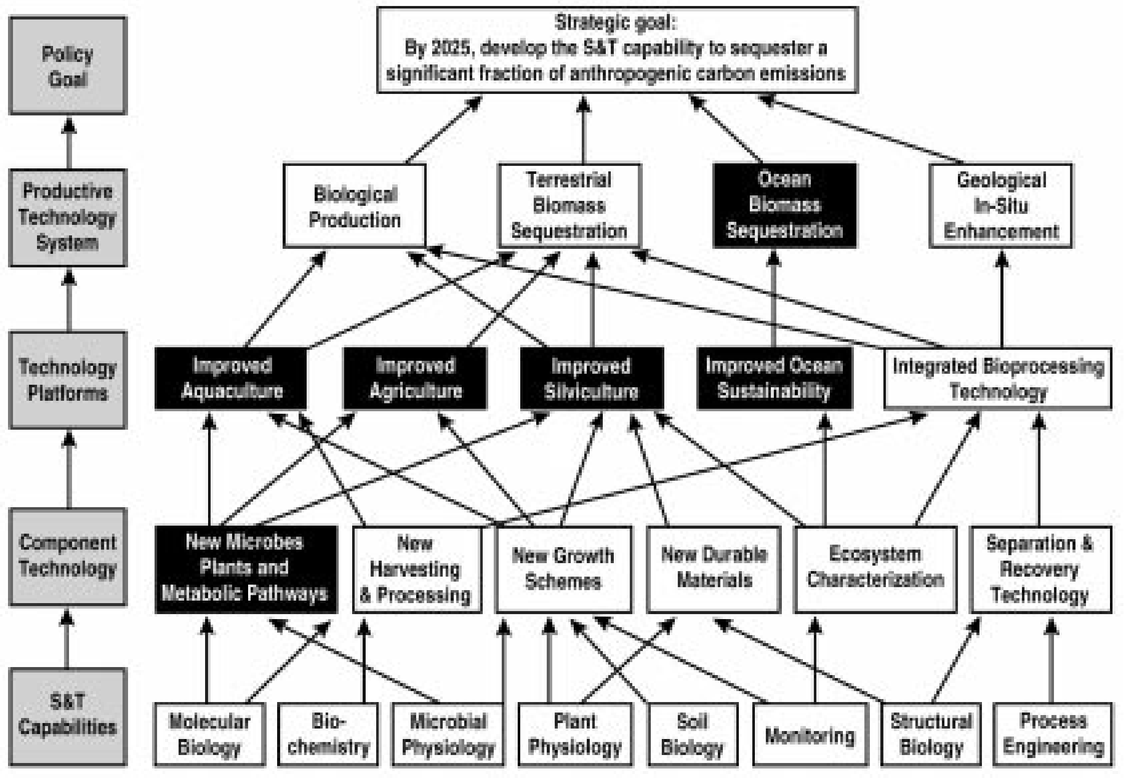

Fig. 6.4. Key elements of the R&D road map for advanced biological processes.

Table 6.1 ranks the strategies discussed in this chapter by technical feasibility, timeliness, and potential effects. Rankings would probably differ if other relevant factors, such as economics, public policy, and risks (health and environmental), were also considered. Some rankings are subjective because of the ill-defined scope of some options. For example, genetic engineering of crop plants for disease and pest resistance is practiced commercially today; hence, this level of engineering is deemed to be highly feasible. On the other hand, targeted genetic manipulation of growth and durability characteristics of conifers is likely to prove difficult and is deemed less feasible.

Table 6.1. Prioritization of advanced biological options

Focus area	Technology description	Technical feasibility 4 = low risk 3 = some risk 2 = moderate risk 1 = high risk (unlikely)	Time 3 = <2005 2 = 2005 25 1 = >2025	Potential impact 4 = very high (>1 Gt/year) 3 = high (>0.25 Gt/year) 2 = moderate (>0.1 Gt/year) 1 = low (<0.1 Gt/year)	Additive component rank (higher score = high priority)
Increase forest productivity	Management	4	1	2	7
	Genetics	2	2	3	7
	Soil sequestration	2	2	4	8
Increase agricultural crop productivity	Soil sequestration	4	3	2	9
	Management	4	3	2	9
	Fuels/chemicals/materials	3	2	3	8
	Nitrogen fixation	2	1	4	7
Alter plant functional structure	Modify plant cell walls	3	2	4	9
Soil biota/ecosystems	Decrease rate of biomass decay	1	2	3	6
	Mycorhizae (P)	2	2	3	7
	Carbonate formation	2	2	3	7
Shift allocation of plant biomass to below-ground organs	Genetic (includes genetic engineering)	3	1	3	7
	Agronomic practices	4	3	2	9
Abiotic stresses	Salt tolerance	3	2	3	8
	Drought tolerance	3	2	3	8
Landfill options	Sequestration	3	3	2	8
	Conversion	4	3	2	9
Materials substitution with renewables	Steel and concrete	2	3	2	7
	Plastics (PHA, PLA; renewable	3	2	2	7
		3	3	2	8
	Durable wood products				
Terrestrial aquaculture	Sequestration in biomass reservoir for C storage)	3	2	3	8
Marine aquaculture	Ocean sediments	2	1	3	6
	Kelp farms	2	1	1	4
	Slow release biofertilization	3	2	4	9
Enzyme and protein	Rubisco CO_2:O_2 fixation ratio	2	1	4	7
	C4 pathway engineering in	2	3	3	8
	Nitrogen fixation	1	1	3	5
	Pathway engineering	3	2	3	8
	Photosystem efficiency	2	2	4	8
Biogeochemical	Bioplugs	2	2	3	7
	Mineralization	1	1	3	5
	Energy-dependent chemical	1	1	2	4

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7 ADVANCED CHEMICAL APPROACHES TO SEQUESTRATION

Vision

Advances in chemical sciences and the resulting technologies allow gaseous CO_2 or its constituent carbon to be transformed into materials that are benign, are inert, are long-lived and contained in the earth or water of our planet, or have commercial value. These transformations represent economical ways to sequester CO_2 or its constituent carbon.

7.1 INTRODUCTION

Advanced chemical processes might lead to unique sequestration technologies or to improvements in our understanding of chemistry that will enhance the performance of other approaches to sequestration. Chemistry is a crosscutting discipline that will interact with virtually all aspects of the sequestration problem. This chapter discusses R&D topics for options not covered in the previous chapters on sequestration technologies but that require advances in our understanding of chemistry.

Advanced chemistry shares significant common ground with separation and capture. Improved methods of separation, transport, and storage will benefit from research into advanced chemical techniques necessary to address sequestration via chemical transformation. Because any sequestration technique will involve storing vast amounts of carbon-rich materials, environmental chemistry is an important cross-linking technology to most of the approaches mentioned in this report. The fate of CO_2 in geological underground storage sites is in part determined by the chemical interaction of the CO_2 with the surrounding matrix, whether it is coal in coal beds or the mineral rock that caps saline aquifers deep underground where brines of carbonic acid can interact. Many issues pertaining to aqueous carbonate/bicarbonate chemistry are relevant to ocean disposal or underground disposal. Carbonate chemistry in very basic solutions may offer potential for extracting CO_2 from air. Because clathrates may be used to separate CO_2 from high-pressure systems, knowledge of their properties may be important to understanding approaches to ocean disposal. Subsurface arctic or marine hydrate formations may also be evaluated as geologic disposal options. Enhancing soil carbon combines biological and environmental chemistry. Similarly, ocean fertilization generates biomass carbon that may interact with ocean chemistry.

7.1.1 Introduction to the Problem and Solutions

Most anthropogenic emissions of CO_2 result from the combustion of fossil fuels. Advanced technologies are being developed to use fossil fuels for co-production of chemicals along with power, including approaches to decarbonizing methane or coal to produce hydrogen. Hybrid approaches may be developed that are an alternative energy source to create hydrogen, making it reasonable to use the hydrogen and captured CO_2 to produce transportation fuels. A number of web sites contain information on the developmental technologies alluded to. See www.nire.go.ip/NIRE/ and www.fe.gov.doe/coal_power/.

The advanced chemical technologies envisioned for the future would work with the technologies now being developed to convert recovered CO_2 economically to benign, inert, long-lived materials that can be contained in the earth or water of our planet or that have commercial value. Most of the advanced chemical approaches identified in this chapter assume that separation and capture processes will make available pressurized CO_2 with minimal (and defined) impurity levels at ambient temperature (i.e., pipeline CO_2). Decarbonization technologies will produce particulate carbon at the site of the process, while advanced power generation technologies may produce a separate stream of carbon monoxide (CO) for use as a feedstock at the plant site. Enhanced chemical processes may also play a role in indirect capture of CO_2 via terrestrial sinks or through ocean fertilization.

7.1.2 Potential Chemical Approaches to Sequestration

One potential approach to sequestration is to transform CO_2 into non-commercial materials that are inert and long-lived, such as magnesium carbonate ($MgCO_3$). Because they have no commercial value, such materials would need to be sequestered in a relatively inexpensive way, such as refilling the mining pits that first provided the magnesium and associated material. After being incorporated in $MgCO_3$, the whole world's 1990 output of carbon could be contained in a space 10 km ´ 10 km ´ 150 m (see sidebar "The Volume of Carbon Sequestration").

The ocean also may provide an inexpensive site for sequestration of carbon. Carbon dioxide can be incorporated in an ice-like material, called CO_2 clathrate, that is long-lived when located at a sufficient depth below the ocean surface. After being incorporated in CO_2 clathrate, the whole world's 1990 output of carbon could be contained in a space with a volume of approximately 80 km^3.

Carbon dioxide, CO, or carbon from energy production also could be recovered and transformed into commercial products (e.g., plastics and rubber) that are inert and long-lived. In 1996, the world's total output of all such products required approximately 206 ´ 10^6 tonnes of carbon or 3.5% of the anthropogenic carbon emitted during that year (SRI 1997). Alternately, bulk commodities for use

The Volume Required for Mineral Sequestration

The aerial photograph shows the Bingham Canyon copper mine on the left-hand side. The town of Copperton, Utah, is located to the right of the mine and to the left of the identification number 242 along the top (1 in. = 1.08 miles). Kennecott Copper extracts some 250,000 tons of rock every day from this mine. Kennecott has been mining this deposit for 90 years. The pit is currently half a mile deep and 2.5 miles wide. If it were a stadium, it could seat nine million people. An average sized power plant, operating at 33% efficiency when firing 12,500 Btu/lb coal, would require approximately 35,000 tons of silicate rock per day to capture the CO_2 produced based on the carbonate reaction shown in Table 7.1. To sequester a full year's carbon emissions—based on typical unit availability and capacity factors—would require space equivalent to 35 days of production from this mine.

Comparison Between the Road Map Goal and Large Industrial Activities

A comparison of the amount of material in sequestered carbon and other large earthmoving activities

- The stated goal of this report is to have the capacity to sequester gigatonnes of carbon by the middle of the next century.
- In 1996, U.S. mines shipped approximately 1 gigatonne of sand and gravel.
- In 1996, U.S. mines shipped approximately 1 gigatonne of coal.
- The Iron and Steel Bureau estimates that the productive capacity of the world steel industry is 1 gigatonne per year.
- According to the Chemical Economics Handbook, the world petrochemical industry bases all of its products on seven precursors. Combined, in 1996 these seven precursors embodied approximately 0.2 gigatonnes of carbon.

Table 7.1 Thermodynamics of chemical/physical transformations involving CO_2

	Chemical/physical transformation	$\Delta H_{298°K}$ (Kcal/mole)
	Energy production	
Coal combustion	$C + O_2 \rightarrow CO_2$	-94.05^a
Natural gas combustion	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-191.76^a
	Sequestration	
Bicarbonate	$CO_2 + 1/2CaSiO_3 + 1/2H_2O \rightarrow 1/2Ca^{2+} + HCO_3^- + 1/2SiO_2$	-15.70^a
Carbonate	$CO_2 + 1/3Mg_3Si_2O_5(OH)4 \rightarrow MgCO_3 + 2/3SiO_2 + 2/3H_2O$	-3.45^a
Oxalate	$CO_2 + CO + CaSiO_3 \rightarrow CaC_2O_4 + SiO_2$	-31.34^a
Clathrate	$CO_2 + 6H_2O \rightarrow CO_2 \cdot 6H_2O$	$-5.68_{(at\ 121°K)}^b$
Liquification	$CO_2(g) \rightarrow CO_2(l)$	$-1.27_{(at\ 298°K,\ 63.5atm)}^c$
	Utilization	
Methanol synthesis	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	-31.30^a
(Hydrogen production)	$(3H_2O \rightarrow 3H_2 + 3/2O_2)$	$(+205.05)^a$
Cyclic organic carbonate	$CO_2 + PhCH{+}CH_2 + 1/2O_2 \rightarrow PhCHO(C{+}O)OCH_2$	-55.3^d

[a] R. C. Weast, M. J. Astle, and W. H. Beyer. *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Roton, Fla., 1988–1989.

[b] S. L. Miller and W. D. Smythe. “Carbon Dioxide Clathrate in the Martian Ice Cap,” *Science*, 170 (1970): 531–532.

[c] W. M. Braker and L. Allen. *Matheson Gas Data Book*, 6th Ed. Matheson, Lyndhurst, N.J., 1980, p. 26.

[d] N. Cohen and S. W. Benson. *Chem. Rev.* 93 (1993):2419–38.

in construction, for example, may represent larger target markets (see the sidebar on potential of sequestration sites and technologies).

In addition, as detailed knowledge is developed, the demands of various sequestration methods may drive the creation of techniques to capture the essence of natural processes. For example, it has been suggested that CO_2 could be sequestered in coal seams. Some of the research needed to investigate that possibility also will bear upon the potential for absorbing CO_2 into other materials that could provide temporary storage; such materials might be used to recover CO_2 from automobile exhaust or directly from the atmosphere. As another example, knowledge of biomimetic chemical techniques—which are essentially models or abstractions of biological processes—might allow us to duplicate these processes under controlled conditions and improve them to enhance reaction rates or reduce the creation of unwanted or hazardous by-products.

7.2 CHEMICAL PROCESSES FOR SEQUESTRATION

Carbon chemistry is very flexible and has helped to create an impressive array of products. Many chemical process options exist for capture and sequestration or reuse of carbon. However, some require as much energy or consume as much raw material as did the original process that emitted the carbon. Such options may have value in a particular niche market, but they are unlikely to represent significant options for long-term sequestration of large quantities of carbon. Whether a process represents a desirable option varies with the economic circumstances and with the attitudes of society; thus it is important to identify a number of approaches that offer a flexible mix of options. Options selected must meet these criteria:

- A process must be environmentally benign.
- It must be stable and sustainable for long-duration storage or disposal.
- It must be safe.
- It must be cost-competitive with alternative approaches to sequestration or avoidance.
- Sufficient knowledge of the process, such as thermodynamics and kinetics, must be developed to allow comprehensive analysis.
- It must be prima facie reasonable, particularly in terms of the energy balance.

This chapter identifies two groups of chemical processes: (1) those that produce materials for sequestration and (2) those that yield useful products of potential commercial value. We examined the knowledge required to determine whether these concepts represent viable options. We also evaluated the current state of knowledge for each process. For each concept, significant R&D needs included (1) an understanding of the basic chemistry and chemical engineering requirements; (2) process development, optimization, scale-up, and environmental control; and (3) systems issues of environmental and ecological impact and economic acceptability. In most cases, the basic chemical reactions have been identified, the basic thermochemical properties have been tabulated, and some process concepts have been established. However, substantial gaps remain.

7.2.1 Inert Benign Long-Term Storage Forms

One goal of this effort is to design chemistry-based processes that can convert separated and captured CO_2 to products appropriate for long-term, environmentally acceptable, and unmonitored storage. It is essential that these options be economically competitive with other approaches to sequestration when performed on the massive scale required to make a significant impact compared with CO_2 production rates. This approach is based on mimicry of natural chemical transformations of CO_2, such as weathering of rocks to form calcium or magnesium carbonates and the dissolution of CO_2 in seawater to yield bicarbonate ions. These two exothermic reactions occur spontaneously in nature. Examples of products for disposal include carbonate ($CaCO_3/MgCO_3$), bicarbonate (HCO_3^-), clathrate ($CO_2 \bullet nH_2O$), and oxalate (CaC_2O_4/MgC_2O_4). Table 7.1 presents data on key chemical reactions—some at the heart of the concepts discussed in this section and others that serve as points of reference. Note that schemes to produce fuels, such as methanol, require hydrogen gas. Combining the methanol synthesis reaction and the hydrogen production reaction shows that the combined process would require a large net energy input.

Four possible approaches to these process are discussed and the knowledge gaps are presented for each.

1. The conversion of natural silicate minerals by CO_2 to produce geologically stable carbonate minerals and silica,

$$(Mg, Ca)_xSi_yO_{x+2y} + x\,CO_2 \rightarrow x\,(Mg, Ca)CO_3 + y\,SiO_2\ ,$$

   is thermodynamically favorable, as is demonstrated by the natural weathering of silicates, albeit at a geologic pace. Current knowledge of this reaction indicates that it is exothermic, that it can be carried out in several steps, and that sufficient raw materials are available to supply the silicates needed. The challenge is to design conditions of temperature, reaction medium, and reactor configuration that will allow this transformation to be carried out at sufficiently rapid rates. An example currently being studied is the use of a hydrous $MgCl_2$ molten salt with a serpentine mineral feed in which HCl/Cl^- appears to play a catalytic role. R&D will need to address novel concepts that allow the key transformations to proceed in a single step, at a faster rate and at affordable cost. Topics requiring study include (1) the mechanism and kinetics for this gas-solid reaction, as well as catalysts and/or reaction media to promote it; (2) thermodynamics and kinetics of the gas-molten salt reactions and the chloride chemistry; (3) designs for solids-consuming, solids-producing reactors, control of the physical form of the solid products to optimize processing, and corrosion control; and (4) the economic and environmental impacts of mining of the silicates, surface disposal of the carbonate/silica product, and the trace metal products that may offer collateral economic benefits.

2. A second chemical system is dissolution of CO_2 in the oceans (or other natural waters) as soluble bicarbonate,

   $$CO_2 + 2H_2O \rightarrow H_3O^+ + HCO_3^- ,$$

   coupled with the need for a source of added alkali to avoid lowering the pH of the body of water. This pathway is important both for sequestration in geologic formations and for ocean disposal. The CO_2 might simply be put in the ocean, where most of it would persist as dissolved gas, carbonic acid, and the bicarbonate ion if the CO_2 were injected far enough below the surface. The bicarbonate ion might be created through development of biomimetic pathways in man-made systems and disposed of near the shore in shallow waters, assuming the needed cations could be provided. The current level of understanding of the process of dissolution and reaction is inadequate to allow development of a process with the potential to sequester CO_2 at the rate at which it is currently produced in power plants. R&D on using bicarbonate to sequester CO_2 should address (1) ocean and fresh water and electrolyte chemistry, the influence of solid surfaces, and the precipitation of carbonates; (2) design of reactors and injectors to facilitate efficient mixing of reactants; (3) the effects of enhanced bicarbonate levels on aquatic life and ecology and on the formation of carbonate deposits by advanced biological approaches; (4) rates of transportation from the atmosphere to the ocean; (5) rates of stimulated growth of candidate organisms to capture and hold CO_2; and, (6) biomimetic pathways to form calcium carbonate, including the process to make the necessary calcium available to the reaction.

3. The clathrate of CO_2 and H_2O (see Fig. 7.1), structurally analogous to the better known methane hydrate, may offer potential as a form for large-scale storage in the cold oceans or in man-made systems that mimic the requisite conditions. Clathrates may be used in CO_2

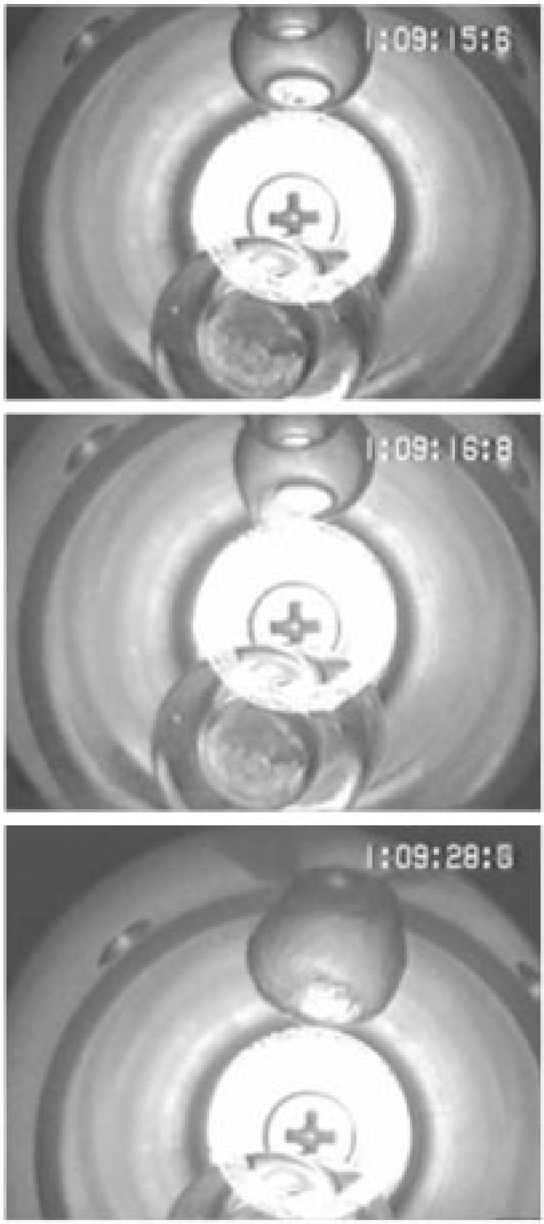

Fig. 7.1. Mixtures of gas clathrates have been found near coasts around the world. These gas hydrates may be mixtures of methane clathrates and CO_2 clathrates. If so, their presence prompts further investigation of the possibility that CO_2 clathrates could be sequestered in the same places. The photos show the formation of a gas clathrate during an experiment.

separation from high-pressure systems, and their properties may be important to understanding both approaches to ocean disposal and geologic disposal options. Forming clathrates as a separation step in an integrated gasification combined cycle power plant could be attractive. Preliminary estimates of the energy required indicate that 3 to 4% of the total plant energy would be needed. This is an improvement over techniques available today. Based on what is now known, additional R&D will be required to (1) improve the definition of the phase diagram, thermodynamics, and physical properties of the CO_2–H_2O system at high pressure in the presence of the electrolytes and impurities found in the ocean, as well as improve the definition of the kinetics of formation and long-term stability of the clathrates; (2) identify practical methods for deep-ocean injection and mixing; and (3) assess the local ecological impacts of hydrate formation. Further exploration would be necessary to determine whether, in the longer term, CO_2 disposal via clathrate formation could be coupled with recovery of methane fuel from the methane hydrate deposits in the oceans.

4. In addition to these process concepts, exploratory R&D is warranted on defining additional low-energy disposal states of carbon that would meet the guiding principles for this topic; examples might include formates and oxalates. Because CO_2 is an acidic gas, it can be captured by using an alkaline substance to form stable compounds with it. A procedure that uses one mole of alkali to transform two moles of CO_2—such as in the transformation of CO_2 to low-energy-state poly-carbon compounds such as calcium/magnesium oxalate (CaC_2O_4/MgC_2O_4)—is desirable because of

the greater CO_2-to-alkaline ratio. Research needs include
(1) development of methods for synthesis of regenerable alkaline compounds and for effective use of alkaline; (2) use of molecular modeling to identify new compounds in which one mole of an alkaline species would tie up several moles of CO_2 (Zeissel 1998); (3) exploration of total energy requirements—which include those for chemical reactions as well as those for chemical processing—for both exothermic reactions involving CO_2 and endothermic reactions requiring a small amount of enthalpy input; (4) research into catalysis reactions, process optimization, surface disposal issues, and environmental concerns. Finally, engineering studies and system evaluations of the types described would be needed.

7.2.2 Products from Carbon Dioxide Utilization

The goal of CO_2 utilization is to design chemical processes that can convert separated and captured CO_2 to useful and durable products that have reasonable lifetimes (tens to hundreds of years). Carbon dioxide either in whole or in part can participate in many chemical reactions (Fig. 7.2).

Such utilization strategies, when examined from the perspectives of the current petrochemical industry, will not have the capacity to handle the bulk of emitted CO_2. However, the products and durable goods that are produced may have greater value and storage lifetimes and lesser environmental impacts than existing means to produce these same products. Additional markets might be developed if R&D were directed toward creation of products with large annual uses, such

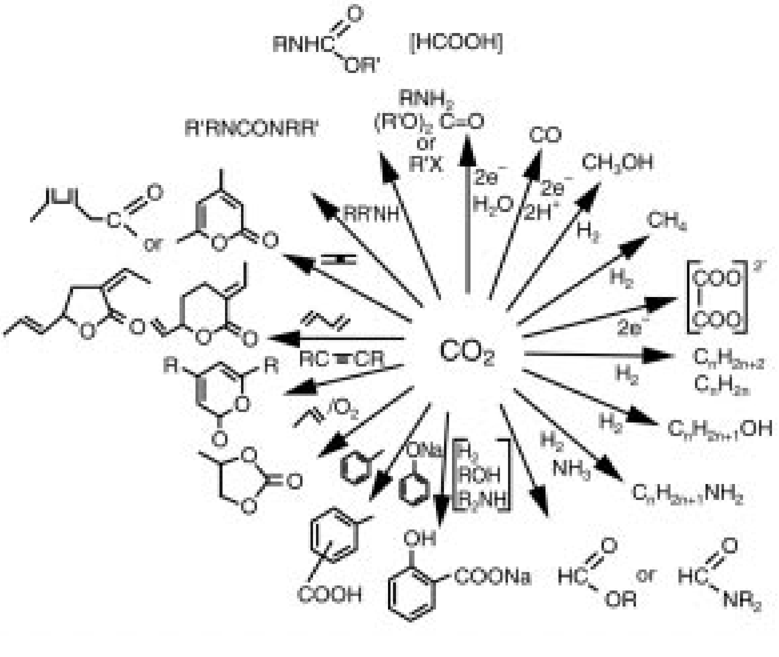

Fig. 7.2. Paths to utilize CO_2 in synthetic chemistry. *Source:* Aresta 1998.

Use of Carbon in Ultralight Vehicles

The Rocky Mountain Institute has performed a number of analyses on development of ultralite vehicles. In December 1996, it published a report titled "Costing the Ultralite in Volume Production: Can Advanced-Composite Bodies-in-White be Affordable?" (Mascarin et al. 1996) that examines the use of a carbon-fiber-composite monocoque body-in-white in an ultralite vehicle or hypercar. The body of the car would be made of parts molded from advanced polymer composites and assembled with adhesives. The composites could be formed from carbon fibers embedded in an epoxy or other resin. The carbon fibers could represent approximately 50% of the total weight.

The typical hypercar prepared from these materials would have a curb weight of 637 kg, of which approximately 190 kg is the weight of the monocoque body. If carbon from the fuel cycle were used to create the products needed for construction of such a vehicle, each body shell might contain 100–150 kg of carbon (the report does not list the actual percentage of carbon in the monocoque body). The report discusses the cost of carbon fiber in terms of the size of the market needed to ensure a low cost for the needed material–a market of approximately 0.6 to 0.9 million carbon-fiber cars per year.

Assume that all the needed carbon from such a car body could be derived from either fuel decarbonization or from products made from CO or CO_2 captured after some or all of the chemical energy had been used for energy production. Then this market might require carbon sufficient to make approximately 750,000 cars/year, each car requiring 125 kilograms of carbon. This usage represents approximately 100,000 tonnes of carbon per year. A total of 750,000 cars per year would represent approximately 10% of the current U.S. new car market.

as construction materials or parts for automobile bodies (see sidebar on use of carbon in ultralight vehicles). However, widespread use of carbon-based products would require large shifts in infrastructure and would face stiff competition from the industries manufacturing the products they sought to displace.

Four end-uses that could be viewed as supporting the need for a particular technology are described in the following paragraphs, and gaps in knowledge are identified. This list is not comprehensive because of the great variety of organic synthesis routes that exist, but it provides a sense of the opportunity and scope of this approach to carbon sequestration. (See also Elsevier 1998 and ACS et al. 1996).

- Particulate carbon, perhaps from methane decarbonization, could be converted into new composite materials and used in durable construction materials such as concrete. The challenge is finding economically viable methods of converting solid carbon into durable goods and new composites. An associated issue is the physical characteristics of the supplied carbon, assuming that the carbon comes from fuel decarbonization processes. Scientific and technological capabilities are needed to define the chemical pathways from hydrocarbons to solid carbon, discover new composite chemistry, and understand how to incorporate carbon into new building materials.

Specific needs include identification of (1) thermochemical processes, (2) new catalysts and reactors, and (3) alternative fuel sources. The lifetime of the product or material is a key variable to be considered in performing life cycle and system cost and performance analyses.

- Many studies have addressed the need to identify ways to use CO_2 as a carbon feedstock for production of plastics or other similar commodities. Needed scientific and technological capabilities include (1) definition of chemical reaction pathways, (2) catalyst development, and (3) process development and optimization. A significant environmental driver is the substitution of CO_2 for toxic substances such as phosgene, which is used as a feedstock to produce isocyanates, polycarbonates, and other products used in industrial processes. Research has uncovered the pathway for this substitution to occur exothermically, implying that more benign processing may be an economic driver as well. Product lifetimes need to be assessed, but we assume that they will be on the order of decades to centuries. Another approach might be partial oxidation (via gasification) to produce energy and some CO that could serve as a feedstock for chemical processes.

- Alternately, it might be possible to use the carbon either from the fuel or from products of the combustion process to create soil amendments to enhance sequestering carbon in natural systems. Similar technical concerns exist about, for example, how to optimize these products for their desired end use. However, the requirements for achieving product purity and for avoiding potential environmental impacts differ.

- Finally, much attention has been focused on carbon-neutral processes in which fuels and chemicals are formed from CO_2 feedstocks via pathways that would use renewable energy sources. Scientific and technological capabilities will be needed to identify new catalysts, electrocatalysts, and efficient reactors. However, this approach requires a source of cheap hydrogen to react with CO_2. Schemes have been proposed to split water to provide a source of hydrogen. Direct use of H_2 as a fuel, as an alternative to reacting hydrogen with CO_2, should be addressed through a systems evaluation of costs and benefits. In general, the question of sequestration or avoidance needs to be addressed with respect to carbon neutral processing.

7.3 ENABLING CHEMICAL TECHNOLOGIES

Previous sections of this chapter described the chemical aspects of sequestering CO_2 for ocean storage of bicarbonates and clathrates; land storage as solid alkaline carbonates; cross-compounds in which a simple cation ties up a number of CO_2 molecules; and storage in durable materials such as plastics, composites, and chemicals. Significant developments in enabling science and associated technologies are needed to support these concepts (see Fig. 7.3). Some processes will be greatly aided by improving computational capabilities related to molecular modeling for novel synthesis routes to make carbon-

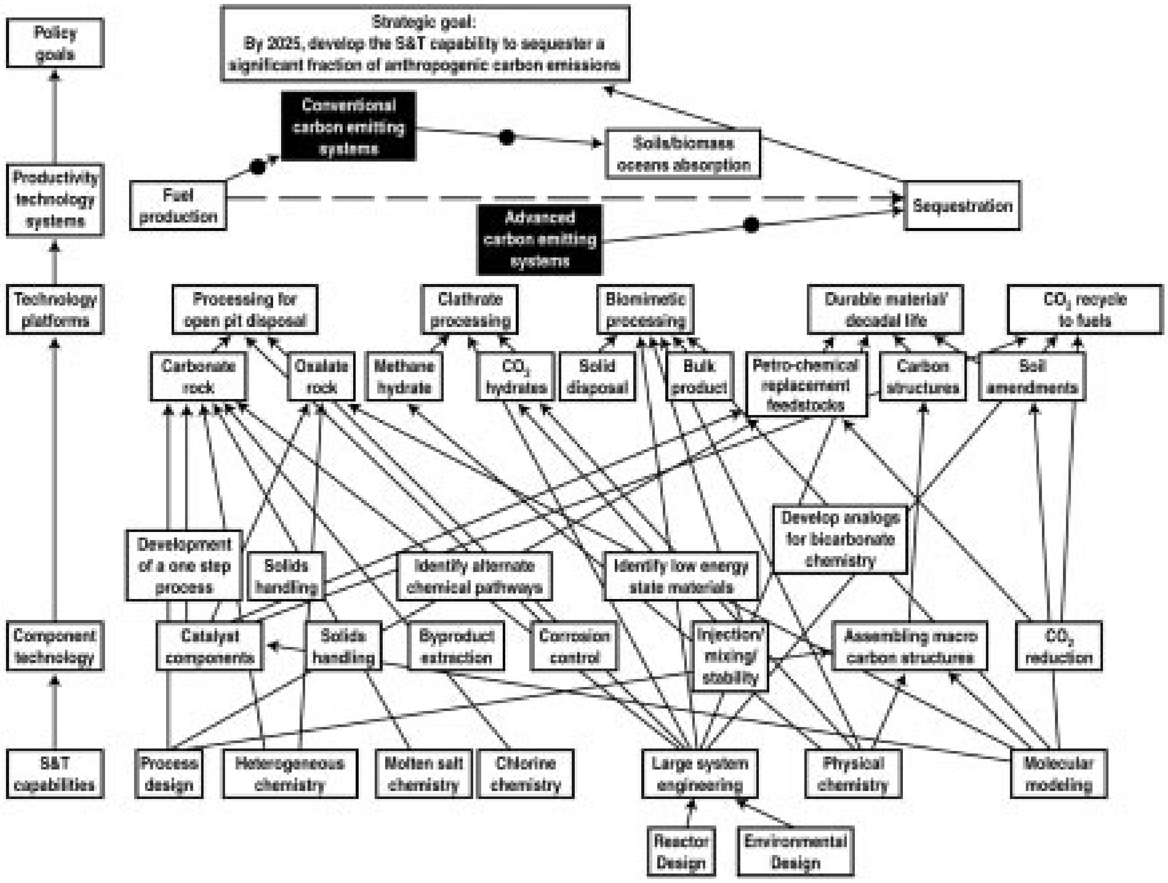

Fig 7.3. A road map of needed research into advanced chemical approaches. The science and technology capabilities address needs of both advanced chemical processes and the other focus areas. These capabilities are topics that need attention in the near term, as are the component technologies that support the carbonate rock option and biomimetic processing (the latter would enhance the chances for success of sequestration in oceans and geologic formations).

based products, or for development of improved solvents such as sterically hindered amines to capture carbon from flue gases. Many of these capabilities are already under development to support creation of new energy and environmental technologies. A partial list of the enabling technologies needed includes

- Develop catalysts needed to enhance geologic sequestration, use of the carbon in CO$_2$, and decarbonization (e.g., mimic photosynthesis; use Ti0$_2$ and sunlight to split CO$_2$)
- Develop new solvents and sorbents for gas separations (O$_2$ from air or CO$_2$ from flue gas)
- Develop a thorough understanding of the chemistry key to CO$_2$ adsorption and methane desorption from coal seams
- Explore novel formulations for fertilizers to be applied to enhance terrestrial or oceanic sequestration concepts
- Create membranes and thin films for advanced separations (e.g., high-temperature ceramic membranes to enable air separation)
- Develop agglomerating agents, binding agents (e.g., coal and lithium zirconate), and coatings

- Improve high-temperature materials, particularly metal oxides (e.g., BaO and BaO_3 cycles for high-temperature separation or NiO or CoO mixed with Yttria-stabilized zirconia for chemical looping combustion)
- Explore novel reactor concepts and the requisite sensors and controls

The development of improved catalysts and other new materials is particularly important.

Catalysis. Developing effective catalysts capable of multiple electron reduction chemistry is the major challenge for creating an effective technology for reducing CO_2 to high-energy intermediates. Considerable success has been achieved in the design, synthesis, and analyses of donor and acceptor assemblies capable of light-driven, one-electron charge separation processes. Current research demonstrates that remarkably enhanced catalytic efficiencies are achieved in natural and artificial photochemical systems by inducing redox chemistry on surfaces in constrained, structured environments.

Novel structured catalytic assemblies capable of initiating single-step, multiple-electron, reductive chemistry are needed. Redox assemblies capable of cooperative charge accumulation mimic the biological process of CO_2 reduction in photosynthesis and would provide a photoelectrochemical system that could use CO_2 as a chemical feedstock for synthesis of carbon-based chemicals.

New catalysts will be required to enhance the rates of formation of alkaline carbonates and oxalates Additives that could enhance geologic sequestration of CO_2 also are needed. These materials would be injected with CO_2 early in the period of use to coat the cap rock or features toward the boundary of the reservoir. Over time, say after 5 years, they would begin to react with the injected CO_2 to seal the reservoir and reduce the potential for leakage.

New materials. New materials are needed to handle the extreme process conditions of molten salt chemistry. Chemical approaches (e.g., barium oxide and barium peroxide) to air separation or chemical looping combustion (nickel oxide or cobalt oxide mixed with yttria-stabilized zirconia) should be studied because they can take advantage of the high temperatures available at power plants. Binding and agglomeration processes must be defined both for the fabrication of products from particulate carbon and for other uses, such as the capture of CO_2 from vehicles. For example, materials like lithium zirconate might be good CO_2 absorbers and thus enable the capture of some CO_2 from vehicle emissions, a hitherto overlooked approach that merits long-range high-risk research. As another example, composite materials that might result from adding carbon to plastics, polymers, glasses, cements and ceramics should be studied.

7.4 SUMMARY

This chapter explored three approaches to carbon sequestration using advanced chemical technologies:

1. Develop benign by-products for disposal. This avenue may offer the potential to sequester large (gigatonne) amounts of anthropogenic carbon.

2. Produce commercial products. This topic probably represents a lesser potential (millions of tonnes) but may result in collateral benefits tied to pollution prevention.

3. Conduct enabling studies that may impact the ability of technologies under development in other focus areas to meet their potential.

Based on our review of advanced chemical concepts, and recognizing needs identified in other focus areas, priority should be placed on obtaining the chemical knowledge required to

- Absorb/adsorb CO_2 in coal seams.
- Create magnesium carbonate as described in the carbonate reaction in Table 7.1. The product is inert and benign.
- Understand and exploit CO_2 clathrates, ice-like materials that precipitate out of mixtures of water and CO_2 under the proper conditions.
- Form and dispose of aqueous solutions of carbonates, the bicarbonate ion being the most prominent, in the ocean or other appropriate bodies of water.
- Develop commercial products made from CO_2, CO (from advanced power system concepts), or carbon created via decarbonization.

Table 7.2 provides more information about these approaches.

The materials above the double line (that is, oxalates, etc.) have virtually unlimited carbon sequestration potential. The ones below the line are less likely to play a major role based on both thermodynamic considerations and the potential size of target markets. Given current consumption patterns, only a small percentage of fossil carbon feedstocks is used for producing carbon-based goods. The rest goes toward energy production. Reduced carbon will be of interest in niche markets that are driven by the value of the products they generate. The chemical industry could use new chemical processes for producing valuable chemicals and materials, as well as avoid potential environmental penalties for continued CO_2 emissions. The economic benefits of new processes might provide increased technological competitiveness for industry and the ability to use CO_2 as a feedstock for chemical production in addition to current petroleum-based feedstocks. However, the overall effect of product development on carbon

Table 7.2 Approaches to sequestration using chemical processes and examples of their use

Chemical form of carbon	Examples of implementation
Aqueous carbonate ions: CO_3^{**}, HCO_3^{*}	Ocean disposal, deep saline aquifers
Solid carbonates: $CaCO_3$, $MgCO_3$	Terrestrial, ocean floor, underground disposal
Clathrates: $CO_2 \bullet nH_2O$, n ~ 6	Ocean, ocean floor disposal
Carbon adsorption of CO_2	Coal bed methane extraction
Other low-energy states of carbon, such as oxalates	Novel disposal technologies
Solid carbon	Underground disposal, feedstock for composite materials
Carbon-based fuels (e.g., methanol)	CO_2-based fuel cycles, alternative energy
Carbon bound in durable commercial goods (e.g., plastics)	Long-lived construction materials

sequestration is likely to be small unless new products that are used in large quantities can be developed, such as building materials or materials for automobile bodies. Based on the scale of sequestration that may be needed, our analysis favors research into those chemical options that offer the greater sequestration potential. Thus we consider stable and benign end products for disposal a more promising approach to the problem. In addition, enabling studies should be pursued that benefit both other sequestration methods and the development of chemical means to mimic natural processes under controlled conditions.

7.5 END NOTES

1. In hydrate-clathrate, the maximum ratio of guest molecules (e.g., CO_2) to water molecules is approximately 1/7. (See E. Denude, Sloan, Jr., 1998. *Clathrate Hydrates of Natural Gases*, Marcel Dekker, New York, p. 53.) The density of ice is approximately 0.9 grams/cm^3. To establish the needed order of magnitude, we assume that one gram-mole of ice (18 grams) occupies 20 cm^3 and that at most 1/7 gram-moles of CO_2 (44/7 grams) occupies the same 20 cm^3. Thus 1/7 gram-mole of carbon occupies at least 20 cm^3, probably more. Hence we estimate the maximum effective density to be 12/7 grams of carbon per 20 cm^3, which is 0.085 grams carbon per cm^3. Thus after 109 tonnes of carbon was incorporated in CO_2 clathrate, this clathrate would occupy a volume of at least 1.2 ´ 10^{11} m^3 or 12 km^3.

2. The ratio of the mass of $MgCO_3$ to the mass of carbon, incorporated therein, is 7. It follows that 109 tonnes of carbon would be bound within 7 ´ 109 tonnes of $MgCO_3$. The density of crystalline magnesium carbonate is 3 grams/cm^3. In practice, powdered material with a bulk density of somewhat less would be sequestered. Perhaps about 10% more space would be needed for powder than for crystal (e.g., 2.7 grams/cm^3). If so, 7 ´ 109 tonnes of $MgCO_3$ would occupy 2.6 ´ 109 m^3 which is the volume of a box whose sides are 10 km by 10 km and whose height is 26 m.

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8 DEVELOPING AN EMERGING TECHNOLOGY ROAD MAP FOR CARBON CAPTURE AND SEQUESTRATION

8.1 INTRODUCTION

Road-mapping techniques are being used by numerous industrial firms, industry collaborative groups, and government agencies in their planning processes. The term “road mapping” has been broadly applied to many kinds of activities, and there are many types of road maps.

The purpose of an emerging technology road map is to provide—and encourage the use of—a structured scientific R&D planning process. Emerging technology road maps furnish a framework for managing and reviewing the complex, dynamic R&D process needed to achieve important strategic goals. These road maps show graphically how specific R&D activities can create the integrated technical capabilities needed to achieve strategic objectives. This chapter describes the creation of an emerging technology road map for the capture and sequestration of CO_2.

Vision

Emerging technology road maps furnish a framework for managing and reviewing the complex, dynamic R&D process needed to achieve important strategic goals.

8.2 A CARBON CAPTURE AND SEQUESTRATION SYSTEM

An emerging technology road map seeks to identify the scientific and technological developments needed to achieve a specific technology goal. The process of identifying the needed science and technology must be focused by developing a concept of the technological system that would enable achievement of that goal. This task is particularly difficult in the case of carbon capture and sequestration because there is no paradigm for such a system.

Today, carbon is emitted to the atmosphere from energy technologies that were not designed to capture, let alone sequester, these emissions. There are many ideas for, and even demonstrations of, technology to capture and sequester carbon from fossil fuel combustion. However, we must consider that the current energy system could be modified significantly to make an economical capture and sequestration system possible. Thus the emerging technology road map for carbon capture and sequestration cannot be constructed apart from consideration of current and emerging energy technologies. It will involve an iterative process to connect this road map with others being developed by DOE for various parts of the energy technology system.

Figure 8.1 gives a top-level picture of a carbon capture and sequestration system and its linkages to the energy system. Within the current fossil energy system, carbon is processed in several forms by different fossil fuel technologies in many different parts of the energy system. To keep it from being emitted to the atmosphere, this carbon must be captured, processed in some way to separate or purify it, and changed to a solid, liquid, or gaseous form that is convenient for transport. It can then be transported in an engineered system to a site for sequestration or for transformation into a long-lived end product. Alternatively, the carbon could be emitted as CO_2 and transmitted through the atmosphere if sequestration by bio-absorption can be assured in some part of the natural carbon cycle.

This report has concentrated principally on the new scientific understanding and technology (shown in white in Fig. 8.1) that are needed for specific capture and sequestration functions. Transportation technologies (shown in gray) have not been addressed. However, particularly in Chaps. 2 and 7, reference is also made to specific changes in components of the existing energy system (shown in black) that would simplify and/or lower the cost of capture and sequestration.

The close relationship between fuel transformation—from natural hydrocarbons to refined fuels for transportation and/or dispersed energy technology—is of particular importance in this regard. Changes in the carbon content of refined fuels can alter the flow of carbon through the capture and sequestration system. Lowering the carbon contents of transportation fuels can change the balance between carbon transported through the atmosphere and that which must be handled in potentially more expensive engineered systems. The form of fossil-fueled electricity-generating technology also plays an important role in determining the form and cost of capture and sequestration technology. The cost and applicability of the individual capture and sequestration technologies shown depends fundamentally on the particular fossil-fueled electricity-generation technology employed. These are two areas for particular emphasis in coordinating this road map with other DOE transportation and fossil energy technology road-mapping efforts.

The major capture and sequestration technologies are listed in Fig. 8.1 and are discussed in detail in Chaps. 2–7. Each can be developed and improved individually. However, the economic cost and effectiveness of the overall carbon capture and sequestration system depend on the effective combination of many technologies.

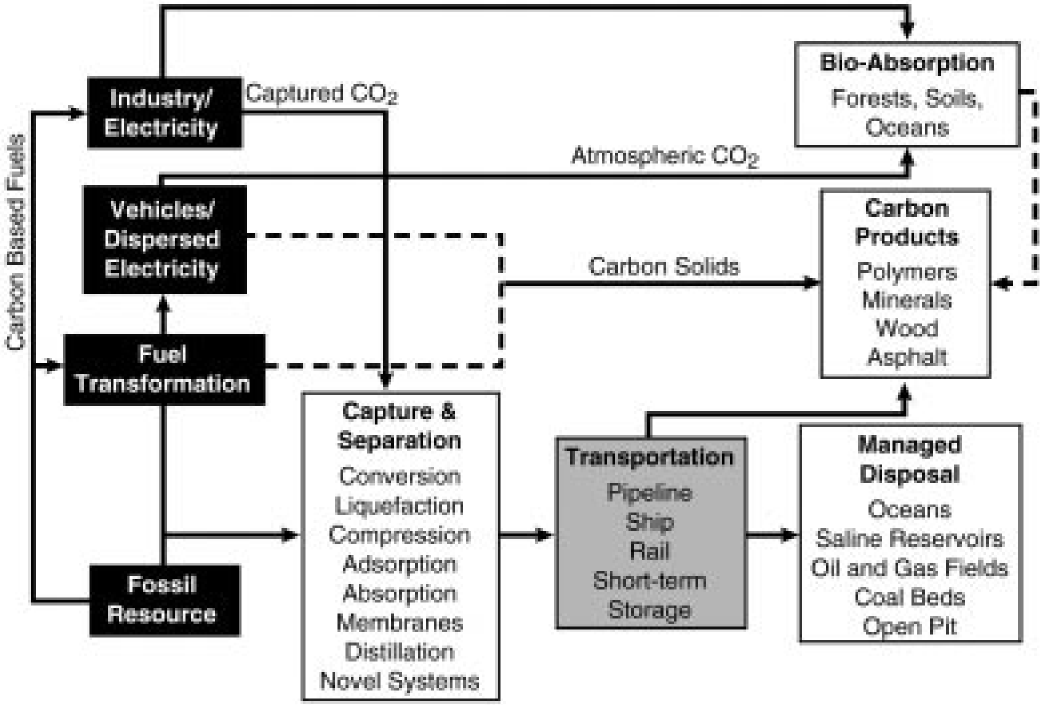

Fig. 8.1. The top-level diagram of a carbon capture and sequestration technology system showing the relationship to the fossil energy system.

Their relative importance must finally be judged in the context of the integrated technology system. The system shown in Fig. 8.1 is adequate for taking the first steps in developing a carbon capture and sequestration emerging technology road map, but a more detailed system engineering effort will be required to add economic and engineering substance to this sketch before the requirements needed to plan an R&D program can be generated.

8.3 BUILDING AN EMERGING TECHNOLOGY ROAD MAP

After identifying the technology goals and the integrated technology system needed to satisfy those goals, the next step in developing an emerging technology road map is to assess the alternative technological pathways that might lead to achieving the integrated technology system. The approach is to construct these pathways within a technological hierarchy. The highest level of the hierarchy is the integrated technology system—in this case, the carbon capture and sequestration system. The hierarchy ends with the science and technology capabilities that are needed to develop the technologies that make the system economical and effective.

Analyzing the integrated technology system in terms of its component functions and the performance required to meet the strategic goal connects these extremes. First, we identify the critical technology platforms that might provide high value in the operation of the integrated technology system. The technological components that make up the technology platforms can also

Definitions of the Technology Hierarchy

Technology platform: A combination of components; intellectual property; and market, business, and technical know-how that can be applied to a family of process needs.

Component: A technology or specific knowledge that performs, or allows the performance of, a unit function supporting one or more technology platforms.

S&T Capability: General science, engineering, and management knowledge and skills that enable development of components and technology platforms.

frequently be identified within the integrated technology system. However, the performance or development requirements of these components must be determined from the needs of the technology platforms, which are aimed at increasing the economic performance of the whole system.

As applied to emerging technologies, the hierarchy includes technology in different stages of development. In fact, not all of the science or technology in an emerging technology road map is well defined. Some elements may well be represented by little more than functional requirements and a technical intelligence–gathering plan to identify scientific or technological approaches. Thus after assembling the framework of the road map by working downward through the hierarchy from policy goals to capabilities, one must also work upward from the capability level to identify possible pathways and to map a course of development.

8.4 BUILDING THE CARBON CAPTURE AND SEQUESTRATION ROAD MAP

Chapters 2–7 are organized by related areas of scientific expertise. These chapters were prepared by experts in each science and technology area that would be needed to develop a carbon capture and sequestration system such as that shown in Fig. 8.1. The material provided by these expert groups is the foundation for developing a carbon capture and sequestration road map.

To develop the outline of an emerging technology road map from this material, the carbon capture and sequestration system outlined in Fig. 8.1 was broken down into its functional components. The result is shown graphically as the capture and sequestration technology system in Fig. 8.2.

Then, using the Graphical Modeling System (GMS), an integration group asked each of the working groups to identify technology platforms that they believed would be critical for the efficient performance of these system functions and that were particularly dependent on the group's science and technology. Within these technology platforms, the groups were asked to identify specific components, again within their science and technology areas, that they believed could be important to the development of these technology platforms. Finally, each group was asked to identify the science and technology capabilities that would be essential for the successful development of the technology that they had identified. They also specified the relationships between the science and technology at each level within this science and technology hierarchy. This exercise enabled each of the working groups to better perceive the

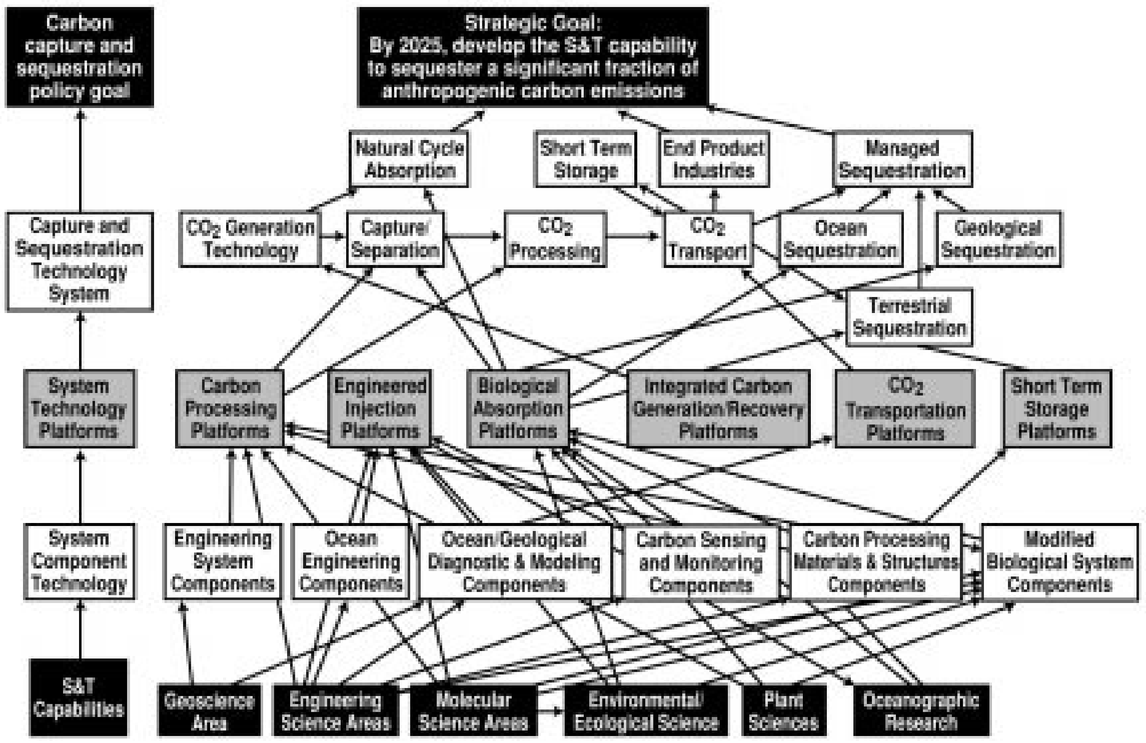

Fig. 8.2. The structure of an emerging technology road map for carbon capture and sequestration. The boxes (nodes) contain the science and technology needs developed by expert working groups in Chaps. 2–7. The lines represent the relationships and performance requirements among technologies.

relationship of its particular technical area to the overall carbon capture and sequestration system. Each of the working groups also adapted this general approach to better illuminate the technical discussion in its chapter.

The integration group assembled all of this expert input into a system-level outline of an emerging technology road map (Fig. 8.2). The outline illustrates the complex interdependence of the science and technology described in the preceding six chapters. To achieve the capability to capture and sequester a significant fraction of anthropogenic carbon by 2025, development is required at each level of this hierarchy supporting a fully functional carbon capture and sequestration system. Even at this stage in the development of a road map, the need for a coordinated science and technology development program is evident from the many science and technology relationships shown in Fig. 8.2.

The science and technology underlying the nodes at each level of the hierarchy in Fig. 8.2 is discussed in more depth in Chaps. 2–7. Each of these items is also shown in summary fashion in Tables 8.1–8.3. Working from the bottom to the top of Fig. 8.2, to support the carbon capture goal, the next step is to assemble the capabilities, develop critical components, create new technology platforms, and integrate them with old technology to form a new carbon capture and sequestration system. From the capability to the systems level, technology becomes increasingly

Table 8.1. System technology platforms

Carbon processing technology platforms	Engineered injection platforms	Biological absorption platforms	Integrated carbon generation and recovery platforms	CO_2 distribution and storage platforms
Durable material processing	Geologic injection	Soils and agriculture	CO_2 recycle combustion	CO_2 hydrates and transportation
Low-temperature distillation	Ocean injection - Tankers - Pipelines	Ocean fertilization	Chemical looping combustion	
Adsorption technology		Algal absorption systems		
Membrane separations		High-productivity plants		
Absorption technology		Microbial CO_2 absorption		
CO_2 to fuels processing				
Bio-mimetic processing				
Clathrate processing				
Microbial biochemical reactors				
Carbonate processing				

integrated as it moves from the research laboratory to commercial application. In the past, these stages of development were often sequential. Today, they are more often overlapping in time and involve extensive interaction through the development and commercialization process. Exploring the path from science to system application consists of identifying the expected technology needs and performance requirements at each level of integration and mapping the relationships between them.

8.5 BUILDING THE R&D CAPACITY

The road mapping presented in this chapter leads to a three-pronged approach to R&D:

- Specific fundamental scientific breakthroughs in chemistry, geology, and biology that are necessary to achieve the vision presented in Chap. 1 are described below and in Chaps. 2–7.
- Large-scale field experiments would help scientists understand the efficacy, stability, and impact of stored carbon, as well as its consequences on humans and the

Table 8.2. System component technologies

Engineering system components	Ocean engineering components	Geological diagnostic and modeling components	Carbon processing materials and structure components	Modified biological system components
Solids handling	Deep sea structural engineering	Reservoir characterization	Catalysis components	Species selection and genetics
Process CO_2 reduction	Hydrate formation technology	Reservoir distribution identification	Gas-liquid contactors	Crop and land management
Corrosion control	Drilling and injection	Geo-monitoring technology	Gas-solid contactors	Photosynthetic system enhancement
Byproduct extraction	Injection mixing and stability		Molecular sieves	Microbial rhizosphere enhancement
Carbon sensor technology	Plume modeling		Enhanced heat and mass transport technology	Soil improvement
In situ ocean carbon monitors			Solvents	Controlled eco-physiology
Tracer technology			Assembling macro-carbon structures	Ecosystem management
			Adsorbents	Fertilizer design and delivery
			Electro-swing adsorption materials	Microbial CO_2 transformation
				Environmental technology
				CO_2 fixation optimization

environment. These might be accomplished by piggy-backing on projects being conducted for other purposes in collaboration with industry, other federal agencies, and/or international programs.

- A coordinated program would take advantage of advances in basic research and findings from field studies. These data and conclusions should be coordinated, communicated, and integrated to better target additional scientific research and the design of future field experiments.

8.5.1 Advanced Sensors and Monitoring Systems

This three-pronged approach is supported by three system technology

Table 8.3. Science and technology capabilities

Engineering science areas	Geoscience areas	Chemical and molecular science areas	Environmental/ ecological science areas	Plant science areas	Oceanographic research areas
Reactor design	Multiphase flow	Surface modeling	Ecosystem modeling	Plant physiology	Ocean general circulation modeling
Large system engineering	Fluid dynamics	Kinetic modeling	Ecological monitoring - Field testing - Long-term	Plant pathology	Ocean chemistry
Environmental design	Geochemical reactions and kinetics	Molecular modeling	Ecological inventories	Metabolic engineering	Oceanic biosphere
Process design	Reservoir modeling	CO_2 hydrate chemistry	Environmental impact assessment	Genetic engineering	
Multiphase flow	Geophysical detail resolution	Heterogeneous chemistry	Ecosystem dynamics	Molecular biology	
Fluid dynamics	Geomechanics - In situ stress - Reservoir leakage and integrity	Chlorine chemistry	Microbial ecology (genomics)		
Environmental design		Physical chemistry			
Process design		Molten salt chemistry			
Reservoir modeling		Soil bio-chemistry			
Geophysical detail resolution		Material synthesis			
Geo-mechanics - In situ stress - Leakage/ integrity					

platforms and one system component technology that cuts across all focus areas.

The cross-cutting systems component technology is advanced sensors and monitoring systems. There is a continuing need to build more robust and sensitive sensors for measuring various biological and chemical species. These sensors need to be developed for making precise and accurate measurements in remote and/or hostile environments. Continuous improvements must also be made in monitoring systems to ensure that data are available in real time and the overall measurement systems will operate under a variety of conditions. The need for advanced sensors and monitoring systems is important for four reasons: (1) The nature of separation, capture, storage, and removal of CO_2 from the atmosphere needs to be quantified in order to measure the efficacy of the technology. Without such characterization, it will be difficult to understand the underlying processes. (2) The stability of the sequestration methods must be validated. We need to know how long the carbon will stay. This will be particularly necessary for oceanic, terrestrial, and geological sequestration. New sensors will need to be developed to measure carbon speciation in soils and CO_2 chemical and physical behavior in geological formations. (3) We must have measurement systems to evaluate impacts due to carbon sequestration. These impacts will need to be shared with the public. This will require development of sensors and monitoring systems for measurement of possible impacts in ocean, geologic, and terrestrial reservoirs. (4) Carbon sequestration will need to be monitored and verifiable if it is to play a role in international agreements.

8.5.2 Carbon Processing Platforms

The first technology platform is carbon processing. The focus of this platform is the development of advanced chemical technologies, which are in turn platforms for capture and separation and the development of technologies with collateral benefits. The effectiveness of capture and separation technologies in isolating relatively pure CO_2 for transport and sequestration will also determine the potential efficacy of geological and ocean sequestration options. The technology platforms that will be required include:

- Chemical/physical absorption, such as the synthesis of novel absorbents
- Chemical/physical adsorption
- Advances in membrane technologies, such as the development of polymeric membranes for increasing dissolution/diffusion rates
- Mineralization/biomineralization, such as developing better reaction paths for formation of carbonates and bicarbonates for geologic and ocean dissolution and sequestration
- Low-temperature distillation systems
- Novel concepts, such as better methods for producing CO_2 clathrates and use of algal bioscrubbers on emissions streams

Capture and separation technologies can also be developed based on engineering and/or chemistry advances of existing technologies already being used in industries such as oil and gas refineries. An important side benefit can be the capture and separation of hydrogen to be used as a clean fuel.

Advances in chemistry research can specifically support oceans and geological sequestration. Geological sequestration will require a better understanding of corrosion, as well as of silicate/carbonate complex interactions. Research will be needed in chemistry and materials sciences to support these geological options. Chemical research in biomimetic processing and the production of clathrates can enhance the effectiveness of engineered solutions for the sequestration of CO_2 in the oceans. In particular, the ability to sequester carbon as bicarbonates or carbonates cost-, resource-, and energy-efficiently will markedly increase the time for which carbon is effectively sequestered.

Chemistry research also has the best potential for developing collateral benefits. Carbon species can be manufactured into commercial commodities, thus giving sequestration an additional economic driver for commercialization. Two problems exist with this approach. First, removing carbon prior to combustion may increase its economic potential but will reduce its energy content. Second, the current market cannot properly use the potentially large amounts of carbon-containing materials produced as part of these processes. New markets and uses will need to be created. Some of these may be in the development of durable materials that could be used for construction materials or soil amendments. Other enabling technologies that would be developed as part of this research would include new catalysts, chemical sensors, and manufacturing process chemicals.

It is important to note that, while there is a huge amount of information on the inorganic and organic chemistry of carbon dioxide, sequestration needs will require new breakthroughs.

8.5.3 Biological Absorption Platforms

Biological absorption is the second system technology platform. Scientific research in this area will be necessary to enhance the ability of terrestrial and soil sinks to sequester CO_2, which will be based on advanced biological research. Plant sciences must develop new rapid-growing species and new, commercially viable woody species. Genetic engineering and molecular biology advances must be used to create new plant species and enhance microbial rhizospheres to increase plant productivity. Research must be done to increase understanding of soil biogeochemistry to enhance carbon uptake and sequestration in soils. As is the case with ocean sequestration, ecosystem dynamics must be better understood to evaluate potential impacts of new farming methods, introduction of new species, control of pests, and increased carbon content in soils. Finally, a potential way of enhancing ocean sequestration may be coupled with advanced biological research. Bioengineered solutions for increasing the primary productivity of oceans will allow for improved biological mechanisms of increased CO_2 uptake. Additionally, the development of algal scrubbers for CO_2 separation and capture may enhance technologies in this area.

8.5.4 Engineered Injection Platforms

The third key system technology platform is engineered systems. The emphasis for sequestration in oceans and geological sinks is similar: although progress has been made in the geological arena, improved injection systems must be developed to enhance the delivery of CO_2 to these sinks. In addition, many research advances in chemistry will require innovative engineered systems to effectively implement new technologies.

All of these findings are interrelated. For example, ocean and geological sequestration will not be effective unless efficient capture, separation, storage, and transportation technologies are developed to deliver CO_2 to sink locations. Capture and separation technologies in turn must rely on advances in chemistry and concomitant engineered solutions to make these technologies efficient and cost-effective.

It is clear from Tables 8.1–8.3 that the technology platforms are not all equally developed. One of these platforms, short-term storage, has not been examined at all because the carbon capture and sequestration system has not yet been sufficiently specified. It is included simply because the current natural gas transmission system, although small by comparison to an eventual CO_2 transmission system in terms of gas volume, requires large short-term storage capacity to operate.

Other platforms, such as integrated carbon generation and recovery, are bridges to other road-mapping efforts. For instance, the road map supporting Vision 21 (a proposed description of the future evolution of fossil fuel technology) is considering modifications to fossil power systems that could significantly simplify the capture of CO_2. Some platforms, such as CO_2 transportation or engineered injection, are brief because of an assumption that a great deal of experience has already been accumulated in these areas. This assumption will require further examination after a more detailed system engineering picture of a carbon capture and sequestration system is developed.

The most elaborated platforms are carbon processing and biological absorption. This is natural for the carbon processing platform because of the wealth of known chemical engineering techniques that might be adapted to this problem. This platform will become more focused as the conditions under which carbon must be captured and processed become more clear from system analysis and other energy and fossil fuel transformation road maps.

On the other hand, one might expect the elements within the biological absorption platform to expand even further as the wealth of possibilities presented by progress in the biological sciences is further explored. This richness is also reflected in the technology components supporting this platform.

The inclusion of the biological absorption platform is a genuine departure from traditional lines of energy technology development. It brings with it ties to agricultural and ecological research that have been tenuous at best in the history of energy development. Once carbon capture and sequestration become a feature of energy planning, scientific and technological progress in these fields assumes a key role in future energy development.

Recognizing linkages between disparate fields of knowledge such as these is a key feature of the road-mapping process. Developing and exploiting these linkages requires further effort.

8.6 NEXT STEPS

This chapter has described the first stage in developing an emerging technology road map for carbon capture and sequestration. Starting from a potential DOE policy goal, the technology system to achieve that goal has been sketched out. The areas of scientific and technological development needed to support this general technology system have been identified, including new areas foreign to traditional energy technology development.

Although mutual relationships and dependencies of scientific and technological development in all of these fields have been identified and are indicated by the links in Fig. 8.2, the corresponding performance requirements have not yet been developed. Nor has the phasing of potential R&D schedules been considered. Overlaps have been eliminated to some extent, but priorities and gaps in the technology needs have not been examined. More work needs to be done on specifying the economic constraints and technology needs of the integrated carbon capture and sequestration system illustrated in Fig. 8.1. This work can be done in parallel with the steps outlined in the following paragraphs, but it must be done to provide substance to the final road map.

The road map outline described is a valuable product. It should be used as a framework for Phase II of the Carbon Sequestration Road Map in developing a quantitative evaluation of the science and technology requirements for a carbon sequestration system. This is an essential aspect of building a usable road map with all of the requisite characteristics.

Road maps should integrate planning and implementation. The road map should consider all the plans of the organization, such as mission and visioning, market analysis, and portfolio analysis. But it goes beyond mere vision to develop a general plan for developing capabilities. Actionable items should naturally flow from the road map. The primary purpose of the emerging technology road map is to influence future events, not to predict them. Program objectives set for the future should, of course, be based on realistic expectations about market, policy, and technical trends. However, no one can predict the future. The value of emerging technology road maps derives from the fact that the future can be shaped by new technological developments. Road maps are intended for revision. A road map is not a plan for the future that is unchangeable when it is completed. As events unfold and new research results emerge, the plan must be changed to address the most current state of knowledge—and to build beyond the new frontier. The road map should provide a mechanism for accommodating serendipity—external events and new research results that should be incorporated into the technology development plans. The process of reaching a consensus is as important as the product. To be truly effective, the road map should be a vision of the future reached by consensus among all parties who have responsibility for the R&D—the funders, developers/deliverers, and implementers/users of technology.

Thus, the process of road mapping is as important as the final product of the process—the road map itself. Frequent communication with upper management along the way, involvement of all layers and functions of the DOE organization, and stakeholder participation are keys to success. Based on the results obtained so far, the stakeholders include other government agencies and the agricultural industry in addition to the energy industry. Many different views and priorities must be considered and synthesized into a coherent plan to carry out R&D on carbon capture and sequestration. This will develop the support needed as DOE attempts to implement the emerging technology road map.

9 FINDINGS AND RECOMMENDATIONS

Vision

"To protect the climate cost-effectively, technology breakthroughs, technology incentives, and the elimination of barriers for the deployment of existing technologies are needed. Broad-based cooperative programs to stimulate markets and develop and disseminate new and existing technology to industrialized and developing countries must be a high priority" (World Resources Institute, British Petroleum, General Motors, Monsanto 1998).

The options for sequestering carbon are diverse. Some are being implemented already, and others will require advances in scientific and engineering disciplines. Many options will require long lead times prior to implementation. In this chapter we identify issues central to the development of an R&D program that would enable us to make viable carbon sequestration options available for the 2025 to 2050 time frame.

The existing R&D program should be expanded soon. If carbon sequestration is to have a significant impact, it will necessarily involve changes of a large magnitude. Decisions made today about the energy infrastructure are likely to be with us for the greater part of a century. New information will help us develop an infrastructure with the flexibility to operate in tandem with carbon sequestration options. Therefore, research should anticipate substantially any necessary carbon reduction efforts.

For carbon capture and sequestration to become a viable large-scale option, it must be cost-competitive, safe, and acceptable. The R&D program should be oriented toward understanding more fully the fate of sequestered CO_2 and the impacts it will have on the environment and on human safety, and toward developing options to ensure a flexible response.

Given the federal government's role in supporting high-risk R&D in the long-term national interest, a carbon sequestration research and technology development program should be significantly expanded on the strength of the eventuality that such technology will be needed in the energy marketplace some time in the first quarter of the next century. This message is consistent with a recent report of the President's Council of Advisors on Science and Technology and other investigations. We should begin this R&D now, because the options available in 2025 and beyond will be determined by research being conducted today.

The first section of this chapter discusses overarching issues that became apparent during the development of this preliminary road map. They are key aspects of carbon sequestration that must be acknowledged and addressed in the planning and implementation of an expanded R&D program. The second section presents our recommendations resulting from an analysis of the focus areas discussed in the previous chapters and from discussions during the workshops.

The implementation of carbon capture and sequestration science and technology must be based on public acceptance. Even though some strategies seem inherently beneficial (e.g., planting more forests and protecting wetlands), it may be a challenge to gain public acceptance of some sequestration options because of their large scale, the fact that they are new and may be viewed as adding costs without adding value, and uncertainties about their environmental consequences. Although some current sequestration activities are presumably safe and benign, such as the Sleipner West Project in the North Sea, other options have largely unknown consequences.

Some sequestration options with potentially large environmental impacts may evoke strong concerns from the public. Whether a sequestration option is successful will depend not only on predicted consequences but also on public acceptance, based upon understanding of benefits and costs.

9.1 FINDINGS

- **Carbon sequestration is a broad topic with many internal linkages; combining processes often can provide ancillary benefits**

The ancillary benefits of many carbon sequestration options are appealing. Thus one of the ways to improve the prospects for carbon sequestration is to combine different processes and benefits so that the larger system is more attractive than individual parts. One example is the increased production of oil that would result from the use of CO_2 for enhanced oil recovery or the enhanced production of methane from injecting CO_2 into coal beds—sequestering CO_2 while extracting fossil resources. Another example discussed in Chap. 6 on advanced biological processes is the energyplex, referred to by DOE as the "Vision 21 Plant," which is a series of modular plants (an industrial ecosystem) that integrate the production of power, heat, chemicals, and fuels to maximize the use of available energy while capturing and sequestering carbon emissions. Another example of combining processes would be using captured carbon to make construction materials or soil enhancements that would otherwise be unavailable.

As Fig. 8.1 in Chap. 8 illustrates, carbon sequestration involves many technological paths and connections or feedbacks. The need to connect processes is evident. Costs and capacities of alternative sequestration options must be based upon consistent assumptions. For instance, the characteristics of a particular CO_2 stream—its location, temperature, pressure, concentration, or impurities—may make it more suitable for sequestration in one type of sink, such as a geological formation, than in another, such as an ocean.

The number of disciplines involved in carbon sequestration R&D is large. Much can be gained by coordinating research programs with related scientific and engineering activities; for example, scientists studying the oceanic carbon cycle and deep sea injection may need to collaborate with the offshore energy companies developing deep-sea technology.

We found that many research topics involve critical links in several of the focus areas. The development of monitoring systems is important across all the focus areas, and advanced biological and advanced chemical topics have potential impacts in several focus areas. In addition, for sequestration options that cannot rely on taking CO_2 directly from the atmosphere, efficient CO_2 capture, separation, and transportation methods are critical. If the cost of capture is very high or the delivery system cannot accommodate the large amount of carbon that must be sequestered, no degree of cost reduction or efficiency improvement for any sequestration option would be sufficient for it to compete with other carbon reduction efforts.

- **Many carbon sequestration options can work within the existing infrastructure; other scenarios would require a new distribution system**

A primary benefit of many sequestration options is that they use the existing infrastructure; indeed, sequestration may allow for continued use of fossil fuels and may be based upon current infrastructure. Sequestration also is consistent with the development of new advanced fossil-fuel-fired generation plants. Sequestration is likely to start with the easiest opportunities, which may require few infrastructure changes, such as the Sleipner West project in the North Sea or improved agricultural and forestry practices.

Other scenarios might require significant infrastructure changes. For instance, shifting to hydrogen-powered transportation to reduce carbon emissions would require a new hydrogen distribution system. The issues in developing a new distribution system, perhaps by making it cost-competitive before it reaches a critical size, are outside the purview of this report, but they are significant.

- **Carbon sequestration is an appropriate topic for government-sponsored R&D, which will be critical to successful implementation**

The prior findings suggest carbon sequestration is not a trivial challenge. The integration required to obtain industrial participation, address environmental issues, and gain public acceptance suggests that an expanded government initiative is needed. In addition, unlike for clean energy and energy efficiency, no economic or regulatory incentives exist at this time for carbon sequestration, suggesting the need for more governmental than private responsibility for support of research and technology development programs. This conclusion was also reached by the DOE-sponsored Stakeholders’ Workshop on Carbon Sequestration held in June 1998 (Herzog 1998), at which industry sent a strong message that “the research agenda for the moment must be led, and funded, by government.”

Most possibilities for carbon sequestration involve immature technologies and ideas. The carbon sequestration options include topics that are inadequately investigated compared with many other energy research areas, making the opportunities for significant breakthroughs high. Government-sponsored R&D could result in surprising advances that might change the rules of the game. Although little private sector R&D is under way at this time, there is evidence (witness recent announcements by British Petroleum and others) that the private sector will attempt to implement carbon mitigation approaches that are known to be technically and economically feasible. Domestic and international forest projects also are being conducted by the electric utility industry. These may offer unique opportunities for an R&D program to identify complementary links to industrial practices that could lead to early demonstration opportunities.

- **Some carbon sequestration options could be used as near-term measures until other carbon management technologies, including other carbon sequestration technologies, can be implemented**

There is much we cannot predict with confidence about the reaction of the natural system to increases in atmospheric CO_2 concentrations. There may be “nonlinear” responses derived from positive feedbacks. An altered climate could bring an increased release of greenhouse gases through, for instance, more rapid mineralization of soil organic material, altered ocean currents, or offgassing of CO_2 and/or methane from permafrost regions.

If scientists were to predict with some degree of reliability that there would be a nonlinear response in the near future, it might result in the need to emphasize development and implementation of near-term sequestration alternatives even though the lifetime of the sequestered carbon might be less permanent than is desirable. In this case, one sequestration option might target R&D to provide techniques and technologies to stall the nonlinear response until some other more permanent solution could be implemented.

9.2 RECOMMENDATIONS

9.2.1 Beginning the R&D Program

The following recommendations should apply to the carbon sequestration research program.

- **Ensure that the carbon sequestration research program develops technologies and practices that are cost-effective and benign**. For carbon sequestration to be a viable option, it must compete favorably with other carbon management programs with respect to cost and effectiveness. Carbon sequestration should be safe, predictable, reliable, measurable, and verifiable. Research programs should lead to these ends. To be cost-effective, the research program will need to reduce costs associated with the current separation and sequestration technologies and processes and support the development of new, innovative technologies and processes.

- **Ensure that the research is integrated with other, related**

research programs. The research program will be linked to related, ongoing research programs so as to leverage the efforts. For instance, results from biomass or carbon cycle research could help in developing the biological understanding needed for terrestrial sequestration.

The research program should be conducted collaboratively among the offices in DOE and with other government agencies. Ties to other countries through research programs or through scientific bodies, such as IEA's Greenhouse Gas R&D Programme, should be made. The research program should also collaborate with the research and other activities undertaken by the private sector.

- **Ensure that the research program is flexible and targets a wide variety of approaches.** Carbon sequestration is an immature field, so multiple approaches and scales are warranted. There are many prospects for significant advances. An expanded R&D program should be broad-based, including both basic and applied, theoretical, laboratory, and field-based research, and all sources and sinks. A robust R&D program is needed that has the flexibility to evolve over time as new scientific advances are incorporated into the overall energy system. For example, deregulation of utility companies may lead to market penetration by highly distributed power systems whose individual emissions would be difficult to capture, aggregate, and sequester. Changes in the availability of oil and in the use of nuclear power because of geopolitical reasons could alter the energy mix and the accompanying CO_2 emissions. Future demand for materials made from CO_2, such as acetate or bioplastics, may increase dramatically. Changes in other related technologies, such as batteries and fuel cells, will influence the effectiveness of various technology pathways. Our understanding of the safety and potential environmental consequences of various sequestration options will evolve. An approach is needed that has a long-term goal but has the flexibility to respond to changes in public policy and energy systems, as well as to the successes and failures of its own research activities.

- **Initiate field-scale investigations to help guide other carbon sequestration research and increase understanding of processes at the field scale.** An important facet of any carbon sequestration R&D program will be to include some early field-scale investigations. Some sequestration options may be sufficiently ready for pilot- or field-scale research, such as sequestering CO_2 in soils and vegetation, geological formations, or in deep coal beds from which methane is extracted. Selection of these investigations should be based on existing information and the opportunities for early results that could provide rapid assessment and feedback to fundamental R&D needs. Large-scale long-term field studies should test research concepts and reduce economic, environmental, and operational uncertainties associated with the new technologies.

- **Ensure that the research program develops an integrated approach to setting R&D priorities and evaluating the probability of success for different sequestration options.** One potential research topic is the development of an integrated framework for carbon sequestration. A context for the overall research program would be useful because so many of the issues cross disciplines and related activities. The integrative modeling would include investigations into life-cycle analysis, risk, uncertainty, and, to the extent possible, economics. One goal would be to generate a clear model of the carbon flows, including the form that the carbon takes (gaseous, compressed liquid, elemental, carbonate, clathrate, etc.). A second goal would be to keep track of the upstream "costs" associated with the carbon in the form in which it is found. It is important to measure the energy penalties associated with providing carbon in a particular form at any particular place in the system. This research would precede actual economic analysis of many of the more complicated sequestration options.

- **Ensure that the results of the R&D program are provided to policymakers to aid them in developing policy and selecting the most efficient and effective solutions to the issues of climate change.** This report is not intended to modify the policy process that determines what, if anything, should be done about climate change. But those policy processes should be informed about the availability, costs, and ancillary benefits of various sequestration options. Research and reporting on monitoring, verification, effectiveness, and environmental consequences of carbon sequestration technologies and practices are an essential element in an iterative process, the goal of which is to help policymakers design more efficient and effective solutions to carbon management.

9.2.2 Developing the Road Map

The following recommendations should apply to the continuation of this road map.

- **Criteria for setting research priorities should include the magnitude of the impact of the carbon sequestration option.** Further development and refinement of this road map could include setting priorities for the research. Many priorities and discussions of staging—that is, which research topics should be conducted first and which should come later—are included in the focus area chapters 2–7. Chapter 8 offers further general criteria that could be used in setting priorities. Although sequestration will likely be achieved through the use of a number of technologies, only those research topics should be targeted that have the potential for significantly reducing CO_2 emissions with acceptable environmental impacts and costs (in either real dollars or energy losses). Longer-term research should focus on the benefits of sequestration mechanisms that will be effective on scales from multiple decades to millennia. Those approaches with shorter sequestration time horizons will provide important relief in the short term, but they must be augmented with more substantial solutions in the longer term.

- **This roadmap should be developed further and refined.** This report is only a first step and should be enhanced by engaging a broader community in discussions of the various sequestration pathways outlined in the roadmap. The understanding of carbon sequestration is still in its early stages, and R&D pathways are still being formulated. Technology pathways are outlined in this road map, but more explicit pathways can be generated for some of the focus areas. Some explicit recommendations are made in the focus area chapters, but phasing of potential R&D schedules has not been done. The next step should include more intense participation by stakeholders, such as the private sector and non-governmental organizations.

9.3 PRINCIPAL FOCUS AREA RECOMMENDATIONS

9.3.1 Separation and Capture of CO_2

There are numerous options for the separation and capture of CO_2, and many of these are commercially available. However, none has been applied at the scale required as part of a CO_2 emissions mitigation strategy, nor has any method been demonstrated for all the anthropogenic sources considered in this R&D map. Many issues remain regarding the ability to separate and capture CO_2 from anthropogenic sources on the scale required, and to meet the cost, safety, and environmental requirements for separation and capture. In our assessment of the scientific and technological gaps between the requirements for CO_2 separation and capture and the capabilities to meet these requirements, many explicit and specific R&D needs were identified.

- Geologic or ocean storage sequestration options that use a concentrated source of CO_2 require low-cost carbon separation and capture techniques to be viable options. The scale of the industrial system required to process gigatonnes of carbon warrants investigation into new solvents, adsorbents, and membrane separation devices for either pre- or post-combustion separation.

- A science-based and applications-oriented R&D program is needed to establish the efficacy of current and novel CO_2 separation processes as important contributors to carbon emissions mitigation. Important elements of such a program include the evaluation, improvement, and development of chemical and physical absorption solvents, chemical and physical adsorbents, membrane separation devices with selectivity and specificity for CO_2-containing streams, molecular and kinetic modeling of the materials and processes, and laboratory-scale testing of the selected processes.

- Field tests are needed of promising new CO_2 separation and capture options in small bypass streams at large point sources of CO_2, such as natural gas wells and hydrogen production plants.

9.3.2 Ocean Sequestration

- The ocean provides a large potential reservoir. Active experiments are already under way in iron fertilization and other tests of enhanced marine biological sequestration, as well as deep CO_2 injection. Improvements in understanding marine systems will be needed before implementation of major marine sequestration campaigns.

- Field experiments of CO_2 injection into the ocean are needed to study the physical/chemical behavior of the released CO_2 and its potential for ecological impact.

- Ocean general circulation models need to be improved and used to determine the best locations and depths for CO_2 injection and to determine the long-term fate of CO_2 injected into the ocean.

- The effect of fertilization of surface waters on the increase of carbon sequestered in the deep ocean needs to be determined, and the potential ecological consequences on the structure and function of marine ecosystems and on natural biogeochemical cycling in the ocean need to be monitored.

- New innovative concepts for sequestering CO_2 in the ocean need to be identified and developed.

9.3.3 Carbon Sequestration in Terrestrial Ecosystems

- The terrestrial biosphere is a large and accessible reservoir for sequestering CO_2 that is already present in the atmosphere. Natural carbon fluxes are huge, so that even small forced changes resulting from R&D advances would be very significant. It will be important to address the consequences of altering the natural flux.

- The terrestrial ecosystem is a major biological scrubber for atmospheric CO_2 (present net carbon sequestration is ~2 GtC/year) that can be significantly increased by careful manipulation over the next 25 years to provide a critical "bridging technology" while other carbon management options are developed. An increase in carbon sequestration to perhaps as much as 5 to 10 GtC/year may be achieved as a result of directed R&D. Ecosystem protection is important and may reduce or prevent loss of carbon currently stored in the terrestrial biosphere. The focus for research, however, should be on increasing the rate of long-term storage in soils in managed systems.

- Research on three key interrelated R&D topics is needed to meet goals for carbon sequestration in terrestrial ecosystems:

  — Increase understanding of ecosystem structure and function directed toward nutrient cycling, plant and microbial biotechnology, molecular genetics, and functional genomics.

  — Improve measurement of gross carbon fluxes and dynamic carbon inventories through improvements to existing methods and through development of new instrumentation for in situ, nondestructive belowground observation and remote sensing for aboveground biomass measurement, verification, and monitoring of carbon stocks.

  — Implement scientific principles into tools such as irrigation methods, efficient nutrient delivery systems, increased energy efficiency in agriculture and forestry, and increased byproduct use.

- Field-scale experiments in large-scale ecosystems will be necessary to understanding both physiological and geochemical processes regulating carbon sequestration based upon integrative ecosystem models. Such carbon sequestration experiments are needed to provide proof-of-principle testing of new sequestration concepts and integration of sequestration science and engineering principles.

9.3.4 Sequestration in Geological Formations

Although there is extensive industrial experience in geologic sequestration of CO_2, many important issues must be addressed to reduce costs, ensure safety, and gain public acceptance. Implementation of the recommendations outlined will provide the information and operational experience needed to address these issues.

- Limited geological sequestration is being practiced today, but it is not yet possible to predict with confidence storage volumes and integrity over long time periods. Many important issues must be addressed to reduce costs, ensure safety, and gain public acceptance.

- Fundamental and applied research is needed to improve the ability to predict, optimize, and monitor the performance of sequestration in oil, gas, aqueous, and coal formations. Elements of such a program include multiphase flow in heterogeneous and deformable media; phase behavior; CO_2 dissolution and reaction kinetics, micromechanics and deformation modeling; coupled hydrologic-chemical-mechanical-thermal modeling; and high-resolution geophysical imaging. Advanced concepts should be included, such as enhancement of mineral trapping with catalysts or other chemical additives, sequestration in composite geologic formations, microbial conversion of CO_2 to methane, rejuvenation of depleted oil reservoirs, and CO_2-enhanced methane hydrate production.

- A nationwide assessment is needed to determine the location and capacity of the geologic formations available for sequestration of CO_2 from each of the major power-generating regions of the United States. Screening criteria for choosing suitable options and assessing capacity must be developed in partnership with industry, the scientific community, and public and regulatory oversight agencies.

- Pilot-scale field tests of CO_2 sequestration should be initiated to develop cost and performance data and to help prioritize future R&D needs. The tests must be designed and conducted with sufficient monitoring, modeling, and performance assessment to enable quantitative evaluation of the processes responsible for geologic sequestration. Pilot testing will lay the groundwork for collaboration with industrial partners on full-scale demonstration projects.

9.3.5 Advanced Biological Processes

The 21^{st} Century has been referred to as the “Century for Biology.” Indeed, many new molecular tools have been developed that will aid in new discoveries and assist in providing solutions to key problems facing humankind and the planet. The difference that advanced biological techniques can make will be evident when they are integrated with land, subsurface, and ocean management practices. The following recommendations will promote cost-effective and stable biological solutions to carbon sequestration.

- Advanced biological techniques may produce improvements too radical to predict. Biologic processes can yield sequestered carbon products at the least cost. New carbon sequestration options could become feasible and others could be improved using advanced biological techniques.

- Research should be initiated on the genetic and protein engineering of plants, animals, and microorganisms to address improved metabolic functions that can enhance, improve, or optimize carbon management via carbon capture technology, sequestration in reduced carbon compounds, use in alternative durable materials, and improved productivity.

- The objectives and goals of the advanced biological research should be linked to those specific problems and issues outlined for carbon sequestration in geological formations, oceans, and soils and vegetation so that an integrated research approach can elucidate carbon sequestration at the molecular, organism, and ecosystem levels.

- Short-, mid-, and long-term goals in advanced biological research should be insituted so that a mimetic yardstick can be employed to assess scale-up issues, genetic stability in natural settings, and efficacy in the field.

9.3.6 Advanced Chemical Approaches

- Most carbon sequestration options rely on chemical reactions to achieve benign, stable, and inert products. Studies to enhance the relevant chemistry almost certainly will reduce the costs or increase the effectiveness of these options. Results from R&D on advanced chemical topics also may make it possible to generate useful and marketable byproducts.

- The proper focus of R&D into advanced chemical sciences and technologies is on transforming gaseous CO_2 or its constituent carbon into materials that either are benign, inert, long-lived and contained in the earth or water of our planet, or have commercial value.

    — Benign by-products for sequestration should be developed. This avenue may offer the potential to sequester large (gigatonne) amounts of anthropogenic carbon.

    — Commercial products need to be developed. This topic probably represents a lesser potential (millions of tonnes) but may result in collateral benefits tied to pollution prevention.

- The chemical sciences can fill crucial gaps identified in the other focus areas. In particular, environmental chemistry is an essential link in determining the impact and consequences of these various approaches. Studies to address the specific gaps identified in Chap. 7 should be conducted to ensure that other focus areas meet their potential.

9.4 REFERENCES

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Appendix A

CARBON SEQUESTRATION WORKING PAPER CONTRIBUTORS AND WORKSHOP ATTENDEES

Appendix A

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Note: Bold text indicates attendees at October 28–29, 1998, workshop

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Appendix B

DETAILED DESCRIPTIONS OF ECOSYSTEMS AND RESEARCH AND DEVELOPMENT NEEDS

Appendix B

DETAILED DESCRIPTIONS OF ECOSYSTEMS AND RESEARCH AND DEVELOPMENT NEEDS

1. Forests (Rich Birdsey, Mac Post, Marilyn Buford, Ken Skog)

Long-term baseline estimates show that increases in biomass and organic matter on U.S. forest lands from 1952–1992 added 281 MMTC/year of carbon to forest ecosystems (25% of U.S. emissions for the period). Projections suggest continuing increases averaging 177 MMTC through 2040. For the period 1990–92 approximately 250 MMTC/year were sequestered in standing trees (~50%), and forest floor/coarse woody debris/ soils (~50%). The gain in forests is net of wood removed for products, and net of mortality from all causes including fire, pests, and disease. Carbon in wood used for products in 1990 was added to the pool of carbon in products in use, and products in landfills—for an additional net increase of carbon in products of about 60 MMTC/year.

Research on basic processes, measurement and monitoring, implementation methods and risk assessment in the forestry sector can provide cost-effective, environmentally sound methods in which to sequester more carbon. But, evaluation of the most effective forestry sector methods requires life cycle analyses that compare tradeoffs among alternate ways to use land area (forest and nonforest) for products for sequestration, and among alternate products (forest- and nonforest-based) to satisfy end use-needs. With that caveat, it is clear that research in a number of areas can improve forest sector contributions to sequestration. Areas where research is needed to improve cost effectiveness and environmental effects knowledge include: afforestation of marginal cropland; reducing deforestation; reforestation and improved forest management for sequestration; substituting wood products for more energy intensive products; reducing energy use in timber growing, harvesting, product production, and in end use; reducing wildfires; use of biomass fuel in place of fossil fuel with regrowth of biomass; increasing the amount of carbon in durable wood products and uses; increasing paper and wood recycling; planting trees in urban and suburban areas; enhancing soil carbon through species selection and management practices, including understory and ground cover management.

Current capabilities

Research is conducted in a broad range of forest sector disciplines that contribute to an understanding of, and means to alter, carbon accumulation in forests and forest products. These include soil science, tree physiology, tree genetics, ecological systems, forest pathology, forest entomology, forest mycology, fire science, forest mensuration, silviculture, forest management, forest economics, forest operations, wood products technology, and pulp and paper science.

Future needs

Research needs to be focused on (1) understanding basic biological, industrial, and socioeconomic processes that can increase sequestration in the forestry sector, (2) measurement, monitoring, and modeling of ecosystem function and the forestry economic sector to evaluate the effectiveness of means to alter sequestration, (3) evaluation of alternative combinations of alterations to the forestry sector to increase sequestration and compare them to other uses of land and use of nonwood products for end-use needs (life cycle assessment), and (4) evaluation of risks of unwanted changes to ecosystem functions.

Strategies and objectives

Afforestation of marginal cropland and pasture. Substantial gains in carbon storage in biomass and soils on afforested lands are possible. This technology is limited primarily by the availability of suitable land (for ecological or economic reasons), nursery capacity, willingness of landowners to participate, and availability of technical assistance. Size of program and cost estimates vary widely because of differences in how and where proposed programs would be implemented and because of differences in carbon accounting. If the new forest land is managed for wood products, then the disposition of carbon in wood products, byproducts, and disposal must also be considered.

Improved forest management. There are opportunities to improve carbon storage by changing silvicultural practices on certain sites and forest conditions. The magnitude of increased carbon storage may be difficult to quantify since silvicultural practices are usually developed and applied for another purpose, such as increasing timber growth, and will not necessarily increase biomass growth and soil carbon storage. Nevertheless, some forest stands may not be growing at biologically potential rates because of suboptimal stocking levels. These stands offer the best opportunities for enhanced carbon storage. Also, silvicultural practices may be designed to maximize the amount of carbon eventually stored in harvested wood products.

Reduce conversion of forest land to nonforest use (reduce deforestation). Conversion of forest land to nonforest use usually means permanent loss of all or a substantial part of live biomass and reduction of organic matter in soils and the forest floor. CO_2 and other greenhouse gases are emitted when the removed biomass and organic matter is burned or decomposes. Some carbon may be sequestered in wood products if the removed biomass is utilized. Protecting and conserving forests should maintain or increase carbon pools in the short term, as long as natural disturbance rates do not reach catastrophic levels.

Increase sequestration of carbon in wood and paper products. Wood harvested from forests remains sequestered and is emitted to varying degrees depending on how products are made, used, and disposed of. Sequestration in products and uses can be increased by altered processing methods, shifts in products used, shifts in end-use durability, and shifts in landfill management. Sequestration in forests and products can be increased by coordinated understanding of forest ecosystems and products utilization.

Objectives

Aboveground

- Increase and maintain area of forest cover.
- Maximize biomass accumulation.

- Maximize average standing stock of biomass.
- Increase carbon retention in wood products and landfills.

Objectives

Belowground

- Increase and maintain area of forest cover.
- Increase soil organic matter on depleted soils.
- Minimize soil and litter disturbance during forest operations.
- Employ management techniques that increase soil organic matter in existing forest.

Research and development needs understanding

Aboveground

- Develop genetically improved plantation species to maximize growth and wood density.
- Develop silvicultural practices (e.g., stocking control, understory management, and prescribed burning) that maximize biomass accumulation.
- Enhance wood and paper products characteristics that increase sequestration (e.g., durability, lignin, recyclability).
- Improve understanding of the interactions between natural disturbances (weather, fire, pests), management practices, and forest protection, with regard to impacts on long-term carbon storage.
- Determine socioeconomic causes (e.g., social institutions) of deforestation.

Belowground

- Develop silvicultural practices and/or selections of species or genotypes that result in a higher humification efficiency (i.e., increase the fraction of dead organic matter that is converted into stable soil humus during decomposition). Much of the litter applied to the surface, including most wood, never enters the soil as humus. Material that enters via the soil has a higher humification efficiency. Material that has a higher lignin content has a higher humification efficiency. Research is needed to assess species or management that affects allocation and tissue composition on soil carbon accumulation.
- Litter and soil decomposition is affected by a number of physical, chemical, and biological factors. Physical factors amenable to management include soil temperature and moisture. Chemical factors include nutrient content and pH. Biological factors include microorganisms, micro- and macro-invertebrates. Research to determine manipulations of these factors to decrease decomposition rates without drastically affecting tree growth is required. Research to create deeper rooting zones would also be important.

Measurement

Aboveground

- For major ecoregions, quantify the potential biomass gains from converting agricultural use to forest using different stand establishment techniques and species (comparative cross-sectional studies; existing long-term research sites).
- Identify existing forest conditions that result in suboptimal biomass accumulation.

- Compare carbon mitigation of burning wood, recycling wood/paper, shifting to longer-lived uses, landfilling (with limited decay).
- For monitoring and verification of changes in aboveground carbon storage, improve and integrate use of data from forest inventory, remote sensing, and Ameriflux collection methods.

Belowground
- For major ecoregions, quantify the potential soil carbon (including organic layers) gains from converting agricultural use to forest using different stand establishment techniques and species (comparative cross-sectional studies; existing long-term research sites).
- For monitoring and verification of changes in below ground carbon storage, improve national forest inventory collection of periodic data on soil organic matter, litter, and coarse woody debris.

Implementation

Aboveground
- Develop and use national models to identify high sequestration combinations of genetically improved species, forest management intensities, products utilization, and landfill management.
- Perform life cycle analyses for major tree species, silvicultural systems, and wood products. Note that this involves analysis of energy inputs throughout the life cycle.

Belowground
- Develop methods to improve the efficiency of the humification process for logging residue.

Assessment

- Evaluate the impact of changes in forest growth/sequestration on essential ecosystem functions.
- Evaluate the risk that disturbances to forests (e.g., fire, pests) and climate change induced changes in productivity or species viability may thwart various activities to increase sequestration.

General

- Develop interagency coordination of research and interagency coordination of strategies to increase sequestration.

Links to other ecosystems

- Use comparative studies to evaluate carbon tradeoffs from converting agricultural use to forest use.
- Understand the socioeconomic tradeoffs of converting agricultural use to forest use.
- Determine the impacts of deforestation to agricultural or developed use on major forest ecosystem carbon pools.

2. Agricultural and Grassland Ecosystems (Keith Paustian, Julie Jastrow, Margaret Torn, Ron Follett, Mary Firestone)

The carbon sequestration potential in agricultural and grassland ecosystems is primarily centered in the soil. Standing stocks of aboveground biomass are modest (typically < 10 Mg C/ha) compared to forests and, in the case of annual crop systems, may be entirely absent for part of the year. In contrast, grassland and agricultural soils may contain several hundred mg/ha of carbon, comparable to amounts aboveground in densely forested communities.

The high levels of carbon achievable in grassland and agricultural soils are the result of the accumulation of plant and microbial-derived residues which become increasingly recalcitrant through recurring cycles of decomposition by soil organisms. In addition, association of organic matter with soil minerals, through binding to colloidal surfaces and occlusion within soil aggregate structures, reduces their accessibility to microbial decay, enhancing organic matter accumulation.

Soil carbon levels are determined by the balance of carbon additions from roots and aboveground litter and the decomposition rates of the organic matter present in soils. Hence, carbon sequestration (i.e., increasing standing stocks of carbon) can be promoted by increasing carbon input rates, decreasing decomposition rates, or both. Carbon input rates are a function of the net productivity of plants, the allocation of that productivity between removals (i.e., harvest, fire) and residues returned to soil, and organic matter imports (e.g., manure, sludge). Soil organic matter decomposition rates depend on the composition and activity of soil organisms, which are influenced by their abiotic environment (temperature, moisture, aeration, mineral nutrients, pH), the physiochemical quality of the organic substrates (its chemical composition, particle size) and the accessibility of these substrates to soil organisms (influenced by soil texture and soil structure relationships). Ecosystem management to increase carbon stocks will be based on the manipulation of these controls on inputs and decomposition rates.

Current carbon sequestration capabilities of grassland and agricultural ecosystems

Cropland currently occupies about 150 Mha of land area in the U.S. (contiguous 48 states) with an additional 14 Mha of formerly cultivated lands in grassland and forest set-asides (mainly Conservation Reserve Program Lands). Agricultural and set-aside lands represent about 20% of total land area of the U.S. Soil carbon stocks (0–1 m) under cropland are on the order of 15–20 Pg (based on extrapolations from surface soil estimates (0–30 cm) by Kern and Johnson 1993)), compared to the 60–80 Pg total for all ecosystems in the contiguous U.S. (Kern 1994, Waltman and Bliss 1997). Historically, these lands have suffered a net loss of carbon, on the order of 5–6 Pg, following conversion of the native ecosystems to cropland. More recently, increased productivity and improved management practices have probably reversed this trend such that overall carbon levels have now stabilized or begun to increase (Cole et al. 1993, Lal et al. 1998). Existing management practices which are responsible for improving carbon levels include reduced tillage intensity, productivity increases through genetic improvements and increased management inputs (fertilizer, pesticides, irrigation); intensified crop rotations (e.g., reduced summer-fallow); and set asides of marginal cropland to perennial vegetation, mainly grasses (Paustian et al. 1997). Recent estimates of the potential for carbon sequestration in U.S. agricultural soils, using existing technologies, are on the order of 50–200 Tg/year over the next 2–3 decades (Bruce et al. 1998, Lal et al. 1998). The range of these estimates reflects both uncertainties in carbon accumulation rates for different practices and soil/ climate conditions and uncertainty in the projected rates and extent of adoption of carbon conservation practices.

Grasslands include both extensively managed native rangelands as well as intensively managed pastures. In the lower 48 states, there are about 160 Mha of nonfederal rangelands and 50 Mha of pastures (1992 National Resource Inventory). Conventional management factors that can impact soil carbon levels on grasslands include grazing management, burning, species selection, and production inputs (i.e., fertilizer, irrigation). Intensively-managed grasslands (i.e., pastures), where productivity and management inputs are relatively high, probably have the greatest opportunities for increasing soil carbon through improved practices such as rotational grazing and application of fertilizers (Nyborg et al. 1997). On rangelands, traditional management is largely restricted to manipulating grazing intensity, which has variable impacts on soil carbon. In general, where vegetation cover and production of rangelands are not adversely affected by grazing, there is little change in SOM (Burke et al. 1997, Milchunas and Lauenroth 1993). Compared to agricultural lands, there is less field data upon which to base estimates of current carbon sequestration potential in grasslands. Bruce et al. (1998) estimated potential rates of sequestration for U.S. pastureland at 10 Tg/year. The greatest opportunities for carbon sequestration in rangelands involves rehabilitation of degraded areas. Unfortunately there is no existing national data base from which to estimate rangeland conditions and the potential for improvement of degraded rangelands. Widespread but slow rates of carbon sequestration may be occurring in many grasslands due to CO_2 fertilization and increased anthropogenic nitrogen deposition, but reliable estimates are currently lacking.

Strategies and objectives for carbon sequestration in grassland and agricultural ecosystems

Strategies for increasing carbon stocks in these soils revolve around maximizing the amount of carbon that can be delivered to the soil and subsequently maximizing its residence time in the soil (by reducing rates of decomposition). Ultimately nearly all carbon that enters the soil is recycled back to the atmosphere, but the amount of carbon in the soil will increase in direct proportion to its mean residence time. Since croplands and grasslands represent the primary food production systems for society, it’s important that carbon sequestration strategies be compatible with the maintenance of food and feedstock supplies. Fortunately, many measures to increase primary productivity also increase plant residue production, and increasing soil carbon levels are generally beneficial for maintaining highly productive systems. However, tradeoffs do exist. For example, increasing the yield component of crop plants without increasing total net productivity will come at the cost of reducing carbon inputs to soil, and retirement of cropland to perennial grassland (or trees) may yield higher carbon sequestration rates but with a loss of food production capacity.

A variety of strategies can be conceived to increase net primary productivity and carbon inputs to soil, through increased photosynthetic efficiency, increased nutrient and water use efficiency, and shifts in allocation of photosynthate to the belowground component. For extensively managed grasslands (rangelands), strategies to increase carbon inputs would be based largely on restoring degraded, poorly managed areas through control of invasive species, elimination of severe overgrazing, and active restoration on severely degraded rangelands. In pastures and croplands, a wider variety of more management-intensive strategies exist, including improved grazing management (e.g., rotational grazing); fertility management; pest control; species selection; and genetic improvements, including plant bioengineering.

On the decomposition side, strategies include manipulating the abiotic environment in favor of plant growth vs microbial (decomposer) activity, while still maintaining the function of the soil microbial community. For example, increasing water use efficiency of plant production (e.g., reduced summer-fallow, higher plant density, more efficient plant water extraction), reduces “excess” water, producing drier soils and reduced microbial activity. Many grass and crop species have lower temperature optima than the majority of microflora. Thus somewhat cooler temperatures (e.g., with use of surface mulches) may reduce decomposition rates while optimizing plant carbon inputs. Soil organic matter typically shows a substantial increase in age with depth (e.g., Paul et al. 1997) due, in part, to lower rates of decay at depth, from lower temperatures, reduced aeration and other factors. Thus, developing and/or using deeper rooting plants can place more carbon in locations where its residence time is increased. The susceptibility of plant residues to decay is influenced by their chemical composition, so that increasing the amounts of recalcitrant substances (e.g., lignin, polyphenols) in residues could enhance carbon storage. Decomposition rates in soils are inhibited by the close association of organic substances with mineral colloids (clays, oxides) and the occlusion of organic matter within soil aggregates. Tillage tends to reduce aggregate stability; thus reducing or eliminating tillage can help maintain the physical protection capacity of soils. Development of reduced and/or zero-tillage systems for a wider variety of crops and environments is an important strategy. Increased use of perennial grasses and legumes, alone or in rotation with annual crops, is effective in building soil carbon stocks. Other opportunities might include the use of artificial colloidal amendments to sorb and “protect” organic matter in soils. Finally, direct manipulation of microbial communities through bioengineering could conceivably be used to reduce decomposition rates, although the unlikelihood of success (i.e., a reduced ability to metabolize organic matter would make for poorly competitive organisms) and the potential for undesirable side effects (i.e., disruption of the biogeochemical cycling function of soils) argue against the desirability of such strategies.

Strategies to sequester carbon in agricultural and grassland ecosystems also need to factor in the carbon cost in terms of fossil fuel subsidies (e.g., fertilizer and herbicide production, farm machine use, irrigation pumping) for various production practices, as well as the potential effects on other soil-emitted greenhouse gases, chiefly N_2O and CH_4. Previously described strategies directed at increasing primary production efficiency (i.e., increased nutrient and water use efficiency), increased use of nitrogen fixation by legumes in crop rotations (to replace fertilizer nitrogen), increase dependence on mycorrhizae and adoption of zero-tillage systems (Frye 1984) would reduce fossil carbon requirements. Agricultural ecosystems are usually net sources of N_2O, particularly from soils with high amounts of inorganic nitrogen. In addition, methane is generated by ruminant livestock and also by waterlogged soils, notably rice paddies. While CO_2 is much more abundant in the atmosphere, N_2O and CH_4 are, molecule for molecule, more potent greenhouse gases relative to CO_2. The impact of carbon-sequestering practices on the potential emissions of these other gases, therefore, cannot be ignored. Although the secondary effects of carbon-conserving practices are often difficult to quantify, any proposed practice should be carefully assessed to ensure that the benefits in carbon stored are not seriously reduced by the emission of other gases.

Research and development needs

Research is needed to promote a better understanding of key soil processes, in order to assess how and to what degree they can be manipulated to promote carbon sequestration. In addition, there are major R&D needs that relate to the estimation and quantification of current and future carbon stocks as a function of environmental and management factors. These later needs cut across all the major ecosystem types.

For specific R&D priorities related to understanding controls on primary productivity and plant allocation, we refer to the section under Biomass Croplands. R&D priorities related to soil processes and controls and inventories of current and future carbon stocks are outlined below:

Research needs for fundamental understanding of soil processes and controls

A. Increase depth of soil carbon
   1) Species-soil-climate interactions controlling root depth distribution
   2) Controls on decomposition at depth
   3) Deep movement of organic and inorganic carbon
   4) Effect of tillage systems on rooting depth
B. Increase root mass
   1) Controls on aboveground to belowground carbon allocation for different plants
   2) Species selections that dramatically increase root mass
   3) Nutrient controls and feedback on productivity
   4) Adaptations to CO_2 increases, temperature increases, and pH tolerance
C. Transform Labile carbon to Recalcitrant carbon
   1) Isolation and characterization of recalcitrant organic matter
   2) Controls on formation of recalcitrant SOM
   3) Role of soil structure in SOM physical protection
   4) Role of soil minerals and cations on chemical protection of SOM
   5) Effect of litter quality on decomposition rate

  6) Effect of rhizodeposition and exudation on decomposition rate
  7) Effects of microbial community structure on SOM cycling and stabilization
- D. Create less favorable abiotic environment
  1) Soil moisture-microbial community interactions affecting decomposition
  2) Community and biome variability in thermal responses of microorganisms
  3) Effect of nitrogen addition (as fertilizer, deposition, biological nitrogen-fixation) on decomposition

Research needs for improving inventories of carbon stocks in agricultural and grassland ecosystems

- A. Dynamic inventories of land cover and land management system distributions
  1) Development of coverages with improved spatial resolution to differentiate fragmented land covers
  2) Improved differentiation of crop and grassland species assemblages
  3) Remote sensing techniques to resolve different management regimes within landcover/vegetation types (e.g., tillage management, cover crops, grazing intensity)
- B. Survey data
  1) Global metadata compilation of national land use/management information
  2) Standardization and/or cross comparison of survey/inventory approaches and definitions
  3) Synthesis (within United States) and cross validation of national level survey data (e.g., USDA/NRI, FS, BLM, USDA/ERS)
- C. Information on distribution and characteristics of soils
  1) More information on soil carbon concentrations at depth
  2) Synthesis and integration of data from distributed pedon data holders (e.g., universities, state agencies)
  3) Standardization (international) of attributes (e.g., carbon analytical methods, bulk density, texture, drainage, and depth) and techniques needed to estimate soil and litter carbon stocks and soil bulk density (e.g., as part of USDA/NRCS and ISRIC collaboration).
  4) In situ, nondestructive determinations of soil carbon

Needs for quantification and prediction of carbon sequestration

- A. Development of modeling approaches
  1) Testing and refinement of models for less studied systems; for example, flooded and poorly drained soils, highly weathered soils (e.g., Ultisols, Oxisols), volcanic-derived soils
  2) Representation (in simulation models) of SOM fractions that are analytically determined, concomitant with experimental science to improve functionally meaningful characterization of SOM
- B. Enhancement of SOM monitoring networks
  1) In field relocateable, resampling points designed to minimize spatial variability, tied into existing monitoring systems (e.g., NRI). Measure change under a variety of cropping/grassland systems (steady-state/aggrading/degrading) in a variety of climates and soil types
  2) Increased deployment of ecosystem CO_2 flux systems, coordinated so as to

leverage information from existing long-term experimental sites (e.g., establish new flux measurements for soil, crop and management variables where long-term experimental records exist) and intensified soils research at existing CO_2 flux tower facilities

C. Coordinate and synthesize spatially referenced data coverage for important model driving variables.

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3. **Biomass Crop Lands** (Lynn Wright, Sandy McLaughlin, Jerry Tuskan, Don Reimensneider, and Carl Trettin)

Biomass production and harvesting systems are being developed to optimize aboveground plant productivity per unit area in a way that conserves and improves soil resources, maintains or improves water quality and wildlife habitat, provides profit potential to the landowner, and supplies low-cost, uniform feedstocks to energy providers as a means of displacing fossil fuel. The crops under development for this land use are primarily perennial crops, including several grass and tree species worldwide. These crops are grown using agronomic techniques such as cultivation or herbicide use for site preparation, fertilization, pest and disease control for crop maintenance, and periodic removal of the aboveground portion of the crop. The grass species are harvested annually or more frequently while the tree crops have 3–10 year harvest intervals. It is generally assumed that the trees or grasses will be grown in relatively large blocks for ease of harvest, handling, and utilization. Alternative methods of biomass production include mixing annual and perennial crops (agroforestry), using shelterbelts or riparian zones to produce biomass, and mixing species in production stands.

A critical assumption for carbon sequestration analysis is that these perennial crops will be established on idled or surplus crop or pasture land, on cropland that is occasionally flooded, or on lands marginally profitable for annual crop production because of poor soil quality, erosion sensitivity, nutrient degradation, or other reasons. The rate of conversion of agricultural cropland to biomass cropland will be economically and policy driven but is also dependent on the development of new, more efficient biomass production and bioenergy conversion technologies. In some areas of Europe, idled agricultural cropland is already being converted to biomass crop production for energy end-use. In other places, such as the United States, the biomass cropping systems described above are being used to produce fiber products with energy production as a by-product.

Current carbon sequestration capabilities of biomass cropland

The greatest carbon emission reduction gain from biomass cropland will be obtained when economic or policy conditions result in the use of biomass cropland to produce feedstocks that substitute for carbon emitting fossil fuels such as coal and oil. Since adequate economic and policy drivers are not yet in place in most areas of the world, very little land currently is managed as biomass cropland. In the United States about 50,000 ha have been converted from agricultural cropland to production of woody crops. Several million ha of cropland were converted to switchgrass and other grass mixtures as part of the Conservation Reserve Program in the United States from the mid-1980s to mid-1990s. However, those lands have not received fertilization or pest control and thus are not highly productive. Similar types of land conservation programs were instituted in Europe for similar reasons. In addition, many parts of the former Soviet Union have large amounts of idled cropland reverting to natural ecosystems with the change from centrally managed to private managed agricultural systems. For purposes of a carbon sequestration analysis, some combination of the current carbon sequestration capabilities of annual crop systems and pastureland should be used as the biomass cropland baseline.

Strategies and objectives for biomass cropland carbon sequestration

Since biomass cropland systems are at a very early stage of development, the opportunity exists to select and develop perennial plant species and management systems that optimize both aboveground production and belowground carbon sequestration while providing profit to the landowner. The primary research strategy here is to increase the per unit land area rate of carbon fixation in the aboveground (economic) portion of the perennial plant biomass by 2 to 4 times. A policy/economic strategy is to develop markets for biomass crops to assure periodic removal of the crops for sequestration in bioproducts (e.g., wood products, bioplastics, etc.) and bioenergy (fossil carbon substitution). Development of the markets could be enhanced by genetically improving the characteristics of perennial biomass crops for bioenergy or bioproduct utilization

One risk associated with biomass croplands is public acceptance of land use change. Because of this, biomass croplands will have to provide more than just carbon sequestration and energy benefits in order to be accepted. Some level of optimization of carbon sequestration and plant productivity may have to be sacrificed in order to assure that water quality, soil conservation, and wildlife benefits are provided as an inherent component of biomass cropland ecosystems. Thus realizing the high rates of carbon sequestration that deployment of biomass production systems can offer additionally requires; (1) land use policy that facilitates biomass cropland implementation without violating strongly held ideas about land use, (2) multiple environmental benefits associated with the land use change and, (3) achievement of high carbon fixation and storage rates with low fossil carbon inputs.

The amount of carbon sequestration in biomass cropland will ultimately depend on the scale of land use conversion that occurs. Conversion of between 10 and 15% of current crop and pasture land worldwide to biomass production appears to be a feasible goal that would not substantially impact food and fiber production and which could provide observable regional environmental benefits.

Research and development needs

All plant productivity research could benefit from improving our understanding of plant and soil processes. Research on plant process understanding must integrate with genetic improvement and crop management activities focusing on carbon sequestration impact. Genetically improved stock should optimally combine high-yield potential, with disease and pest resistance, high water-use and nutrient efficiency and optimal feedstock properties for conversion. Genetic potential needs to be achieved in concert with crop management techniques that minimize carbon inputs but assure sustainability of yields over time. Functional genomics will use molecular genetics to identify and modify plant growth and development processes, including individual gene expression, host-microbial interactions, all physiological responses, and plant assembly mechanisms. Integrated physiology, entomology, pathology, and agronomic studies are needed to elucidate plant growth and stress resistance mechanisms (i.e., studies focused on CO_2 fixation and respiration processes, carbon allocation, efficiency of carbon capture per unit of nutrients and water available, and pest and disease resistance are required). The selection and deployment of improved planting stock and crop management techniques must be optimized for each soil type and climatic zone.

Similar to most plant ecosystems, process understanding is critical to improving belowground carbon sequestration in biomass croplands starting with improving our understanding of the processes controlling the movement of aboveground carbon to soil carbon pools. Carbon storage process studies should include; (1) determination of how carbon fractionation influences labile and recalcitrant forms of carbon, (2) quantification of how existing carbon levels affect storage rates and, (3) determination of factors affecting the rate and form of downward carbon migration in soils. The process research should be supplemented with extensive surveys documenting how carbon forms vary with soil type, depth, temperature, physical properties, and chemistry as well as types of crops and cropping strategy. In evaluating crops and cropping approaches it will be important to link effects of nitrogen management and tillage practices to carbon storage rates, stability of carbon gains over time, and the equilibrium conditions. Finally, a better understanding how climate change events (such as nitrogen deposition, regional ozone levels, changing precipitation patterns, and overall global warming) may feedback to affect carbon inputs and storage will add valuable information for predicting long-term effects.

The measurement and quantification research that would non-destructively determine carbon sequestration in the soil in biomass croplands would be very beneficial. Remote sensing approaches could also improve our ability to survey large areas of land thus predicting levels of standing biomass. Research to improve our understanding of the linkage between above- and belowground carbon gains would be helpful in estimating soil carbon gains based on tons of biomass harvested annually.

Implementing the strategy for increasing carbon sequestration in biomass cropland requires the initiation of research that will lead to (1) technologies that are economically viable and environmentally sound and (2) analytical techniques that will assist policy makers in determining optimal land use allocation strategies for achieving carbon sequestration goals. Carbon sequestration will not increase in any ecosystem unless there are appropriate economic and policy drivers.

One risk associated with biomass croplands is public acceptance of land use change. This is part of the reason why biomass croplands will have to provide more than just carbon sequestration and energy benefits in order to be accepted by the public. Thus some level of optimization of carbon sequestration and plant productivity may have to be sacrificed in order to assure that water quality, soil conservation, and wildlife benefits are provided as an inherent component of biomass cropland ecosystems.

Linkages

Biomass cropland R&D will be similar to that proposed for traditional agricultural crops, intensively managed forests, and managed grasslands since in all cases, a major goal is the production of biomass for removal from the site. Improvement of plant growth on degraded ecosystems could also share some similarities in approach with biomass croplands, since stress tolerance will be a component of both systems.

Biomass and agricultural cropland R&D will differ in that the former will focus primarily on perennial plants and the latter on annual plants and that most of the products from biomass crops will have a longer sequestration residence time. Basic plant research may be able to address some topics common to both, but perennial and annual plants have very different requirements for survival, and thus many differences in basic plant mechanisms.

Biomass cropland and managed forest or grassland ecosystems will differ by the fact that biomass crops will likely be established on former agricultural lands that are carbon depleted, while forest and grassland soils will likely have less opportunity for soil carbon increases.

A major cross cutting issue is to develop appropriate decision models and analytical techniques for optimizing land use allocation under various economic and policy scenarios. In the context of this report, consistent decisions have to be made on accounting for carbon removed from sites, considering portions that return to the atmosphere with no fossil substitution and portions that are sequestered or substitute for fossil carbon.

4. **Wetlands** (Carl Trettin, Ron Thom, Patrick Megonigal, Walter Oechel)

Global wetlands cover about 7% of the total land surface, and contribute about 10% of the total global net primary productivity (NPP). Many systems have a high turnover rate (production:biomass) indicating loss and export rates are high. In addition, loss to sedimentation in deep portions of lakes and oceans may be great. Wetlands produce 40% of the global methane emissions. The degree to which wetlands produce methane is intimately tied to the hydrology of the system. Systems, such as rice paddies, that are wet much of the time, have greater methane emission rates. Marshes and some other wetland systems can be nutrient limited. Wetlands have the highest carbon density among all terrestrial ecosystems. Because of their low drought stress, high nutrient availability, and ability to expand below ground biomass in enriched conditions, wetlands have a relatively great capacity to sequester additional carbon dioxide.

Wetlands sequester carbon through accretion of sediments and organic matter. Accretion is great in coastal systems where sediment input to estuaries is high. Marshes, in particular, form land through progradation. Very limited studies have shown that coastal marshes under enriched CO_2 conditions, can sequester more carbon in the below ground biomass. Carbon sequestration through peat formation is an active process especially in boreal systems. Because of their position at the interface between land and water bodies, wetland export large quantities of carbon to deeper portions of lakes, estuaries and oceans, where carbon can be sequestered through burial.

Wetland soils contain a significant proportion of the terrestrial soil carbon (20–25%), despite the relatively small proportion of the total land area occupied. In North America, approximately 50% of the wetlands are forested. They are an important carbon sink, and a major source of atmospheric methane. Carbon dynamics in wetland soils also affect non-point pollutants, ground and stream water chemistry, and biogeochemical processes. Although soil carbon in wetlands is recognized as being an important component of global carbon budgets and future climate change scenarios, relatively little work has been done to consider the role of terrestrial ecosystems in managing carbon sequestration. Wetlands are among the most productive ecosystems in the world. They also have properties that reduce the rate of organic matter turnover from the ecosystem. Hence wetlands inherently have the two primary factors controlling carbon sequestration, (1) high rates of organic matter input, and (2) reduced rates of decomposition. There is considerable opportunity for managing that capability to affect enhance carbon sequestration while sustaining the other valued ecosystem functions. However, considerable research is needed to provide the knowledge foundation for the resource management decisions.

In the United States, 50% of wetlands have been lost or converted to other uses (e.g., crop and grazing lands). Globally the loss is undocumented, but could easily be as great. Sea level rise is causing net loss of some coastal wetlands, and carbon sinks in temperate and boreal wetlands have decreased by 50% (from 0.2 to 0.1 GtC year^{-1}) due to development and resource extraction. Loss in tropical systems could likely exceed this amount. The leading causes of wetland loss are conversion, deforestation, development, and hydrological modifications.

Because of the global losses of wetlands, restoration of damaged, degraded and converted ecosystems represents a major opportunity to improve sequestration in wetlands. We estimate that restoring 25% of the wetlands would result in an increase in carbon sequestration. Hydrological controls could be effectively used to produce a positive balance in favor of carbon sequestration vs methane emission. Some wetland system are nutrient (nitrogen) limited to some degree. Hence, fertilization or other methods to introduce nitrogen into these systems could increase primary productivity and enhance carbon storage. Reduction in the rate of sea level rise would reduce the rate of conversion of intertidal wetlands to subtidal mud bottom. Massive restoration efforts presently underway on the Mississippi River delta through the Coastal Wetland Protection, Preservation and Restoration Act (CWWPRA) represent an excellent opportunity to evaluate the effects of large scale restoration on carbon sequestration and comparison of forest, shrub, and herbaceous wetlands.

Strategies

- Identify degraded wetlands and develop management/conservation strategies to rehabilitate processes that sequester soil carbon. These lands have the inherent characteristics to sequester large amounts of carbon; reestablishing anaerobic processes and managing inputs have the potential for large amounts of long-term carbon storage. Especially important opportunities exist in prior-converted agricultural lands.
- Implement vegetation management strategies that sustain the soil carbon resources while producing woody crops.
- Increase soil carbon storage by identifying sites that have high productivity potential through managing water and nutrient resources.
- Conserve wetland landscapes that are inherently effective at carbon storage.
- Mitigate carbon loss through created wetland systems.

Objectives

- Increase soil carbon sequestration in managed wetlands to rates above the norm for natural or unmanaged systems.
- Increase acreage of wetlands within selected landscapes thereby enhancing both above and below ground carbon storage.
- Increase the volume of wood products derived from the resource that enter stable products classes.
- Implement planning / decision systems that consider carbon sequestration at the landscape level.
- Consider the value of carbon sequestration in designing mitigation projects.

There may be inherent limits on the potential for any given wetland to simultaneously have both very high productivity and extremely slow decomposition rates. Such limits will be important to understand if we wish to manipulate wetlands to enhance carbon sequestration. One limit that is incompletely understood in wetlands is the link between carbon and nitrogen cycling. Plants require a substantial nitrogen supply to support high photosynthesis rates. Most of the annual nitrogen demand in wetlands is supplied by decomposition of soil organic matter, a process that produces both plant available nitrogen and CO_2. Thus, wetlands cannot necessarily support high rates of photosynthesis and low rates of decomposition simultaneously. A basic research needed in wetlands is understanding how nutrient inputs and hydrology can be managed to optimize net ecosystem production in wetlands.

Coastal marshes have high rates of primary production due to tidal subsidies of water and nutrients, and high rates of carbon sequestration in soils due to low decomposition rates and burial by sediments. Global sequestration in these systems is perhaps 0.025 to 0.05 Pg carbon per year. One of the largest coastal marsh systems is the Mississippi River delta, which has an area of ~30,000 km^2, roughly 10% of all coastal marshes. Both natural and artificial impacts are causing annual losses of 66 km^2 of freshwater and saltwater wetlands in the basin, and efforts to slow these losses are underway. Halting the current losses would save about 0.03 Tg y^{-1} in soil carbon sequestration. Restoring these wetlands would increase this amount by perhaps 20-fold.

R&D Needs

Aboveground

- Improve the understanding of the processes controlling vegetative production and community dynamics.
- Improve the understanding of the hydrologic controls on above and belowground carbon allocation and carbon uptake vs emission.
- Develop a modeling framework to consider the role of wetlands in carbon sequestration at the landscape scale.
- Develop an understanding of how wetland plants (i.e., trees) will respond to increased levels of atmospheric CO_2.
- Develop techniques to sustainably manage wetland ecosystems.
- Determine the differences among forest and herbaceous communities in carbon sequestration.

R&D Needs

Belowground

- Improve the understanding of the processes controlling biomass allocation to roots among different wetland species.
- Develop an understanding of the role of mychorrizae in carbon fixation and plant productivity.
- Determine how different land management practices affect soil carbon storage.
- Determine the feedback of changes in soil carbon storage on ecosystems functions (e.g., habitat, water quality, hydrology).
- Determine the interactions of nutrient levels, temperature, redox and organic matter quality on carbon turnover and sequestration.
- Determine the organic matter sources affecting soil carbon storage.
- Role of fire in limiting carbon sequestration.
- Explore opportunities for creating wetland/carbon storage systems as an integral components of the landscape. Such a system would provide environmental benefits (e.g., water quality, habitat, recreation) and provide long-term carbon storage.
- Improve the understanding of the hydrologic controls on processes controlling carbon sequestration.

Linkages

Wetlands are inherent to most landscapes where soil carbon storage is important. Accordingly, whether the management system is on the upland, adjoining the wetland, or directly within the wetland, wetlands are probably involved in attempts to affect carbon sequestration on the land. The linkages are controlled primarily by the movement of water. Hence understanding the functional linkages among ecosystems or management zones is critical to developing sustainable management systems. Wetlands effect soil carbon storage primarily as a result of reduced rates of organic matter turnover caused by anoxia. Factors affecting hydrology or aeration may affect the processes controlling soil carbon storage. Accordingly, there are direct linkages to land use (i.e., water use, waste disposal, urbanization) that must be considered at the landscape scale. Altered climates factors including temperature, precipitation, and atmospheric CO_2 should be expected to change wetland processes and carbon storage. Studies of the effects of climate change factors on wetlands have largely been ignored. Accordingly, there is a critical need to develop an understanding of climate change influences on wetland processes so that those influences can be considered in conjunction with current and planned management approaches.

There is considerable interest in the United States in mitigating wetland loss through banking and project-specific approaches. The carbon sequestration function is not currently considered as part of the wetland value. Hence, it is likely that carbon losses are occurring with questionable prospects for long-term parity. Accordingly, there is an opportunity to design mitigation systems to provide, and perhaps enhance, carbon sequestration functions. Wetlands are productive ecosystems. There is considerable opportunity to enhance that productivity while sustaining valued ecosystem functions at the landscape scale. However, development of integrated assessment systems based on knowledge of ecosystem processes is required.

5. Deserts and Degraded Lands (F. Blaine Metting and Rattan Lal)

Deserts and degraded lands are considered together because restoration of these ecosystems to sequester carbon can require highly manipulative strategies. Many of the same strategies can be applied to both systems, with some modifications.

The definition and areal extent of degraded lands is somewhat difficult to assess. Included under different definitions are both “natural” and anthropogenic degradation. Worldwide, there are approximately 1965×10^6 ha of degraded soils, 4% from physical degradation, 56% from water erosion, 28% from wind erosion and 12% from chemical degradation. With proper management these soils have the combined potential to sequester between 0.81 and 1.03 Gt C/year. Categories include saline, sodic, saline-sodic, mine spoils, and eroded or severely eroded soils.

Erosive processes are as a consequence of overly intensive tillage often combined with climate change and other inappropriate practices, such as use of marginal lands and steep topographies, and over grazing. One result is desertification. Estimates of land areas subject to degradation and desertification vary from $\sim 1–2.5 \times 10^9$ ha. Annual desertification rates vary from $\sim 5–27 \times 10^6$ ha, half of which is occurring on rangelands.

Depending on the basis for their definition (i.e., evapotranspiration or other aridity indices, vegetation, soil taxonomy), deserts account for between 11–12% of the Earth’s land surface. Estimates vary from 10^8-to-$2^+ \times 10^9$ ha and include hyper-arid regions receiving <200 mm annual precipitation (ppt.) and arid areas with <200 mm of winter ppt. or <400 mm total annual ppt. Addition of semi-arid areas receiving 200-500 mm of winter ppt. or 400–600 mm of summer rainfall increases the areal extent of deserts to $\sim 5 \times 10^9$ ha. The principal feature of these regions is their negative water balance, which is reflected by generally sparse and often seasonal plant cover and low primary production. With open or absent plant canopies, much of the soil surface of deserts is exposed to full sunlight. One result is the evolution of unique microbial ecosystems dominated by autotrophic bacteria, microalgae and/or lichens known variously as cryptobiotic or algal crusts and desert pavement. Organic carbon stocks are much smaller than other ecosystems, but desert soils (primarily in the Aridosol soil order) often contain significant concentrations of inorganic carbon, principally as caliche. Other features of desert soils are:

- Aridosols occupy $\sim 1.7 \times 10^9$ ha
- Average carbon density of desert soils ~3–3.5 kg/m^2/m depth
- World wide desert soil stock ~59 Gt total C, 4.7 Gt N
- Global caliche accretion rate ~0.05 Gt C/year

Strategies for enhanced carbon sequestration

Strategies for enhanced carbon sequestration have different objectives for deserts and degraded lands. For deserts, enhanced sequestration strategies are largely innovative uses of otherwise under utilized resources. Restoration of degraded lands and strategies to minimize or reverse desertification processes, on the other hand, are as much aimed at reversing loss of carbon to the atmosphere as they are to enhancing sequestration. With the exceptions of the use of saline and brackish groundwater resources for (1) crop irrigation or (2) microalgal mass culture, strategies for deserts and degraded lands largely focus on below ground sequestration. The greatest potential may be the discovery and application of innovative ways to enhance the accumulation of inorganic carbon stocks.

1. Control desertification (minimize, reverse) and restore degraded lands by means of improved land management practices
2. Delineate “bright” (trigger) spots for desert carbon sequestration. That is, identify area(s) to focus short-to-mid term desert carbon sequestration efforts.
3. Exploit under utilized desert resources to create wetlands and large-scale aquaculture projects with saline and brackish surface and groundwaters
4. Use existing plant and microbial resources together with biotechnology and genetic engineering:
   - Screen, identify and adapt C4 and CAM plants
   - Engineer enhanced water use efficiency, salt tolerance, high pH tolerance into select species for desert regions
   - Engineer for desired root physiology/metabolism and architecture
   - Encourage and manipulate surface and rhizosphere microbial communities to enhance sequestration
5. Expand the use of land application of organic and inorganic soil amendments:
   - Organic matter
   - Inorganic nutrients (e.g., Ca to enhance caliche development)
   - Microbial inocula to promote the development of desert crusts

Objectives

The objectives of the strategies for enhanced soil carbon sequestration in deserts and for restoration of degraded lands are to:

1. conserve soil and water, enhance water use efficiencies
2. utilize neglected and underutilized resources
3. strengthen/direct desired biogeochemical cycles/processes
4. enhance vegetal cover and effective carbon sequestration by plants and microbial communities

Research and development needs

Research and development needs for enhanced carbon sequestration in deserts and degraded lands falls within seven categories. These include research to establish global databases in biotechnology and land management, and to better understand natural plant, microbial, and soil processes and their interrelationships in arid and disturbed ecosystems. Specific research and development needs include:

1. *Quantify and categorize the extent and severity of degraded lands on a global scale*. The availability and quality of this information is inadequate. Campaigns to collect, archive and make available data are required to better

understand the extent of degraded lands and for developing effective and prioritized international research programs.

2. *Understand mechanisms and processes controlling carbon pools and fluxes in deserts and degraded lands*. A number of basic biogeochemical mechanisms important to establishing a solid, fundamental understanding of environmental and ecological processes in deserts and degraded lands are poorly understood. Research is needed to better understand the following:
   - Aeolian/dry deposition processes and effects on carbon sequestration
   - Inorganic carbon formation and movement and the role of Ca
   - Influence(s) of soil physical properties on carbon sequestration in arid regions, including the roles of texture, clay mineralogy, and soil structure and aggregation
   - Biogeochemical cycles/controls of carbon sequestration and movement, including N, P, S, Fe, Ca and Cl
   - The microbial ecology of desert soil surfaces and rhizosphere microbial communities
   - Physical, mechanical, and species-mediated weathering of exposed subsoil or parent material on eroded sites
3. *Management practices for desertification control and soil restoration*
   Desert lands are, by definition, water limited. Thus, fewer than 10% of arid regions are cropped. Therefore, key management strategies for utilizing deserts and reversing desertification must focus on minimizing the water deficit. Important objectives are:
   - The use of appropriate plant species. In particular, many arid land plants have evolved special photosynthetic mechanisms for enhanced water use efficiency. These include the C4 photosynthetic fixation pathway and the crassulacean acid metabolism (CAM) pathway. There are many advantages to growing C4 and CAM plants in arid regions based on their improved water and soil nutrient use efficiencies at high temperatures. Research is needed to improve understanding of global biodiversity of C4 and CAM plants that could be screened for innate carbon sequestration traits of interest and used in field research projects.
   - Supplementary irrigation and the use of under utilized saline and brackish surface and ground waters. Growing crops or mass culturing microalgae that tolerate saline and alkaline water is another strategy for which expanded research efforts are required.
   - Research focused on techniques for soil erosion control, particularly as suited to arid lands is required. This research needs to be integrated with management efforts to optimize soil fertility, residue use, salinity control and the possible use of novel microbial and chemical amendments.
4. *Molecular biology and plant genetic engineering*
   Biotechnology to improve plant performance in desert environments is needed and should focus on:
   - Development of genetic transformation tools and methods in new plant species for desert growth and carbon sequestration, including C4 and CAM plants.
   - Genetic engineering of desired traits into existing crop and forage plants, including salinity tolerance, water use efficiency, etc. One approach is to engineer desirable C4 and CAM metabolic traits into C3 crop plants.

5. *Microbial biology*
   Microorganisms and microbial communities in and on desert soils are unique in comparison to agricultural and forest soils. In some arid and hyper-arid settings, microbial communities are the only mechanism for biological CO_2 fixation. They are also responsible for nitrogen input via biological N_2 fixation and for weathering of primary minerals and nutrient release. Fundamental research is needed in desert plant rhizosphere microbial community function and diversity of cryptobiotic communities (i.e., desert pavement, and lichen and microlagal crusts). In addition, applied research to develop and demonstrate microbial inoculants for rhizosphere and soil crust manipulation and development is needed.
6. *Desert ecology*
   Ecosystem-scale research is required to better understand integrated ecological roles of desert plant and animal communities, including the role and global significance of arthropods in soil carbon cycling and sequestration. Ecological research is also needed to determine the appropriateness and extent of expansion or modification of grazing practices in arid and semi-arid regions.
7. *Economic, social and policy research*
   In all cases, research is required for cost-benefit and risk analysis for all technical and management options for enhanced soil carbon sequestration in deserts and degraded lands. This includes the need for life cycle analysis all approaches to determine the overall energy and carbon budgets for implementation.

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6. Urban and Suburban Forested Areas (John Hom, David Nowak, Richard Pouyat, Marilyn Buford)

Carbon storage by urban forests nationally is estimated between 400–900 million tons (aboveground tree and shrub biomass only, Nowak 1995). Within the urban area, the largest carbon tree storage is found in institutional lands dominated by vegetation (e.g., parks, preserves, cemeteries, golf courses), in residential land use (1–3 family residential buildings), multiresidental areas (apartments) and vacant lots. Small trees account for the majority of the trees in urban areas. In comparison, U.S. forested ecosystems store approximately 52.5 billion tons of carbon (Birdsey 1992) and have 3–4 times higher live carbon/ha than urban forests, due to the lower average percent tree cover in urban sites (~28%). The estimates of suburban forest carbon storage are not well known, and are sometimes included in carbon estimates for urban forests, as they fall between the inventories of rural and urban forests.

Land use is one of the most significant factors affecting urban vegetation. Urbanization eliminated 10 million ha of agricultural and forested land in the United States between 1960 and 1980 (Alig and Healy 1987). It is estimated that 80% of the U.S. population will live in urban areas by the year 2025, up from 74% in 1986 (Alig and Healy 1987). Urban areas account for less than 1% of the total terrestrial life zones. The total amount of land dedicated to urban uses was 26 million hectares in 1992 (World Resource 1996).

Soil carbon densities for urban soils are relatively high compared to other biome types, higher than temperate forest soils, and comparable to wet boreal forest (17.5 and 23.7 kg/m^2, Pouyat, personal communication). Data suggest that long term urban forests soils may store more carbon than in rural forest soils with less labile carbon and greater passive carbon pools (Groffman et. al. 1995).

Urban forests are unique as they perform the dual function of directly sequestering atmospheric carbon and by indirectly conserving energy use of structures through shading, reducing the “heat island effect” by transpirational cooling, and reducing turbulent transfer losses. It was estimated that planting 10 million urban trees annually over the next 10 years would sequester and offset the production of 363 million tons of carbon over the next 50 years, with 20% due to direct carbon sequestration and 80% due to avoided carbon emission from energy conservation under optimal tree location. The total sequestration and energy offset of carbon reduction under this scenario is less than 1% of the carbon emissions projected for the United States over the same 50 year period (Nowak 1995).

Strategies

Urban forest planning and management to direct urban forest structure to desired outcome of increasing forest cover, increase rate of carbon capture, and long-term maintenance of standing stock within space and land-use limitations.

Sustain or enhance existing tree health to maximize sequestration while minimizing losses due to tree mortality (hold on to existing carbon).

Establish properly selected and located urban trees in available planting areas. Planning to maximize building energy conservation will yield greatest relative carbon benefit.

Objectives

Aboveground

1. Increase and maintain area of urban and suburban forested areas
2. Maximize biomass accumulation within space and land use limitations
3. Minimize mortality losses under multiple stress conditions within urban environment
4. Increase net carbon retention in maintenance (pruning), landfill (disposal), and recycling (leaf and chipping) practices.

R&D needs

Aboveground

Identify and select tree species and genotypes, for the urban and suburban environment that meets objectives of increasing sequestering carbon and reducing emissions.

Evaluate physiological responses and carbon allocation of urban trees and shrubs to those in rural environments. Urban trees are exposed to elevated CO_2 and temperature gradients within an urban-suburban environment as well as multiple stress interaction with ozone and atmospheric deposition of nitrogen and sulfur compounds.

Identify policy and management issues that would lead to preserving existing urban forests and increasing tree planting: energy conservation, economic development, natural resources planning, social-economic values.

Full life-cycle analysis on carbon budget of urban and suburban forests to increase carbon sequestration and reduce emissions. Trees in the urban environment require greater energy inputs in establishment, maintenance and disposal (fertilizer, site prep, pruning, leaf litter, chipping, transport and disposal). Trees offset energy use by energy conservation on buildings through shading, reduction of heat island effect, and turbulent transfer losses.

Objectives

Belowground

1. Increase and maintain urban and suburban forest cover
2. Increase soil carbon densities
3. Employ planning and management practices to minimize soil, litter disturbance and maximize soil carbon retention

R&D needs

Belowground

Will urban land uses result in greater soil carbon storage? Soil carbon densities for urban soils are relatively high compared to other biome types. Long term urban forests soils may store more carbon than in rural forest soils.

Determine litter quality changes and soil decomposition rates in the urban environment. The urban environment receives elevated chemical and atmospheric inputs. This can produce changes in litter quality by air pollution (ozone) or exotic plant species. Temperature increases in the urban environment and greater nitrogen deposition will increase decomposition rates. Heavy metal and air pollution damage to plant tissue should decrease decomposition rates. Changes in microbial and soil invertebrate composition across urban to rural environments may change rates of decomposition.

Develop urban land use management practices to increase soil carbon. Management practices, such as irrigation and fertilization make up for site limitations restricting plant and root growth.

Investigate effects of drastic soil disturbances that occur in urban areas on soil carbon

Links to other ecosystems:

1. Determine the net conversion of land use (i.e., agricultural and forested lands to suburban and urban forested lands).
2. Determine extent of urban land uses in other vegetation life zones (e.g., coastal areas, wetlands conversion to urban and suburban use).

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Table B.1 Assessment of carbon storage and sequestration by urban forests in the United States

Region	Urban land[1]	Urban tree cov[2]	Total C stored[3]	Total C gr. seq[4]	Total C net seq[5]	Per meter stored[6]	Per meter gr. seq[7]	Per meter net seq[8]
NE	48,646	15,814	131,876,000	4,668,000	679,000	2,718	95.9	13.8
NC	51,724	17,118	142,748,000	5,052,000	735,000	2,768	97.6	14.3
SE	46,413	15,562	129,775,000	4,593,000	668,000	2,792	98.8	14.3
SC	65,930	15,926	132,807,000	4,701,000	684,000	2,026	71.4	10.4
RN	5,331	2,402	20,028,000	709,000	103,000	3,756	132.9	19.3
RS	22,447	2,447	20,407,000	722,000	105,000	914	32.1	4.7
PSW	27,348	2,949	24,589,000	870,000	127,000	890	31.9	4.7
PNW	7,958	2,537	21,155,000	749,000	109,000	2,669	94.1	13.6
GP	4,710	907	7,562,000	268,000	39,000	1,606	56.8	8.2
Misc[9]	492	142	1,183,000	42,000	6,000	2,397	85	12.4
U.S.[10]	281,000	75,803	632,129,000	22,373,000	3,255,000	na	na	na

Ref. David J. Nowak, Daniel E. Crane, and Jack C. Stevens, personal communications-DRAFT
Note: all urban tree carbon numbers are for aboveground only

[1] urban land in km^2
[2] urban tree cover in km^2
[3] total carbon stored in metric tons (t)
[4] total gross annual carbon sequestration in metric tons (t/year)
[5] total net annual carbon sequestration in metric tons (t/year)
[6] carbon stored per acre of land (g/m^2)
[7] gross annual carbon sequestration per acre of land ($g/m^2/yr$)
[8] net annual carbon sequestration per acre of land ($g/m^2/yr$)
[9] Miscellaneous land-urban land that crossed state borders and could not be assigned to an individual states
[10] U.S. total
na-not analyzed

U.S. Regions:
Northeast (NE): NY, PA, MD, WV, DE, NJ, CT, RI, MA, NH, VT, ME, DC
North Central (NC): MN, IA, MO, IL, WI, MI, IN, OH
Southeast (SE): VA, NC, SC, GA, FL
South Central (SC): KY, TN, AL, MS, AR, LA, OK, TX
Rockies-north (RN): MT and ID.
Rockies-south (RS): NV, UT, AZ, CO, WY, NM
Pacific SW (PSW): CA
Pacific NW (PNW): OR, WA
Great Plains (GP): ND, SD, NE, and KS

Table B.2. Urban soil carbon storage

Life zone groups	Area* (x 10^{12} m^2)	Carbon density(kg m^2)	Soil carbon (x 10^{15}g)
Tropical forest-moist	5.3	11.4	60.4
Temperate forest-warm	8.6	7.1	61.1
Boreal forest-wet	6.9	19.3	133.2
Warm desert (1)	14.0	1.4	19.6
Wetlands (2)	2.8	72.3	202.4
Urban (3)	0.26	20.6	5.4
Urban -15% (4)	-	17.5	4.6
Urban +15%	-	23.7	6.2

* After Olson
1. Ratio of warm desert to cool desert after Walter
2. Carbon density for cultivated land and wetland after Schlesinger
3. After Hyun-Kil Jo and E. G. McPherson
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